

UNIVERSIDAD POLITÉCNICA DE MADRID

Escuela Técnica Superior de Ingenieros Navales



**Methanol electrolyser and direct
methanol fuel cell for marine
applications**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Vladimir Luis Meca López

Naval Architect & Marine and Oceanic Engineer (M.Sc.)

Madrid, 2024



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Under the supervision of:
Dr. Teresa J. Leo Mena
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To you, Nititi, my steadfast companion on this thrilling voyage...

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Abstract

Energy sources and the energy transport play crucial roles globally. From fossil fuels to renewable energy, they form the backbone of the world energy infrastructure. Efficient distribution of energy relies on various transportation methods, including electrical grids, pipelines and maritime transport systems. Furthermore, advancements in sustainable and efficient transportation technologies, coupled with the transition towards cleaner and renewable energy sources, are reshaping the global energy landscape and shaping the future of energy and transportation worldwide. Amidst this context, the use of methanol as energy vector emerges, central topic of this doctoral thesis. Recent decades have witnessed heightened interest in methanol, particularly in maritime transportation and fuel cell applications, as well as its more recent role in hydrogen production, evolving it beyond just an energy vector to a hydrogen carrier. The main aim of this doctoral thesis is to explore the viability of methanol as an energy vector for marine applications, analysing the economic feasibility of e-methanol as a hydrogen carrier and experimentally studying the use of methanol for electricity generation via Direct Methanol Fuel Cells (DMFCs) and hydrogen production through Methanol Electrolysis Cells (MECs).

This thesis conducts a technoeconomic study comparing the use of e-methanol and liquefied hydrogen as energy vectors transporting both fuels by ship. Additionally, two alternatives for obtaining hydrogen at the destination are compared: methanol reforming process and methanol electrolysis. The study sheds light on when it is advantageous to produce hydrogen locally or import it, and which vector is preferable in each scenario.

Within the scope of methanol utilization as an energy vector, DMFCs offer a means to generate electrical energy from methanol. The operational conditions and geometry of the anode flow field significantly influence DMFC performance. Therefore, this thesis evaluates the combined influence in the DMFC behaviour of DMFC temperature, methanol concentration and the volumetric flow rate of methanol solution introduced into the DMFC. Furthermore, a series of anode serpentine channel geometries are designed as a preliminary step towards experimentally assessing its impact on DMFC performance.

As for methanol utilization as a hydrogen vector, there has been increased interest in MECs viability as hydrogen production systems from methanol over the past two decades. This thesis conducts for the first time an experimental study on the

influence of operational conditions, akin to what has been done for DMFCs, and geometrical parameters (open ratio, channel width and channel depth) of the anode serpentine flow field, applying the Response Surface Methodology to analyse experimental results. Additionally, it includes an experimental study on different non-noble metal-based electrodes, important components of MECs, conducted during the stay at the Università degli Studi di Palermo, Italy.

Through these studies, the significance of operational conditions on the performance of both devices and the feasibility and potential of methanol as an energy and hydrogen vector for marine applications are underscored. The study concludes that e-methanol is a competitive option at certain hydrogen mass flow rates transported, especially when incorporating technological improvements. Key processes impacting viability include hydrogen liquefaction, methanol synthesis and methanol electrolysis. Regarding the use of this methanol in DMFCs and MECs, optimal methanol concentration and devices temperature significantly enhance DMFC and MEC performance. Furthermore, improvements in electrodes and geometric configurations of the anode flow field enable enhancement of the methanol electrolysis process, contributing to the development of sustainable hydrogen production technologies.

Resumen

Las fuentes de energía y el transporte de esta energía juegan roles cruciales a nivel global. Desde los combustibles fósiles hasta la energía renovable, conforman la columna vertebral de la infraestructura energética mundial. La distribución de la energía depende de diversos métodos de transporte, como redes eléctricas, oleoductos y sistemas de transporte marítimo. Los avances en tecnologías de transporte sostenible y la transición hacia fuentes de energía más limpias y renovables, remodelan el panorama energético global y dan forma al futuro de la energía y el transporte a nivel mundial. En este contexto, emerge el uso de metanol como vector energético, tema central de esta tesis doctoral. Las últimas décadas son testigo de un aumento en el interés por el metanol, especialmente en el transporte marítimo, aplicaciones de pilas de combustible y su reciente papel en la producción de hidrógeno, destacando su relevancia como vector energético y portador de hidrógeno. El objetivo principal de esta tesis es explorar la viabilidad del e-metanol como vector energético en aplicaciones marítimas, analizando la viabilidad económica del metanol como vector de hidrógeno y estudiando experimentalmente el empleo de metanol para la generación de electricidad mediante Pilas de Combustible de Metanol Directo (DMFCs) y producción de hidrógeno con Celdas de Electrólisis de Metanol (MECs).

Esta tesis desarrolla un estudio tecnoeconómico comparando el uso de metanol e hidrógeno licuado como vectores energéticos, transportándolos por barco. Además, compara dos alternativas para obtener hidrógeno en destino: reformado de metanol y electrólisis de metanol. El estudio arroja luz sobre cuándo es económicamente rentable producir hidrógeno localmente o importarlo, y qué vector es preferible en cada caso.

Dentro del uso de metanol como vector energético, las DMFCs permiten generar electricidad a partir de metanol. Las condiciones operativas y la geometría del canal del ánodo influyen significativamente en el rendimiento de las DMFC. Por ello, esta tesis evalúa la influencia combinada en el comportamiento de este dispositivo, de la temperatura de la DMFC, la concentración de metanol y el flujo volumétrico de metanol introducido en la DMFC. Además, se diseñan una serie de geometrías de canales en serpentín de ánodo como un paso preliminar hacia la evaluación de su impacto en el comportamiento de una DMFC.

En cuanto al uso de metanol como vector de hidrógeno, en las últimas dos décadas ha aumentado el interés en la viabilidad de las MECs como sistemas de producción

de hidrógeno a partir de metanol. Esta tesis realiza por primera vez un estudio experimental sobre la influencia en una MEC de las condiciones operativas, análogo al realizado para DMFC, y los parámetros geométricos (open ratio, ancho de canal y profundidad de canal) del canal en serpentín del ánodo, aplicando la Metodología de Superficies de Respuesta. Además, incluye el estudio experimental de electrodos con metales no nobles, componentes importantes de las MECs, realizado durante la estancia en la Università degli Studi di Palermo, Italia.

A través de estos estudios, se resalta la importancia de las condiciones operativas en ambos dispositivos y la viabilidad y potencial del metanol como vector energético y de hidrógeno para aplicaciones marítimas. Se concluye que el e-metanol es una opción competitiva para ciertos flujos máscicos de hidrógeno transportado y al incorporar mejoras tecnológicas. Procesos clave que impactan en la viabilidad incluyen la licuefacción de hidrógeno, la síntesis de metanol y la electrólisis de metanol. En cuanto al uso de este metanol en DMFCs y MECs, la concentración óptima de metanol y la temperatura mejoran significativamente su comportamiento. Además, avances en los electrodos y en la geometría del campo de flujo permiten potenciar el proceso de electrólisis de metanol, contribuyendo al desarrollo de tecnologías sostenibles de producción de hidrógeno.

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Abbreviations and Acronyms

ABS	Acrylonitrile Butadiene Styrene
ANOVA	Analysis Of Variance
BP	Bipolar Plate
bTNTs	Black Titania Nanotubes
CCD	Central Composite Design
CCUS	CO ₂ capture, Utilization and Storage
CL	Catalyst Layer
CNG	Compressed Natural Gas
CSIC	Spanish National Research Council
CTS	Chitosan
CV	Cyclovoltammetry
DMFC	Direct Methanol Fuel Cell
DoE	Design of Experiments
EIS	Electrochemical Impedance Spectroscopy
FIO	Free In and Out
FRA	Frequency Response Analyser
GDL	Gas Diffusion Layer
GHG	Greenhouse Gas
GO	Graphene Oxide
HBSPE	Highly Branched Sulfonated Polyarylene Ether
HER	Hydrogen Evolution Reaction
HESC	Hydrogen Energy Supply Chain
HFO	Heavy Fuel Oil
HHV	Higher Heating Value

HPLC	High Performance Liquid Chromatography
ICE	Internal Combustion Engine
IEA	International Energy Agency
IGC Code	International Gas Carrier Code
IGF Code	Safety Code for Ships Using Gases or Other Low Flashpoint Fuels
IPHE	International Partnership for Hydrogen and Fuel Cells in Economy
IRENA	International Renewable Energy Agency
ISO	International Organization for Standardization
LC50	Lethal Concentration 50
LCOE	Levelized Cost Of Energy
LCOH	Levelized Cost Of Hydrogen
LH2	Liquefied Hydrogen
LHV	Lower Heating Value
LNG	Liquefied Natural Gas
LOHC	Liquid Organic Hydrogen Carrier
LR1	Long Range 1
MEA	Membrane Electrode Assembly
MEC	Methanol Electrolysis Cell
MGO	Marine Gas Oil
MeOH	Methanol
M-L	Mid-life renewal cost
MOR	Methanol Oxidation Reaction
MR	Membrane Reactor
NF	Nickel Foam
O&M	Operation and Maintenance
OCV	Open Circuit Voltage
OCP	Open Circuit Potential
OER	Oxygen Evolution Reaction

OPEX	Fixed Operational Expenditures
OR	Open Ratio
ORR	Oxygen Reduction Reaction
PAEK	Polyarylene Ether Ketone
PBI	Polybenzimidazole
PBR	Packed Bed Reactor
PEM	Proton Exchange Membrane
PFSA	Perfluorosulphonic acid
PID	Proportional Integral Derivative controller
PVA	Polyvinyl Alcohol
RFNBO	Renewable Fuel of Non-Biological Origin
RO	Reverse Osmosis
RSM	Response Surface Methodology
SEBS	Styrene Ethylene Butylene Styrene
SEM	Scanning Electron Microscope
SGO	Sulfonated Graphene Oxide
SOLAS	Safety Of Life At Sea
SPAES	Sulfonated Polyarylene Ether Sulfone
SPEEK	Sulfonated Polyether Ether Ketone
SPES	Sulfonated Polyether Sulfone
SPI	Sulfonated Polyimide
sPVdF	Sulfonated Polyvinylidene Fluoride
SS	Stainless Steel mesh
SWIP	Seawater Intake and Pre-treatment
TCI	Total Capital Investment
TiFelt	Titanium Felt Anodized
TiFoilNTs	Titanium Foil with Nanotubes
TRL	Technology Readiness Level

UPM	Universidad Politécnica de Madrid
USD	United States Dollars
VLCC	Very Large Crude Carrier

1. Introduction

1.1. Motivation

In the discussion about meeting the world energy needs, it is the opinion of most scientists and experts in the field of energy that the future of mankind depends on how humans will produce energy in future years (Owusu & Asumadu-Sarkodie, 2016). There is an urgent need to move from fossil energy dependent models to alternative energy systems to meet the environmental constraints affecting power generation systems. These alternative systems must be sustainable, reliable and decarbonised, driven by climate change and its environmental challenges.

With global population growth and accelerated industrialisation, the energy demand is rising every year (International Energy Agency, 2020). Until now, this trajectory has been linked to the use of fossil fuels, leading to environmental problems such as greenhouse gas emissions and climate change (L. Chen et al., 2022). This dependence on fossil fuels not only worsens the environmental situation, but also forces national economies to be at the mercy of geopolitics and resource scarcity. In addition, the finite nature of fossil fuels makes it necessary to explore alternative energy sources that can help to improve the current global situation.

Renewable energies produce clean energy, avoiding the emission of greenhouse gases and pollutant emissions. Moreover, their diversity, availability and abundance make it possible to use them in various parts of planet Earth (BP, 2021). The rise of these types of energy, such as solar, wind, hydro and geothermal, together with the support for these energies from the United Nations through actions such as the Paris Agreement (Rogelj et al., 2016), make them a possible viable alternative to the current fossil fuel-centred system. In addition, the European Union is pursuing a greener, more digital and resilient Europe, and is demonstrating this through the Recovery Plan for Europe (European Commission, 2021a). It also aims to reverse climate change and curb its effects, and has therefore presented the "EU Green Deal" (European Commission, 2021b). With this information, it can be thought that there is a consensus and a political horizon in the international community in favour of the decarbonisation of economies on a local and global scale, guiding a transition towards a new energy system possibly based on renewable energies (Gracia et al., 2018).

The development of technology related to these types of clean energy is crucial for combating climate change and limiting its effects on the environment (Dincer et al., 2013). For this reason, an in-depth analysis of the different alternatives available is needed, considering various renewable energy sources, energy vectors that help to transport the energy, geographical routes and appropriate distribution hubs (Khan et al., 2019).

The pressure on technicians to solve the problems related to the renewable energy supply grid and its integration with existing energy grid is increasing due to the urgency and need for alternative energy sources to fossil fuels (Klinge Jacobsen & Schröder, 2012). In the search for solutions for the integration of renewable energy, there is a need for adaptive energy models that can adapt to the stochastic and intermittent nature of renewable energy sources, such as wind and solar. (Ioannou et al., 2017). The integration of renewables into the current energy pull causes other power facilities, such as combined cycle plants, to operate under off-design conditions, producing inefficiencies related to frequent start-up and shut-down cycles (G. Zhao & Ravn Nielsen, 2017). This highlights the need to be able to store and transport the energy obtained from renewable energy sources.

Energy carriers, also called energy vectors, are substances capable of transferring energy, allowing energy to be transmitted from an external source, either primary or secondary, and stored and transported over time. This scheme enables this energy to be released when it is needed for consumption (IBT Connecting Energies GmbH, 2022). The decision to use either carrier depends on a number of factors, including energy density, cost, available technology, transportability, sustainability and government policies (Aba et al., 2024). Energy carriers such as coal or natural gas have been used for power generation for decades (Denny Ellerman, 1996), with oil playing a major role in the transport industry (Kulagin et al., 2020). Within this transport sector, solutions are currently being sought for the transmission and storage of energy from renewable energy sources, including the use of hydrogen and hydrogen-derived substances such as synthetic natural gas, formic acid or products derived from the Fischer-Tropsch process (Preuster et al., 2017).

Hydrogen is the most abundant substance in the universe, assuming around 75 % of total mass (Stolten et al., 2016). It was first artificially generated by Henry Cavendish in 1776. Nowadays, it can be produced using conventional technology, such as steam reforming with methane, coal gasification, partial oxidation of hydrocarbons, or cleaner methods such as water electrolysis using renewable

energy from sources as solar or wind power (International Energy Agency, 2019a). However, despite numerous investments in hydrogen technologies, national hydrogen plans, as well as strategies and roadmaps that have been made and planned in recent years (Incer-Valverde et al., 2023; World Energy Council, 2021), an 83 % of the hydrogen produced in 2022 was still based on the use of fossil fuels, mainly from steam methane reforming without employing CO₂ capture, utilization and storage technologies (CCUS) (International Energy Agency, 2023a).

Depending on the type of production process and the origin of the energy used to obtain it, hydrogen has carbon emissions related to this process, hence the importance of knowing the origin of the hydrogen used in each application. To solve this issue, a colour code has been proposed, where hydrogen is colour-coded to classify hydrogen according to its origin and associated carbon emissions (International Energy Agency, 2019a). However, this terminology has presented problems during its use, with a lack of standardisation and a need to reduce the number of colours to avoid misunderstandings (Incer-Valverde et al., 2023). In addition, this colour coding has proved impractical for use in contracts underpinning hydrogen technology investments, prompting the proposal for the use of an internationally agreed emissions accounting framework (International Energy Agency, 2023b). The International Energy Agency proposes to use the methodology presented by the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) to assess the greenhouse gas (GHG) emissions of each hydrogen production route and thus establish the basis for an international standard for calculating the GHG emissions intensity of hydrogen supply. In fact, the International Organization for Standardization (ISO) is defining the methodology for this implementation, including elements related to hydrogen transport. Besides, the Renewable Energy Directive (RED II) specifies that Renewable Fuels of Non-Biological Origin (RFNBOs) must present a GHG reduction of at least 70 % compared to a fossil fuel benchmark (equivalent to around 3.4 kgCO₂/kgH₂) (Erbach & Svensson, 2023; Motola et al., 2023).

Apart from the different ways of producing hydrogen, it is necessary to evaluate the ways of transporting this fuel, as it is to be used for renewable energy transmission. Hydrogen exporting countries can generate hydrogen from renewable energy at low cost, while importing countries do not enjoy this facility. The latter must bring this fuel from another country to benefit from a reduction in their dependence on fossil fuels and diversify their hydrogen trade with several countries, resulting in less energy dependence.

In year 2023 hydrogen transport was limited to a group of countries such as Belgium, France or the Netherlands that have a network of hydrogen pipelines connecting various industrial areas. There are also some pilot projects working on hydrogen transport by ship (International Energy Agency, 2023a).

Different technologies are being developed for the international transport of hydrogen by sea, including compressed and liquefied hydrogen (Mazloomi & Gomes, 2012). These solutions allow to increase the volumetric energy density of hydrogen, which is low compared to other fuels, as can be seen in Table 1.1 under different states. In this table *HHV* stands for Higher Heating Value.

Table 1.1: Specific energy and energy density of different energy carriers (Chase et al., 1986; Haynes et al., 2016; Lemmon et al., 2013; Moran et al., 2018) Comp. refers to the compressed gas state and liq. refers to the liquid state of the fuel.

Fuel	Density	Specific Energy	Energy Density
	ρ (kg/m ³)	<i>HHV</i> (MJ/kg)	<i>HHV</i> (MJ/m ³)
CH ₄ (298.15 K, 100 kPa) gas	0.65	55.5	36.1
CH ₄ (298.15 K, 27.5 MPa) comp.	201.15	55.5	11163.8
CH ₄ (111.51 K, 100 kPa) liq.	422.59	55.5	23453.7
H ₂ (298.15 K, 100 kPa) gas	0.08	141.8	11.3
H ₂ (298.15 K, 27.5 MPa) comp.	19.09	141.8	2707.0
H ₂ (20.22 K, 100 kPa) liq.	71.02	141.8	10070.6
CH ₃ OH (298.15 K, 100 kPa) liq.	786.33	22.7	17849.7
NH ₃ (298.15 K, 1 MPa) liq.	602.90	22.5	13565.3

Demonstration projects have been developed to test the possibility of transporting liquefied hydrogen by ship (Hydrogen Energy Supply Chain Project, 2024). The possibility of transporting other alternative fuels such as methanol or ammonia has also been demonstrated. The first international transport of 75 tonnes of hydrogen from the coast of Australia to Japan as part of the Hydrogen Energy Supply Chain (HESC) project took place in 2022 (Hydrogen Energy Supply Chain Project, 2024), with plans to increase the amount of hydrogen transported to 225 kt per year in the 2030s (New Energy and Industrial Technology Development

Organization (NEDO) et al., 2023). In 2019, 11 vessels were already in operation using methanol on board as fuel. These vessels carried methanol as cargo and were able to consume it as fuel in two-stroke engines (Ming et al., 2021). Ammonia was used for the first time in 2020 as bunker fuel on board a vessel operating between Saudi Arabia and Japan, carrying on board 40 t of NH_3 . During the years 2022 and 2023 several transports of ammonia have taken place and there are currently several planned transports of this fuel with transport operations of up to 50 kt of NH_3 . (International Energy Agency, 2023a).

Projects based on the transport of compressed or liquefied hydrogen have provided valuable information about this process. To transport this hydrogen from where it is produced to where it is consumed requires, among others, an infrastructure with compression or liquefaction plants, pipelines, pressurised trucks, storage, compressors, dispensers and contaminant detection equipment to ensure the quality of the hydrogen delivered (Office of Energy Efficiency & Renewable Energy U.S. Department of Energy, 2023). This infrastructure and its operation and maintenance, including transport and storage, entail a high cost and a series of energy losses in the process that must be considered (Aasadnia & Mehrpooya, 2018). One of the disadvantages of the process of transporting liquefied hydrogen by sea is the problem of the boil-off produced during the loading and unloading processes or storage on board of liquefied hydrogen (Rivard et al., 2019). This boil-off consists of the evaporation of liquid hydrogen when it is subjected to temperatures above its boiling point. This drawback can be mitigated by using this gaseous hydrogen as fuel for propulsion, as on board re-liquefaction would be an energy-consuming process (Cardella, Decker, & Klein, 2017). Another disadvantage of transporting liquefied hydrogen, apart from the economic and energy costs, would be the need for large storage infrastructures such as spherical tanks on board the ship, which imply a great loss of space on board, increasing the size and cost of the ship (Moon et al., 2005).

In this scenario, other alternative fuels emerge to be used as hydrogen carriers. These include chemical hydrogen carriers such as ammonia (NH_3) and liquid organic hydrogen carriers (LOHC) such as methanol (CH_3OH) (Ortiz-Cebolla et al., 2021). Other hydrogen transport options, such as the use of metal hydrides could be considered in the long term, but currently they need to be further developed for use in the maritime transport of large quantities of hydrogen (Drawer et al., 2024).

Unlike ammonia, which is a liquid at lower temperatures or higher pressures than ambient (239.56 K at 0.1 MPa or 298.15 K at 1.0 MPa), methanol is a liquid

chemical compound at ambient temperature and pressure, making it much easier and cheaper to handle and store than a gaseous fuel.

Methanol production has increased in recent years, reaching 98 Mt in 2019, with a production capacity of 150 Mt in 2020 (International Renewable Energy Agency & Methanol Institute, 2021). Around 65 % of its production comes from natural gas reforming, with coal gasification accounting for almost all the remaining 35 %. Only 0.2 % comes from renewable energy sources. The main producer and consumer country is China, with more than 50 % of methanol consumption, followed by other Asian countries, Europe, North America and South America. More than 60 % of methanol production is used to synthesise chemicals such as formaldehyde, acetic acid, ethylene and methyl methacrylate (International Renewable Energy Agency & Methanol Institute, 2021). These further processed products are used in the production of hundreds of manufactures of daily life, such as paints and plastics or building materials and car parts. Methanol is also used as a solvent, antifreeze or in water treatment plants. Its use as fuel, either directly or in the manufacture of other products such as biodiesel or dimethyl ether, has increased since the 2000s, currently accounting for about 31 % of its consumption. In addition, its direct use as fuel has seen a large increase in recent years, rising from 1 % in 2000 to more than 14 % in 2021.

The maritime industry has also had a growing interest in methanol in recent years. Currently, 25 ships operate with methanol as fuel. Although they represent only 0.04 % of gross tonnage, there are several companies interested in this type of vessels, and there are several vessels under shipyards' order books (Forsyth, 2023). In 2015 Stela Line, Waterfront Shipping and Wärtsilä collaborate to launch the first methanol-fuelled dual-fuel ferry into operation (Methanex, 2023), while the first tanker using a methanol-fuelled dual-fuel engine, the Lindanger, was built in 2016 (DNV, 2023). Table A.1 in Annex A lists some of the companies with ships using methanol as fuel under design, construction or in service since 2015 (Methanol Institute, 2023b). Based on the information provided in the Table A.1 in Annex A, the number of commercial projects related to each type of vessel is presented in Figure 1.1.

Due to the increasing interest in methanol as fuel in the maritime industry, seen through the increase of methanol-fuelled ships in recent years, either in operation or in the order book, and the qualities of methanol as fuel, which allow it to be stored as a liquid at ambient temperature and pressure thus facilitating its

transport, the use of methanol as an energy carrier or hydrogen carrier in the maritime sector should be considered.

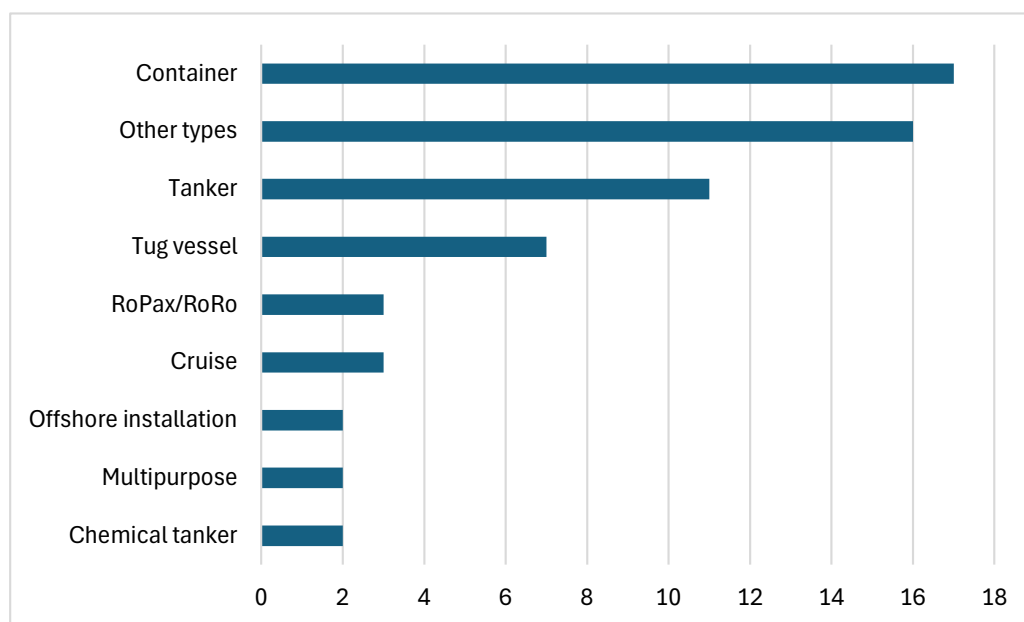


Figure 1.1: Number of current methanol-based propulsion ship commercial projects per ship type

The conversion of energy from renewable sources into fuels, in addition to enabling the transport of such energy, can consist of an environmentally friendly process (Pethaiah et al., 2020). The application of methanol as an energy vector is an energy transport option that has been little studied (American Bureau of Shipping, 2021) and which could be an effective way of transporting clean energy from its source to its place of consumption.

For the use of methanol as an energy carrier to be considered a carbon neutral process, this fuel must be obtained from biomass or renewable energy. Methanol obtained from residual materials derived from forestry and agriculture, biogas, sewage, municipal solid waste and black liquor generated in the pulp and paper industry, is called bio-methanol. If obtained from carbon dioxide and renewable hydrogen, it is called e-methanol. Bio-methanol and e-methanol sourced from renewable origins and processes exhibit identical chemical properties to fossil fuel-based methanol. However, they result in substantially lower GHG emissions throughout their entire life cycle. Moreover, the adoption of renewable methanol can diminish reliance on fossil energy imports and promote the growth of local economies. Several companies worldwide are presently engaged in the production

of bio-methanol and e-methanol (International Renewable Energy Agency & Methanol Institute, 2021).

Figure 1.2 outlines the process of obtaining, transporting by ship and using e-methanol as an energy vector and hydrogen carrier. The process begins by capturing or obtaining CO_2 and generating renewable hydrogen. Through a synthesis process with these two compounds, e-methanol is obtained, which is carbon neutral and easy to transport and store as methanol is liquid at room temperature and pressure. After the synthesis process, e-methanol can be transported by sea and can also be used as fuel on board. Once it reaches its destination, the e-methanol can be used as fuel in various devices to produce mechanical or electrical energy, or this e-methanol can be converted back into hydrogen. For this reason, it is considered interesting to study and develop devices that can obtain hydrogen or electrical energy from methanol in aqueous solution.

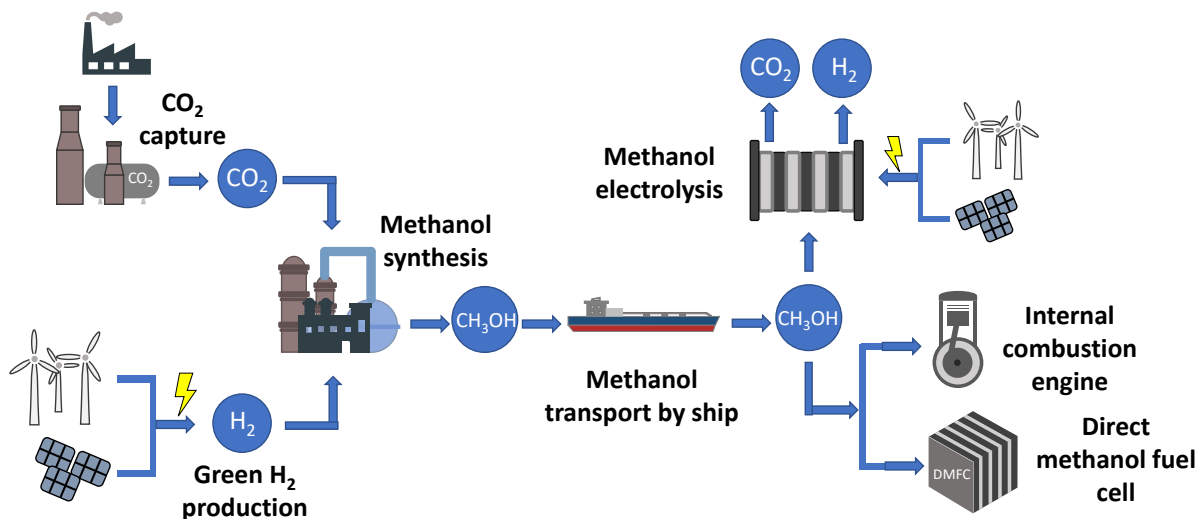


Figure 1.2: Diagram of the use of methanol as energy vector and hydrogen carrier

E-methanol can be used as fuel in different devices, such as internal combustion engines (ICEs) or direct methanol fuel cells (DMFCs). The efficiency of ICEs is limited by Carnot efficiency and these devices are currently commercially available with efficiencies of around 45 % (Ming et al., 2021). However, DMFCs are not limited by Carnot efficiency and although they are between 20-45 % efficient (Campanari & Guandalini, 2020; Glösen et al., 2020), they have potential for improvement in their design, the materials used and their operating conditions. In addition, due to its operational and design characteristics, the CO_2 emitted during the operation of a DMFC is separated from the gas stream of the other products of

the electrochemical reactions, making it easier to capture than the CO₂ emitted by an ICE. This highlights the interest of these devices in the chain of using methanol as an energy carrier, and the need to study this technology to improve its performance.

For the conversion of e-methanol into hydrogen there are different possibilities, among which steam reforming and methanol electrolysis are the most relevant (Basile & Dalena, 2017).

Methanol reforming is already a mature technology and available on a commercial scale. High temperatures are required for this process (250-350 °C) as well as purification steps of the gas stream leaving the reactor to obtain a hydrogen purity higher than 80 % (X. Li et al., 2023; Q. Liu et al., 2024), which increases the size of the installation and its cost.

The process of obtaining hydrogen using methanol electrolyzers is not a mature technology and has been of interest in recent years (Pethaiah et al., 2020). Methanol electrolysis is produced at low temperatures (30-80 °C) and a hydrogen purity of more than 99 % can be obtained without any purification process of the hydrogen produced (Sasikumar et al., 2008). The production of hydrogen by methanol electrolysis can be an important part of the logistics chain for the transport and storage of renewable hydrogen, and the technology has yet to mature to reach the commercial scale. It is therefore interesting to study this technology to advance its Technology Readiness Level (TRL).

To increase the power and efficiency of DMFCs and enable their use for electricity generation from methanol the designs of their components and their operating conditions can be improved. The same applies to methanol electrolyzers, which are currently not commercially available and which, if their hydrogen production capacity is increased, could be an interesting technology for large-scale production of hydrogen from methanol.

Specifically, improving DMFC performance requires studying the designs of the channels through which methanol flows inside the DMFC, as well as the operating conditions of these devices. Factors like open ratio, channel width and depth affect fluid flow, mass transfer and CO₂ bubble evolution in a DMFC. While methanol flow rate, concentration and DMFC temperature also impact performance, so identifying the influence of these parameters is crucial for improving DMFC operation.

A challenge in methanol electrolysis lies in improving performance through effective channel design and operational adjustments, as in DMFC. This involves selecting suitable configurations for the flow field to ensure uniform methanol distribution and efficient CO₂ bubble removal. Operational parameters like methanol concentration and electrolyser temperature significantly influence performance. In fact, no studies have been found on the influence of the serpentine flow field geometry or the volumetric flow rate of methanol supplied to the methanol electrolyser on the behaviour of this device. Therefore, further research is needed to assess the impact of methanol flow rate, combined temperature, concentration and flow rate effects, and the influence of anode channel geometries on methanol electrolyser performance.

1.2. Objectives

The general objective of this doctoral thesis is to study the use of e-methanol as an energy vector for marine applications, focusing on the study of hydrogen production by means of a methanol electrolyser and the production of electrical energy by means of a DMFC, both based on proton exchange membranes. Specifically, this thesis investigates the circumstances under which methanol can be economically viable as a hydrogen vector or energy carrier. Additionally, it assesses the combined influence of various geometric parameters of the serpentine flow field in a methanol electrolyser, as well as the impact of operating conditions on DMFCs and methanol electrolyzers.

To achieve this general objective the following specific objectives are set:

1. Analyse the processes necessary to transport hydrogen obtained from renewable energy by sea to its place of consumption using methanol as a vector and investigate under what conditions this process can be cheaper than the direct transport of hydrogen.
2. Design and build a test bench to study the behaviour of a methanol electrolyser and a DMFC.
3. To identify the most significant parameters influencing the performance of a DMFC by conducting an experimental study of a DMFC single cell designed and built as part of this thesis.
4. To identify the influence of the operating conditions and anode channel geometry parameters of a methanol electrolyser by conducting an

experimental study of methanol electrolyser single cells designed and built in this thesis.

1.3. Structure of the thesis

This doctoral thesis is divided into five chapters, briefly described as follows:

- Chapter 1: Introduction. This chapter provides an overview of the context of the topics addressed in this thesis, defines specific objectives, and outlines the thesis structure. It covers the need for energy transportation from renewable sources, the use of alternative fuels such as hydrogen or methanol for this purpose, the utilization of methanol as an energy vector, and its application in fuel cells and methanol electrolysers.
- Chapter 2: State of the art. This chapter discusses the current state of energy transportation by ships, as well as the characteristics of DMFCs and their components, and the operating characteristics and components of methanol electrolysers.
- Chapter 3: Materials and methods. This chapter describes the procedures and materials, including test benches, used to obtain the results of this thesis.
- Chapter 4: Results and discussion. Here, the results of the technoeconomic analysis of using methanol as a hydrogen vector and energy vector are presented and discussed, along with the experimental results of the DMFC and methanol electrolyser under several working conditions.
- Chapter 5: Conclusions and future work. The thesis concludes by summarizing the main findings related to the initial objectives and discussing potential future research directions arising from these conclusions.

2. State of the art

Methanol, also known as methyl alcohol (CH_3OH), is a chemical compound consisting of methyl and hydroxyl groups. It has a simple chemical structure and can be rapidly synthesised from a variety of carbon-containing materials (Díaz-de-Baldasano et al., 2014). In small quantities and at low concentrations, methanol is present in the environment. It is liquid at ambient temperature and pressure, making it suitable for transport, storage and energy use. However, methanol energy density is lower than that of traditional fuels used in the transport sector. For example, compared to marine gas oil (MGO), methanol has an energy density of 17.8 GJ/m^3 , while MGO has 36.6 GJ/m^3 (Methanol Institute, 2023a). This implies that, on a methanol-powered vessel, fuel and storage tanks will take up approximately 2 times more room space than on a vessel using MGO. Despite this disadvantage, methanol can be stored in conventional fuel tanks and even in ballast tanks on board a ship, which differentiates it from other fuels such as liquefied natural gas (LNG) and hydrogen (H_2) that require cryogenic storage. In addition, it has a higher energy density than some other alternative fuels, such as LNG, ammonia and hydrogen (see Table 1.1 in the Introduction Section), especially with regard to the size of storage tanks, secondary barriers and cofferdams.

Methanol can be produced from a variety of sources, including biomass, biomethane, renewable hydrogen and CO_2 , as well as fossil sources such as natural gas and coal. The carbon footprint of methanol varies depending on the feedstock and the production route used, as this indicator can be calculated taking into account all the GHG emissions caused directly by the methanol supply chain and by energy and commodities used within this chain. Currently, most methanol is produced from natural gas, where natural gas is used both as a feedstock and as a process fuel. Modern facilities can produce methanol with an estimated carbon footprint of approximately $110 \text{ kgCO}_2\text{eq/GJ}$ ($110 \text{ gCO}_2\text{eq/MJ}$) (Methanol Institute, 2023a). In the case of biomethanol, it can be produced from natural materials and also using cheaper, non-food feedstocks such as biomass.

Methanol synthesis is a well-established process, with an annual production of approximately 100 Mt, and industrial experience in handling, storage and transport. Besides, there are several synthesis routes to produce methanol. Conventional synthesis process involves the use of synthesis gas, the so-called syngas. The syngas mainly contains carbon monoxide, carbon dioxide and

hydrogen. Generally methanol is obtained using syngas produced from natural gas by steam reforming, partial oxidation or auto-thermal reforming (Araya et al., 2020). In addition to natural gas, other alternative sources include coal or coke oven gas on the fossil side, and on the renewable side, syngas produced by biomass gasification. For large-scale renewable methanol production, the option of electricity-based methanol, produced by means of hydrogen obtained through the electrolysis of water and carbon dioxide, is widely discussed in the literature (Bos et al., 2020; Marlin et al., 2018; Meunier et al., 2020; Schorn et al., 2021; Y. Sun et al., 2019). The main reactions that take place in the methanol synthesis process from syngas are expressed in Eqs. 2.1-2.3 (Araya et al., 2020; Lawes et al., 2023).



Production from renewable sources, such as biomethane, solid biomass, municipal solid waste and renewable energy, has a low carbon footprint. Most of these pathways achieve emissions of 10-40 kgCO₂eq/GJ (10-40 gCO₂eq/MJ) (Methanol Institute, 2023a). Once emissions from well to propeller are considered, bio-methanol and renewable methanol are among the marine fuels with the lowest emissions.

According to the International Renewable Energy Agency (IRENA), by 2050, e-methanol and biomethanol, *green* methanol, are expected to account for approximately 80 % of total production, which could reach 500 Mt per year (International Renewable Energy Agency & Methanol Institute, 2021). Whether produced from diverse feedstocks, the methanol molecule will have the same physical properties, facilitating the introduction of this fuel over time, as more low-carbon and net carbon-neutral methanol enters the global supply chain. Regarding e-methanol production, it is estimated that by 2050 it could reach 250 Mt per year. This level of e-methanol production would require around 350 Mt of CO₂ and 48 Mt of H₂.

In terms of its use as an industrial and energy feedstock, methanol is traded today as a chemical commodity and is a building block for a wide range of useful materials, including fuels, adhesives, plastics, solvents and antifreeze (Araya et al., 2020). In addition, it is used as an industrial feedstock, for thermal and electrical power generation, as fuel for mobility and considered as a member of the LOHC family.

Methanol itself can be used in the transport and chemical sectors and is receiving particular attention among researchers as a viable marine fuel for the future. Due to its vast range of possible applications, simple handling and potential to leverage existing infrastructure, the idea of a "methanol economy" was already considered and proposed in 2006 (Olah, 2005).

As a globally traded chemical commodity, the expected future demand for renewable methanol for the chemical sector alone is substantial. Within the transport sector, methanol can generally be used as a blend or, in its pure form, in internal combustion engines. In fact, ship operators with methanol fleets could purchase methanol relatively easily, with methanol available in more than 120 ports worldwide and currently being transported globally (Methanol Institute, 2023a).

In terms of the logistics and infrastructure required for the supply of methanol as a marine fuel, the development of different supply methods, such as bunkering by truck, by barge and at port terminals, is noteworthy. These methods offer flexibility and adaptability to meet the bunkering needs of ships in different locations and operational situations. In particular, methanol bunkering by truck has proven to be a viable and widely used option in a number of ports (Ellis et al., 2021). On the other hand, barge bunkering allows for both in-port and offshore methanol bunkering, which provides greater autonomy and flexibility to vessels in terms of route planning and operations. In addition, port terminal bunkering offers a long-term solution for methanol supply, especially for vessels operating on fixed, high-capacity routes. This can facilitate the integration of methanol bunkering infrastructure in ports and encourage the adoption of methanol in shipping worldwide.

In terms of fire hazards and prevention, it is important to note that methanol has a low flash point 284 K (11 °C). This means that 284 K is the lowest temperature at which methanol vapours are released in sufficient quantities to form a flammable vapour-air mixture. In addition, the flammability range of methanol in dry air is between 6.7 % and 36.5 %, which can create an explosive or flammable environment (Andersson & Márquez Salazar, 2015). The flammability characteristics and the fire and explosion hazards of this fuel are given in Table 2.1. Methanol burns at a relatively low temperature and its flame is almost invisible during the day. In addition, the molar mass of methanol (32 kg/kmol) is slightly higher than that of air (28 kg/kmol), so methanol vapour tends to accumulate near the ground. Methanol does not dissipate in enclosed, unventilated

areas. These characteristics require specific safety measures to prevent the formation of methanol vapour and the installation of adequate ventilation, leak detection, heat detection and fire extinguishing equipment.

Table 2.1: Properties of Marine Diesel Oil (MDO), Liquefied Natural Gas (LNG) and methanol (CH_3OH) (Andersson & Márquez Salazar, 2015; Zamboni et al., 2024)

Fuel	MDO	LNG	CH_3OH
Density (kg/m^3)	830-880 ^a	423 ^b	786 ^a
Boiling Point (101.3 kPa) (K)	436-672	112	337
Boiling Point (101.3 kPa) ($^{\circ}\text{C}$)	163-399	-161	64
Specific energy (HHV) (MJ/kg)	45.5	55.5	22.7
Energy density (HHV) (MJ/m^3)	37765-40040 ^a	23454 ^b	17850 ^a
Auto-ignition temperature (K)	530	853	737
Auto-ignition temperature ($^{\circ}\text{C}$)	257	580	464
Flash point (K)	325-369	137	284
Flash point ($^{\circ}\text{C}$)	52-96	-136	11
Lower flammability limit (% vol in air)	1.0	4.2	6.7
Higher flammability limit (% vol in air)	5.0	16.0	36.5

^a Temperature and pressure of 298.15 K and 100 kPa

^b Temperature and pressure of 111.51 K and 100 kPa

In terms of toxicity, methanol is metabolised by humans to formic acid, which makes it toxic if ingested, absorbed through the skin or inhaled in high concentrations. Exposure to methanol can cause blindness, kidney failure and, if the dose is high enough or exposure is prolonged, death. Ingesting 10 ml of pure methanol can cause critical optic nerve damage and the average lethal dose, when ingested, is approximately 100 ml (Methanol Institute, 2023a). Methanol poisoning can be counteracted with an antidote such as fomepizole or ethanol. Haemodialysis or hemodiafiltration may be indicated to remove methanol and its toxic by-products from the bloodstream.

From an environmental contamination standpoint, methanol is relatively benign compared to other fuels because it is completely water miscible and biodegradable.

As a result, a methanol spill would likely have limited impacts on marine life unless it is delivered in very high concentrations (Methanol Institute, 2023a). In addition, methanol is readily broken down by microorganisms into CO₂ and water at concentrations of less than 3 kg/m³ (3000 mg/l). However, methanol is toxic to aquatic organisms at concentrations above 1 kg/m³ (1000 mg/l) and especially at 10 kg/m³ (10000 mg/l) and above. The toxicity of a chemical is often presented as the Lethal Concentration 50 (LC50), which is the dose that is lethal to 50 % of the organisms in a given population. In a water body, the LC50 of methanol for fish is 15.4 kg/m³ (15400 mg/l) (European Chemical Agency, 2023), compared to only 7.9 · 10⁻² kg/m³ (79 mg/l) for Heavy Fuel Oil (HFO) (Shell Global, 2023). This implies that it would take 200 times more methanol than HFO to kill the same number of aquatic species.

Due to the flammability and toxicity characteristics presented above, the handling of pure methanol at filling stations is considerably more complex and may come with the exchange of certain facilities and safety measures. In addition, methanol is corrosive to aluminium and titanium alloys, which are commonly used in fuel systems for natural gas and distillate fuels (Methanol Institute, 2023a). To solve this problem, corrosion-inhibiting additives or coatings can be applied, provided they are not susceptible to damage by acidic impurities. Alternatively, or additionally, non-metallic materials such as nylon, neoprene or non-butyl rubber can be used in fuel tanks and piping.

As a liquid fuel at ambient temperature and pressure, the onboard methanol supply and combustion system is designed so that crew members do not come into direct contact with methanol. However, crews must be adequately trained in methanol handling and know how to deal safely with a methanol leak or spill. The IMO's Safety Code for Ships Using Gases or Other Low Flashpoint Fuels (IGF Code), adopted in November 2020, provides mandatory guidelines and criteria to minimise risks to crew members on board methanol-fuelled ships (International Maritime Organization, 2016).

2.1. Energy transport by ship

This subsection presents the evolution in the use of coal, oil, natural gas, hydrogen and methanol as energy carriers through their transport by ship, including the characteristics of specialisation and type of ships used for its transport. It shows the importance of the transport of energy by sea in chemical form and its implication on the socio-economic status worldwide.

Before the 17th century, ships were already being used to transport coal, being one of the pillars of the growth of the English Merchant Navy in this century (Hatcher, 1993). During the 18th century there was a rapid growth in productivity in the transport of coal by sailing ships, although this was not only due to increased ship life or innovation in ship design, but also to improvements in dock and harbour systems and intermodal transport including railways (Solar et al., 2023). These changes allowed ships carrying coal to make a greater number of voyages per year, have smaller crews and carry more coal per tonne of ship. These changes and their implications for the coal trade made shipping a major contributor to the growth of British trade. In the late 18th century Englishman Benjamin Outram invented the first container ship for transporting coal. The logistics of transporting the coal from the mine to the ship relied on animal traction, see Figure 2.1, as did the process of loading and unloading the coal (MC Containers, 2024).

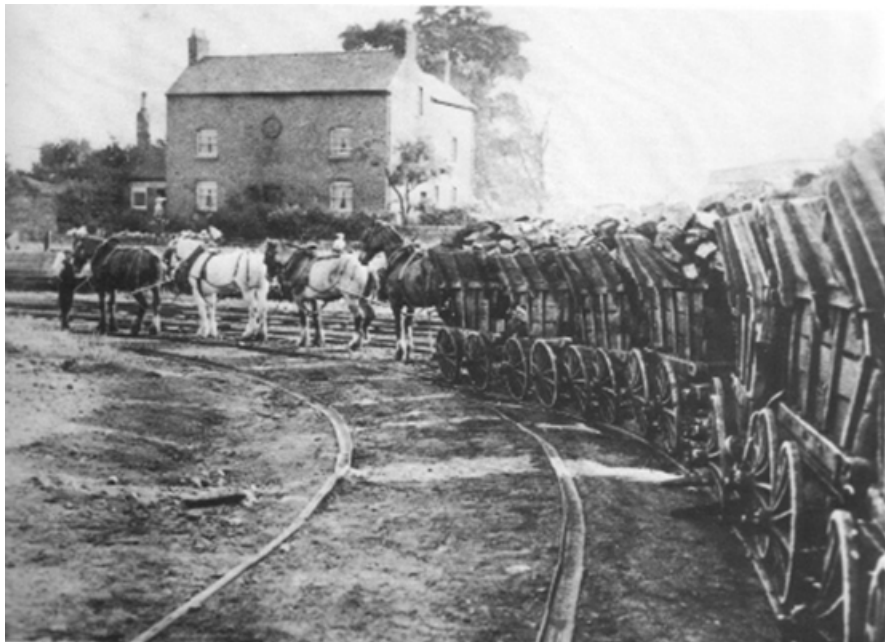


Figure 2.1: Image of the transport of coal from the mines to the ship using horses. Image "Illustrated History of the Railroads" via Wikimedia Commons (Wikimedia Commons, 2023)

From the 1860s steamships displaced sailing ships in the coal trade and by 1874 steamships were carrying almost all the coal that reached London by sea (Solar et al., 2023). Between the late 19th and early 20th centuries the UK had the largest production and export of coal, both as a cargo and as fuel (Castillo Hidalgo & Honorato, 2023). British shipowners were the first to employ steamships for long

sea voyages and their companies enabled British coal to be shipped to distant ports at competitive selling prices, even cheaper than prices in other producing countries (Fletcher, 1975). The world economy at the end of the 19th century was based on the use of coal and the reduction of transport costs both by sea and land. Without this fuel, neither the railways nor the steamship would have made such technological advances (Buchet & Rodger, 2017). In the 1880s and 1890s advanced new-built large iron and steel square-rigged ships, similar to the vessel shown in Figure 2.2, were used to transport coal to the American coasts in the Pacific, while traditional sailing ships continued to be used to transport coal in the Baltic until the end of the century, albeit with a smaller presence (Buchet & Rodger, 2017). At this time, liner shipping services and later the tramp sector (ships without a fixed commercial route, without fixed schedules or ports) adopted steam technology as propulsion for ships, most of which were built in British shipyards and were characterised by relatively low propulsive power and medium capacity and size, although they were built in various types and could carry different cargoes apart from coal, such as ore or grain.



Figure 2.2: Iron square-rigged ship Herzogin Cecilie. Source: State Library of Victoria (Wikimedia Commons, 2019)

Only on certain short, usually coastal, sea routes steam colliers were used, see Figure 2.3, ships whose use on these routes was more economical and which specialised in the transport of coal (Buchet & Rodger, 2017). A reduction in the consumption of coal as a marine fuel coincides with the end of the Great War and the beginning of the use of oil as fuel for this sector. This was due, among other reasons, to the possible reduction in the number of ships' crews using this new fuel, a situation necessitated by the shortage of manpower caused by the war (Zimmermann, 1921). Moreover, the use of this new fuel allowed the United States to counterbalance the United Kingdom primacy in fuel stations by promoting the use of oil.

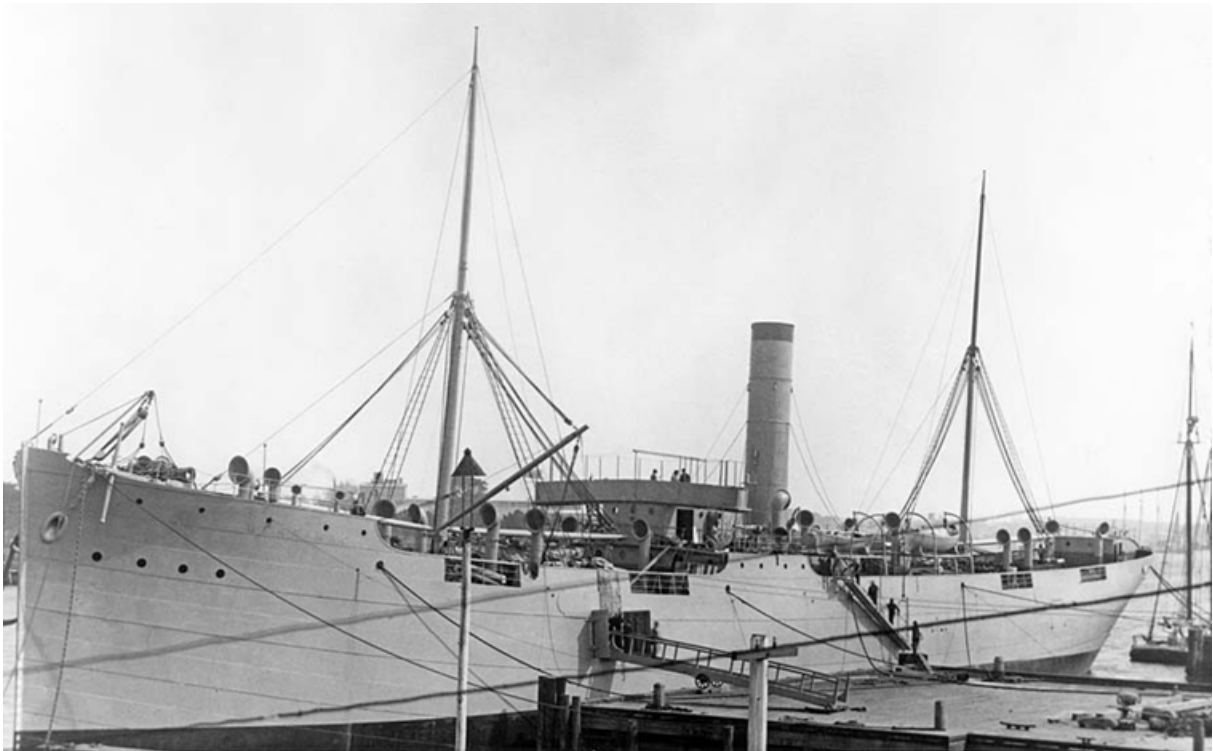


Figure 2.3: Image of collier ship USS Merrimac. Source: Naval History & Heritage Command Collection (Naval History and Heritage Command, 2018)

Although steam shipping recovered its previous pace after the end of the war and coal supplies were restored to normal, eventually, the economic crisis of the 1930s and the unstoppable competition from liquid fuel caused this phenomenon to languish after World War II, almost disappearing during the 1950s (Fletcher, 1975). In 1960, Europe accounted for half of the international coal trade. Russia was the main supplier to Eastern Europe and Germany to Western Europe. With the reduction of coal exports, when it seemed that oil would lead the energy

transport sector, becoming at this time the most used fuel in the world, oil price increased in 1973. Due to this increase in oil prices among other factors, 1979 encouraged the conversion of power stations to coal and the generation of new coal-fired power stations. Such was the increase in demand of coal that by 2000, with exports accounting for a small share of total coal production, 85 % of international trade in coal was seaborne (Buchet & Rodger, 2017). Although in 2020 fuel trade by ship was dominated by the oil transport, coal was still among the most transported fuels by sea (International Chamber of Shipping, 2022).

The evolution in the use of coal as fuel at a global scale, together with the evolution in the characteristics, propulsion systems, specialisation and type of ships used for its transport, highlights the importance of the transport of chemical energy from a fuel by sea and its implication at a global level in terms of policy, technology and impact on the transport system itself.

As mentioned above, another fuel that has had an implication for energy transport technology by sea and its global consumption is oil. The use of this fuel began to spread in the 20th century, becoming a strategic resource militarily, politically and economically (Castillo Hidalgo & Honorato, 2023). In 1859 Colonel Edwin Drake struck oil at Titusville, beginning drilling in Pennsylvania for crude oil. Initially, this fuel was transported in barrels, and then in tin cases (Buchet & Rodger, 2017). These barrels were transported in break-bulk boats and barges.

The first major transport of oil by this means took place in 1861, when the brigantine Elizabeth Watts transported 1329 barrels (about 182000 kg) of crude oil from Philadelphia to the United Kingdom, see Figure 2.4. However, the transport of oil in barrels involved a series of problems, including long loading and offloading times, the high cost and weight of the barrels, which accounted for 20 % of the total weight of the barrel loaded with oil, and safety problems during cargo handling (Tolf, 1976). To solve these problems, work began on solutions for transporting crude oil in bulk, evolving into the Zoroaster steamship shown in Figure 2.5.



Figure 2.4: Image of Port of Philadelphia 1861, more than 1300 barrels were loaded aboard the Elizabeth Watts ship. Source: American Oil & Gas Historical Society (Wikimedia Commons, 2011)

Zoroaster steamship was the first oil tanker, built in 1878, with a steel hull and iron cargo holds to carry the crude oil. This ship, built in Sweden, was able to navigate the Baltic Sea and rivers leading to the Volga River to reach the Caspian Sea (Lichtman & M.D., 2017).

The considered precursor of the current tankers, the Glückauf (Devanney & Beach, 2006), was built in 1886 and had a waterline bulkhead, a cargo capacity of 2300 dwt (deadweight tonnes) and a service speed of 10 kn (5.14 m/s, 18.52 km/h).

Another milestone in the transport of energy in chemical form using oil as fuel was the ship Murex, which in 1892 became the first tanker to pass through the Suez Canal (Shell Global, 2024).

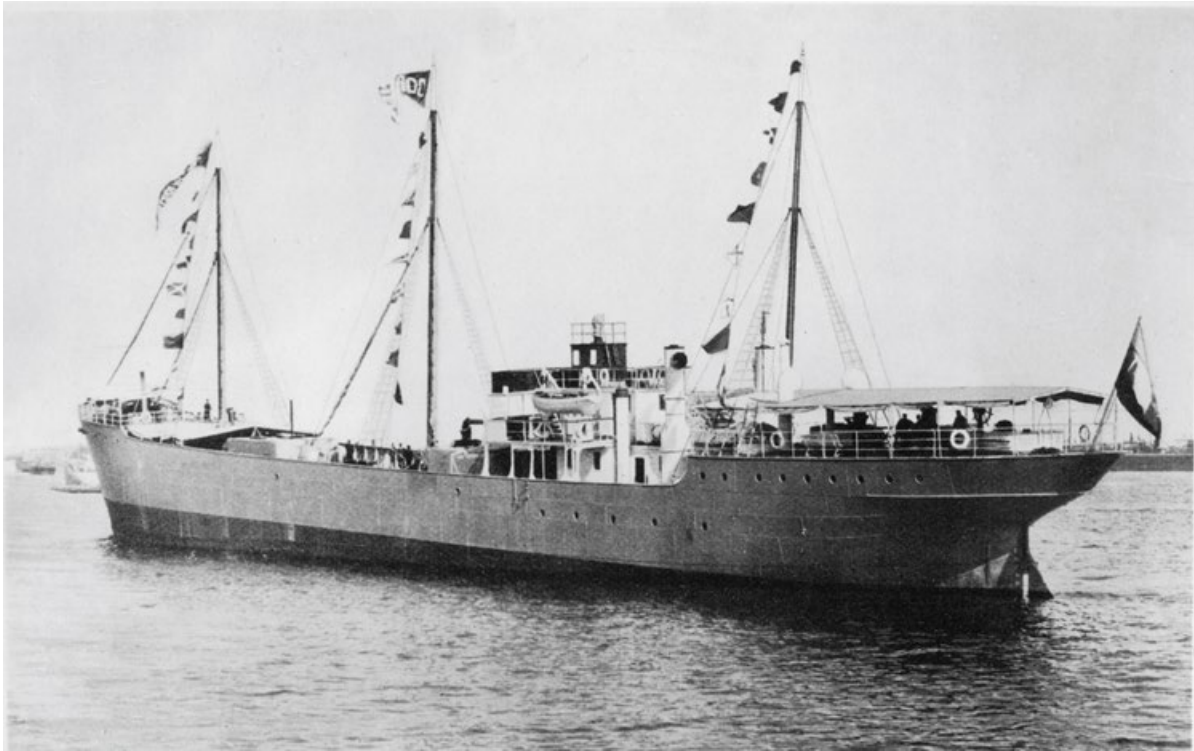


Figure 2.5: Zoroaster steamship oil tanker. Source: Swedish National Museum of Science and Technology (Okänd, 2019)

From the 1890s until 1930, North America and Russia/USSR had the largest oil production. From 1929 onwards, the quantity of oil transported began to increase in relation to other cargoes, with oil accounting for 42.9 % of the total tonnes of cargo transported worldwide in 1950 (Buchet & Rodger, 2017). This evolution in the transport and consumption of oil was reflected in advances in tanker design. In 1903, the ships Vandal and Sarmat were built, which were already diesel-powered (Buchet & Rodger, 2017). In 1908, the Isherwood system was introduced, which was notable for incorporating a longitudinal structure design instead of the conventional transverse structure. This development allowed the construction of longer ships, with the Paul Paix tanker, see Figure 2.6, being the first to be built using the design proposed in this system (Science Museum Group, 2024). In addition, from 1916 to 1921, 316 tankers totalling 3.2 Mdwat were built in American shipyards, and in 1931 the tanker fleet reached 9 Mdwat.

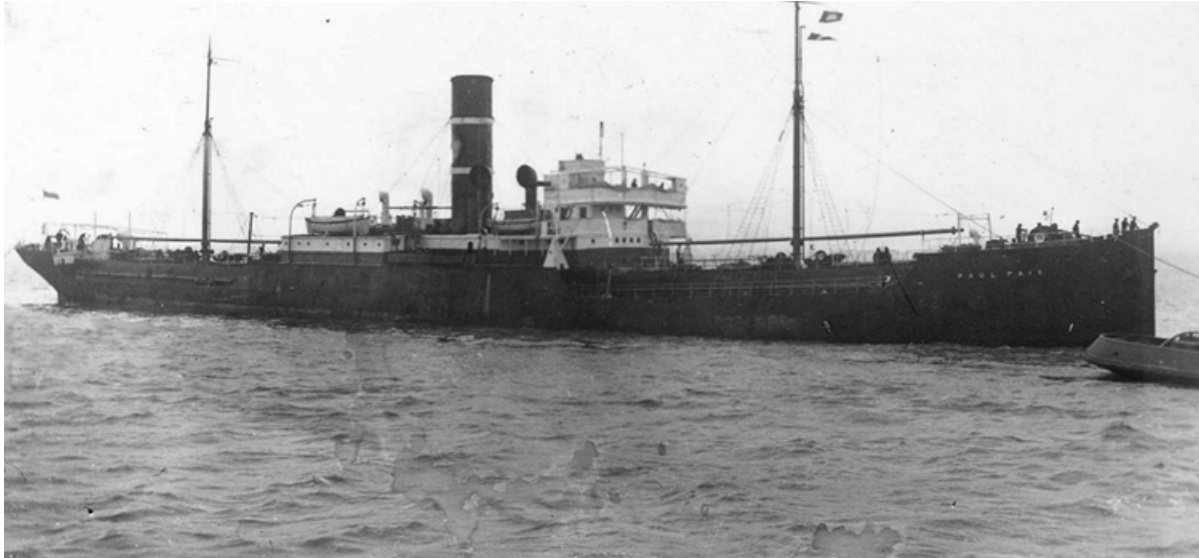


Figure 2.6: Image of Paul Paix tanker. Image courtesy of Harold Appleyard. Used with permission from Tees Built Ships (Tees Built Ships, 2024)

The transport of oil, its overall consumption and the large size of the fleet underline the importance of this fuel in these decades, with political and economic implications. However, this transport also entailed several accidents of potential risk to crews, coastlines and the environment. This led to the search for solutions, and in 1933 tank inert gas systems were incorporated in all Sun Oil tankers (Devanney, 2010).

Until 1956 the size of tankers navigating from Europe to Middle East Countries had been designed with the Suez Canal geometrical constraints in consideration. However, its closure in that year, forcing ships to pass through the Cape of Good Hope, led shipowners to look for vessels with larger cargo capacity. This led to an increase in size within a few years, reaching 100000 dwt in 1958 with the tanker Universe Apollo. The further closure of the Suez Canal between 1967 and 1975 led to a further increase in the size of these vessels, which became known as Very Large Crude Carriers (VLCC) with cargo capacities of over 200000 dwt. Since then, advances have been made in the safety of these vessels making them less prone to oil spills, with additions to its structure such as the double hull, thus reducing the likelihood of cargo spillage due to collision.

Along with these changes in tanker size and design, in 1959 the Methane Pioneer with a cargo capacity of 5000 m³ became the first ship to carry liquefied natural gas (LNG); and the Methane Princess, with a cargo capacity of 27400 m³, started transporting this fuel from Algeria to Canvey Island in UK in 1964 (Ship

Technology, 2014). The delay of this type of fuel and its transport is partly due to technical reasons, since this fuel at ambient temperature and pressure has a density of 0.65 kg/m^3 , which can be increased to 201 kg/m^3 if the storage pressure is increased to 27.5 MPa at 298.15 K or to 423 kg/m^3 if the temperature is lowered to 111.5 K at a pressure of 100 kPa, the latter being the most widely used option at present. Keeping this fuel cold and storing it on board required solving many technical problems that have been resolved over the past decades. Some of these are boil-off management and the design and materials of storage tanks to maintain the conditions for storing liquefied natural gas.

Boil-off consists of a process whereby part of the liquefied gas, on receiving thermal energy from the environment, becomes gaseous, producing an undesired increase in pressure in the storage tanks. This pressure can be maintained by releasing part of this generated gas, for example by using it as onboard fuel or by a liquefaction process.

Regarding the structure and construction of LNG storage tanks on board, the International Gas Carrier Code (IGC Code) sets out the regulations to be followed for gas tankers built from 1986 onwards (International Maritime Organization, 2019). Among the most important characteristics are the construction of double skin vessels, with aluminium or nickel tanks to avoid the transition from ductile to brittle due to low temperatures, and with adequate thermal insulation to protect the mild steel outer hull and to reduce the loss of cargo due to boil-off. The construction of the tanks is also taken into account, with a distinction being made between independent or free-standing tanks and membrane tanks. The construction and operation of this type of vessel requires a series of very strict safety precautions to be followed (Buchet & Rodger, 2017).

Since the voyage of the Methane Princess in 1964 the size of the vessels has been increasing. In the 1960s the vessels SCF Polar and SCF Arctic came into operation with a cargo capacity of 71500 m^3 . In the 1970s the vessels Gemini and Aquarius, see Figure 2.7, were built, which used the Moss spherical tank system and had a cargo capacity of 126300 m^3 and a service speed of 20.4 kn (10.5 m/s, 37.78 km/h) (Noble, 2009).



Figure 2.7: Model of Aquarius LNG carrier. Source: National Maritime Museum, Greenwich, London (Royal Museums Greenwich, 2024a). Licensed under CC BY-NC-SA 4.0 DEED

The tanks on these ships allowed for increased cargo capacity and consisted of double-walled spherical tanks with an empty space between walls, allowing for leak detection and improved safety on board (Mokhatab et al., 2014). However, such tanks, due to their large dimensions, are expensive and difficult to build requiring large and specialised facilities.

The 1980s brought advances in power generation systems for these vessels, with marine engine companies developing engines capable of consuming natural gas and fuel oil, which made it possible to use the boil-off produced on board for ship propulsion (Bakas, 2015). These were the engines that enabled the breakthrough to the first dual fuel engine introduced by Wärtsilä in 1995 (Wärtsilä, 2024a).

In the late 20th and early 21st century, advances were made in the construction and design of tanks for storage of liquefied natural gas on board, see Figure 2.8, with the patenting of membrane tanks that are cheaper and easier to build than spherical tanks (Dhellemmes & Jean, 1999).



Figure 2.8: Model of Methane Heather Sally LNG carrier. Source: National Maritime Museum, Greenwich, London (Royal Museums Greenwich, 2024b). Licensed under CC BY-NC-SA 4.0 DEED

The year 2005 saw advances in LNG carrier design with the Q-Flex and Q-Max series, which incorporated improvements to the propulsion system with twin engines and shafts, improving propulsion safety and reducing the environmental footprint, as well as twin rudders to ensure safety during navigation and manoeuvrability (Noble, 2009). In addition, these vessels have cargo reliquefaction plants on board, as well as slow speed diesel engines, which are more efficient than the steam turbines usually employed for LNG carriers' propulsion. These vessels have a cargo capacity of between 210000 and 266000 m³.

In 2023 there were 709 LNG carriers in the water and another 373 on the orderbook, reaching in November 2023 a total cargo capacity of 110 Mm³ (Jallal, 2023).

All the fuels mentioned above as energy carriers (coal, oil and natural gas) are fossil fuels. The political dependence on these types of fuels and the greenhouse gas emissions and pollutant emissions associated with their transport and consumption make governments look for renewable energy sources to cover at least part of their energy needs. To achieve the goals of the Paris Agreement and reduce greenhouse gas emissions, nations are also looking for solutions to reduce energy consumption (mainly by increasing the efficiency of processes and machinery), reduce the consumption of coal, oil and natural gas, achieve rapid electrification of various sectors of the global economy and achieve a growth in the use of lower-carbon fuels such as hydrogen. These changes have a direct implication for the maritime sector, as 36 % of the current trade of shipping sector is transporting energy products, such as coal, oil, natural gas and biomass. In the near future, ships could be transporting different fuels, in different quantities, between different countries, which implies a series of challenges and opportunities (International Chamber of Shipping, 2022).

To reduce global fossil fuel consumption for energy applications by increasing the use of energy from renewable sources, energy storage and transport systems are also needed, because renewable energy sources are usually not located close to where the energy is consumed. One of the possibilities to achieve their transport and storage is the transformation of electrical energy from renewable sources into chemical energy of a fuel. Among the most studied options for using a fuel as a renewable energy carrier is hydrogen. Like natural gas, hydrogen can be transported by ship as a compressed gas or by lowering its temperature, transporting it as liquefied hydrogen at 20 K and 0.1 MPa (d'Amore-Domenech et al., 2023).

The technology related to hydrogen transport by ship is very recent. In 2020, the construction of the first liquefied hydrogen transport vessel was completed, the Suiso Frontier, with a cargo capacity of 1250 m³ of liquefied hydrogen at a temperature of 20 K and a pressure of 100 kPa. This vessel completed its maiden voyage in February 2022, departing from Australia and arriving off the coast of Japan (Hydrogen Council, 2022). This vessel has a cargo tank system with a vacuum-insulated double-wall structure and a high thermal insulation capacity.



Figure 2.9: Illustration of H2Neo carrier design. Used with permission from Provaris Energy Ltd (Provaris Energy Ltd, 2024)

Another way of transporting hydrogen by ship is as compressed gas, and this is the system on which the company Provaris is basing its designs. This company is developing compressed hydrogen transport ships such as the H2Neo, see Figure 2.9, with a cargo capacity of 430 t and the H2Max designed to transport 2000 t of H₂, both designs with a pressure of 25 MPa and ambient temperature. They are also working on the H2Leo storage barge design with a capacity of between 300 and 600 t at 25 MPa and ambient temperature (Provaris Energy Ltd, 2024).

The use of other fuels that can be used as energy carriers for renewable energy sources is now also being considered, one of the options being methanol (Harahap et al., 2023). Methanol transport by ship and its bunkering are possible and can be carried out, after modifications, with existing infrastructure in a cost-effective

manner. Moreover, as one of the most widely used chemicals commodities, port storage of this fuel is available in more than 120 ports (Methanol Institute, 2023a).

Although tanker ships had already been used to transport methanol and other chemicals by ship, a vessel built and intended for methanol transport, the Celchem Catalyst, entered service in 1981. This single skin vessel had tanks for the transport of 6000 m³ of methanol (Methanol Institute & DCS Logistics, 2016). In 1983 the first Japanese methanol carrier, the Kohzan Maru, was built by Mitsui O.S.K. Lines for Mitsubishi Gas Chemical, since then they have formed a partnership focused on methanol transportation (Mitsui O.S.K. Lines Ltd., 2014; SAFETY4SEA, 2023). During the 1980s, the Safety Of Life At Sea (SOLAS) regulations were revised due to the problem of explosions and safety issues related to low flash point fuels under 60 °C. Methanol, with a low flash point of 11 °C, was included in this regulation, conditioning the design and construction of ships carrying this fuel from 1986 onwards. According to these regulations, oil tankers had to use inert gas during loading and unloading manoeuvres to prevent the explosive mixture of fuel with air in the cargo tanks. Chemical tankers had the option of not using inert gas, but if not including this solution, they had to have tanks of less than 3000 m³ (Methanol Institute & DCS Logistics, 2016). Because onboard N₂ generation systems were expensive at this time, the smaller tank solution was a sensible alternative. In the 1990s, interest in methanol as a chemical commodity grew and in 1999 a Japanese ship with a large ship-based nitrogen generator system was built, the methanol carrier Millennium Explorer (Wärtsilä, 2024b). Its N₂ generation system is based on membrane technology. The nitrogen generated is used to protect the methanol cargo during sea voyages and loading or unloading operations.

In 2016, the methanol Carrier Cajun Sun, see Figure 2.10, was built, with a cargo capacity of 50000 dwt and a 2-stroke dual-fueled low-rev main engine propulsion power generation system, which enables the use of methanol as propulsion fuel (Mitsui O.S.K. Lines, 2016). This ship completed the first net zero emissions voyage with bio-methanol as fuel in 2023 (Methanol Institute, 2023a). Since then, several orders have been announced for methanol tankers with the possibility of using their cargo as fuel and a capacity of around 50000 dwt (Labrut, 2023; Riviera News, 2023).



Figure 2.10: Image of Cajun Sun methanol carrier ship. Source: Flirck (Mik, 2017).
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Regarding the technical characteristics of the cargo tanks and the handling of methanol as cargo and marine fuel, the structure of the vessels and the loading/discharging systems is similar to that of crude oil tankers. Due to the similar characteristics of methanol and diesel, methanol can be stored in conventional tanks (Rigas et al., 2023). However, the cargo tanks are constructed using corrosion-resistant materials such as stainless steel, and coatings are used inside the tanks and piping to prevent corrosion due to methanol characteristics (Mitsui O.S.K. Lines Ltd., 2023; Yildirim, 2024). In addition, due to methanol flammability characteristics, tanks cannot be located adjacent to manned or open access spaces (Rigas et al., 2023). The current regulations governing the use of methanol on board are mainly MARPOL (Annex VI regulates green house gas and pollutant emissions) and the regulations issued by IMO (IMO Green Voyage 2050, 2024; Rachow et al., 2018; Svanberg et al., 2018). SOLAS Chapter II regulates low-flashpoint fuels through Part G and IGF code, and Part F and circulars MSC.1/Circ.1212/Rev.1 and MSC.1/Circ.1455. The IGF Code does not directly regulate the use of methanol on board, but MSC.1/Circ.1621 provides guidelines for the safety of ships using this fuel. According to the IBC Code methanol presents a risk to human life or marine resources, and ISO/AWI 6583 is under development entitled "Specification of methanol as fuel for marine applications".

Regarding the use of methanol as a hydrogen vector, in the last years several publications have analysed the cost of transporting this fuel by sea, even including

an analysis of methanol production processes (Araya et al., 2020; Parris et al., 2024; Schorn et al., 2021; Svanberg et al., 2018). Besides, some publications compared methanol transport cost and its characteristics with those of other alternative fuels also used as energy carriers (Aba et al., 2024; Hampp et al., 2023; Meca et al., 2022; Moritz et al., 2023; Runge et al., 2020; Villalba-Herreros et al., 2023). However, in the methanol use as an energy carrier, no study includes the comparison of the methanol reforming process with the methanol electrolysis process to obtain hydrogen at destination, and this study is carried out in this thesis.

2.2. Direct Methanol Fuel Cells

Direct Methanol Fuel Cells (DMFCs) are electrochemical devices that transform the energy of methanol into direct current electrical energy. Therefore, within the chain of the use of methanol as an energy vector, these devices are located in the last steps, in the consumption of this fuel to obtain energy needed in different devices, such as vehicles or electrical and electronic devices (Kundu & Dutta, 2016). As methanol is consumed in these devices and this fuel is liquid at ambient temperature and pressure, they are devices that have simpler fuel storage and handling systems than a gaseous fuel, such as hydrogen. Therefore, most DMFC applications are geared towards those where fuel availability, storage or handling could be a constraint. Some of these applications are small and portable devices, autonomous underwater vehicles, unmanned aerial vehicles or military equipment. In 2015 the use of DMFCs was on the rise, with an increase of about 2000 units per year, with a use of about 10000 DMFCs in that year. The average power of the units in service was below 1.5 kW, and most were installed in the United States, Europe and Japan (Methanol Institute, 2013). In 2018 another 3700 units were marketed and in 2022 they reached 7800 units (Hart et al., 2022). However, despite the high growth in the number of DMFCs placed on the market, only 0.9 MW annual capacity is reached among all units sold in 2022.

DMFCs have a power density between 0.5 and 1.0 W/cm² and a specific power of 10 to 30 W/kg (Z. Wang et al., 2024). Their operation is based on electrochemical reactions that occur when methanol and oxygen are supplied. A DMFC single cell basically consist of two electrodes, cathode and anode, and an electrolyte that separates them, in addition to bipolar plates and an external electrical circuit. The most used electrolyte in DMFCs is a solid electrolyte, a polymeric membrane. This membrane together with the electrodes forms the so-called membrane electrode

assembly (MEA). During operation of a DMFC with a proton exchange membrane (PEM), aqueous methanol is introduced at the anode and oxygen at the cathode, see Figure 2.11. The fuel, methanol, oxidises at the anode producing CO_2 and releasing electrons and protons. The electrons travel through an electrical circuit to the cathode, while the protons pass through the membrane to the cathode. Oxygen is reduced at the cathode by reacting with the protons and electrons, producing water. The main reactions that occur at the cathode and anode, as well as the overall reaction, are shown in Eqs. 2.4-2.6.

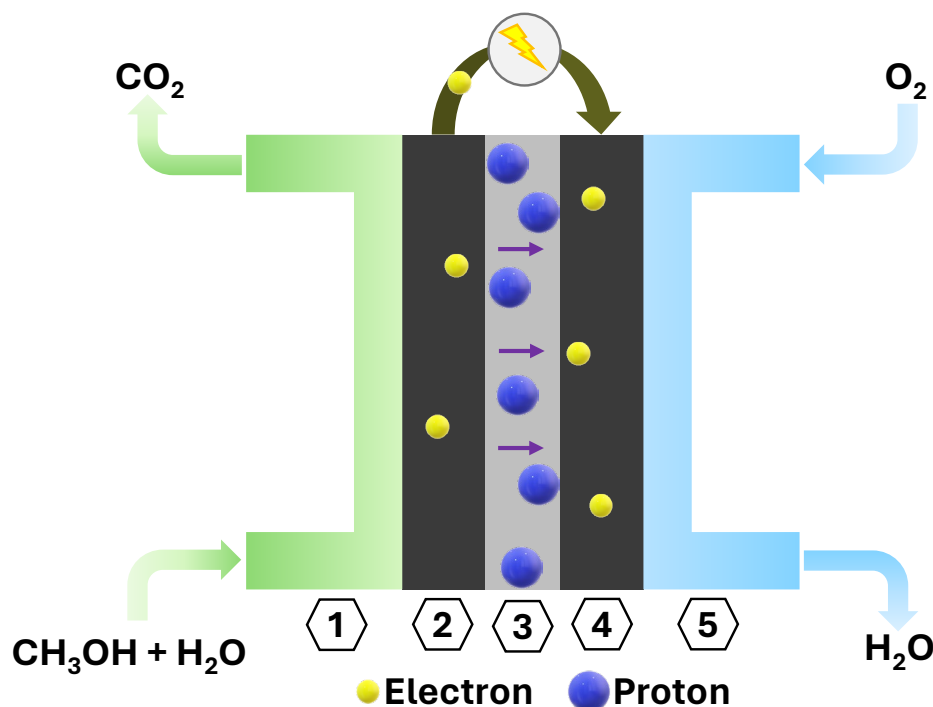
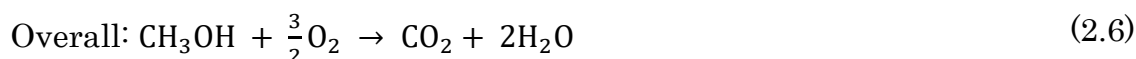
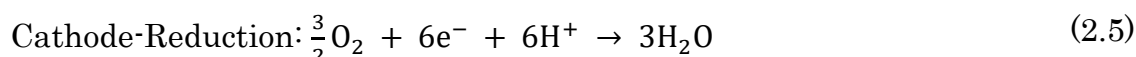
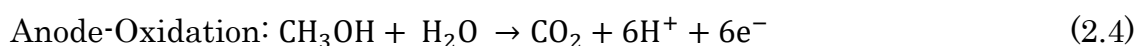


Figure 2.11: Schematic diagram of the basic operation of a Direct Methanol Fuel Cell. 1 – Anode side. 2 – Anode. 3 – Membrane. 4 – Cathode. 5 – Cathode side

From the expressed redox reactions, an electric current with a potential difference of 1.2 V at 25°C is obtained. To increase this voltage, and thus the output of a DMFC, several of the cells as the one shown in Figure 2.11 are placed in series. If the DMFC consists of only one cell it is called a single cell, see Figure 2.11, if it consists of several cells it is called a stack.

There are basically two types of DMFCs depending on the type of the electrolyte they use: acidic DMFCs or alkaline DMFCs. The alkaline technology was first developed in 1951 (Wee, 2006). In the 1960s, DMFCs were operated using acidic medium (Hogarth & Hards, 1996). The use of alkaline electrolyte offers a number of benefits compared to acid electrolyte DMFCs, including (Dutta, 2020; Higa et al., 2020; Hyun & Kim, 2023; Merle et al., 2011):

- Faster methanol oxidation reaction kinetics. This makes it possible to reduce the load of noble metal-based catalysts or even to avoid them by replacing them with others such as nickel.
- Reduced corrosion problems in bipolar plates and components due to high pH, which can lead to lower costs due to simpler and more durable materials.
- The reduction of methanol crossover from anode to cathode, partly due to the passage of anions from the cathode to the anode. So not only does the electro-osmotic drag not facilitate the crossover, but it opposes this phenomenon.

However, alkaline DMFCs feature problems of carbonation of the electrolyte due to the production of CO_2 at the anode. Therefore, during their operation, there is a continuous precipitation of carbonate salts, which leads to a loss of alkalinity of the electrolyte and reduces the lifespan (Santiago Carretero, 2021). For this reason, the present work focuses on the use of DMFCs with acid electrolyte, looking for solutions featuring less degradation and a longer lifetime.

DMFC technology can also be divided in two types: active DMFCs and passive DMFCs. In the active DMFCs the fuel is supplied to the device by a convective phenomenon. This involves the use of pumps that drive the fuel, facilitating its circulation in the device. In the passive DMFCs the fuel is transported by a diffusion phenomenon, avoiding the electrical consumption of pumps to drive the methanol. However, passive DMFCs only reach power outputs of around 10 to 20 W in scientific literature, so the study of DMFCs in this work for marine applications will focus on active DMFCs.

A DMFC stack consists of different components. The main ones, shown in Figure 2.12, are: membrane, electrodes (anode and cathode), bipolar plates and end plates (Santiago Carretero, 2021). The characteristics of each of these components are developed in the following subsections.

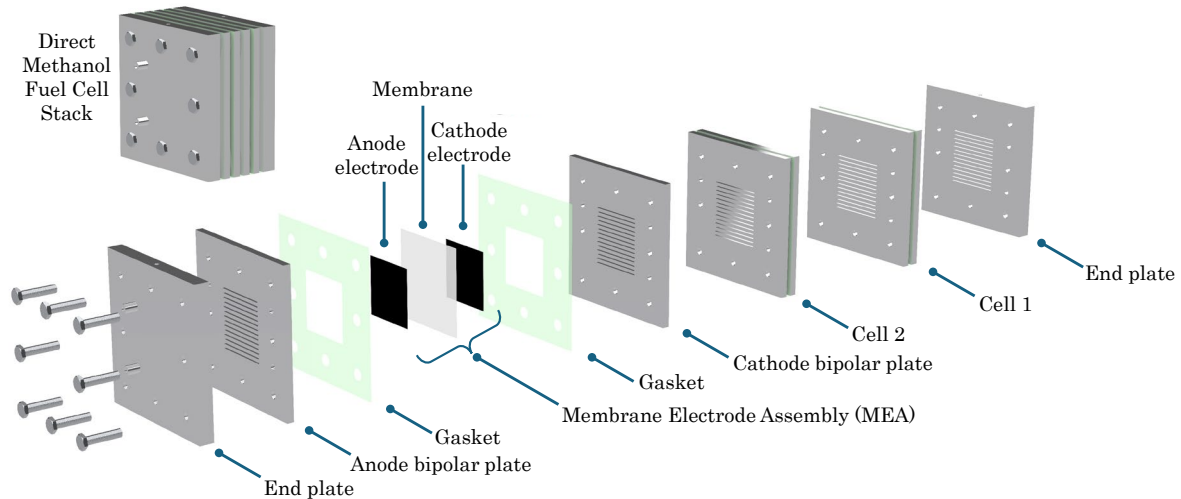


Figure 2.12: Exploded view of a Direct Methanol Fuel Cell stack

2.2.1. Membranes for DMFCs

Proton exchange membranes used in DMFCs must feature high proton conductivity, rejecting electron transport, good mechanical, chemical and thermal stability and must prevent the crossover, the passage of fuel from the anodic to the cathodic side, therefore they shall exhibit low methanol permeability (Hosseini et al., 2019). In fact, the crossover of methanol across the membrane is one of the major problems in DMFC, decreasing the power obtained with these devices due to the loss of part of the methanol that is not oxidised at the anode and which, on reaching the cathode, reacts with oxygen reducing the cathode potential (Dalena & Basile, 2018; Pinto et al., 2018). The crossover is mainly caused by a diffusion phenomenon, convection due to a differential pressure between cathode and anode sides of the membrane, and electro-osmotic drag, created by the passage of protons from the anode to the cathode, which drag the methanol molecules. Most of the membrane requirements mentioned above are characteristics of perfluorosulphonic acid (PFSA) membranes, such as Nafion®. This material is synthesised by DuPont, with a high proton conductivity and a high electrochemical stability, but with high methanol crossover (Ko et al., 2010; Prapainainar et al., 2020). However, Nafion® is the most widely used material in DMFCs because of its properties. Nafion® membranes need water to allow the transport of protons, in fact their proton conductivity is reduced when their hydration decreases (Y. Wang et al., 2022). This dependence on water is due to the mechanisms of proton transfer in this type of membrane: *Grotthuss* and *vehicle* mechanisms (L. Liu et

al., 2016; Ng et al., 2023). The *Grotthuss* mechanism is based on the cleavage and creation of hydrogen bonds in the water molecules that allow the proton to cross the membrane through a network of hydrogen bonds with the water molecules. By this mechanism the proton binds to a water molecule forming a structure such as a hydronium ion (H_3O^+), and when this cation releases the proton it bonds with a molecule such as SO_3^- or another water molecule forming a hydrogen bond. In this way, the proton travels from molecule to molecule until it reaches the cathode. On the other hand, the *vehicle* mechanism is based directly on the transport of the proton in a water molecule in the form H_3O^+ , H_5O_2^+ and H_9O_4^+ , etc. into the hydrophilic Nafion® channels. These mechanisms, apart from their relation to the need to maintain adequate membrane hydration, are also related to the crossover produced in Nafion® membranes, since methanol molecules can also be dragged together with protons (J. Zhou et al., 2021). To avoid the crossover phenomenon, a thicker membrane could be used, but this is counterproductive due to the increase of the ohmic potential caused by the higher resistance to the passage of protons (Aricò et al., 2015). Therefore, if the modification of the geometry does not improve the properties, one of the possible solutions lies in the modification of the membrane material. Two possibilities stand out for these modifications: adding inorganic compounds to the Nafion® structure that reduce the crossover while maintaining the proton conductivity (Ng et al., 2022), or directly synthesising new low-cost membranes that help to solve these problems (Ahmad et al., 2022).

There are materials, such as hygroscopic inorganic oxides, which when added to the Nafion® structure allow for increased water retention due to their high porosity, thus improving the transport of protons (Sigwadi et al., 2021). One of the problems to be improved in the use of these materials is the homogeneous dispersion in the membrane, which can be enhanced by the use of nanosized and high surface area particles (Velayutham et al., 2017). Adding nanosized hydrophilic filler also improves the proton conductivity by creating hydrogen bonding sites and even creates a blockage in the hydrophilic region that hinders the passage of methanol. This improves proton transport via the Grotthuss mechanism but can worsen transport via the vehicular mechanism. In fact, the concentration of these particles in the membrane must be considered, as adding too much filler can limit proton transport by covering sulfonic acid groups and worsen the mechanical properties of the membrane (Ng et al., 2022). One hydrophilic ion-conducting material that has been used in DMFC membranes is zeolite. Its use in a Nafion® membrane has permitted to increase the DMFC power density to more than double

of the peak power density obtained with commercial Nafion® (X. Sun et al., 2020). Some of the materials used in DMFC membranes to prevent crossover and increase the proton conductivity are TiO₂ (Ercelik et al., 2017), SiO₂ (C. W. Yang et al., 2017), ZrP (Sigwadi et al., 2019) and graphene oxide (GO) (Prapainainar et al., 2019). In fact, in addition to its high chemical and mechanical stability, GO allows crossover to be reduced. Moreover, GO has hydroxyl and carboxylic groups that allow an improvement of the ion exchange capacity (Sha Wang et al., 2015).

To reduce the cost of DMFC membranes, different non-Nafion® based materials are being studied. Polybenzimidazole (PBI) is one of the materials on which DMFC membranes are based due to its resistance to methanol crossover and its chemical and thermal stability (J. Zhou et al., 2021). However, it presents problems due to its low proton conductivity, which makes the incorporation of fillers necessary (S. Wang et al., 2018). Another material used is polyvinyl alcohol (PVA), which, despite its high water selectivity over methanol, has low ionic conductivity. To improve this characteristic, fillers with proton conducting properties can be introduced or PVA can be combined with acid groups or polymers (Duangkaew & Wootthikanokkhan, 2008). Sulfonated polyvinylidene fluoride (sPVdF) has shown its hydrophobicity characteristics during its use as a DMFC membrane material, which prevents the passage of methanol but hinders ionic conductivity (kumar et al., 2010). Fillers such as Fe₃O₄/SiO₂ can be used to promote proton transport of sPVdF membranes (Ranjani et al., 2018). Styrene-ethylene-butylene-styrene (sSEBS) has also been used as a DMFC membrane material, reducing methanol crossover and improving DMFC performance (Pascual-Jose et al., 2023; Santiago et al., 2020). Other materials used include sulfonated polyimide (SPI), polyarylene ether ketone (PAEK), Sulfonated polyether ether ketone (SPEEK), sulfonated polyarylene ether sulfone (SPAES), chitosan (CTS), sulfonated polyether sulfone (SPES) and highly branched sulfonated polyarylene ether (HBSPE) (J. Zhou et al., 2021). The last two materials mentioned have a high proton conductivity but need to increase their resistance to methanol crossover with solutions such as the incorporation of sulfonated graphene oxide (SGO). The rest of the materials mentioned above can be combined with other materials and introduce fillers in their matrix to increase their proton conductivity. Membranes based on these materials can be an alternative to Nafion®, showing better results than this commercial material in DMFC performance tests, mainly against methanol crossover.

2.2.2. Electrodes for DMFCs

The elements of a DMFC that are in contact with the membrane are the electrodes, one corresponding to the anode and one corresponding to the cathode. The electrodes consist mainly of two layers, a gas diffusion layer (GDL) and a catalyst layer (CL). The main functions of the GDL of anode and cathode electrodes are to facilitate the transport of the reactants, methanol and oxygen, respectively, to the catalyst layer of anode and cathode. In addition, the GDL can assist the transport of water into the membrane, which enables its hydration. To meet these characteristics, the GDL must have, among other properties, adequate porosity, good fluid permeability and diffusivity, durability, good thermal and electrical conductivity and mechanical strength to serve as a support for the catalyst layer (Peinador et al., 2022). The CL is the part of the electrode that is in direct contact with the membrane and acts as catalysts increasing the reaction rate of the methanol oxidation reaction (MOR, see Eq. 2.4) and the oxygen reduction reaction (ORR, see Eq. 2.5).

The most used catalysts for DMFCs are based on the utilization of noble metals such as Pt. The cost of these catalysts is another of the parameters of this type of fuel cell that makes their commercialisation difficult, as the catalyst load to promote the MOR and ORR reactions is between $1 \text{ mg} \cdot \text{cm}^{-2}$ and $4 \text{ mg} \cdot \text{cm}^{-2}$, with the anode requiring more catalyst loading due to the very sluggish MOR reaction (Gong et al., 2018; Scott & Xing, 2012). Besides, CO can be produced at the anode during the MOR reaction and this compound will poison the Pt in an adsorption process, which degrades the anode catalyst during the operation of the DMFC (Moura et al., 2017). Apart from the catalyst material, the morphology and structure of the catalyst, the support used and the distribution of the catalyst influence the reactions rate and the overall performance of the DMFC (Gong et al., 2018; Moura et al., 2017). In fact, the mass transport efficiency and the interaction of the catalysts with each support are related to the catalytic activity and the utilization of the catalyst load used (Zuo et al., 2022).

The most studied catalysts for MOR and ORR are based on the use of Pt and Pd, through the reduction of the catalyst load and/or its combination with other elements, with a smaller number of publications in recent years related to the use of nonprecious metal catalysts such as transition metals and metal oxides (Zuo et al., 2022). The following is a brief review of the catalysts used in DMFCs as anode and cathode based on the use of Pt and/or Pd or other metal catalysts.

Within the catalysts using Pt, it has been demonstrated that different geometries of this catalyst can be created, such as nanowires, nanotubes or nanoflowers (Ensafi et al., 2014). These geometries can allow for increased mass and electron transfer, increasing electrocatalytic activity. Using a combination of Pt and Pd can also increase the catalytic activity compared to using Pt or Pd separately, promoted in part by the synergistic effects of the bimetals (Y. C. Shi et al., 2017; H. Zhang et al., 2010). This combination of Pt with other metals improves CO tolerance and enables to reduce the Pt catalyst load. In fact, Pt-Ru is the most widely used commercial bimetallic catalyst for DMFC anode because the effect of Ru promotes the complete oxidation of the CO adsorbed on Pt, thus reducing poisoning problems (Jackson et al., 2017; Sahin & Kivrak, 2013). The synergy effect of Pt and Au has also been studied, showing an enhancement of activity towards anodic and cathodic reactions (Gowthaman et al., 2018; Xie et al., 2017). Some other noble metals have been combined with Pt showing enhanced electrochemical activity, such as Ag (Cao et al., 2015), Ir (Holt-Hindle et al., 2008) and Rh (Choi et al., 2004). Other bimetallic catalysts based on Pt and the use of transition elements such as Cu (Cao et al., 2018), Ni (Kwon et al., 2020) and Co (L. Zhang et al., 2019) have also been studied, showing an increase in activity due to alloyed composition and an increase in the active surface and active sites in the catalytic layer. Trimetallic catalysts based on Pt and Ru, such as PtRuCo (Q. Zhao et al., 2016), PtRuNi (Shang et al., 2019), PtRuSn (Saravanan et al., 2020) and PtRuFe (Rethinasabapathy et al., 2017), have also been studied, allowing the catalytic loading of noble metals to be reduced.

The use of non-platinum based catalysts has also been studied, one of the most attractive being Ag due to its chemical stability, low price compared to platinum, high electrical conductivity and appropriate corrosion resistance. The combination of Ag with TiO₂ may be a good candidate, as it reduces the activation potential with the latter compound (Mohamed et al., 2016). Other oxides have also been studied in combination with Ag, such as ZnO and Bi₂O₃ (Balachandran et al., 2016). The Ag-Au catalyst has also been studied, which can enhance the electrocatalytic performance (Atar et al., 2015).

Pd alone does not show activity towards MOR reaction in acidic media (Antolini, 2009; A. Chen & Ostrom, 2015). However, its combination with Ag and TiO₂ allows to obtain promising non-Pt catalyst for the MOR reaction with high catalytic activity thanks to the interaction between the metal and the nanofiber support (J. Ju et al., 2013). Most of the studies on catalysts based on transition metals and

their oxides focus on the study of MOR in an alkaline media (Dutta, 2020). However, there are some studies, such as the use of Ni with partially sulfonated polyaniline (Das et al., 2015), which demonstrate the possibilities for the development of these catalysts for MOR in acidic media. Co has also been studied in acidic media through the characterisation of a cobalt-tungsten composite (Vernickaite et al., 2016). With low content of W the Co-W alloy dissolved in the acidic environment, but an increase of the W up to 30 % allowed to create a layer coating the active surface and avoiding the dissolution of alloyed particles.

2.2.3. Bipolar plates for DMFCs

The bipolar plates of DMFCs have several functionalities and are one of the elements that represent an 80 % of the mass and nearly the total volume of the electrochemical device (Dutta, 2020; Santiago et al., 2019; Shen et al., 2014). Among their different functionalities, the following stand out:

- Drive the reactants to the electrodes, ensuring a good distribution over the entire active surface, and to evacuate the products of the reactions taking place in the DMFC.
- Prevent contact between reactants belonging to the cathode and those belonging to the anode.
- Transfer electrons from the anode of one cell to the cathode of the next.
- Transfer the thermal energy that needs to be dissipated during operation of the DMFC, either to the environment or to a refrigerant in an external circuit.
- Act as a structural element for the DMFC, separating different MEAs and preventing their collapse.

To fulfil all these functions, bipolar plates must have several properties: good impermeability for both cathodic and anodic fluids, good chemical stability, good electrical and thermal conductivity, good mechanical strength and behaviour, and ease of fabrication. Besides, low degradation rate, low cost and good corrosion resistance, are desirable to reduce the total cost of the stack as the bipolar plates are one of the elements that can account for up to 45 % of the total cost of the stack. The two factors that will most affect these properties and the functionality of the bipolar plates are the material from which they are constructed and the fluid field through which the reactants circulate.

The materials used in DMFC bipolar plates can be grouped into three categories: carbon-based, metal-based and composite materials (X. Gao et al., 2024).

Within carbon-based category, compact graphite is one of the most widely used materials in the fabrication of DMFC bipolar plates due to its good property as a current conductor. However, it is also a brittle material, so the manufacture of plates with this material is a process in which fractures can occur. Furthermore, its installation in environments subject to vibrations or forces is not recommended due to these same mechanical properties. Research on DMFC with bipolar plates made of this material is carried out due to the good properties against corrosion, deficiency of contaminants, low contact surface resistance or interfacial contact resistance (Karimi et al., 2012). However, it is a brittle material with poor mechanical properties and is permeable to gases. Besides, the manufacture of channels in sheets of this material implies the need for machining, which increases the cost and production time (Tawfik et al., 2007). Also due to these mechanical properties and fluid permeability, graphite bipolar plates have a limitation in their minimum thickness, whereby requirements for mobility and transport applications such as low volume or high power density are compromised due to the intrinsic volume of these plates (Karimi et al., 2012). To solve these problems, plates made by combining graphite with other elements or compounds, graphite-composite plates and graphite-metallic plates, have been studied (Dutta, 2020). Graphite-composite plates are composed of a thermoplastic material, such as polypropylene, or a thermoset resin, such as epoxy, and a filler, mainly carbon-based. The higher the proportion of filler, the better the electron conduction, but also the worse the mechanical properties. Graphite-metallic plates, consisting of graphite sheets with a thin metal foil, have good properties due to the corrosion resistance offered by the graphite and the mechanical strength provided by the metallic material, resulting in durable and lightweight plates (Pinto et al., 2018).

The main characteristics of the metallic materials used for the production of bipolar plates are their good mechanical properties, electrical conductivity, fluid impermeability and manufacturability. In addition, one of the most interesting features is the possibility of manufacturing metal plates by stamping, which makes it possible to obtain very thin plates (Alo et al., 2017). However, metallic materials are less resistant to corrosion, which affects their durability and performance (Wilkinson et al., 2010). To minimise these effects, corrosion resistant coatings and surface treatments have been proposed (Hamilton & Pollet, 2010; H. Wang & Turner, 2010). Between the most used metallic materials for the manufacture of

DMFC bipolar plates are stainless steel (Yi et al., 2019), aluminium alloys (Alegre et al., 2019) and titanium alloys (P. Gao et al., 2018), with the use of iron-based alloys being the most common due to their low cost (Karimi et al., 2012). When using titanium and stainless steel plates, an oxide layer is created on the surface of the metal when it is in contact with oxygen. This layer protects the plates from corrosion but decreases the conductivity of the material as it increases the interfacial contact resistance with the electrodes, especially in the case of titanium. Therefore, ways are being sought to reduce the thickness of this layer or to remove it and apply films of conductive and corrosion resistant materials (Bhosale & Rengaswamy, 2019). Another metal that stands out for its low density and cost is aluminium when compared to steel, but it presents even greater corrosion problems than stainless steels.

Although the coating reduces the corrosion problems of metallic materials, this effect as well as the conductivity of the resulting plate depends on the materials used as base and coating, the technique used to apply the coating and the resulting thickness of the coating (Santiago Carretero, 2021). It should also be noted that these coatings increase the cost of bipolar plates, and metallic materials have a high density, so the use of such bipolar plates may not be suitable for applications requiring low mass and cost.

Composite materials have also been studied for use as bipolar plates, consisting of a polymer that acts as a matrix and a filler. Since the polymer normally lacks good electrical conduction properties, this characteristic is provided by the filler. There are mainly two types of schemes depending on the filler material: polymer-metal and polymer-carbon. Due to the high density and low corrosion resistance of metallic materials, polymer-metal composite materials are the least studied composite materials for use as bipolar plates compared to polymer-carbon composite materials (Planes et al., 2012). Polymer-carbon composites have good corrosion resistance properties and low cost and mass when compared to bipolar graphite or metallic plates (X. Gao et al., 2024). To reduce ohmic losses in bipolar plates, fillers of carbon black, carbon nanotubes, graphene and graphite are used in polymer-carbon composites (Jeong et al., 2021). In general, the use of fibre materials increases the electrical conductivity and mechanical strength of the composite material compared to materials with spherical particles. However, they still do not have the high conductivity of metallic materials (X. Gao et al., 2024). It is also important to study in these materials the compatibility between the filler and the polymer that serves as matrix, which can present problems due to the low

wettability of the filler and lead to the permeability of fluids through the plates, necessitating an increase in the interfacial compatibility (Jeong et al., 2021).

Among the bipolar plates functions mentioned above is the role of conducting the reactants to the diffusion and catalyst layers of the electrodes, ensuring their correct distribution over the entire active area. These plates must also allow the correct evacuation of the reaction products. The flow field is the element of the bipolar plates that is responsible for these functions and is mainly composed of the manifolds of the DMFC stack and the flow patterns.

The manifolds are the elements that distribute the reactants from the inlet of the stack to the bipolar plates and collect the products of the reactions and take them to the outlet of the stack. Depending on the direction of fluid flow within the stack, two main configurations differ, U shape and Z shape. The U shape configuration consists in the reactant inlets and product outlets of the stack being located at the same end of the stack, following the distribution shown in Figure 2.13. In this way, the inlets and outlets follow opposite flow directions, resulting in an inhomogeneous distribution of the fluid along the cells of the stack. This can lead to a degradation of the stack and a non-uniform distribution of reactions in the cells. In contrast, a Z shape, although involving a larger stack size by placing the inlets and outlets on opposite sides of the stack, allows the fluid to follow the same direction at both inlets and outlets. This allows a better distribution of the fluid through the succession of cells in the stack and can therefore lead to better performance.

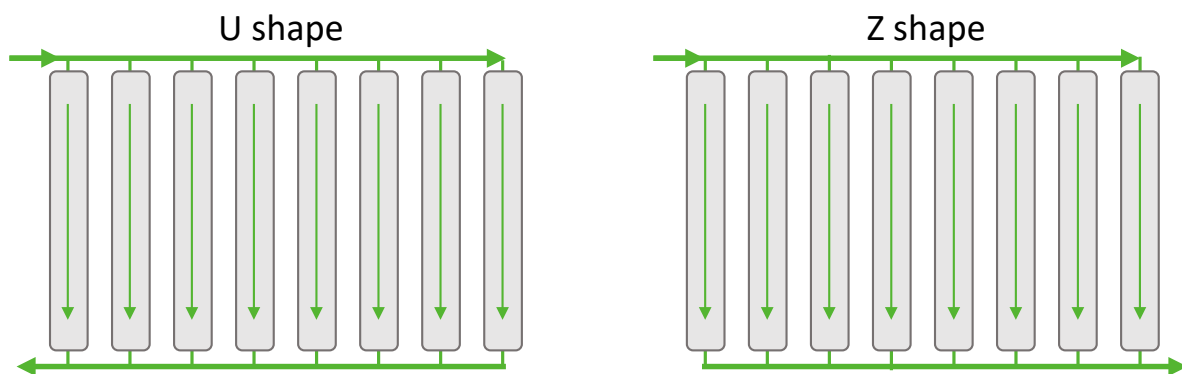


Figure 2.13: Schematic of fluid distribution inside a DMFC stack with U and Z shape configurations. The horizontal lines represent the stack manifolds and the vertical lines represent the fluid flow through the cells

The flow patterns allow the reactants to be distributed over the active area. They consist of a series of channels machined in the bipolar plates through which the reactants enter and the products of the electrochemical reactions are removed. Depending on the geometry of the channels, various flow pattern designs can be distinguished, including parallel channels, serpentine, multi-serpentine, spot, interdigitated and bio-inspired, see Figure 2.14.

The parallel design consists of two collectors placed one at each end of the bipolar plate face, see Figure 2.14a. One collector in the area where the reactants enter and the other in the area where the products are collected and expelled from the bipolar plate. Both collectors are connected by a series of parallel channels that allow the fluid to pass through the active area. In this design the reactants are not evenly distributed over the entire active area, with a lower flow through the central channels compared to the flow observed in the end channels. In addition, the central channels can be blocked by CO₂ bubbles at the anode, especially when there are a large number of channels or at low methanol flow rates and high current densities as there is a low pressure drop in these channels, which is insufficient to eject these bubbles. This behaviour produces a decrease in DMFC performance, as the reactants do not reach part of the active surface due to the blockage formed by the bubbles, as well as non-uniform temperature distribution throughout the cell. In addition, the convective flow under the ribs of the channels is negligible due to the low pressure drop between the channels, as they have a similar pressure in this design. Due to this phenomenon, the reactants access the catalytic layer under the ribs mainly by diffusion, just as the reactants leave this area by the same phenomenon. This can also lead to clogging under the ribs, reducing the catalytic area reached by the reactants.

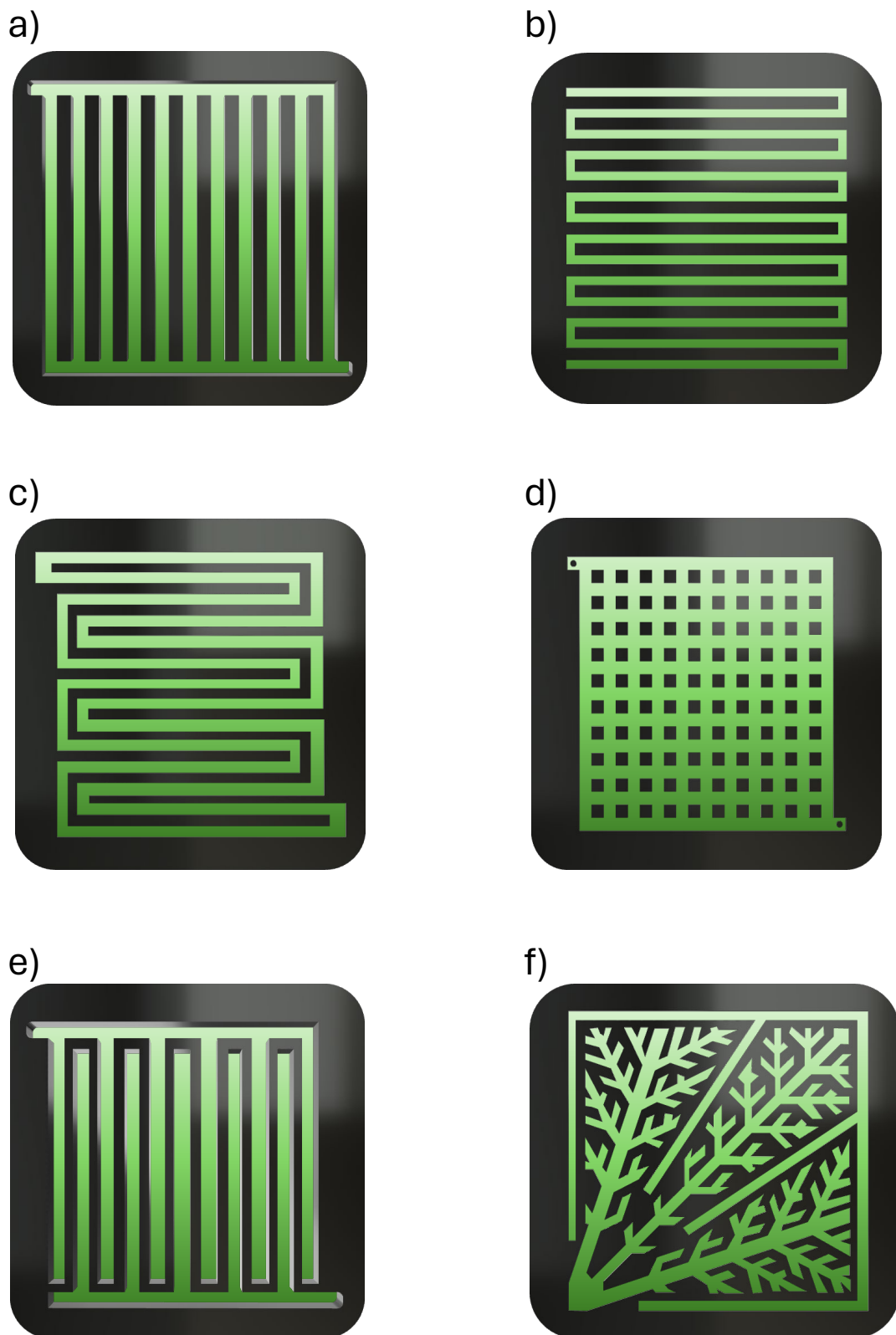


Figure 2.14: Schematic of flow pattern geometries. a) Parallel design. b) Single serpentine design. c) Multi-serpentine design. d) Spot design. e) Interdigitated design. f) Bio-inspired designs

The serpentine-based fluid field design, see Figure 2.14b, consists of a single channel with changes in fluid direction at the ends of the active area and thus fluid direction in the part of the channel that is distributed over the entire active area. Due to this design there is a higher pressure drop along the channel compared to parallel flow, which helps to expel the reaction products and avoid clogging (H. Zhou et al., 2023). In addition, there is a convective flow between the parallel sections of the channel, below the ribs, thanks to the higher pressure difference of these sections. These features help to improve the distribution of reactants in the catalytic area and the evacuation of the products avoiding blockages. The comparison between the parallel channel design and the serpentine design has been studied both experimentally and theoretically using mathematical models (H. Yang & Zhao, 2005; H. Zhou et al., 2023). These studies show a better behaviour of the serpentine channel both for the removal of reaction products and for the overall improvement of the DMFC performance. However, despite these improvements, the methanol concentration distribution is affected by this design as methanol is consumed at the anode as the fluid moves through the channel, reducing its concentration. In addition, the higher pressure drop also means higher energy consumption of the device driving the methanol through the DMFC. For these reasons, this geometry is normally used in small bipolar plates.

The multi-serpentine design, see Figure 2.14c, helps to overcome some of the problems posed by a single serpentine, showing a lower pressure drop across the channel. This design consists of several serpentine channels that are distributed along the active area but share the reactant inlet and product outlet. With this design, a lower pressure drop is achieved by having a shorter length of serpentine channel, as several channels cover the same area (Oliveira et al., 2010). Although the problems of clogging found with the parallel channel design can occur, the pressure drop in the multi-serpentine design is usually enough to evacuate the reaction products properly.

Spot design, as presented in Figure 2.14d, provide a low pressure drop and a good methanol mixture at high methanol flow rates due to the reduced contact area between ribs and MEA, which enhances fuel access to the electrode (Scott et al., 1998). However, the reduced contact also leads to increased ohmic losses due to inhomogeneous current distribution, which results in reduced DMFC performance, and this design also presents difficulties in removing CO₂ bubbles (T. Y. Chen et al., 2012).

In the interdigitated design, see Figure 2.14e, the fluid is transported mainly by convective phenomenon, with diffusion phenomenon having less influence (Aricò et al., 2000). This fluid field design does not have an inlet connected directly through one or more channels to an outlet. Instead, it has an inlet to a series of closed channels, forcing the fluid to pass under the ribs until it reaches another series of channels with an opening to allow the products to be discharged. The interdigitated design, due to the influence of the fluid passing under the ribs, allows for faster mass transport, but also implies a higher pressure difference to be overcome with the devices driving the fluid in the active DMFC.

Bio-inspired flow field designs, see Figure 2.14f, in fuel cell bipolar plates are an active field of research at present, with designs such as those based on fluid distribution in the leaves of different plants (Yağız et al., 2023), fluid distribution in lungs (Ozden et al., 2017), or those inspired in fishbones (Y. Wang et al., 2021). These designs have different characteristics depending on the design used, but in general they show a balanced pressure change between inlet and outlet, an improvement in the distribution of the reactants and an improvement in the evacuation of the products, among other characteristics, showing an improving or a worsening of the DMFC power density compared to more traditional flow fields, but normally improving the DMFC general performance (Yagiz et al., 2024). These new DMFC flow field designs with structures based on highly efficient transport networks due to their evolution in nature show promising results for the improvement of DMFC characteristics. However, the fabrication process of these patterns can be more difficult and therefore economically costly than more traditional geometries. Table 2.2 displays a summary of the advantages and disadvantages of the different flow pattern designs described.

Table 2.2: Summary of advantages and disadvantages of different flow pattern designs

Flow Pattern Design	Advantages	Disadvantages
Parallel	Low energy demand to drive the fluid due to low pressure drop	Non-uniform fluid distribution, CO ₂ bubble blockage and negligible flow under the ribs
Serpentine	Improved fluid distribution and product evacuation	Higher pressure drop and concentration gradient between inlet and outlet
Multi-serpentine	Improved fluid distribution and product evacuation with lower pressure drop than serpentine geometry	Blockage problems may occur, although with low probability
Spot	Low pressure drop and good methanol mixing	Increased ohmic losses and difficulties in CO ₂ bubble removal
Interdigitated	Faster mass transport and excellent flow under the ribs	Higher pressure drop
Bio-inspired	Balanced pressure change, improved fluid distribution and effective removal of the reaction products	More difficult and costly to manufacture and difficult scale-up

Regarding the design of the channel geometries, within the different patterns there are parameters that need to be studied to improve the characteristics of the flow field. In the case of flow fields using serpentine-based designs, the most important parameters are the open ratio, the channel width and the channel depth. The open ratio can be defined as the ratio between the active area directly exposed to the fluid in the channels of the bipolar plate and the total active area of the MEA (Oliveira et al., 2010; H. Yang & Zhao, 2005).

In the work of Yang and Zhao (H. Yang & Zhao, 2005) the effect of open ratio in a serpentine channel was studied by testing three single cells with different values of this parameter: 26.3 %, 52.7 % and 79.3 %. In order to modify the open ratio, the length of the serpentine was changed, thus modifying the rib width and fixing the channel width. It was found that a low open ratio, i.e. a high rib width for the same channel width, limits the contact area between the fluid and the GDL. This results in a non-uniform distribution of the fluid in the active area of the MEA, worsening the methanol mass transport and thus causing degradation. However, an increase in the open ratio, i.e. a narrower rib, leads to an increase in crossover by having a larger area of the MEA exposed to the methanol flow. The possibility of increasing ohmic losses by reducing the contact area between the bipolar plate and the MEA when the open ratio is increased has also been studied, but the change in open ratio shows only a small variation of ohmic resistance. For these reasons, it is necessary to work with a suitable open ratio to allow good methanol mass transport but low crossover. Following this line of research on the open ratio, the effect of channel width has also been studied by fixing the ribs width, with open ratios of 59.3 %, 67.9 % and 76.3 % (Park et al., 2012). This study also reveals that for the intermediate value of open ratio the DMFC performance improves. A large open ratio (76.3 %), with a very wide channel (1.5 mm), reduces the fluid velocity and pressure drop in the channel, which limits the convective flow of methanol under the ribs and the evacuation of reaction products. Whereas a very low open ratio (59.3 %), with a very narrow channel (0.7 mm), limits methanol mass transport compared to an open ratio of 67.9 % with an intermediate channel (1.0 mm). The effect of channel width without significant modification of the open ratio has also been studied by modifying the channel length (B. Yu et al., 2013). It has been shown that a decrease in channel width from 0.889 mm to 0.737 mm results in an increase in pressure drop across the channel due to the increased serpentine length. The higher pressure drop leads to an increase in the methanol velocity in the channel and in the GDL, improving the mass transport efficiency. However, this increase in pressure drop also implies a higher energy consumption of the pump or compressor driving the fluid through the DMFC (Kianimanesh et al., 2012). In addition, operation with a very narrow channel can lead to blockages due to CO₂ bubbles, especially at high current densities. The effect of channel depth on the performance of a DMFC has also been studied for three values 2.0 mm, 1.5 mm and 1.0 mm (Alizadeh et al., 2013). At low current densities the behaviour of the DMFCs with each of these channel depths is similar, but at high current densities the channel depth of 1.0 mm provides better results. This effect is due among other

reasons to the low flow velocity at higher channel depths and thus to the accumulation of bubbles on the electrode surface, which limits the mass transport of methanol into the catalytic layer. However, as in the case of channel width, an excessive decrease of the channel depth may imply a worsening of the DMFC performance due to the clogging caused by CO₂ bubbles that are not properly evacuated (Wong et al., 2006).

By studying the modification of the different geometrical parameters of the serpentine, it has been seen that they mainly affect the fluid velocity, the mass transfer and the evolution and evacuation of the reaction products, in particular the CO₂ produced at the anode. The effect of this CO₂ is greater the higher the amount of CO₂ in the channel, so the higher the current density, the more noticeable the effect. Due to this effect, it is possible that the increase in overpotential at high current densities is partly caused by the evolution of these bubbles (Calabriso et al., 2015). This CO₂ evolution is current density dependent, with the amount of CO₂ increasing as this parameter increases, showing different patterns depending on the current density for the same reactant flow. At low current densities, small discrete bubbles appear, increasing their accumulation forming gas slugs at moderate current densities, and at high current densities a predominance of long gas slugs appears (H. Yang et al., 2005a). The pattern observed for these bubbles is also affected by the flow velocity when the current density is fixed, with a greater number of smaller bubbles observed when the volumetric flow rate is increased (Calabriso et al., 2017).

Methanol volumetric flow rate, methanol concentration and DMFC temperature are also three factors that affect the performance of the DMFC, defining part of its operating conditions. Low methanol volumetric flow rate may imply poor methanol mass transfer due to ineffective removal of CO₂ bubbles formed in the anode channel (Kumaresan et al., 2022), while a very high volumetric flow rate can increase methanol crossover, worsening the DMFC performance. In addition, a high methanol volumetric flow rate can lead to a decrease in the temperature of the catalytic layer, which worsens the kinetics of the methanol oxidation reaction (Yuan et al., 2016). The methanol concentration affects the DMFC performance as it is also related to the mass transport and the availability of methanol in the catalyst layer. Low methanol concentration can lead to high concentration polarization when operating at high current densities due to the low availability of methanol in the catalyst layer (Yuan et al., 2016). However, high concentration can also worsen DMFC performance due to increased crossover (Liao et al., 2007).

An increase in temperature results in improved reaction kinetics at both anode and cathode (Alizadeh et al., 2013). However, high temperature can also lead to an increase in methanol crossover due to increased methanol diffusion across the membrane as the temperature increases (Raso García et al., 2017).

As seen in this section, the DMFC performance is affected by the parameters of the serpentine pattern geometries in DMFC bipolar plates (e.g. open ratio, channel width and channel depth), as well as by the operating conditions of this device, mainly its temperature, methanol volumetric flow rate and methanol concentration. Even some of these parameters show combined influence on the peak power density of the DMFC, and it is required to identify these combined effects and the values of the geometrical parameters and operating conditions that allow to improve the overall performance of the DMFC.

2.3. Methanol Electrolysis Cells

When methanol is not to be used directly as fuel for electricity generation after the transport process, as in the case of DMFC use, but hydrogen is required at the destination, a methanol electrolysis process can be employed. Methanol electrolysis process is used to electrochemically reform methanol to obtain high-purity hydrogen (Wei et al., 2018). During the methanol electrolysis process, electrical energy is supplied to break down the methanol molecule into its basic components, H_2 and CO_2 . The use of this process dates back to 1948, as documented in the NASA Brief Technical Report (Coutanceau & Baranton, 2016; Jeffries-Nakamura B et al., 1948). Later, a system capable of producing hydrogen based on the electrolysis of aqueous organic solutions was patented (Narayanan, 1998). Methanol electrolysis is carried out in a device that can be called methanol electrolysis cell (MEC). This device consists mainly, like DMFCs, of two electrodes, an electrolyte, bipolar plates and an external electrical circuit. During operation, methanol is introduced at the anode, but no reactant is introduced at the cathode, see Figure 2.15. By supplying an electric current, methanol is oxidised at the anode, as in a DMFC, giving rise to CO_2 and protons. These protons pass through the polymer membrane to the cathode, where they are reduced to hydrogen by the hydrogen evolution reaction (HER). The main reactions occurring at the anode and cathode and the overall reaction can be expressed by Eqs. 2.7-2.9 (Lamy, 2020; Xiao et al., 2017).

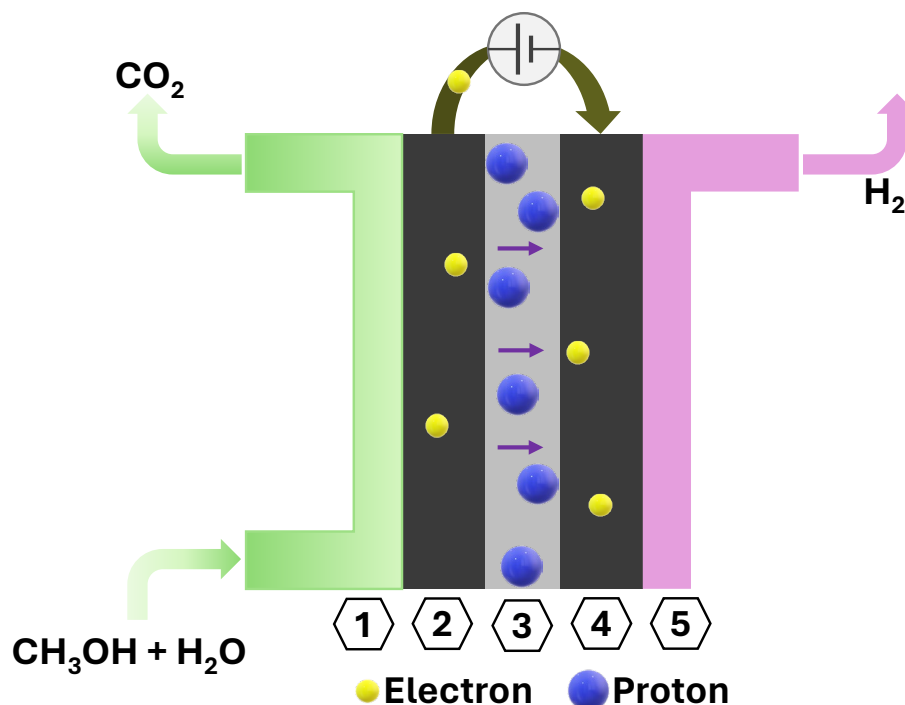
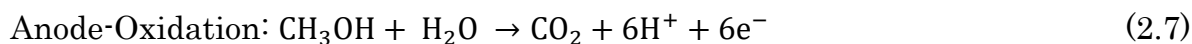


Figure 2.15: Schematic diagram of the basic operation of a Methanol Electrolysis Cell. 1 – Anode side. 2 – Anode. 3 – Membrane. 4 – Cathode. 5 – Cathode side

From the expressed redox reactions, an electric current with a theoretical potential difference of 0.016 V at 25 °C need to be applied (Lamy et al., 2020). However, the minimum experimental voltage obtained so far is around 0.4 V, so the improvement potential of this process is still high (Pethaiah et al., 2020). To increase hydrogen production, several of the cells as shown in Figure 2.15 are connected in series.

As in the case of DMFCs, two types of MECs can be differentiated according to the electrolyte used: acidic or alkaline electrolyte. MECs with an alkaline electrolyte have been less studied than MECs using a proton exchange membrane. Alkaline MECs have a higher reaction rate, associated with a lower anodic overpotential. However, they also have higher ohmic losses associated with the low conductivity of the alkaline membranes compared to the Nafion® membrane (Sapountzi et al., 2019). Due to its similarity to the structure of a DMFC with a proton exchange membrane, the study of methanol electrolysis in this thesis focuses on acid

electrolyte, although a large part of the current literature on catalysts focuses on alkaline electrolyte as it presents better reaction kinetics for the methanol oxidation reaction (Tuomi et al., 2013).

MECs are a less commercially developed technology than DMFCs, with increasing interest in the last two decades due to their hydrogen production capacity. A MEC stack consists of different components, mainly membrane, electrodes (anode and cathode), bipolar plates and end plates. The characteristics of each of these MEC components are developed in the following paragraphs.

2.3.1. Membranes for MECs

The membranes used in a MEC share the requirements with those used for DMFC, such as high proton conductivity, rejecting electron transport, good mechanical, thermal and chemical stability and low methanol permeability. Most scientific publications on methanol electrolysis with proton exchange membrane use Nafion® as electrolyte because of its good proton conductivity, as well as good mechanical, chemical and thermal stability (Pethaiah et al., 2020). The performance of a MEC has been compared by modifying the thickness of the Nafion® membrane, observing an improved ionic conductivity by reducing the thickness, but an increase in methanol crossover. To avoid this crossover, the use of Pt-catalysed Nafion® membranes has been studied (Sethu et al., 2014). These membranes are prepared by a non-equilibrium impregnation-reduction method, by depositing the catalyst on the membrane. The catalysed membrane showed a better performance especially at high current densities, due to a better catalyst utilization. Following this line, the use of Pt-Pd impregnated Nafion® nanocomposite membrane has also been studied, showing a better catalytic activity and also a better resistance to methanol crossover (Sethu et al., 2015). As in the case of DMFCs, the incorporation of inorganic compounds to the Nafion® structure has also been studied for MEC, as in the case of polyaniline (Sanchez et al., 2022). By incorporating polyaniline, water retention is improved, which increases proton conductivity. The use of low-cost membranes not based on Nafion®, such as SPVDF/ZrP composite membrane, has also been studied (Narreddula et al., 2018). The use of this membrane in MEC allows more stable results to be obtained than with a Nafion® membrane and presents a lower crossover due to the hydrophobic nature of PVDF. The use of SPES-based membranes has also given good results, with a lower methanol crossover and a reduction in economic cost (Muthumeenal et al., 2016).

2.3.2. Electrodes for MECs

MECs have two electrodes, one corresponding to the anode and the other to the cathode. These electrodes allow the mass transport of methanol at the anode and the formation of hydrogen at the cathode, acting as catalysts for the methanol oxidation reaction and the hydrogen evolution reaction. As in DMFCs, these electrodes consist mainly of a gas diffusion layer (GDL) and a catalytic layer (CL). The main functions of the GDL are to facilitate methanol transport and hydrogen formation and release, to transmit electrons to the CL, to increase the reaction rate and to facilitate the transport of water to the membrane, which allows its hydration. CL acts as catalysts increasing the reaction rate of the methanol oxidation reaction (MOR, see Eq. 2.7) and the hydrogen evolution reaction (HER, see Eq. 2.8).

Pt and Ru alloys are most commonly used in the anode of MECs due to their CO-tolerant nature (Ali & Pickup, 2022). In fact, the patent for the device for hydrogen production from organic molecules is based on a MEC using a Nafion® 117 membrane as electrolyte and Pt and Pt-Ru electrodes for cathode and anode, respectively (Narayanan, 1998). However, other MEC catalysts for hydrogen production from methanol have also been studied, although most of them are based on the use of noble metals. Pt-based catalysts have been studied such as PtPd-WC (M. Wu et al., 2007), Pt₁/CeO₂ (L. N. Chen et al., 2019), Pt-WC/C (Hu et al., 2007), PtSn/C, Pt/C-SnO₂, Pt/C-CeO₂ and PtRu/C-SnO₂ (H. K. Ju et al., 2017). The use of Pd nanoparticles for hydrogen evolution at the cathode has also been studied, showing similar behaviour to carbon supported Pt electrocatalyst (Naga Mahesh et al., 2016). Limited information has been found on the use of non-noble metal based catalysts used in MEC for hydrogen production in an acidic environment. Mo carbide nanoparticles and Ni functionalised carbon nanotubes have been used in this device showing high durability (Tuomi, 2019).

The exploration of cost-effective and highly active non-noble metal electrocatalysts for MOR reaction is an imperative concern (Cheng et al., 2021). Transition metal oxides, including Mn, Cu, Fe, Co, and Ni-based oxides, have garnered significant attention in MOR, whether for use in the anode of a DMFC or in the anode of a MEC, owing to their economical nature, abundant reserves, and promising electrocatalytic activity (Anantharaj et al., 2021, 2022; Candelaria et al., 2017; Yaqoob et al., 2020). However, most of its use is restricted to the alkaline electrolyte MECs. In this thesis, a study of the use of transition metals with

different supports for methanol electrolysis in an alkaline environment has been carried out. Therefore, in the following paragraphs, the use of these catalysts in the anode of a MEC or a DMFC is discussed.

Ni has been shown to be highly active as a catalyst for MOR (Abdelrazek et al., 2022). This material has strong surface oxidation properties (Y. Shi et al., 2021), and can be used to prepare electrodes with high activity and prolonged stability (N. Wu et al., 2020). Ni-based electrocatalysts have proven to exhibit high activity, selectivity, and stability for both the hydrogen evolution reaction (HER) and the methanol oxidation reaction (MOR) in strongly alkaline media, particularly at high current densities (Arshad et al., 2022; J. Liu et al., 2022; J. Wang et al., 2022; Ysea et al., 2022). Cu-based catalysts have a high MOR efficiency, such as CuO and Cu(OH)₂ (Anantharaj et al., 2022). The activity of these catalysts in the methanol oxidation reaction is enhanced in the presence of Ni. The fabrication of electrodes by hydrothermal method using Mo and Ni as catalyst for the MOR reaction has also been studied, demonstrating increased methanol electrooxidation activity (Jothi et al., 2015).

Different supports, apart from carbon-based ones, have also been used for the study of MOR, including stainless steel, Ni foam, and Ti foils. Stainless steel mesh has been used as a support for Ni/Ni-Co catalyst to study the methanol oxidation reaction (Durgadevi et al., 2016). Foams made of metallic materials have a high porosity, high specific surface area, good mechanical strength, and good mechanical resistance, so the use of Ni foam can offer good results (Abdelrazek et al., 2022; Verlato et al., 2012). Ti felt, Ti foil and black titania nanotubes (bTNTs) with Pt as catalyst have been used for the study of the MOR, showing an exceptionally high mass-specific activity exhibited by Pt/bTNTs and Pt/Ti-felt, that renders these electrodes favourable candidates for anodes in MOR, for its use in DMFCs and MECs (Touni et al., 2022).

2.3.3. Bipolar plates for MECs

The bipolar plates of a MEC must conduct the methanol to the anode, ensuring a good distribution throughout the catalytic layer, as well as collecting the hydrogen produced at the cathode and evacuating the rest of the reaction products. They must also separate the fluids present at the anode and cathode, while transferring electrons from one cell to the other. As in a DMFC, the bipolar plates in MEC must transfer the thermal energy produced during the operation of the device to

dissipate it to the environment or to an external circuit. In addition, they must act as a structural element, separating different MEAs and preventing their collapse.

In both the comparative study of bipolar plate materials and the comparison of the flow field configuration for MEC, not much information has been found in the literature, with most studies using stainless steel and carbon-based materials and a flow field based on parallel channels or a serpentine. Several studies using a stainless steel porous metal flow field stand out (Pham, Baba, & Shudo, 2013; Pham, Baba, Sugiyama, et al., 2013; Tuan & Shudo, 2012). This porous flow field has been compared to a parallel channel flow field, demonstrating improved MEC performance due to a uniform distribution of methanol in the catalytic layer using the porous material, together with improved CO₂ bubble evacuation. In addition, a lower interfacial contact resistance was also achieved with the porous metal flow field. Besides, stainless steel and Ni-base alloy have been compared for its use as flow field material, both showing similar MEC performance, so the use of Ni-based alloy C276 due to its corrosion properties may be a good material for MEC (Pham, Baba, & Shudo, 2013). Pore size is another parameter studied in these works, showing that a smaller pore diameter in the metal flow field can reduce the interfacial contact resistance between the GDL and the bipolar plate, increasing the current intensity at the same voltage.

The MEC operating conditions have also been studied, showing their influence on the performance of the device. Specifically, the parameters methanol concentration and MEC temperature have been studied because of their great influence on the MEC operation characteristics. At low current densities, a modification of the methanol concentration does not reveal a large influence on the electrical power consumed by a MEC, however, by increasing the methanol concentration when operating at higher current densities the MEC performance improves, possibly due to an improvement of the methanol mass transfer between the bipolar plates and the catalytic layer (H. K. Ju et al., 2017). However, a very high methanol concentration can lead to a worsening of the performance of the MEC by increasing the methanol crossover, producing a mixed potential at the cathode that reduces the catalyst activity (Hu et al., 2007; Take et al., 2007). In addition, a high concentration of methanol can also hinder proton transfer in the membrane by decreasing the amount of water available for ionic transfer in this electrolyte (Uhm et al., 2012). Despite the proven influence of concentration on electrolyser operation, some studies show that temperature is a more influential parameter on MEC performance (Guenot et al., 2015; Lamy, 2020; Lamy et al., 2015). These

studies show that an increase in MEC temperature leads to an increase in the reaction kinetics of methanol oxidation and decrease in MEA ohmic resistance, thus leading to a better performance of the MEC. However, too high MEC temperature can also lead to an increase in methanol and water crossover, due to the increased diffusion of these species in the membrane, resulting in a loss of part of the fuel (Uhm et al., 2012).

Regarding hydrogen production in a MEC, no dependence on temperature, methanol concentration or even the catalyst used has been found, showing a clear relationship between hydrogen production and current density (Lamy, 2020). However, the power consumed in the electrolyser does depend on these parameters, providing a different voltage for the same current density.

The purity of hydrogen obtained with methanol electrolysers was also analysed. Values of up to 99.80 % of purity have been reported, the remaining 0.20 % being due to the presence of CO₂ in the cathode (Sasikumar et al., 2008).

The importance of the study of the operating conditions of methanol electrolysers has been shown in previous paragraphs. The effects of both temperature and methanol concentration on the performance of a MEC have been reported in the literature. However, no information has been seen on methanol volumetric flow rate or on the combination of temperature or concentration with this parameter, nor about the influence of anode channel geometries on the performance of a MEC. For these reasons, this thesis studies the effects of the MEC operating conditions (MEC temperature and methanol concentration and volumetric flow rate), the influence of their combination on the performance of this device, as well as the influence on the MEC performance of the geometrical parameters of a flow field with serpentine pattern (open ratio and channel width and depth).

3. Materials and methods

In this chapter, the methodology and materials utilized to derive the findings of this doctoral thesis are presented. The chapter is structured into four main sections.

Firstly, the methodology employed in studying methanol as an energy carrier is discussed, including the development of technoeconomic models comparing hydrogen and methanol for energy transportation via ships.

The second section introduces the Response Surface Methodology (RSM) utilized in this thesis during the experimental investigation of Direct Methanol Fuel Cells (DMFCs) and Methanol Electrolysis Cells (MECs) to identify the operational parameters or geometric design parameters of the anode flow field that most influence the devices performance, with the aim of improve their designs and working conditions to enhance their performance.

The third section focuses on the experimental study of a Direct Methanol Fuel Cell for generating electrical energy from methanol, an integral component in the latter stages of methanol utilization as energy carrier.

Finally, the methodology and materials used in experimentally investigating a Methanol Electrolysis Cell for producing hydrogen from methanol are exposed, highlighting its critical role in the final stages of methanol use as a hydrogen carrier.

3.1. Methanol as energy carrier

This section presents the methodology followed to compare the use of hydrogen and methanol as energy carriers to transmit energy by transporting these fuels by ship.

The efficient transmission of energy from renewable sources to the centres of consumption is a crucial challenge in the transition towards a more sustainable energy system that is less dependent on fossil fuels.

In this context, there is a need to evaluate and compare different energy carrier options in order to identify which option is the most suitable in each situation. This study focuses on the comparison between two potential energy carriers: hydrogen and methanol. The proposed methodology covers several key aspects along the energy supply chain, with a particular focus on the costs associated with each stage. First, the production of both energy carriers from renewable sources is analysed, with a particular focus on the electrolysis process for obtaining hydrogen.

In this way, the origin of the energy and the starting point of the study for both fuels is the same, considering the transport of the hydrogen obtained at source either as liquefied hydrogen or using methanol as a hydrogen vector.

Subsequently, it is examined the packing process, which consists of increasing the density of the fuel to prepare it to be transported by ship. This process involves the conversion of hydrogen gas into liquid form, a liquefaction process, or the production of methanol from a synthesis process using CO₂ as a commodity and hydrogen produced with energy from renewable sources. The costs associated with these operations are considered, as well as any inherent energy consumption. Storage facilities for both fuels at the loading terminal are also considered.

The next step addresses the transport of energy carriers over long distances, focusing on the use of ships as a means of transport. The logistical and energy costs of this step are assessed, considering factors such as the cargo capacity and other characteristics of the vessels specialised in the transport of each fuel, as well as the consumption of each fuel for the propulsion of the vessels.

Finally, the unpacking process at the final destination is analysed, which includes the reconversion of liquefied hydrogen to its gaseous form and the reconversion of methanol to hydrogen by means of two possible processes, methanol reforming or methanol electrolysis. The costs of the facilities or their operation are studied, as well as any associated energy consumption. Storage facilities for both fuels at the receiving terminal are also considered.

This study adopts a systematic and comparative approach to provide a comprehensive assessment of different energy carrier options in terms of their technical and economic feasibility in the context of transporting energy from renewable sources. The proposed scheme, covering the stages of production, packing, transport and unpacking, serves as an analytical framework to guide research and facilitate informed decision-making in the search for sustainable and efficient energy solutions. In an international context, there is a need to assess the economic viability of both local production of green hydrogen and its importation from other locations. This analysis becomes crucial when considering whether importing hydrogen is cheaper than producing it locally, especially in the context of lower renewable energy costs in other regions. In addition, it becomes essential to determine the most cost-effective method of transporting this hydrogen, taking into account various factors such as the distance between production and destination, as well as the amount produced and transported.

To get a clearer picture of these considerations, three different alternatives are compared in this study: liquefied hydrogen transport and subsequent regasification, methanol transport and subsequent electrolysis and methanol transport and subsequent reforming. Each alternative is evaluated under different scenarios, which involve different electricity prices, distances and mass flow rates of H_2 produced for the transport of green hydrogen from its place of origin to its final destination. In each scenario, transport options are evaluated, either via liquid hydrogen or via e-methanol, with the necessary conversions both in the production processes of each fuel and in the processes to obtain hydrogen after transport. Thus, this study seeks to shed light on the complex interaction between hydrogen production costs, electricity prices, transport distances and production and transport hydrogen amounts, with the aim of providing valuable information for international clean energy decision-making.

3.1.1. Definition of maritime transport alternatives

This study examines various alternatives for the maritime transport of hydrogen produced from electricity from renewable sources. The alternatives analysed are presented in Figure 3.1 to Figure 3.3. The first one, shown in Figure 3.1, is based on the generation of hydrogen from renewable electricity, followed by its transport in liquid form and subsequent regasification.

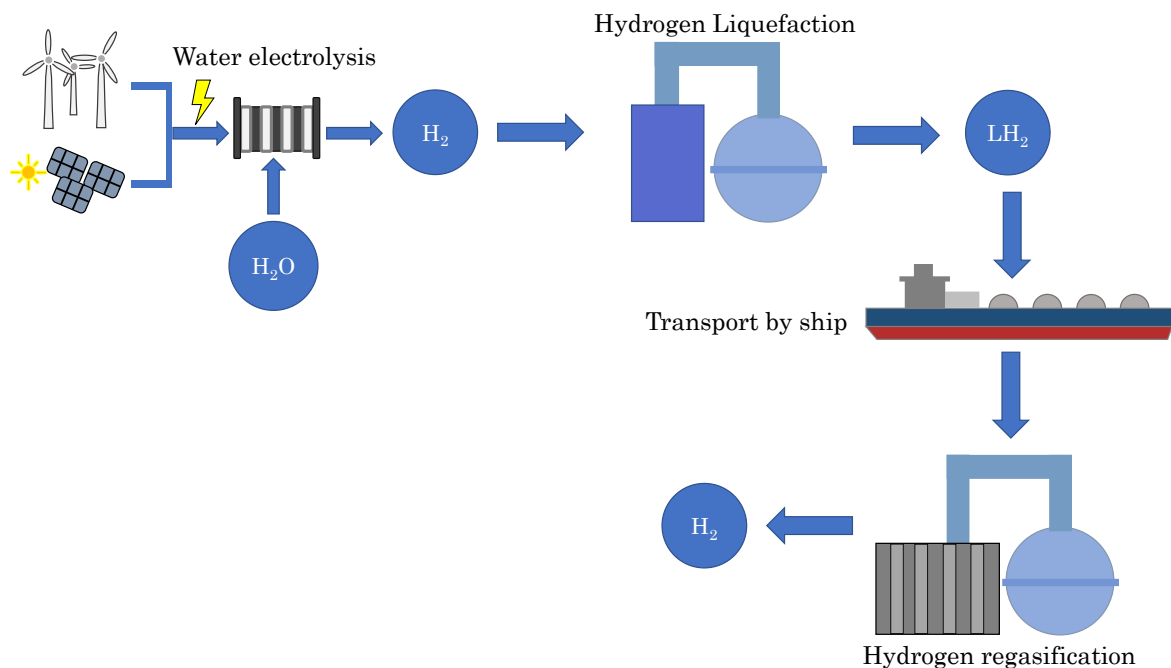


Figure 3.1: Diagram of hydrogen transport based on liquefied hydrogen and its regasification

Meanwhile, the second alternative, see Figure 3.2, involves the generation of hydrogen from renewable electricity, followed by a synthesis process to use methanol as a hydrogen vector, then methanol transport, and finally a methanol electrolysis process to obtain hydrogen at the destination.

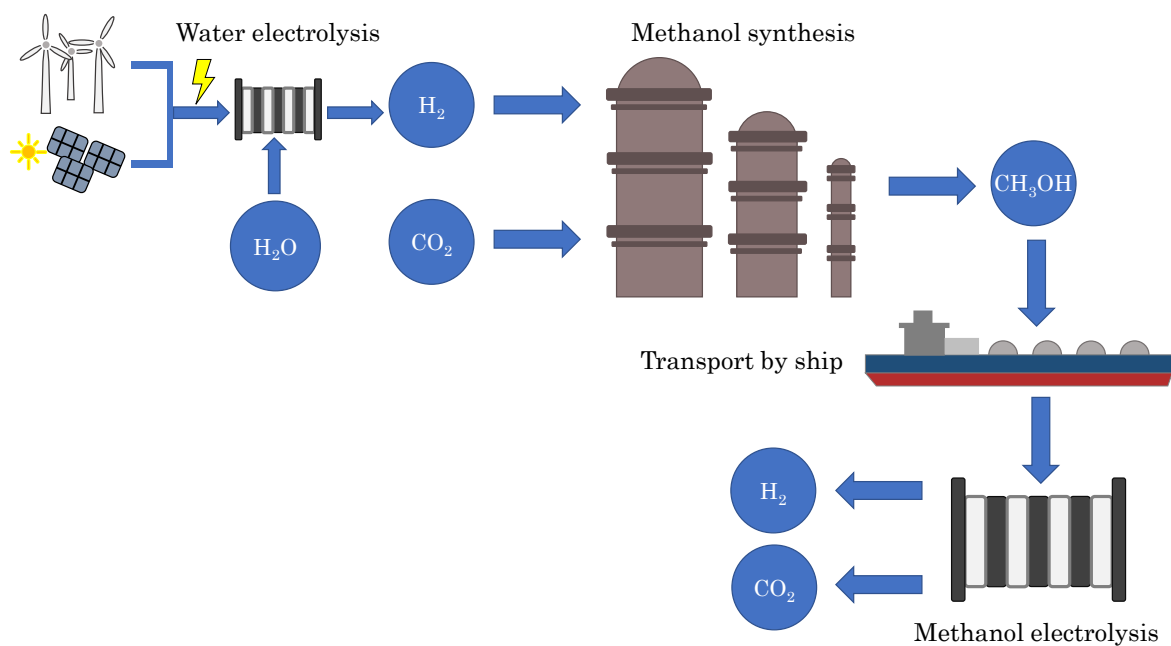


Figure 3.2: Diagram of hydrogen transport based on e-methanol and its electrolysis

The third alternative, presented in Figure 3.3, in comparison with the second alternative follows a similar scheme, but instead of using methanol electrolysis a reforming process is carried out to obtain hydrogen at destination.

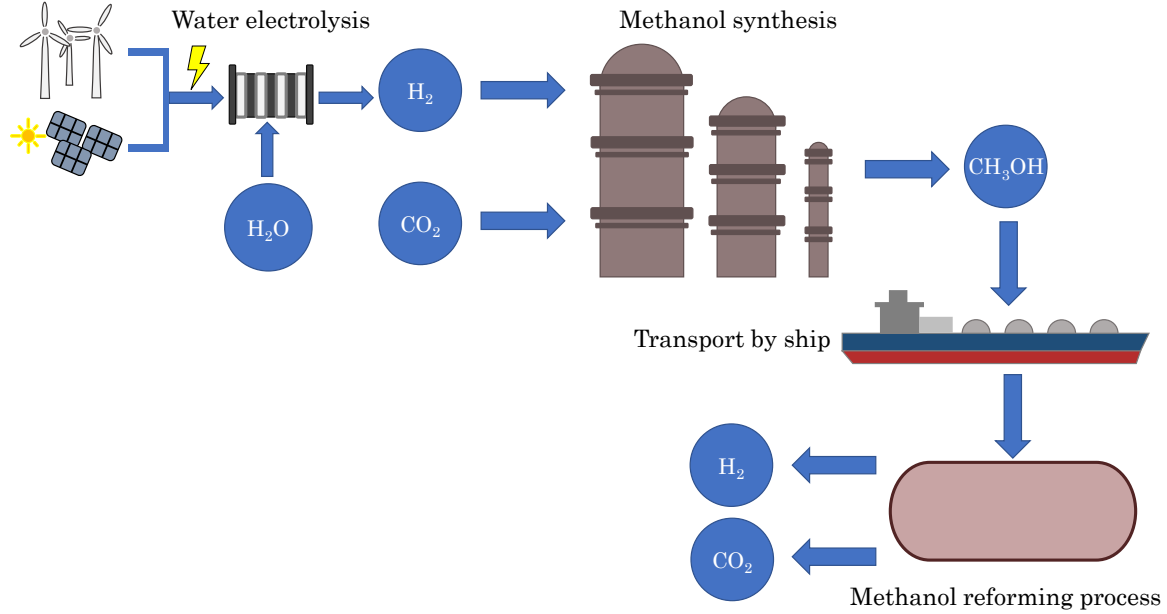


Figure 3.3: Diagram of hydrogen transport based on e-methanol and its reforming

Table 3.1 presents a summary of the different facilities used in this study that make up each of the three alternatives analysed. Table 3.1 indicates which of the facilities are part of each of the alternatives.

Table 3.1: Indication of the facilities analysed in this study and their inclusion in each of the alternatives studied

Facilities	LH ₂	CH ₃ OH+electrolysis	CH ₃ OH+reforming
Water treatment plant	X	X	X
Water Electrolysis plant	X	X	X
Methanol synthesis plant		X	X
Hydrogen liquefaction plant	X		
Methanol storage facilities (Export)		X	X
Liquid hydrogen storage facilities (Export)	X		

Methanol carrier ship		X	X
LH ₂ carrier ship	X		
Methanol storage facilities (Import)		X	X
Liquid hydrogen storage facilities (Import)	X		
Methanol electrolysis plant		X	
Steam reforming plant			X
Hydrogen regasification plant	X		

Within the field of scientific research on energy transport alternatives, it is imperative to establish a coherent framework for comparison. A number of assumptions and methodological considerations are presented here to facilitate consistent assessments between various options:

- **30-Year Life Cycle Assumption:** at the core of the analysis is the adoption of a 30-year operational life cycle for all alternatives. This assumption allows for a longitudinal assessment and facilitates the projection of long-term impacts.
- **Calculation of costs in 2021 US Dollars (USD):** to streamline financial evaluations, all costs are expressed in 2021 USD, year in which the study was carried out, and published in early 2022 (Meca et al., 2022). This standardisation minimises currency related problems, such as the use of specific exchange rates, and improves comparability of economic metrics.
- **Currency conversions:** initial currency conversions are performed using the prevailing exchange rates, adjusted for inflation to maintain time consistency between currencies.
- **Constant Inflation Rate of 2.5 %:** a constant annual inflation rate of 2.5 % is assumed, in line with global averages when this study was carried out (Central Intelligence Agency, 2021). This assumption underpins the financial projections and ensures the realism of long-term cost estimates.

- **Cost Breakdown:** comprehensive cost delineation encompasses infrastructure, operation and maintenance expenditures, mid-life refurbishment investments, and end-of-life decommissioning costs. This granularity allows for a nuanced understanding of the financial implications throughout the lifecycle.
 - **Infrastructure cost:** covers the expenses directly involved in the construction of the energy link infrastructure.
 - **Operation and maintenance (O&M) cost:** includes expenses related to the operation and ongoing care of the infrastructure. Costs associated with energy losses or exceptional interventions are not considered here. Normally, the annual O&M cost is estimated as a percentage of the total investment cost.
 - **Mid-life renewal cost (M-L):** generally, these renewals are carried out in one or several stages during the lifetime of the energy link. They are mainly carried out to modernise obsolete systems or to replace components with a shorter lifetime than the complete infrastructure.
 - **End-of-life:** at the end of the lifetime of the link, it is likely that existing obsolete installations will have to be removed. This implies additional costs. Although other end-of-life strategies exist, they are not considered in this method in order to keep the analysis simple.
 - **Energy Loss Costs:** the monetary valuation of energy losses throughout the life cycle of energy transmission is incorporated into the analysis. This inclusion takes into account the inefficiencies inherent in energy transfer processes and provides a holistic view of the economic ramifications. As the pricing hinges on the electricity rates at the exportation terminal, the authors propose investigating rates of 100 USD/MWh (27.8 USD/GJ), 150 USD/MWh (41.7 USD/GJ), and 200 USD/MWh (55.6 USD/GJ).
- **Thermodynamic Properties:** the use of thermodynamic data derived from REFPROP software informs the estimation of energy losses. The thermodynamic knowledge gained from REFPROP tools facilitates the quantification of inefficiencies, thus improving the knowledge of energy loss assessments.

By adhering to these principles, comparative analyses of energy alternatives can generate crucial information for informed decision-making in the search for sustainable energy solutions.

3.1.2. Methodology

After presenting the maritime transport alternatives and the hypotheses that will guide this methodology, each of the facilities considered in this study is detailed. The equations outlined in this section to determine the expenses linked to each facility are executed within Excel, facilitating an assessment of the projected costs for each facility and the entire energy transport alternatives. This analysis allows to understand the distinctive characteristics of each facility, as well as their specific implications in the context of the research.

As can be seen in Table 3.1, there are two facilities shared between all the alternatives analysed, namely the water treatment plant and the water electrolysis plant.

The evaluation of the cost of the reverse osmosis (RO) plant to obtain fresh water from salt water is based on economic models using data provided by El-Emam & Dincer (El-Emam & Dincer, 2014). This system is presented in Figure 3.4 and consists of a water treatment plant composed of saltwater pumps, a filter, a chemical treatment system, a valve, RO cartridges, a Pelton turbine and a mixing chamber. The process starts with seawater entering through a low-pressure pump, which directs it to the filter to remove coarse impurities. The water then undergoes chemical treatment to further purify it. It is then pumped by a high-pressure pump to the RO system, where salts and other impurities are separated from the fresh water. The brine water is sent to the Pelton turbine, while the treated water is diverted. At the end of the process, the treated water is mixed with fresh seawater to obtain the desired solution. This methodology allows the constant production of high quality fresh water, meeting supply needs.

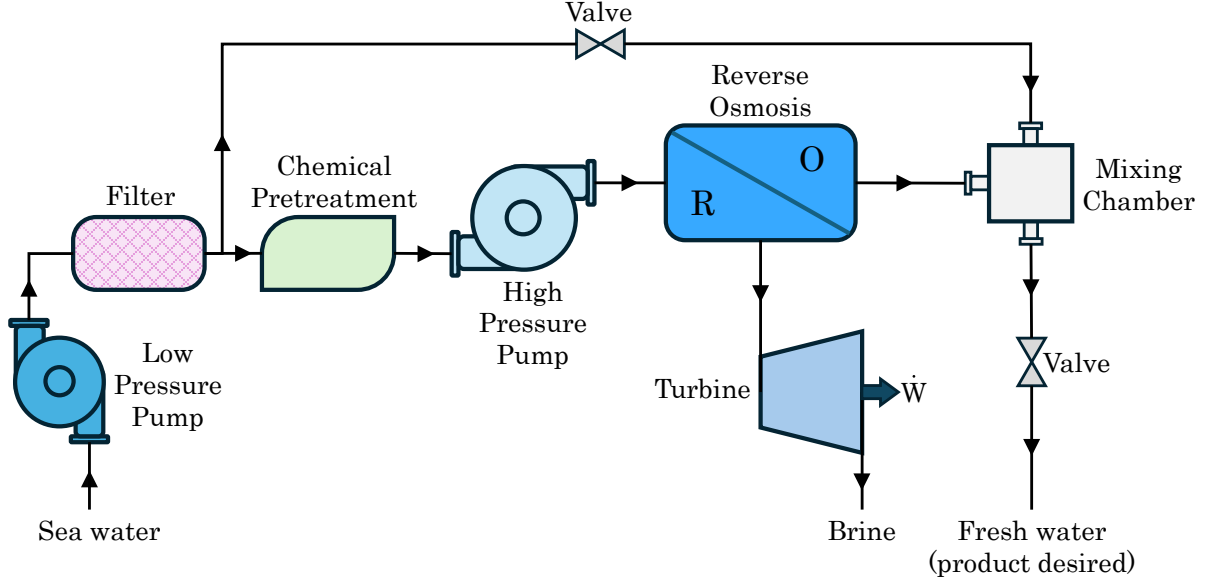


Figure 3.4: Schematic diagram of the reverse osmosis plant based on information from (El-Emam & Dincer, 2014)

The seawater intake and pre-treatment section (SWIP) consists of a low pressure pump, a filter and chemical treatment. The acquisition cost of the equipment in USD is estimated using a correlation of El-Emam & Dincer (El-Emam & Dincer, 2014), adjusted for annual inflation:

$$PC_{SWIP} = 1184 \cdot \dot{V}_t^{4/5} \quad (3.1)$$

where $\dot{V}_t$ represents the total fed seawater volumetric flow rate in m^3/day .

The annual energy cost in USD/year of the low-pressure pump is calculated in this study using the following equation:

$$\dot{C}_{e,SWIP} = p_{SWIP} \cdot \dot{V}_t \cdot f_1 \cdot C_e / \eta_{SWIP} \quad (3.2)$$

where p_{SWIP} represents the pressure after the pump in kPa; $\dot{V}_t$ corresponds to the total fed seawater volumetric flow rate in m^3/s ; f_1 is the plant load factor, varying between 0 and 1; C_e represents the price of the electricity at the origin in USD/(kWyear) and η_{SWIP} is the low-pressure pump efficiency.

The estimate of the acquisition cost of the high-pressure pump is based on the equation presented by El-Emam & Dincer adjusted for annual inflation (El-Emam & Dincer, 2014):

$$\log_{10} \left(\frac{PC_{HPP}}{1.189} \right) = 3.389 + 0.054 \log_{10}(p_{HPP} \cdot \dot{V}_{RO} \cdot f_1 / \eta_{HPP}) + 0.154 [\log_{10}(p_{HPP} \cdot \dot{V}_{RO} \cdot f_1 / \eta_{HPP})]^2 \quad (3.3)$$

in this equation p_{HPP} represents the pressure after the high-pressure pump in kPa; $\dot{V}_{RO}$ is the water volumetric flow rate of the pump expressed in m³/s and η_{HPP} stands for the high-pressure pump efficiency.

To calculate the annual energy cost of this pump, the same method is used as for the low-pressure pump, substituting the values of pressure and water flow rate after the pump, as well as its efficiency (90 %).

The cost of reverse osmosis membranes is determined by the following equation (El-Emam & Dincer, 2014):

$$PC_{RO} = 10 \cdot N \cdot A \quad (3.4)$$

where N is the number of membranes used and A is the area of each membrane.

The purchase cost of the Pelton turbine is established based on the expression of El-Emam & Dincer adapted for annual inflation (El-Emam & Dincer, 2014):

$$\log_{10} \left(\frac{PC_{PT}}{1.189} \right) = 2.248 + 1.497 \log_{10}(p_{PT} \cdot \dot{V}_{brine} \cdot f_1 \cdot \eta_{PT}) - 0.1618 [\log_{10}(p_{PT} \cdot \dot{V}_{brine} \cdot f_1 \cdot \eta_{PT})]^2 \quad (3.5)$$

where p_{PT} stands for the pressure upstream of the turbine in kPa; $\dot{V}_{brine}$ denotes the brine volumetric flow rate through the turbine in m³/s, and η_{PT} represents the efficiency of the turbine.

O&M expenses for the low-pressure pump, high-pressure pump, RO cartridges, and turbine are set at 5 %, 4 %, 1 %, and 4 % of the Total Capital Investment (TCI), correspondingly. The TCI is defined as the total cost required for planning, designing, constructing, and commissioning the facility. For this study, TCI is calculated as 6.32 times the equipment purchase cost (Bejan et al., 1996).

The yearly expense for chemical treatment is determined as follows (El-Emam & Dincer, 2014):

$$\dot{C}_{op,ch} = \dot{V}_t \cdot f_1 \cdot C_{ch} \quad (3.6)$$

where $\dot{V}_t$ represents the total volumetric flow rate of seawater intake in m³/year, and C_{ch} is the cost of the chemical treatment per water volume, 0.018 USD/m³.

Throughout the lifespan of the plant, two replacements of the low-pressure pump, high-pressure pump and turbine are anticipated. The yearly replacement cost of RO cartridges is computed as (El-Emam & Dincer, 2014):

$$\dot{c}_{op,RO} = r_m \cdot cc_{RO} \cdot \dot{V}_{RO} \quad (3.7)$$

where r_m stands for the membrane replacement factor, set at 0.01; cc_{RO} is the cost of cartridge filters, at 0.01 USD/m³, and $\dot{V}_{RO}$ represents the water volumetric flow rate through the membranes in m³/year.

The values of the parameters used in the technoeconomic model to derive the results for the water treatment plant are listed in Table 4.1 of Section 4.1 Methanol as energy carrier.

In dissecting the expenses of the entire hydrogen infrastructure, the electrolysis plant emerges as a pivotal component. Linear models are dismissed due to their failure to account for scale effects in larger setups. Hence, investment costs must, at the very least, reflect the scale effects of hydrogen output and the nominal efficiency of the plant. Operating under a designated efficiency, the electrolyser works at a specific current density continuously with electricity from renewable sources, so the capacity factor assigned for this study is 1. In this context, the empirical equation proposed by Lmmen et al. (Lmmen et al., 2019), based on an earlier model by Oi & Wada (Oi & Wada, 2004), for estimating the cost of a proton exchange membrane (PEM) electrolysis plant, denoted as C_{EC} , proves suitable. Updated to 2021 currency values, the equation, expressed by the nominal mass flow rate of hydrogen, is as follows:

$$C_{EC} = 9.06 \cdot 10^7 \cdot \frac{\dot{m}_{H_2}^{0.79}}{j^{0.32}} \quad (3.8)$$

where $\dot{m}_{H_2}$ is expressed in kg/s and the current density j in A/cm².

The expected annual O&M cost amounts to 1.5 % of the installed cost (Godula-Jopek, 2015). The lifespan of an electrolyser can extend up to 100000 h (Godula-Jopek, 2015), necessitating at least two complete midlife refurbishments.

The basic reaction for the electrolysis of water can be described as follows (Shiva Kumar & Lim, 2022):



Considering Eq. 3.9, the electrical power consumed by the electrolysis plant $\dot{W}_{ext,electrol}$ can be computed by:

$$\dot{W}_{ext,electrol} = \frac{\dot{m}_{H_2} \cdot h_{H_2} + \dot{m}_{O_2} \cdot h_{O_2} - \dot{m}_{H_2O} \cdot h_{H_2O}}{\eta_{electrol}} \quad (3.10)$$

where $\dot{m}_{H_2} = M_{H_2}/M_{H_2O} \cdot \dot{m}_{H_2O}$, $\dot{m}_{O_2} = M_{O_2}/M_{H_2O} \cdot \dot{m}_{H_2O}/2$, and the enthalpies are computed as follows:

$$h_{H_2} = \Delta h_{f_{H_2}}^0 + [h_{H_2}(T, p) - h_{H_2}(T^0, p^0)] \quad (3.11)$$

$$h_{O_2} = \Delta h_{f_{O_2}}^0 + [h_{O_2}(T, p) - h_{O_2}(T^0, p^0)] \quad (3.12)$$

$$h_{H_2O} = \Delta h_{f_{H_2O}}^0 + [h_{H_2O}(T, p) - h_{H_2O}(T^0, p^0)] \quad (3.13)$$

Here, $\Delta h_{f_i}^0(T^0, p^0)$ represents the enthalpy of formation of substance i at (T^0, p^0) and $[h_i(T, p) - h_i(T^0, p^0)]$ is the enthalpy increment of substance i from (T^0, p^0) to (T, p) .

The power consumed by the electrolysis plant does not equate to energy loss since electrical energy is converted into chemical energy in the form of hydrogen $\dot{m}_{H_2} \cdot HHV_{H_2}$. To determine the total energy lost in the electrolysis process the First Law of Thermodynamics can be applied to the electrolyser system:

$$\begin{aligned} -\dot{Q}_{ext,electrol} + \dot{W}_{ext,electrol} \\ = \left. \frac{dE}{dt} \right|_{CV} + \sum \dot{m}_{H_2} h_{H_2} + \sum \dot{m}_{O_2} h_{O_2} - \sum \dot{m}_{H_2O} h_{H_2O} \end{aligned} \quad (3.14)$$

For steady state $\left. \frac{dE}{dt} \right|_{CV} = 0$:

$$-\dot{Q}_{ext,electrol} + \dot{W}_{ext,electrol} = \sum \dot{m}_{H_2} h_{H_2} + \sum \dot{m}_{O_2} h_{O_2} - \sum \dot{m}_{H_2O} h_{H_2O} \quad (3.15)$$

If considering energy losses all but the hydrogen obtained, total energy lost, $\dot{E}_{lost}$, in the electrolyser system can be calculated as follows:

$$\dot{E}_{lost} = \dot{W}_{ext,electrol} - \sum \dot{m}_{H_2} h_{H_2} \quad (3.16)$$

Thus, by considering the Eq. 3.15 and 3.16 the total energy loss of the electrolyser can be obtained as:

$$\dot{E}_{lost} = \dot{Q}_{ext,electrol} + \sum \dot{m}_{O_2} h_{O_2} - \sum \dot{m}_{H_2O} h_{H_2O} \quad (3.17)$$

For calculating the levelized cost of hydrogen, $\dot{W}_{ext,electrol}$ will be used. However, for the life cycle cost of the system $\dot{E}_{lost}$ is employed.

The values of the parameters used in the technoeconomic model to derive the results for the water electrolysis plant are listed in Table 4.2 of Section 4.1 Methanol as energy carrier.

The characteristics and technoeconomic models of the facilities that are exclusively part of the alternative based on liquefied hydrogen transport are described below.

For estimating the costs of the hydrogen liquefaction plant various cost prediction models have been identified, all based on H2A models (Elgowainy & Reddi, 2015). Given that the largest hydrogen liquefaction plant handles 0.35 kg/s (30 t/day) (Aasadnia & Mehrpooya, 2018), it is recommended not to extrapolate beyond 2.31 kg/s (200 t/day) (T.-P. Chen, 2010). However, the International Energy Agency (IEA) report on the future of hydrogen assumed a plant capacity of 8.24 kg/s (712 t/day) with an estimated cost of 1400 MUSD (International Energy Agency, 2019b). Attempting to extrapolate for 8.24 kg/s using the prediction model from Chen yields an estimated cost of around 669 MUSD (T.-P. Chen, 2010). However, utilizing the prediction model from HDSAM produces a result of 1427 MUSD. Hence, despite some uncertainty, the cost prediction model from HDSAM allows reasonably accurate extrapolations for high liquefaction rates. The infrastructure cost for the liquefaction plant, denoted as C_{LP} , in 2021 USD is estimated by the Eq. 3.18 (Elgowainy & Reddi, 2015).

$$C_{LP} = 2.59 \cdot 10^8 \cdot \dot{m}_{H_2}^{0.8} \quad (3.18)$$

here, C_{LP} is expressed in USD, and $\dot{m}_{H_2}$ in kg/s.

Liquefaction plants are very reliable, with an annual availability of 98.5 % (T.-P. Chen, 2010). The total annual O&M cost, excluding electricity, is approximately 3 % of the total installation cost (Elgowainy & Reddi, 2015). Several mid-life refurbishments are anticipated, as compressors, turbines, and pumps of the liquefaction plant will require replacement. Approximately 40 % of the total capital cost is allocated for this purpose, based on the assumption that around 20 % of the total cost is associated with components subject to mechanical wear, such as turbines, compressors, and pumps.

The conversion of hydrogen into a liquefied state is deemed an energy loss in this context, as energy recovery systems are not considered. Consequently, energy losses will be calculated by multiplying the mass of produced hydrogen in the lifecycle of the liquefaction plant by the specific work for hydrogen liquefaction, denoted as w_{liquef} .

The values of the parameters used in the technoeconomic model to derive the results for the hydrogen liquefaction plant are listed in Table 4.3 of Section 4.1 Methanol as energy carrier.

After being obtained through the liquefaction process, liquefied hydrogen needs to be stored before being loaded onto the ship. Storing large quantities of liquid hydrogen most cost-effectively is achieved through double-walled spherical tanks. Typically, the outer wall is constructed of lightweight steel, while the inner wall is often composed of austenitic stainless steel. Perlite fills the annular space between the walls, with the air evacuated to prevent condensation on the cryogenic inner wall. HDSAM Version 3.0 incorporates specific cost data for such tanks, including capacities of 280 t and 70 t, with uninstalled costs of 7.217 MUSD (2014) and 1.684 MUSD (2014), respectively (Elgowainy & Reddi, 2015). The IEA report on hydrogen's future also provides data for a 3190 t capacity tank, priced at 290 MUSD (2018) (International Energy Agency, 2019b). Other works offer a predictive model for spherical tank costs based on size (T.-P. Chen, 2010), though a new regression is conducted for a more recent cost model, denoted as C_{LHT} . This regression follows a potential model, aligning best with available data (d'Amore-Domenech et al., 2021). The resulting equation from this potential curve fit is:

$$C_{LHT} = 0.51 \cdot m_{H_2}^{1.344} \quad (3.19)$$

where C_{LHT} is expressed in USD and m_{H_2} in kg.

The installed cost can be estimated at 1.3 times the uninstalled cost of the spherical tank (T.-P. Chen, 2010). The total O&M cost is approximated at about 3 % of the total installed cost of the tank, with no mid-life refurbishments anticipated for the liquid hydrogen storage system. Energy losses of the tank involve the re-liquefaction energy of the boil-off of stored hydrogen.

The values of the parameters used in the technoeconomic model to derive the results for the liquefied hydrogen storage plant are listed in Table 4.4 of Section 4.1 Methanol as energy carrier.

From a financial standpoint, there are two main approaches to operating a ship for bulk hydrogen transportation: ownership or chartering. Under ownership, one is responsible for all aspects of ship operation, whereas chartering involves hiring a ship and holding the shipowner responsible for some operational expenses in exchange for a charter rate (Figure 3.5).

Fixed costs		Voyage costs		Cargo handling costs		
CAPEX	Fixed operating costs	Proportional costs	Non-proportional costs	Loading and unloading		
Bareboat charter						
Time charter						
Voyage charter						
Vessel ownership						

Figure 3.5: Choices for vessel operations in the bulk transport of goods. The obscured areas denote expenses assumed by the shipowner, while the illuminated areas signify supplementary costs assumed by the charterer

Three common charter types are bareboat charter, time charter, and voyage charter (Mazioli et al., 2019; Plomaritou & Papadopoulos, 2017). In a bareboat charter, the charterer assumes full control and responsibility for the operation and expenses of the vessel (Plomaritou & Papadopoulos, 2017). Conversely, in a time charter, the shipowner covers fixed costs, while the charterer pays for variable expenses. A voyage charter sees the shipowner bearing all voyage-related costs except for cargo loading and unloading under FIO (Free In and Out) terms (Plomaritou & Papadopoulos, 2017). For consistent point-to-point travel, bareboat or time charter options are preferable due to their cost-effectiveness compared to ship ownership or voyage charter. Of the two, time charter is favoured by non-specialized companies due to reduced operating costs. Hence, it is the chosen option.

Time charter rates vary depending on factors like market conditions, cargo type, and vessel size and age. Negotiations determine the final rate, influenced by bargaining power. Despite no operational fleet for bulk hydrogen transportation as of now, the LNG fleet can serve as a reference for estimating LH₂ freight rates, alongside the compressed natural gas (CNG) fleet for compressed H₂ charter rate estimation. Spot charter rates typically cover contracts of six months or less, while long-term rates extend beyond five years (IGU, 2019). Spot rates are volatile, whereas long-term rates provide stability. For LNG, both spot and long-term rates saw a decline post-2012 Fukushima accident. Spot rates dropped from 160 kUSD/day in Q1 2012 to 30 kUSD/day in mid-2015, rebounding to 150 kUSD/day

by late 2018. Long-term rates also decreased from 90 kUSD/day in Q1 2012 to 60 kUSD/day by Q1 2018, rising to 70 kUSD/day by Q4 2018 (IGU, 2019; Steuer, 2019). A long-term benchmark charter rate of 90 kUSD/day is assumed for LH₂.

Ships transporting hydrogen consume part of the cargo, with consumed hydrogen counted as an energy loss. Non-proportional voyage costs like taxes and marine services vary by harbour and vessel (H. Meersman et al., 2015). A fixed 15 kUSD non-proportional voyage cost per land terminal is assumed. Loading and offloading facilities are included in logistic chain analysis, so no additional tolls or fees are expected.

The time for one roundtrip (t_{RT}) can be estimated by Eq. 3.20:

$$t_{RT} = 2 \cdot \frac{l}{s_V} + t_{LS} + \frac{V_H}{\dot{V}_L} + \frac{m_{OL}}{\rho_l(1 \text{ bar}) \cdot \dot{V}_{OL}} \quad (3.20)$$

where l represents the distance between the endpoints, s_V denotes the velocity of the vessel during cruising, t_{LS} signifies the additional time during the approach and departure at both end terminals at low speed, V_H represents the volume of the holds, $\dot{V}_L$ is the loading volumetric flow rate of the liquefied hydrogen, m_{OL} represents the off-loaded mass of hydrogen at the receiving terminal, $\rho_l(1 \text{ bar})$ represents the density of hydrogen as saturated liquid at 1 bar, and $\dot{V}_{OL}$ represents the off-loading flow rate of the liquefied hydrogen.

The offloaded mass of hydrogen m_{OL} is determined by the equation:

$$m_{OL} = m_L - m_C \quad (3.21)$$

where m_L is the loaded mass of hydrogen, which corresponds to the total cargo capacity of the vessel and m_C is the hydrogen consumed during the roundtrip.

The consumed mass of hydrogen m_C is estimated as follows:

$$m_C = 2 \cdot \frac{l}{s_V} \cdot cr_C + \left(\frac{V_H}{\dot{V}_L} + \frac{m_{OL}}{\rho_l(1 \text{ bar}) \cdot \dot{V}_{OL}} \right) \cdot cr_{L,OL} \quad (3.22)$$

here cr_C is the consumption rate of hydrogen during navigation and $cr_{L,OL}$ is the consumption rate of hydrogen during loading and offloading.

The number of ships, N_{ships} , required in the fleet can be calculated by Eq. 3.23:

$$N_{ships} = \frac{\dot{m}_{H_2} \cdot t_{RT}}{m_L} \quad (3.23)$$

where $\dot{m}_{H_2}$ is the mass flow rate of the produced hydrogen.

If the number of ships is not an integer, then the velocity of the ship during navigation is decreased until the Eq. 3.24 yields a whole number. The reduction of the ship velocity, s_V , also reduces the consumption rate of hydrogen during cruising, cr_C , according to the cubic rule:

$$cr_C = \frac{\dot{W}_{nom}}{\eta_{FC} \cdot LHV} \cdot \left(\frac{s_V}{s_{V_{nom}}} \right)^3 \quad (3.24)$$

where $\dot{W}_{nom}$ is the power developed at cruise speed, η_{FC} is the fuel cell efficiency, LHV is the Lower Heating Value of hydrogen, and $s_{V_{nom}}$ is the nominal cruise speed of the ship.

The number of voyages throughout the assumed operational lifetime $N_{voyages}$ can be estimated using Eq. 3.25:

$$N_{voyages} = \frac{t_L}{t_{RT}} \quad (3.25)$$

where t_L is the life cycle time.

The life cycle cost of the fleet of ships C_{fleet} can be estimated by:

$$C_{fleet} = N_{ships} \cdot (t_{RT} \cdot c_{TC} + C_V) \quad (3.26)$$

where c_{TC} is the time charter rate and C_V represents the voyage costs for one round trip.

The values of the parameters used in the technoeconomic model to derive the results for the liquefied hydrogen transport are listed in Table 4.5 of Section 4.1 Methanol as energy carrier.

After the transportation of liquefied hydrogen, the next crucial step involves converting it back into its gaseous state to enable its consumption at the destination. This process is facilitated by a regasification plant.

Certain hydrogen refuelling stations utilize evaporators to generate hydrogen under conditions suitable for storage in vehicles. The HDSAM Version 3.0 incorporates specific cost data for facilities employing this technology. An equation featured in HDSAM illustrates the correlation between the uninstalled cost of evaporators and the mass flow rate of hydrogen obtained. This equation is adjusted to account for annual inflation:

$$C_{Regasif} = (5.95 \cdot 10^5 \cdot \dot{m}_{H_2} + 122) \cdot f_{install} \quad (3.27)$$

here, $\dot{m}_{H_2}$ represents the mass flow rate of hydrogen in kg/s, and $f_{install}$ is the installation factor.

The values of the parameters used in the technoeconomic model to derive the results for the regasification plant are listed in Table 4.6 of Section 4.1 Methanol as energy carrier.

Having discussed LH₂ transportation facilities in preceding paragraphs, the focus now shifts to outlining the commonalities shared with the alternatives based on methanol transportation.

The cost estimation for a methanol synthesis facility in this study is derived from the relationship with the methanol production rate it can achieve. Utilizing economic data on methanol synthesis plants sourced from the International Renewable Energy Agency (International Renewable Energy Agency & Methanol Institute, 2021), a regression analysis is conducted. This dataset encompasses the expenses associated with an electrolysis plant required for hydrogen production essential to methanol synthesis. Consequently, to determine the synthesis facility cost, the calculated cost of the electrolysis plant from this investigation, inclusive of refurbishment, is subtracted from the overall cost derived from the regression equation:

$$C_{Synth} = 5.73 \cdot 10^7 \cdot \dot{m}_{MeOH}^{0.91} - 3 \cdot C_{EC} \quad (3.28)$$

where $\dot{m}_{MeOH}$ is expressed in kg/s.

The O&M expenses of a methanol synthesis plant encompass fixed operational expenditures (OPEX) and the procurement cost of CO₂ necessary for the process. Fixed OPEX is determined as a percentage of the fixed capital investment (Nyári et al., 2020). The mass flow rates of CO₂ and H₂ required for methanol production are acquired from published parameters: 1.397 kgCO₂/kgMeOH and 0.192 kgH₂/kgMeOH, respectively (Nyári et al., 2020). Additionally, the electric energy consumption is correlated with the methanol production rate, estimated at 0.175 MWh/t (Nyári et al., 2020).

The values of the parameters used in the technoeconomic model to derive the results for the methanol synthesis plant are listed in Table 4.7 of Section 4.1 Methanol as energy carrier.

In the process of methanol use as hydrogen vector, it is necessary to consider the storage phase after synthesis and prior to transportation. This intermediate storage stage allows for the optimization of shipping schedules and the facilitation

of timely deliveries to destination. Additionally, storage facilities help to mitigate supply chain disruptions by providing a buffer against production fluctuations and unexpected demand surges. In this investigation, the cost assessment of methanol storage tanks does not capitalize on economies of scale, as the pricing reference is anchored on a 200-ton methanol tank. The cost estimation for the storage facility is determined using Eq. 3.29 (C. Chen & Yang, 2021).

$$C_{SMeOH} = 53.1 \cdot m_{MeOH} \quad (3.29)$$

where m_{MeOH} denotes the maximum storage capacity of methanol storage facilities, expressed in kg.

The values of the parameters used in the technoeconomic model to derive the results for the methanol storage facilities are listed in Table 4.8 of Section 4.1 Methanol as energy carrier.

While there are currently ships designed for methanol transportation (Mitsui O.S.K. Lines, 2016; Wärtsilä, 2024b), insufficient economic data exist for this specific ship type to construct a robust model. Nonetheless, given the similarities between ships transporting methanol and conventional tanker ships, the costs associated with the latter serve as a reference for estimating methanol freight rates. Economic data published for tanker ships indicate an average time charter rate of 16918 USD/day for a Long Range 1 (LR1) type (74000 dwt) tanker ship in 2020 (Clarkson Research Services Limited, 2021). Adjusting for annual inflation and considering a larger ship (120000 m³) currently transporting methanol (Wärtsilä, 2024b), an estimated time charter rate of 19000 USD/day is adopted in this analysis. In terms of consumables, it is assumed that ships transporting methanol as cargo will consume a portion of the methanol cargo for transportation purposes. A fixed non-proportional voyage cost of 15000 USD per land terminal is accounted for. Loading and offloading facilities are included in the logistic chain analysis, thus no additional tolls or fees are anticipated.

The methanol transport model shares similarities with the previously described hydrogen transport model, albeit differing in the characteristics of the vessels involved. The values of the parameters used in the technoeconomic model to derive the results for the methanol transport fleet are listed in Table 4.9 of Section 4.1 Methanol as energy carrier.

Presently, commercial methanol electrolysis units are unavailable. However, models for estimating the cost of methanol electrolyzers can be derived from those used for PEM water electrolysis, see Eq. 3.8, due to the design similarities between

PEM methanol electrolysis and PEM water electrolysis. To adapt the model, differences between methanol and water electrolysis systems are identified, and appropriate adjustments are made to the water electrolysis unit model.

The catalyst composition and content differ between methanol and water electrolysis systems. Methanol Electrolysis Cells (MECs) typically contain Pt and Pt-Ru alloy in the range of 1.5-2.0 mg/cm² (H. K. Ju et al., 2018), whereas PEM water electrolysis cells contain approximately 0.8 mg/cm² of Pt and 2.5 mg/cm² of Ir (Carmo et al., 2019). The catalyst cost for methanol electrolyser is approximately 2.60 · 10⁻² USD/cm², compared to 8.29 · 10⁻² USD/cm² for water electrolysis. Catalyst-coated membranes contribute 25-45 % to the cost breakdown of commercial PEM water electrolyzers, with catalysts accounting for 30-50 % of the membrane cost (Mayyas et al., 2019). Consequently, the impact of these precious metals ranges from 7.5-22.5 % of the total cost. Therefore, for the same area and number of cells in an electrolysis unit, the cost factor for calculating the cost of an equivalent methanol electrolysis cell can be estimated between 0.582 and 0.807. These factors are applied in Eq. 3.8 to account for this difference in catalyst cost with respect to water electrolyzers.

The polarization curves of methanol electrolyzers exhibit lower current densities and decreased faradaic efficiencies. This faradaic efficiency can be defined as the ratio between the amount of the product obtained, in this case the amount of hydrogen, and the amount of theoretical product that could be obtained from the total electrical energy provided. Thus, these characteristics make it necessary larger electrolysis stacks to achieve the same hydrogen production rate. While water PEM electrolysis stacks typically operate at around 1 A/cm² (Carmo et al., 2019), methanol equivalents operate at significantly lower current densities. A suitable balance between electrolysis rate and efficiency may be achieved at 150 mA/cm², with a corresponding cell voltage of approximately 0.5 V. Consequently, the size of the electrolyser equivalent increases by a factor of 6.7, applied in Eq. 3.8 to consider this difference in size.

Assuming a methanol electrolysis standard of 150 mA/cm², to adapt the water electrolyser cost model developed considering a current density of around 1 A/cm² presented in Eq. 3.8, a factor of $j_0^{0.32} = 0.150^{0.32} = 0.54$ is applied.

Besides, methanol electrolysis faradaic efficiencies for 150 mA/cm² current density range typically between 0.70 and 0.75 (Sethu et al., 2014). To maintain the amount of hydrogen that would be produced with a water electrolyser operating at a

faradaic efficiency closer to 1, the size of the methanol electrolyser operating at a faradaic efficiency around 0.70 would have to be increased, so comparing these efficiencies a factor of between 1.3 and 1.4 is applied in Eq. 3.8 to account for this difference in efficiency in the cost of the methanol electrolysis plant.

Applying in Eq. 3.8 all these factor accounting for the differences in catalyst costs and size of methanol electrolyser compared to water electrolyzers, the extrapolated model for the cost of the methanol electrolysis plant can be represented as follows:

$$C_{EC} = (3.1 \pm 0.6) \cdot 10^8 \cdot \frac{\dot{m}_{H_2}^{0.79}}{j^{0.32}} \quad (3.30)$$

where $\dot{m}_{H_2}$ is expressed in kg/s and the current density j in A/cm².

The O&M procedures for methanol electrolyzers are anticipated to mirror those of a water electrolyser. Hence, the anticipated annual O&M cost is 6 USD/kW. The lifespan of an electrolyser can extend up to 100000 hours, thus necessitating at least two complete midlife refurbishments.

The basic reaction for the methanol electrolysis can be described as follows (Lamy, 2020):



Considering Eq. 3.31, the electric power consumed by the electrolysis plant $\dot{W}_{ext, meth-electrol}$ can be computed using the following equation:

$$\begin{aligned} \dot{W}_{ext, meth-electrol} \\ = \frac{\dot{m}_{H_2} \cdot h_{H_2} + \dot{m}_{CO_2} \cdot h_{CO_2} - \dot{m}_{H_2O} \cdot h_{H_2O} - \dot{m}_{CH_3OH} \cdot h_{CH_3OH}}{\eta_{meth-electrol}} \end{aligned} \quad (3.32)$$

where $\dot{m}_{H_2} = \frac{M_{H_2}}{M_{H_2O}} \cdot \dot{m}_{H_2O} \cdot 3$, $\dot{m}_{CO_2} = M_{CO_2}/M_{H_2O} \cdot \dot{m}_{H_2O}$; $\dot{m}_{CH_3OH} = M_{CH_3OH}/M_{H_2O} \cdot \dot{m}_{H_2O}$ and the enthalpies are obtained as:

$$h_{CO_2} = \Delta h_{f_{CO_2}}^0(T^0, p^0) + [h_{CO_2}(T, p) - h_{CO_2}(T^0, p^0)] \quad (3.33)$$

$$h_{CH_3OH} = \Delta h_{f_{CH_3OH}}^0(T^0, p^0) + [h_{CH_3OH}(T, p) - h_{CH_3OH}(T^0, p^0)] \quad (3.34)$$

here, $\Delta h_{f_i}^0$ is the enthalpy of formation of substance i at (T^0, p^0) , and $[h_i(T, p) - h_i(T^0, p^0)]$ is the enthalpy increment of substance i from (T^0, p^0) to (T, p) .

Similar to PEM water electrolysis, the power consumed by the electrolysis plant does not coincide with energy losses. The energy lost, $\dot{E}_{lost}$, in the transformation of electricity into hydrogen can be calculated as:

$$\dot{E}_{lost} = \dot{W}_{ext, meth-electrol} - \sum \dot{m}_{H_2} h_{H_2} \quad (3.35)$$

For the calculation of the levelized cost of hydrogen, $\dot{W}_{ext, meth-electrol}$ is utilized. However, for the life cycle cost, $\dot{E}_{lost}$ is used.

The values of the parameters used in the technoeconomic model to derive the results for the methanol electrolysis plant are listed in Table 4.10 of Section 4.1 Methanol as energy carrier.

In order to compare with methanol electrolysis, this study provides also insights into the characteristics of a methanol steam-reforming plant for hydrogen production. To conduct this investigation, two types of methanol steam-reforming plants have been under consideration: a packed bed reactor (PBR) and a membrane reactor (MR). Although both reactor types produce CO₂ during operation, the CO₂ emission mass flow rate during hydrogen generation in an MR is lower compared to that of a PBR. Various studies have explored methanol reforming in PBRs (Kim et al., 2019). The characteristics of such reactors include high operating temperatures and the necessity for pressure swing adsorption for hydrogen purification. In contrast, MRs combine reforming and separation capabilities, enabling operation at lower temperatures and cost reduction. Given these attributes, this study focuses on analysing the cost of a methanol steam-reforming plant employing a MR.

To derive the cost of the methanol reforming facility, a regression analysis is conducted using data from membrane reactors as reported in Byun et al (Byun et al., 2020). Consequently, an equation is obtained to elucidate the relationship between installation cost and the mass flow of hydrogen produced after reforming:

$$C_{Reform} = 2.13 \cdot 10^6 \cdot \dot{m}_{H_2}^{0.60} \quad (3.36)$$

here $\dot{m}_{H_2}$ is expressed in kg/s.

To derive the O&M cost of the methanol steam reforming facility, a regression analysis is conducted using also data from Byun et al (Byun et al., 2020). This regression yields an equation that correlates the annual operational cost of the facility with the mass flow of hydrogen produced:

$$C_{O\&M Reform} = 4.0 \cdot 10^5 \cdot \dot{m}_{H_2}^{0.28} \quad (3.37)$$

As thermal energy is required to reform methanol into hydrogen, typically involving natural gas consumption, in this study the combustion of methanol arriving at the facility to fulfil the thermal energy requirements is used. The mass

flow of methanol necessary for the reforming process is determined based on the efficiency of a methanol reforming reactor:

$$\dot{m}_{MeOH_{Combustion}} = \dot{m}_{MeOH} \left(1 - \frac{\frac{LHV_{MeOH}}{LHV_{H_2}} \cdot \eta_{reform}}{r_{conv}} \right) \quad (3.38)$$

where $\dot{m}_{MeOH}$ represents the mass flow of methanol arriving at the facility in kg/s, LHV denotes the lower heating value of methanol and hydrogen in MJ/kg, η_{reform} signifies the efficiency of the methanol reforming reactor, and r_{conv} represents the mass ratio of hydrogen converted to methanol in the reforming process, expressed in kgH₂/kgMeOH.

The values of the parameters used in the technoeconomic model to derive the results for the methanol reforming plant are listed in Table 4.11 of Section 4.1 Methanol as energy carrier.

To facilitate the analysis of the results of the Levelized Cost Of Hydrogen (LCOH) obtained by applying the exposed methodology, the processes are grouped into different categories: production, packing, transport and unpacking. Within production, the hydrogen production processes are compiled for each of the alternatives studied. Packing includes the processes necessary to increase the energy density of the fuel for its transport, as well as storage at the terminal of origin. The process of transporting liquefied hydrogen or methanol by ship is then considered, depending on the alternative. Finally, in unpacking, the processes necessary to obtain hydrogen at the destination terminal are compiled, together with the storage of the transported fuel at this terminal. A summary of the cost structure for the calculation of the LCOH for each of the alternatives studied is presented in Figure 3.6, Figure 3.7 and Figure 3.8.

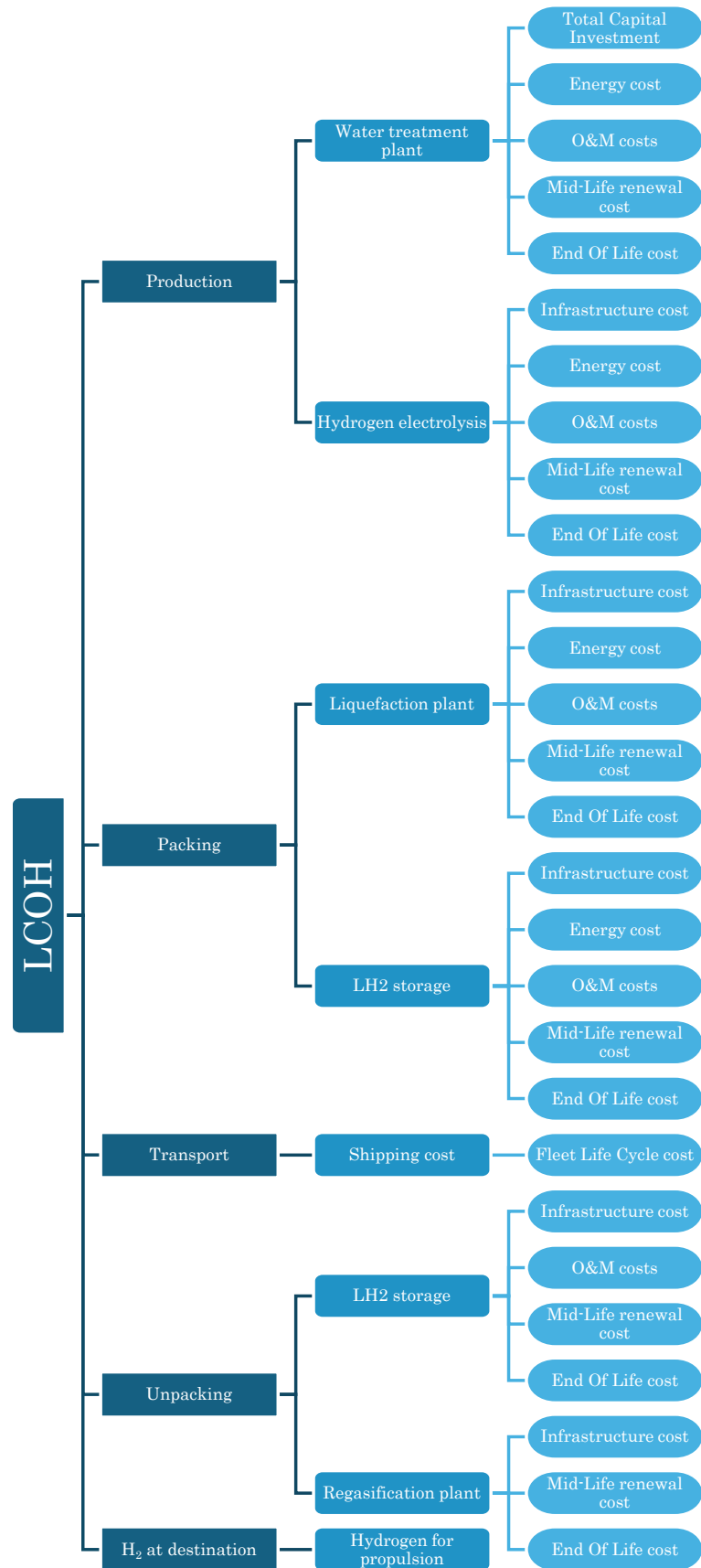


Figure 3.6: Summary of the cost structure for the Levelized Cost Of Hydrogen (LCOH) calculation of the liquefied hydrogen (LH2) alternative

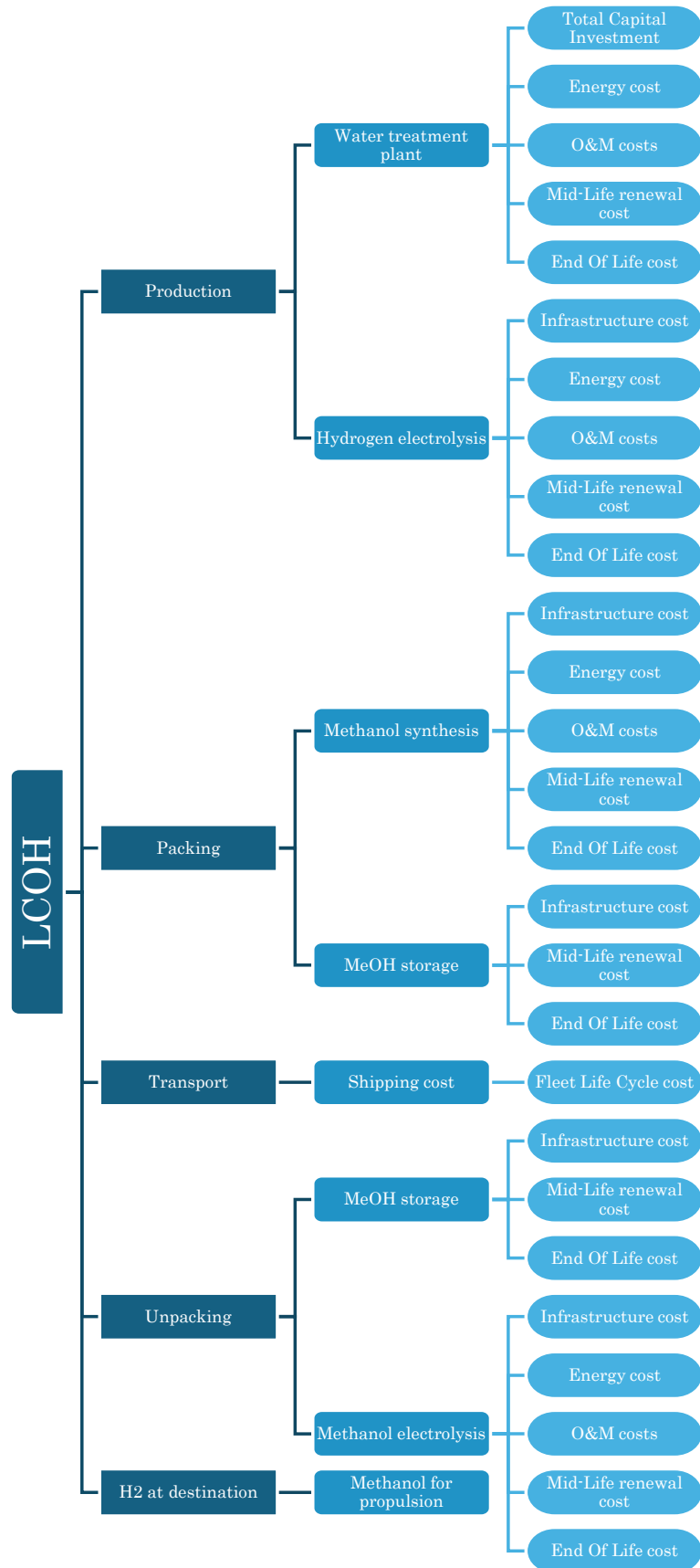


Figure 3.7: Summary of the cost structure for the Levelized Cost Of Hydrogen (LCOH) calculation of the e-methanol (MeOH) and its electrolysis alternative

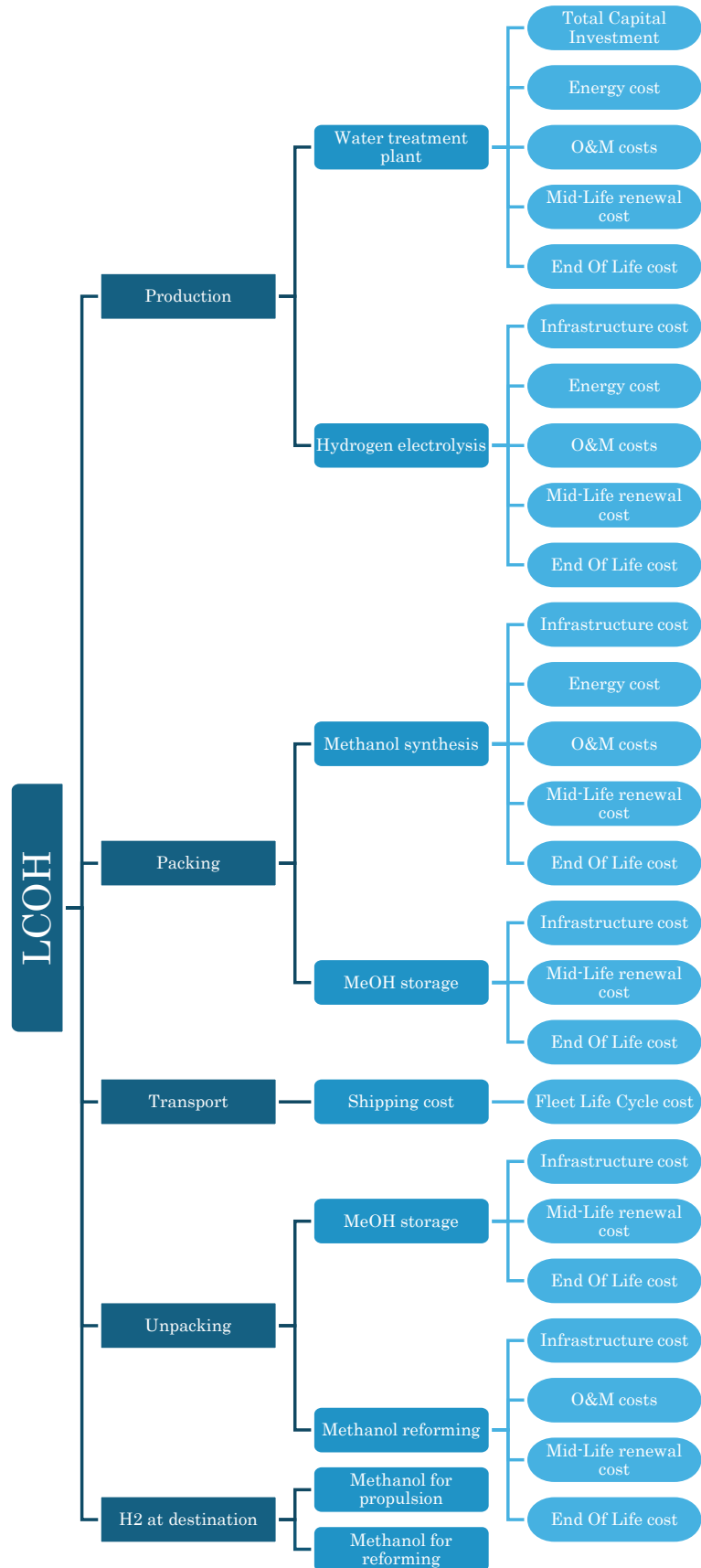


Figure 3.8: Summary of the cost structure for the Levelized Cost Of Hydrogen (LCOH) calculation of the e-methanol (MeOH) and its reforming alternative

3.2. Response Surface Methodology

Response Surface Methodology (RSM) is a statistical technique employed in the study and optimization of processes and systems. It facilitates the exploration and optimization of relationships between multiple variables by analysing the response of a system as a function of input variables, called factors, derived mainly from experimental data (Myers et al., 2016). RSM serves the purpose of optimizing processes, products and systems by identifying the operating conditions to obtain a desired response. It is widely used in various fields such as engineering, chemistry, agriculture and pharmaceuticals to, for example, enhance product quality, minimize production costs, maximize process efficiency, understand interactions among variables and identify optimal parameter settings. The application of RSM usually starts with the design of experiments (DoE), selecting the system and its associated factors to be studied and modifying their corresponding values by systematic variations while measuring the corresponding response of the system operating under these values of the factors. In this way, several steps can be distinguished in order to apply this methodology:

- The system to study is chosen.
- The factors that are related to the expected response of this system are specified.
- The interval of interest to evaluate the values of these factors is determined.
- The variations of the values of these factors and their combination with the values of other factors among those studied are determined on the basis of a design.
- The response of the system to the different combinations of these factors is determined.
- A mathematical model is generated that relates the values of the factors taken as input into the system and the response obtained from the system.
- The mathematical model obtained from experimental data is analysed for its adequacy and significance.
- The mathematical model obtained is used to find maximums or minimums in the response of the system, which will be associated with certain operating conditions of this system.

Within the different designs used to determine the values of the parameters to be studied the Central Composite Design (CCD) is a popular DoE design used in RSM (Myers et al., 2016). The CCD is characterised by its ability to explore both linearity and curvature in the relationship between factors and system response, making it a versatile tool for understanding the influence of multiple factors in a system. This design is based on the choice of *centre* points and determination of *factor* and *axial* points. The points represent a combination of factor values that will serve as inputs to the experiment to obtain the system response associated with that combination. *Centre* points represent typical or normal conditions of system operation. They serve to provide information on how the system behaves when the input variables are at intermediate values. These points help to characterise the response of the system under steady state conditions and to evaluate possible trend or bias effects in the data. *Factor* points allow the main effects of each factor to be assessed, i.e. how the response varies when one factor is changed while holding all other factors constant. *Factor* points are crucial to identify the individual influence of each factor on the response and to detect possible interactions between them. *Axial* points are located at a specific distance from the *centre* points along each design dimension. These points allow to explore extreme regions of the design space and to capture possible non-linear or quadratic effects of the factors. The location of the *axial* points and their distance to the *centre* point is determined by the specific design used. They serve to improve the precision of estimates of non-linear effects and to extend the range of exploration of the experimental design.

A schematic of the CCD when three factors are studied is shown in Figure 3.9, also representing *centre*, *factor* and *axial* points. This figure shows three axes (x_1 , x_2 and x_3), one for each factor studied, and the levels corresponding to each factor, i.e. the number of different values assigned to each factor. In this design, 5 levels can be differentiated for each factor, corresponding to the normalised values ($-\alpha$, -1 , 0 , $+1$ and $+\alpha$), where 0 represents the *centre* point and α determines the study range, value associated with *axial* points. The combinations of factor values to be tested are determined by selecting a *centre* point, the distance to range boundaries and α . The choice of the values corresponding to these levels and their distribution will be explained later.

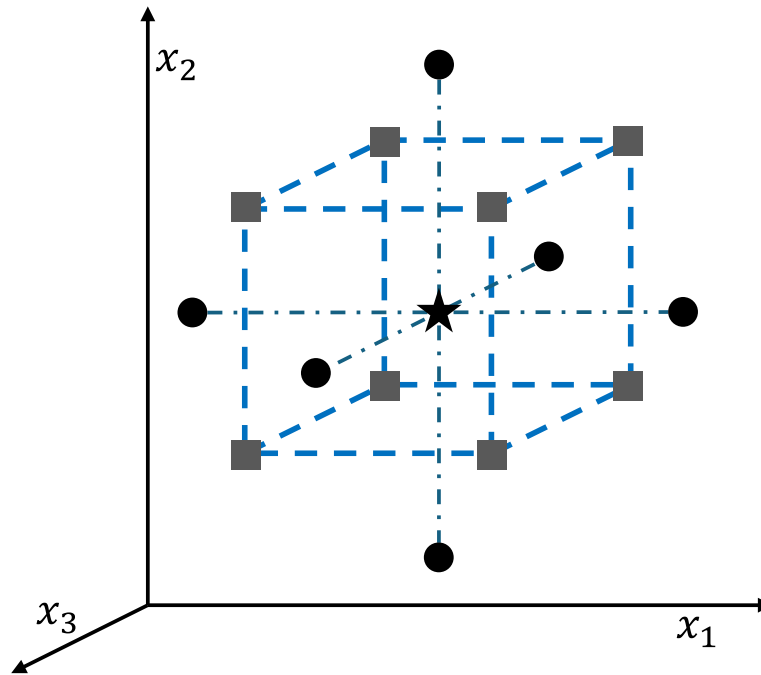


Figure 3.9: Schematic representation of the Central Composite Design (CCD) model for three factors. x_1 , x_2 and x_3 represent the axes corresponding to each of the factors. The stars represent the *centre* point, the squares the *factor* points and the circles the *axial* points of the CCD

Each of the points shown in Figure 3.9 with either stars, squares or circles represents a combination of factor values that will serve as inputs to the experiment to obtain the system response associated with that combination. In this way, the CCD as part of the called *fractional factorial designs*, is a design that does not evaluate all possible combinations of factor levels, but strategically selects a subset of points to minimise the total number of experiments while obtaining meaningful information about the system. This makes it efficient in terms of resources and time required to conduct the experiments.

To define the levels of each of the factors under study, the operating ranges of each factor must be identified. This involves defining the lower and upper limits within which the factors are relevant to the process or system under study. Practical considerations, such as resource constraints, technical viability and safety, must also be taken into account. It is important to select levels that are technically feasible and safe to operate during experiments. Within the CCD, 1, 0 and α values are commonly used to represent factor levels. These coded values are a way of representing the actual factor levels in the experimental design. The central value (level 0) represents the central level of the factor. This level usually corresponds to

the midpoint of the operating range of the factor and is chosen to represent typical or normal operating conditions. It is often used to collect additional data and assess the linearity of the model at this point. High and low values of one of the factors (levels +1 and -1, respectively) are chosen so that they are at a given distance from the centre point of the operating range of the factor. The extreme values ($-\alpha$ and $+\alpha$ levels) correspond to the limits of the study range of the parameter. The α value is a scaling factor used to calculate the distance between the high and low levels of the factor and the central level. The coded values (1, 0 and α) are related to the actual values of the parameters according to the following equation:

$$x_i = x_{0i} + (-1)^m \cdot f \cdot \Delta x_i \quad (3.39)$$

where:

- x_i is the actual value of the i factor.
- x_{0i} is the central value of the i factor.
- m has value 1 for the lower levels (-1 and $-\alpha$) and 2 for the higher ones (1 and α).
- Δx_i is the distance from the central level to the high and low levels of i factor.
- f is the scaling factor, defined as 1 in this study for the factorial points (+1 and -1 levels) and as $\sqrt{3}$ for the axial points (α and $-\alpha$ levels).

In this work the CCD with three factors and five levels ($-\alpha$, -1, 0, +1 and $+\alpha$) for each factor is used.

After carrying out the experiments associated with each of the points defined with the CCD, response data is collected and statistical models are fitted to describe the relationship between input variables and the response. Common models include linear, quadratic, and cubic models. In this work, to account for non-linear effects in the response of the system, quadratic models following the Eq. 3.40 are used (Myers et al., 2016):

$$y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum \sum_{i < j} \beta_{ij} x_i x_j + \sum_{i=1}^n \beta_{ii} x_i^2 \quad (3.40)$$

where y denotes the system response, β_0 is the constant coefficient, x_i and x_j represent the factors; β_i are the linear coefficients, β_{ij} stand for the interaction coefficients and β_{ii} are the quadratic coefficients.

After obtaining the mathematical model, various statistical analyses can be used to evaluate model adequacy and significance before mathematical techniques are applied to identify the desired operating conditions using the fitted response surface model. These statistical analyses include, among others, the items in the following list:

- Regression Analysis: used to fit a mathematical model to the experimental data collected during the RSM application. This analysis allows estimating the coefficients of the model, including main effects, interaction effects and quadratic effects, if applicable.
- Coefficient of Determination (R^2): this coefficient provides a measure of how much of the variability in the response is explained by the model. The values of R^2 lie between 0 and 1. A value closer to or coincident with 1, indicates a good fit of the model to the experimental data.
- Parameter Significance Tests: statistical tests, such as the *t-test* or the *p-values*, are used to determine whether the model coefficients have a significant effect on the response.
- Residual plots: these are used to assess the validity of the underlying assumptions of the regression model, such as normality of the residuals and homogeneity of variance. The residuals are the differences between the observed values from experimental data and the values predicted by the model.
- Analysis of Variance (ANOVA): ANOVA decomposes the total variability of the response into components attributable to the main factors, interactions and residual error. It allows to determine whether there are significant differences between treatments and whether the model is adequate to explain the observed variability in the data.

After obtaining a mathematical model using RSM, this model is analysed and visualised to better understand the relationship between the inputs and the desired response. This can be done by generating three-dimensional response surfaces, which show the relationship between the values of two input factors (two axis) and the response of the system (the third axis) in a three-dimensional space. These surfaces are generated by combining the values of the independent variables and the predicted values of the response according to the mathematical model obtained. By analysing these response surfaces, points can be found that maximise or minimise the desired response. These points represent the theoretical operating

conditions that would maximise the performance of the system or process under study.

In this work, a code has been programmed in MATLAB software to generate the CCD designs related to the three parameters and the boundary conditions chosen by the user, as well as the application of the RSM methodology to obtain the mathematical model and the response surfaces, as well as the ANOVA analysis of the model obtained. This code has been used to apply RSM to conduct the experimental study of the operating conditions of Direct Methanol Fuel Cells and Methanol Electrolysis Cells, using in both cases the volumetric flow rate of methanol, the methanol concentration and the temperature of the devices as factors. In addition, it has also been applied to the study of the effect of the anode flow field serpentine geometry of a Methanol Electrolysis Cell, using the open ratio, the channel width and the channel depth as factors. The three application cases of RSM within this study are summarized in Table 3.2., based on the device and factors used.

Table 3.2: Cases of application of the Response Surface Methodology in this work as a function of the device studied and the factors analysed

Case	Factors
Case 1: DMFC working conditions	• Methanol volumetric flow rate • Methanol concentration • DMFC temperature
Case 2: MEC working conditions	• Methanol volumetric flow rate • Methanol concentration • MEC temperature
Case 3: MEC anode flow field serpentine geometry	• Open ratio • Channel width • Channel depth

3.3. Direct Methanol Fuel Cell

In this work, DMFC single cells designed and manufactured as part of this thesis have been tested. These single cells are composed of 316 L stainless steel single

cell plates, which have been mechanised to incorporate channels with a flow field in a serpentine configuration. In addition, a MEA assembled with a Nafion® 117 membrane has been used, together with commercial Pt-Ru electrodes at the anode and Pt at the cathode. Technical details of the electrodes used in the experimental process to test DMFC single cells are compiled in Table 3.3.

Table 3.3: Characteristics of the electrodes used in the DMFC single cell

Parameter	Value
Anode catalyst	PtRu/C
Anode catalyst charge (mg/cm ²)	3 (molar ratio 1:1)
Anode commercial reference	BC-M100-30F
Anode supplier	Quintech
Cathode catalyst	Pt/C
Cathode catalyst charge (mg/cm ²)	1
Cathode commercial reference	BC-H225-10F
Cathode supplier	Quintech

Before assembling the MEA, the membrane and electrodes are prepared. The Nafion 117 membrane (H2Planet) is cut to the appropriate size to suit the specific design of the single cell being tested. In the case of this work, it is a square membrane of 5x5 cm². A treatment protocol is followed with this cut membrane prior to its use in the MEA assembly:

1. The membrane is immersed in a one-litre solution of 3 % w/v H₂O₂ heated to 353 K for one hour.
2. The membrane is cleaned with distilled water and immersed in one litre of distilled water heated to 353 K for one hour.
3. The membrane is cleaned with distilled water and immersed in a one-litre 0.5 M H₂SO₄ solution heated to 353 K for one hour.
4. The membrane is cleaned with distilled water and immersed in one litre of distilled water heated to 353 K for one hour.
5. The membrane is removed and rinsed with distilled water.

6. The membrane is placed between filter paper and stored for 24 h before assembling the MEA.

To prepare the electrodes, they are cut to the appropriate size to fit the size of the membrane and the design of the DMFC. In this work, electrodes of $4.25 \times 4.25 \text{ cm}^2$ are cut out, with an active area of 16 cm^2 after assembly. After cutting them out, a solution of Nafion® 1100 EW 5 % w (Mervilab) is sprayed onto the catalytic layer and the anode electrode is placed on one side of the Nafion® membrane and the cathode electrode on the other side, making sure that the catalytic layer is in direct contact with the membrane. Once the electrodes are placed on the membrane, they are hot-pressed, applying a pressure of 6 MPa using a hydraulic jack (MEGA MGH-30) at a controlled temperature of 403 K for 3 min to ensure a solid bond between the membrane and the electrodes. Once this process is completed, the MEA is ready for use in a DMFC.

As depicted in Figure 3.10, the assembled MEA is placed between two silicone gaskets and secured in position between two single cell plates by ensuring contact of the GDL of the electrodes with the channels mechanised in the plates and applying a torque of 1.5 N·m to each of the 8 screws which help to ensure uniformity of pressure at all points of the single cell.

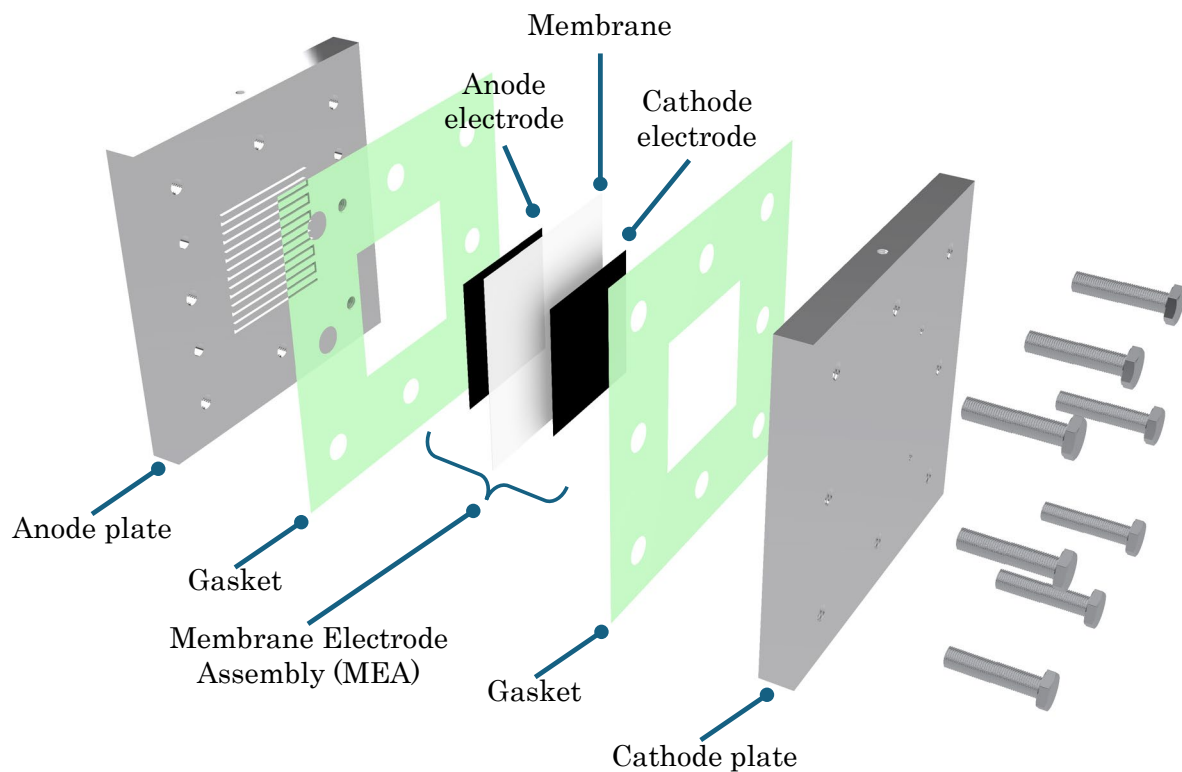


Figure 3.10: Schematic of the DMFC single cell assembly

The plates used in the single cell have dimensions of 10x10x1 cm³. These plates are designed and manufactured with threads to facilitate their fixing and ensure the necessary tightening torque, as can be seen in Figure 3.11. Other key threaded elements are also incorporated, such as the banana plugs necessary for the electrical connections and the fittings to allow the reactants to enter the DMFC. A serpentine flow field with a total area of 4x4 cm² is used for the cathode plate. It has a total of 25 straight channel sections with a rib width of 0.6 mm, a channel width of 1 mm and a channel depth of 0.5 mm. The configuration of the anode flow field varies to allow the study of the geometrical parameters that influence the behaviour of the DMFC. The information on the geometries used in the DMFC anode are shown in Section 3.3.3 DMFC flow field geometry.

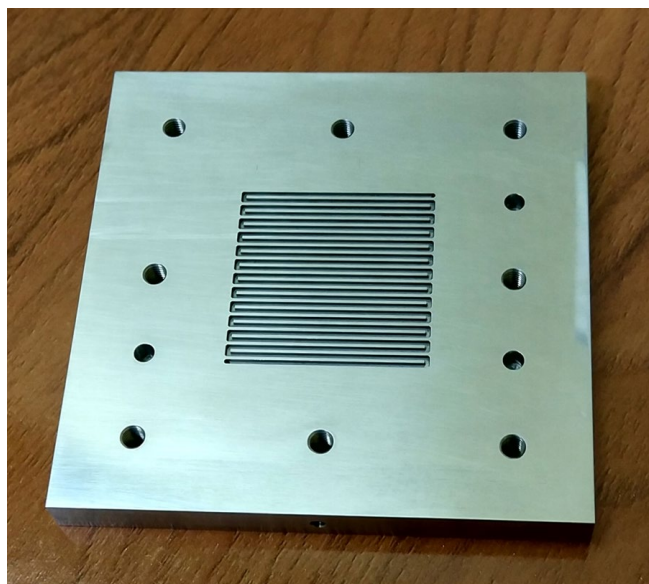


Figure 3.11: Photograph of a DMFC single-cell plate

To evaluate the influence of operating conditions or flow field geometry on the performance of a DMFC single cell the polarization curve test is used, see Figure 3.12, as a fundamental technique to understand and evaluate the electrochemical behaviour of a DMFC.

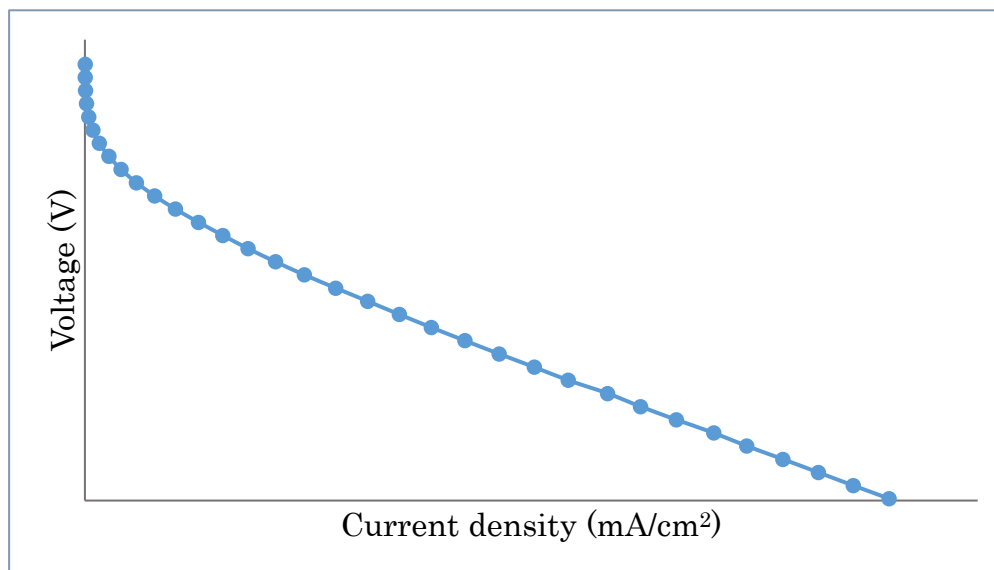


Figure 3.12: Direct Methanol Fuel Cell polarization curve

This procedure is performed during the supply of reactants to the single cell, i.e. passing a methanol flow rate at the anode and an oxygen or air flow rate at the cathode. For the polarization curves presented in this work, methanol (99.9 % purity, supplied by PanReac AppliChem) and oxygen (purity higher than 99.5 %, provided by Messer Iberica de Gases) has been used. Once the single cell is ready, it is connected to an external circuit to control the current or voltage generated by the DMFC single cell, depending on which one of these two is the setpoint signal. During the test, the current and voltage generated by the single cell are recorded as a function of the voltage or current signals used as the setpoint signal. This choice of variable to be monitored depends on the knowledge of the device and what response is to be evaluated. By controlling the voltage and measuring the current of the DMFC, a number of points can be recorded depending on the specific operation of the DMFC to be tested. This occurs because the potential can vary progressively, while controlling the current do not follow this evolution, potentially leading to a loss of control over the reactions occurring in the device when current is regulated. Consequently, exceeding the current limit when controlling the current may trigger another possible undesired reaction. Conversely, voltage control provides greater assurance in operating parameters and reactions. Besides, controlling voltage the polarization curve test can start from the OCV, which varies with changing operating conditions or device components, and gradually decrease with a fixed step until 0 V is reached, detecting the limiting current density. Fixing the current density better controls fuel consumption by fixing the current flowing

through the external circuit, but if the OCV or limiting current density is not known, a high current density step may result in too few points on the curve being recorded. For these reasons, the voltage has been controlled in order to obtain the DMFC polarization curves in this thesis.

The pairs of voltage and current values are used to construct the polarization curve, which is a graphical representation of the relationship between the current density and voltage of the cell. The current density is obtained by dividing the measured current by the active area of the single cell, in this work 16 cm^2 . To plot the polarization curves of the DMFC single cells tested in this work, the voltage is controlled by varying it from the Open Circuit Voltage (OCV) to 0 V with a step of 0.02 V. The OCV is the voltage in the cell with no current flowing through it. Each point on the curve is obtained by holding the voltage constant for 3 min to ensure a stable measurement. During these 3 min, voltage and current signals are recorded every 1 s. To plot the corresponding point on the curve, the values obtained during these 3 min are averaged to obtain the voltage-current density pair of values. The obtained polarization curve provides valuable information about the electrochemical behaviour of the single cell. From this curve, several important parameters can be extracted, such as the OCV. Another important parameter that can be obtained from the polarization curve is the limiting current density, which indicates the maximum current that the cell can supply. From the polarization curve, it is also possible to obtain the power density curve, see Figure 3.13, which shows how the power generated by the cell varies with the applied load.

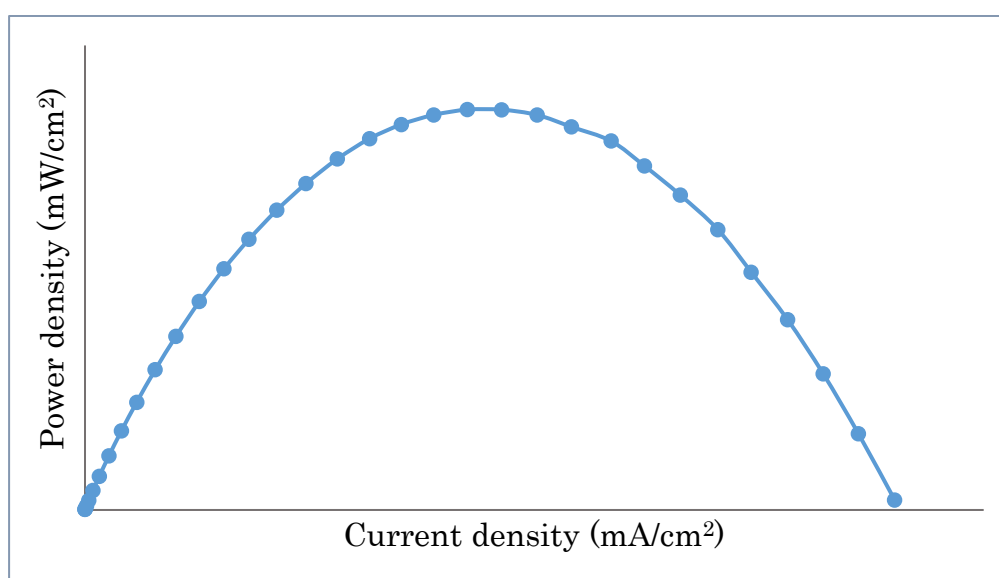


Figure 3.13: Direct Methanol Fuel Cell power density curve

This power density curve, see Figure 3.13, is obtained by multiplying the current density by the voltage at each point on the polarization curve shown in Figure 3.12. The maximum power is found at the point where the slope of the power density curve equals zero, indicating the point of maximum power density of the cell. The maximum power density or peak power density is the parameter most used in this work to evaluate the behaviour of the DMFC single cell studied. To obtain the polarization and power density curves, the test bench presented in the 3.3.1 Direct Methanol Fuel Cell test bench with air treatment system Section is used.

3.3.1. Direct Methanol Fuel Cell test bench with air treatment system

The direct methanol fuel cell test bench used in this research is the result of a previous design and construction, developed with the purpose of providing a controlled and reproducible environment for the evaluation of fuel cells under specific conditions (Santiago Carretero, 2021). This test bench, although already existing at the beginning of this thesis work, has undergone significant modifications during the course of the research to adapt it to the specific objectives of the study.

One of the main modifications made to the test bench has been the incorporation of a fuel cell measurement system using a programmable electronic load. This technical improvement allows a more detailed evaluation of the fuel cell performance under different operating conditions by providing the ability to control and adjust the electrical load applied to the cell in a programmable manner.

In addition to the incorporation of the aforementioned measuring system, improvements have been made to the electrical and pneumatic connections of the test bench. These improvements enhance the reliability and stability of the experimental system, allowing for reproducible data acquisition with less interference.

Another modification made to this test bench is the incorporation of a system that allows the fuel cell to operate using air as a reactant at the cathode and controlling both the temperature and humidity of this air stream. Until now, this test bench has operated with pure oxygen at the cathode of the DMFC with control of volumetric flow rate and pressure. The addition of this cathode air treatment line increases the capabilities of the DMFC study with this test bench.

The DMFC test bench, shown schematically in Figure 3.14, consists of four main systems: the oxidant supply system (Figure 3.14, 1 to 6), the fuel supply system

(Figure 3.14, 7 to 8), the temperature conditioning system (Figure 3.14, 9 to 12), and the operation and data acquisition system (Figure 3.14, 13 to 15).

The oxidant supply system facilitates the introduction of a stream of humidified oxygen at a controlled volumetric flow rate and pressure. The oxygen is stored in a cylinder at 200 bar (Figure 3.14, 1), pressure that is reduced by means of a pressure reducing valve (2) to match the working pressure of the air treatment system. After this valve, the oxygen passes through a volumetric flow controller (3), and then through a humidification system (4). This system consists of two gas scrubber flasks connected in series, filled with Milli-Q grade water and whose temperature is controlled by a thermostatic bath. Subsequently, the humidified oxygen stream is introduced into the cathode of the DMFC (12), from where the excess oxygen and reaction products are led to a water trap (5) to prevent the liquid water produced during the operation of the DMFC from reaching the pressure controller (6). This controller allows to regulate the pressure at which the cathode of the fuel cell works. After the pressure controller, the excess gases leave the oxidant line.

The fuel supply system allows the storage of aqueous methanol at the set point concentration required to feed the anode of the DMFC. An aqueous methanol tank (7) is connected to an HPLC pump (8) that directs the fuel to the DMFC anode (13). Excess methanol and reaction products leave the fuel line after going through the DMFC to be collected in a beaker for safe disposal.

The temperature conditioning system regulates the temperature of the DMFC working environment. The temperature is controlled by two chambers (9), an inner chamber in which the test temperature is measured and controlled and in which the DMFC is located, and an outer chamber to reduce the thermal energy transfer from the inner chamber to the outside. The temperature is controlled by a heating/cooling circulator working with a closed circuit of Milli-Q grade water passing through a heat exchanger (11) at the temperature required to increase or decrease the temperature of the inner chamber. To force the circulation of the air between the two chambers, a fan powered by a DC power source (12) is installed to force air through the heat exchanger.

The operation and data acquisition system facilitates conducting tests to study the performance of the DMFC when its components or operating conditions are modified. This system includes the device under study, the DMFC (13), and an electronic load (14) connected to a computer (15) which allows the voltage at which

the DMFC operates to be controlled while the current intensity is recorded during the tests for subsequent analysis.

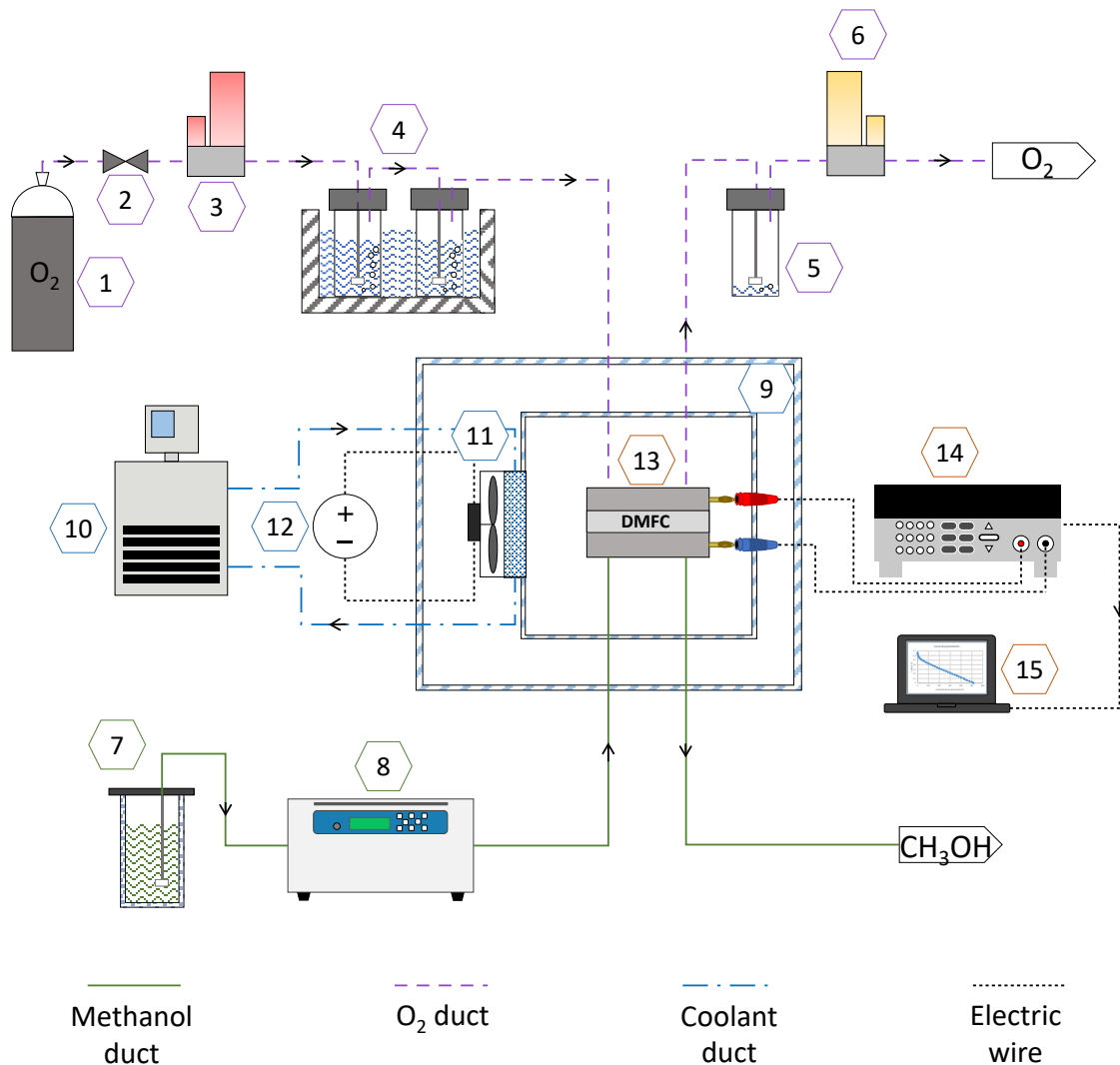


Figure 3.14: Diagram of the Direct Methanol Fuel Cell Test Bench. 1 - Compressed O_2 cylinder. 2 - Pressure reduction valve. 3 - Gas flow controller. 4 - Gas humidification system. 5 - Water trap. 6 - Gas pressure controller. 7 - Aqueous methanol tank. 8 - Methanol pump. 9 - Chambers. 10 - Refrigerating and heating circulator. 11 - Heat exchanger. 12 - DC power source. 13 - DMFC. 14 - Electronic load. 15 - Computer

The test bench presented in Figure 3.14 allows to obtain valuable experimental information to study the influence of the operating parameters and components of a DMFC, both in an experimental and commercial context, thus contributing to the advancement of this technology.

The initial design and concept of the cathode air treatment system are currently under construction and undergoing testing for integration into the DMFC test bench. Once experimental results are obtained with this initial prototype,

opportunities for enhancing its design and automating various processes within the system could be explored.

The conditions of the gas flow supplied to the cathode of a DMFC have a great impact on its operation, especially the temperature, pressure and relative humidity of the air (González-Espasandín et al., 2019; Seo & Lee, 2008; Yousefi et al., 2013). Therefore, the control and recording of these parameters are fundamental elements of the designed test bench. In particular, moisture plays an important role in the performance of a DMFC, especially in the MEA, since if the moisture in the oxidant is non-existent, the membrane undergoes fast drying, which drastically reduces its performance. Therefore, it is important to study the effect of the humidity of the air introduced at the cathode of a DMFC. By using the new oxidant supply system, based on the use of an air treatment system, it will be possible to introduce an air stream with controlled volumetric flow rate, temperature and humidity at the cathode of the DMFC.

In order to be able to modify the conditions of an ambient air stream to achieve the desired humidity and temperature conditions during each test, two fundamental steps are considered in this process: heating and humidification. The air treatment process in the designed system involves a first stage of heating the ambient air and a second stage of humidification by introducing steam into the preheated air stream obtained in the first stage. Figure 3.15 shows the diagram of the engineering concept used for the defined air treatment system.

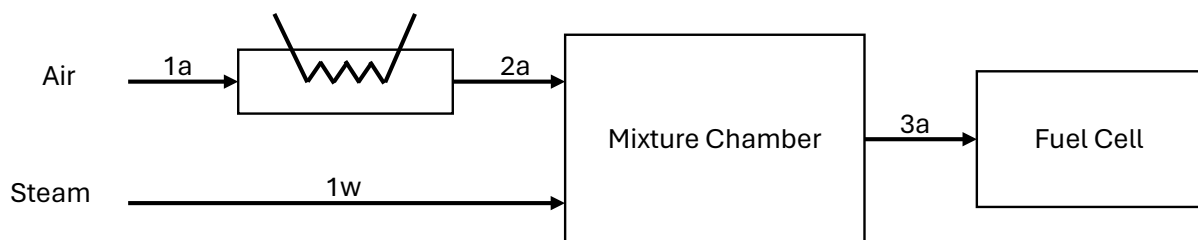


Figure 3.15: Concept diagram of the cathode air treatment system

Figure 3.16 shows the schematic of the constructed air treatment system, which after fine-tuning will be added to the DMFC test bench.

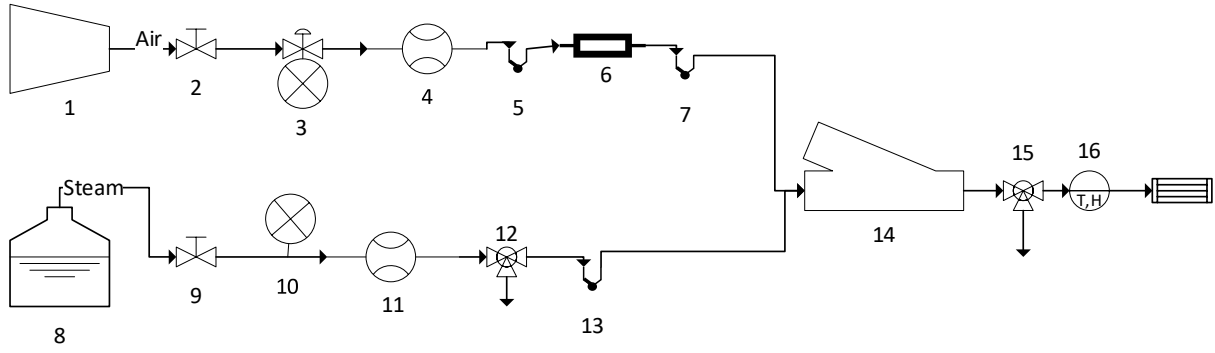


Figure 3.16: Schematic of the air treatment system for use as an oxidant supply system in the DMFC test bench. 1 - Compressor. 2 - Hydraulic flow control valve. 3 - Pneumatic regulator. 4 - Rotameter. 5 - Temperature sensor. 6 - Heater. 7 - Temperature sensor. 8 - Steam generator. 9 - hydraulic flow control valve. 10 - Pressure gauge. 11 - Rotameter. 12 - three-way ball valve. 13 - Temperature sensor. 14 - Mixing chamber. 15 - three-way ball valve. 16 - Temperature and humidity sensor

To obtain the volumetric flow rate of humid air at ambient pressure and desired temperature and humidity, point 16 in Figure 3.16, the volumetric flow rates of humid air from the environment, its temperature, and the volumetric flow rate of saturated vapor generated in the cathode air system must be controlled. The First Law of Thermodynamics and mass balance are applied to the mixing chamber, shown in Figure 3.15, to determine these volumetric flow rates. The temperature in point 2a is obtained from the enthalpy at state 2a, calculated with Eq. 3.49. Considering the ambient air conditions allows for the calculation of its density, and with the mass flow rate of dry air, the volumetric flow rate to be set as a reference in the rotameter can be determined, as seen in Figure 3.16 at point 4. The volumetric flow rate to be set in the vapor rotameter, as shown in Figure 3.16 at point 11, is obtained by applying mass balance in the mixing chamber, see Eq. 3.45, and calculating the density based on the properties of the steam stream, assumed to be saturated vapor in this study. This study employs ideal mixture model and real models for the components of the mixture, considering humid air constituents as dry air and water. The ideal mixture model assumes the fulfilment of the equation:

$$V_m = \sum V_i \quad (3.41)$$

where V_m represents the volume of the mixture and $V_i = x_i \cdot V_m$ where x_i denotes the molar fraction of each component in the mixture.

Relative humidity, symbolized as ϕ , can be defined as:

$$\phi = \frac{x_w}{x_{w_{sat}}} = \frac{p_w}{p_{sat}(T)} \quad (3.42)$$

where x_w represents the molar fraction of vapor, $x_{w_{sat}}$ denotes the molar fraction of vapor at saturation. By considering the ideal mixture model, the second equality stated in Eq. 3.42 can be assumed, where p_w represents the partial pressure of vapor and $p_{sat}(T)$ is the saturation pressure at the temperature of the mixture.

Humidity, denoted as ω , is defined as:

$$\omega = \frac{m_w}{m_a} = \tilde{\omega} \frac{M_w}{M_a} \quad (3.43)$$

where m_w represents the mass of vapor, m_a denotes the mass of dry air, M_w is the molar mass of vapor, M_a is the molar mass of dry air and $\tilde{\omega}$ represents the humidity expressed in terms of amount of substance:

$$\tilde{\omega} = \frac{n_w}{n_a} = \frac{p_w}{p - p_w} = \frac{\phi \cdot p_{sat}(T)}{p - \phi \cdot p_{sat}(T)} \quad (3.44)$$

where p denotes the pressure of the humid air mixture.

The mass balance applied to the mixing chamber for the steady-state case is:

$$\dot{m}_w = \dot{m}_a(\omega_{3a} - \omega_{2a}) \quad (3.45)$$

The application of the First Law of Thermodynamics to the mixing chamber yields:

$$\dot{Q} + \dot{W} = \left. \frac{dE}{dt} \right|_{cv} + \sum \dot{m}_{out} \cdot h_{out} - \sum \dot{m}_{in} \cdot h_{in} \quad (3.46)$$

Under the assumptions of an adiabatic mixing chamber and steady-state flow, it is obtained:

$$0 = \sum \dot{m}_{out} \cdot h_{out} - \sum \dot{m}_{in} \cdot h_{in} \quad (3.47)$$

$$0 = \dot{m}_a[h_{3a} - h_{2a} - h_{1w}(\omega_{3a} - \omega_{2a})] \quad (3.48)$$

from which it is obtained:

$$h_{2a} = h_{3a} - h_{1w}(\omega_{3a} - \omega_{2a}) \quad (3.49)$$

Once obtained the theoretical values of the volumetric flow rate of humid air from the environment, its temperature, and the volumetric flow rate of saturated vapor, the system exposed in Figure 3.16 is used to obtain the volumetric flow rate of humid air at ambient pressure and desired temperature and humidity to be introduced in the DMFC. In this system, a compressor (Figure 3.16, 1) is used to introduce ambient air into the circuit and store it until it is needed. The compressor

is followed by a hydraulic flow control valve (2), a pneumatic regulator (3) and a rotameter (4) to adjust the volumetric flow rate at which the humid ambient air enters the air treatment system. After adjusting the volumetric flow rate, the temperature of the humid air stream is measured with a thermocouple (5) and passed through a heater (6) fitted with an electrical resistance. A thermocouple (7) monitors the temperature of the humid air leaving the heater and this temperature signal is used by a Proportional, Integral, Derivative (PID) controller implemented in an ARDUINO UNO to regulate the electrical power supplied to the heater resistor. This control loop allows the temperature of the heater to be increased or decreased, thus being able to control the temperature of the humid air leaving the heater. After temperature control, the humid air stream is introduced into the mixing chamber (14), where it is mixed with the steam stream.

To obtain the steam stream that reaches the mixing chamber, there is a steam generation and control circuit. This circuit has a high-pressure steam generator (8) that produces steam from Milli-Q grade water. This steam generator is connected to a hydraulic flow control valve (9) that regulates the passage of this steam to the rest of the circuit. A pressure gauge (10) and a rotameter (11) are located downstream of this valve to monitor the pressure and to adjust the volumetric flow rate of steam entering the air treatment system. A three-way ball valve (12) is placed after the steam flow meter to prevent the entry of liquid water, high flow or low temperature steam into the rest of the system. After this valve, the temperature of the steam is recorded with a thermocouple (13) and led to the mixing chamber (14). To prevent the steam from condensing in this line before it reaches the mixing chamber, a circuit preheating system is currently being designed based on the use of electrical resistors to maintain the high temperature of the ducts.

Once the humid air stream at the set temperature and volumetric flow rate and the steam stream with the desired volumetric flow rate are mixed in the chamber (13), the humid air stream with the required temperature and humidity is obtained. As a preventive mechanism, which is not used except in case of failure, a three-way ball valve (15) and a temperature and humidity sensor (16) are placed at the outlet of the mixing chamber to prevent a high volumetric flow of humid air with a temperature and humidity different from those required in the test from entering the DMFC. After checking with this sensor (16) that the temperature and humidity of the air stream are those required in the test, this humid air stream is conducted to the cathode of the DMFC (17).

The components that enable the integration of sensors in the different lines of the circuit, as well as part of the heater and the entire mixing chamber are custom-made using 3D printing with Acrylonitrile Butadiene Styrene (ABS) (provided by Ultimaker) as the extrusion material. ABS is a thermoplastic that has good mechanical properties under the operating conditions of the air treatment system.

This system extends the capabilities of the DMFC test bench by replacing the oxygen stream with air as the oxidising fluid to feed the DMFC cathode at a desired volumetric flow rate, temperature and relative humidity. In this way, the test bench makes it possible to determine the effect of using pure oxygen compared to using oxygen from air on the performance and durability of the DMFC. In addition, the control of the different parameters allows to study the effect of volumetric flow rate, temperature and air humidity on the performance of the DMFC.

3.3.2. DMFC working conditions

The working conditions analysed for the DMFC are its operating temperature (T), the concentration of methanol (M) introduced into the anode and the volumetric flow rate of this reactant ($\dot{V}$). For different combinations of these parameters, polarization curves and the associated power density curves of the DMFC single cell have been obtained. The combinations of these parameters used as input data to perform the DMFC single cell tests are obtained by applying RSM with a CCD design. The operating temperature, T , of a DMFC can typically range from 303 K to 343 K (Govindarasu & Somasundaram, 2020; Raso García et al., 2017; Santasalo et al., 2009), while the methanol concentration, M , can typically range from 0.25 M to 5 M (Celik et al., 2022; X. Li & Faghri, 2013), showing better performance below 5 M. The volumetric flow rate of methanol, $\dot{V}$, can typically range, for single cells with similar characteristics and size to the one used in this work, from 0.5 ml/min to 10 ml/min (Jiang et al., 2021; H. Yang et al., 2005b), showing the best performance of the DMFC when working with $\dot{V}$ higher than 1 ml/min and lower than 8 ml/min. Taking into account these ranges and applying the CCD design, the parameter combinations shown in Table 3.4 are obtained and the polarization curves are plotted to determine the peak power density with each parameter combination.

Table 3.4: Combinations of parameters related to working conditions obtained applying RSM and CCD design and used to study their influence on the DMFC performance

$\dot{V}$ (ml/min)	$10^8 \cdot \dot{V}$ (m ³ /s)	M (mol/l)	$10^3 \cdot M$ (mol/m ³)	T (°C)	T (K)
1.90	3.17	2.00	2.00	50.0	323.0
3.00	5.00	1.00	1.00	40.0	313.0
3.00	5.00	1.00	1.00	60.0	333.0
3.00	5.00	3.00	3.00	40.0	313.0
3.00	5.00	3.00	3.00	60.0	333.0
4.50	7.50	0.27	0.27	50.0	323.0
4.50	7.50	2.00	2.00	32.7	305.7
4.50	7.50	2.00	2.00	50.0	323.0
4.50	7.50	2.00	2.00	67.3	340.3
4.50	7.50	3.73	3.73	50.0	323.0
6.00	10.00	1.00	1.00	40.0	313.0
6.00	10.00	1.00	1.00	60.0	333.0
6.00	10.00	3.00	3.00	40.0	313.0
6.00	10.00	3.00	3.00	60.0	333.0
7.10	11.83	2.00	2.00	50.0	323.0

The tests carried out using as input data the combinations listed in Table 3.4 are performed with an oxygen volumetric flow rate of 110 ml/min humidified at 341 K at a pressure of 100 kPa and an anode plate with flow field in serpentine of 1 mm width and 0.5 mm depth with 25 straight channel sections and a total area of 16 cm². The value of the volumetric flow of oxygen has been fixed after an experimental study of the influence of this parameter on the performance of the DMFCs used in this thesis, varying this value between 80 ml/min and 150 ml/min and finding that for values close to 110 ml/min the maximum peak power densities were obtained.

A systematic process is followed to determine the peak power density corresponding to each combination of parameters. First, a DMFC single cell is prepared and two activation curves are run on the test bench described in Section

3.3.1 Direct Methanol Fuel Cell test bench with air treatment system. These curves involve varying the single cell potential from OCV to 0.4 V, with 0.02 V steps every 3 min. During this 3-minute period, voltages and currents are recorded every second, following a scheme similar to a standard polarization curve. Subsequently, a total of 40 polarization curves are plotted under specific conditions: a methanol flow rate of 3 ml/min with a concentration of 1 M and a DMFC temperature of 333 K. These curves complement the MEA activation process, preparing it for operation at different working conditions. After this process, 2 polarization curves are recorded for each combination of parameters indicated in Table 3.4. From the data of all these curves, the corresponding power density curves are obtained and the peak power density of each curve is calculated. The peak power density associated with each parameter combination is the maximum power density obtained from the DMFC for that parameter combination.

Once the peak power density is obtained for each combination, the second order mathematical model is obtained using the Response Surface Methodology explained in Section 3.2 Response Surface Methodology. From this model, the predicted response surfaces are plotted for different operating conditions and the mathematical model obtained is analysed using ANOVA.

3.3.3. DMFC flow field geometry

The effectiveness of the flow field design in the anode of a DMFC is essential for its performance and efficiency. In this work, the influence of the anode geometry on the DMFC performance is evaluated, addressing critical parameters such as channel width (e), channel depth (d) and open ratio (O_R). These parameters, fundamental for uniform reactant distribution and enhancement of the electrochemical reaction, are selected within specific ranges. The channel width can typically vary between 0.7 mm and 2.0 mm (Calabriso et al., 2017; Park et al., 2012), while the depth typically range between 0.6 mm and 2.0 mm (C. Y. Chen et al., 2006; Oliveira et al., 2010; Park et al., 2012) and the open ratio between 26.3 % and 79.3 % (Oliveira et al., 2010; Park et al., 2012; H. Yang & Zhao, 2005). Using this information and applying a CCD design within the framework of the RSM methodology, serpentine channel geometries can be generated for fabrication and subsequent evaluation in a DMFC. However, geometrical constraints impose practical limitations, resulting in non-integer number of straight channel sections when using the CCD design. To address this limitation, the flow field geometry is parameterized by relating two of the three geometrical variables under study by

means of specific equations, namely the open ratio and the channel width. Once the Eqs. 3.39 and 3.50 to 3.53 are established, iterations are carried out, setting a total area of 4x4 cm², a rib minimum width of 0.4 mm, and adjusting the parameters of channel width and open ratio, as well as minimum variation of channel width and open ratio (Δx_i from Eq. 3.39), until a solution consistent with a CCD design and feasible from the technical point of view, i.e. a number of channel to be a positive integer, is achieved. In this parameterisation the open ratio can be calculated as:

$$O_R = A_c / L^2 \quad (3.50)$$

where O_R represents the open ratio, L is the side of the square that constitutes the total area and A_c is the area bounded by the channels, which can be calculated as:

$$A_c = N_c \cdot L \cdot e + (N_c - 1) \cdot l \cdot e \quad (3.51)$$

where N_c is the number of straight channel sections (13 in Figure 3.17), e the channel width and l the rib width, shown in Figure 3.17. This length can be calculated as:

$$l = \frac{L - N_c \cdot e}{N_c - 1} \quad (3.52)$$

Operating with Eqs. 3.50 to 3.52 an equation can be obtained which allows the number of straight channel sections to be calculated as a function of O_R , L and e :

$$N_c = L \cdot \frac{O_R \cdot L - e}{L \cdot e - e^2} \quad (3.53)$$

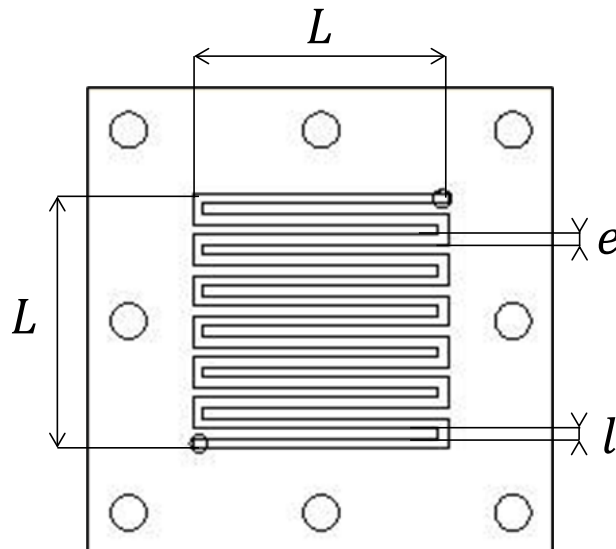


Figure 3.17: Diagram of the parameterisation used to determine the DMFC anode geometries to be studied

The resulting combinations of geometrical parameters (O_R , e and d), obtained through this process, as well as the parameters associated (N_c and l) are recorded in Table 3.5, thus providing a basis for fabrication and experimental evaluation of DMFC anode geometries.

Table 3.5: Combination of geometrical parameters defining the serpentine flow field of DMFC anode plates obtained by applying a Central Composite Design considering geometrical and technical constraints

O_R (%)	e (mm)	d (mm)	N_c	l (mm)
19.2	0.98	1.30	7	5.52
30.3	0.83	0.90	14	2.19
30.3	0.83	1.70	14	2.19
30.3	1.13	0.90	10	3.19
30.3	1.13	1.70	10	3.19
45.4	0.71	1.30	25	0.92
45.4	0.98	0.61	18	1.32
45.4	0.98	1.30	18	1.32
45.4	0.98	1.99	18	1.32
45.4	1.25	1.30	14	1.74
60.6	0.83	0.90	29	0.57
60.6	0.83	1.70	29	0.57
60.6	1.13	0.90	21	0.81
60.6	1.13	1.70	21	0.81
71.7	0.98	1.30	29	0.41

The plates corresponding to the geometries presented in Table 3.5 have been designed and fabricated, and experimental tests have been started, but are not yet completed to be able to incorporate them within this doctoral thesis due to the high test times (minimum of two weeks for each geometry) and the problem of supplies due to the lack of commercial material, such as electrodes. These results will be incorporated into future scientific publications.

3.4. Methanol Electrolysis Cell

The MEC single cells used in this work have a similar structure to that used in DMFC single cells. These MEC single cells are composed of 316L steel plates, gaskets, Nafion® 117 membrane and electrodes, the latter being of a non-commercial nature in the case of MEC. This is due to the fact that in the literature consulted no commercial electrodes have been found for these devices, the authors preparing their own electrodes or using commercial electrodes from DMFCs. As the studies carried out in this thesis on MEC consist of analysing the influence of different operating conditions on the performance of the MEC or the influence of the geometry of the serpentine channel used in the anode of the MEC, the use of non-commercial electrodes, prepared in the same way, can be used to achieve the proposed objectives. Specific details on the characteristics of the electrodes used in the MEC working condition tests, as well as the various flow field geometries, are detailed in Table 3.6. The electrodes are prepared following the protocol described by Jurado et al. (Jurado Egea et al., 2002).

Table 3.6: Characteristics of the electrodes used in the MEC single cell

Parameter	Value
Anode catalyst	PtRu/C 40 %w
Anode catalyst charge (mg/cm ²)	3 (molar ratio 1:1)
GDL anode commercial reference	Toray TGP-H-060
Anode supplier	Collaboration with the Instituto de Cerámica y Vidrio of CSIC (Spain)
Cathode catalyst	Pt/C 40 %w
Cathode catalyst charge (mg/cm ²)	1
GDL cathode commercial reference	Toray TGP-H-060
Cathode supplier	Collaboration with the Instituto de Cerámica y Vidrio of CSIC (Spain)

It is important to highlight that the membrane treatment and assembly process of the MEA are analogous to those carried out in DMFC single cells. Likewise, the characteristics of the single cell plate corresponding to the cathode are identical in both devices.

The polarization curves of the electrolyser are generated using the test bench described in Section 3.4.1 Methanol Electrolysis Cell and Direct Methanol Fuel Cell test bench and introducing methanol (99.9 % purity, supplied by PanReac AppliChem) in the MEC anode. In this context, the current density is used as the setpoint signal, and the voltage is recorded during the MEC polarization curve, as the one presented in Figure 3.18, due to the better control of the hydrogen volumetric flow rate obtained with the MEC following this process as this is closely related to the current density.

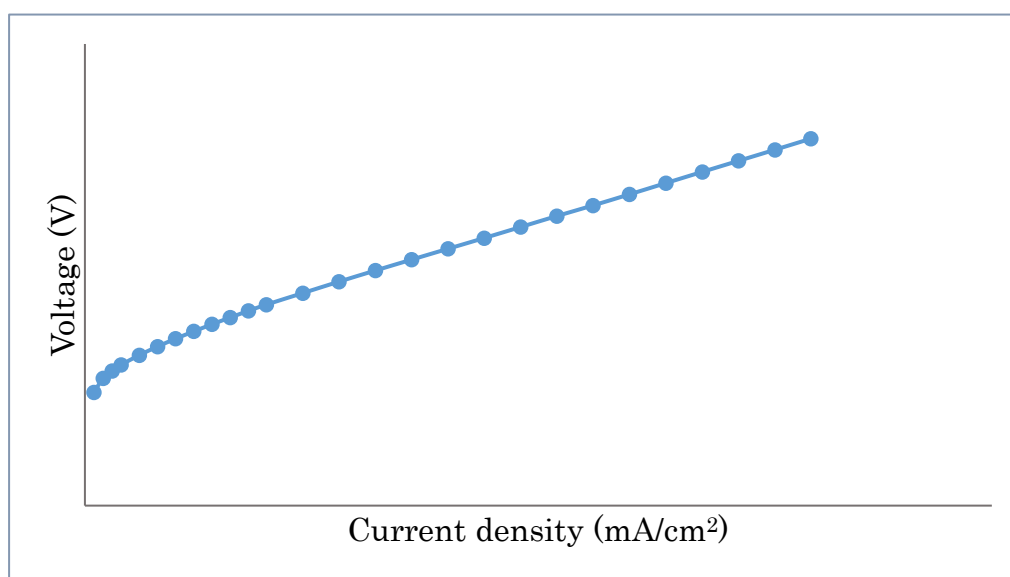


Figure 3.18: Methanol Electrolysis Cell polarization curve

The MEC polarization curves in this study have been plotted over a current density range from 0 mA/cm² to 400 mA/cm², with 20 mA/cm² increments every 3 min. During this process, the voltage and current supplied to the system are recorded every second. To plot each point of the polarization curve on a graph, the average of all the values collected during the 3 min corresponding to each point is calculated using Excel and also a MATLAB code to check that the result is obtained correctly.

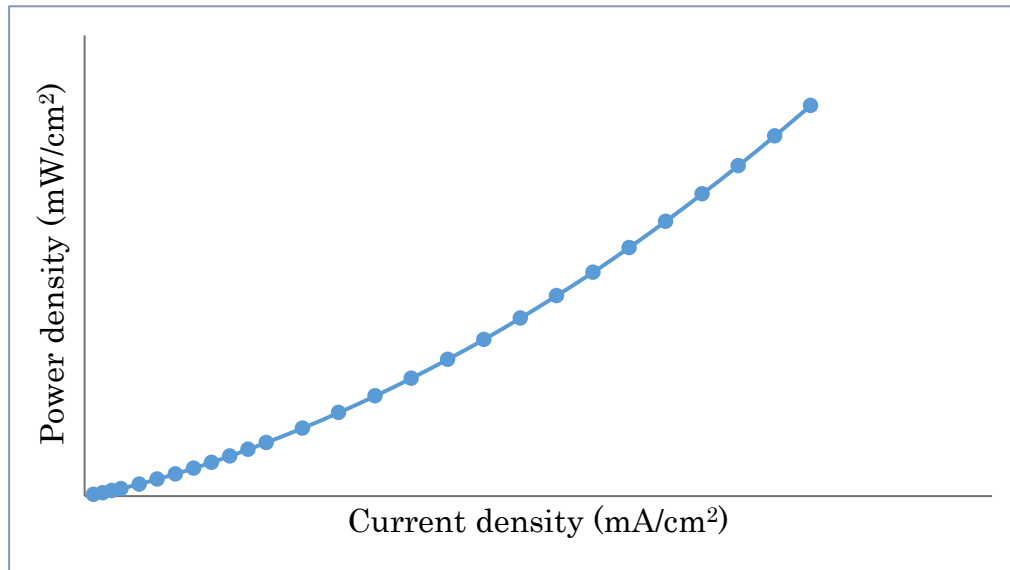


Figure 3.19: Methanol Electrolysis Cell power density curve

In addition, from these polarization curves, the power density curve of the MEC is also obtained, as the one presented in Figure 3.19, by multiplying the current density by the voltage measured at each point of the polarization curve using Excel and a MATLAB code too in order to check the results. To facilitate the comparison between power density curves, the power density parameter corresponding to a current density of 300 mA/cm² has been selected in this study. This value has been chosen because it is within the linear region of the polarization curves obtained, without having entered the concentration overpotential region.

3.4.1. Methanol Electrolysis Cell and Direct Methanol Fuel Cell test bench

A test bench both for DMFC and MEC research has been designed and built during the development of this doctoral thesis. This new bench, which evolves from the model previously used to study exclusively DMFCs (Figure 3.14), presents a series of additional functionalities that significantly extend its scope and versatility. A photograph of the DMFC and MEC test bench used in this thesis is shown in Figure 3.20.



Figure 3.20: Photograph of the Methanol Electrolysis Cell (MEC) and Direct Methanol Fuel Cell (DMFC) test bench designed and built in this thesis and used for MEC tests

One of the features of this test bench is its ability to perform both DMFC and MEC tests. This represents a substantial advance, as it allows the performance of both devices to be investigated and compared in a controlled experimental environment. In addition, the incorporation of a Frequency Response Analyser (FRA) module in the data acquisition system extends the analysis possibilities, facilitating the performance of Electrochemical Impedance Spectroscopy (EIS) tests. In addition, the methanol crossover across the membrane in both DMFC and MEC can also be experimentally determined with this bench.

The general scheme of the test bench is similar to that used for the DMFCs, with modifications mainly in the operation and data acquisition system. The schematic representation of the bench during a MEC test (Figure 3.21) shows the incorporation of a potentiostat-galvanostat with an integrated FRA module. This device allows polarization curves to be plotted for both DMFC and MEC. In the case of MEC, during the polarization curve test, the current density is controlled and the corresponding voltage is recorded, which allows a more accurate assessment of the hydrogen volumetric flow rate produced, given its high degree of dependence on the current density.

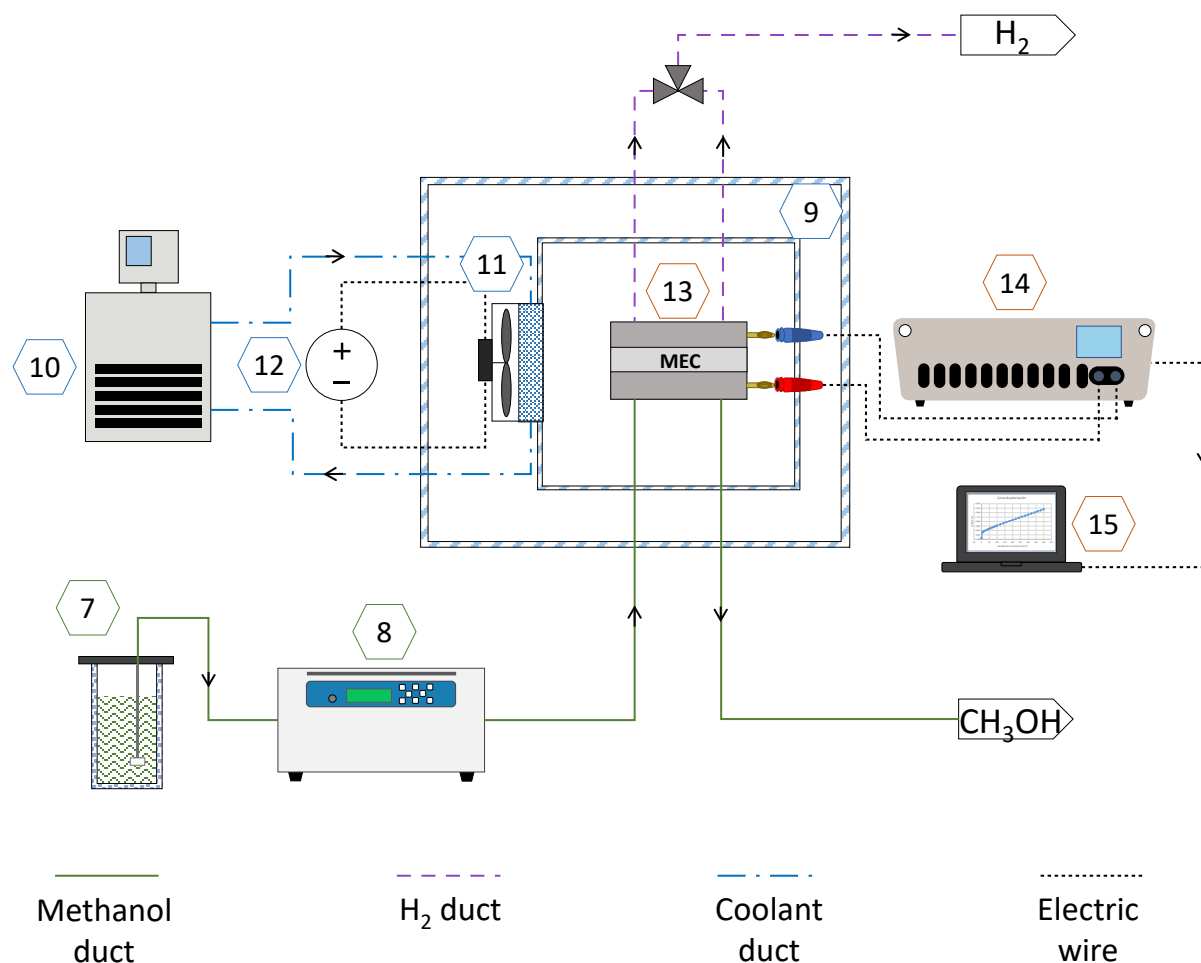


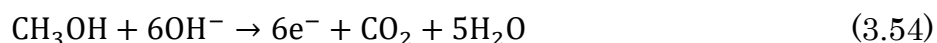
Figure 3.21: Diagram of the Direct Methanol Fuel Cell and Methanol Electrolysis Cell Test Bench during MEC tests. 7 - Aqueous methanol tank. 8 - Methanol pump. 9 - Chambers. 10 - Refrigerating and heating circulator. 11 - Heat exchanger. 12 - DC power source. 13 - MEC. 14 - Potentiostat-galvanostat with FRA. 15 - Computer

Although no forced circulation of gases through the cathode is required during the MEC tests, it is noted that the bench is also equipped with an oxidant supply system similar to that used in DMFCs (Figure 3.14, 1 to 6), hence the start of the numbering in Figure 3.21 is set to the initial number of fuel supply system.

The possibility of also incorporating the cathode air treatment system (Figure 3.16) into the DMFC and MEC test bench is highlighted, allowing the experimental evaluation of the behaviour of a DMFC fed with air instead of pure oxygen. This added functionality further extends the capabilities of the test bench, providing a comprehensive platform for the research and development of energy systems based on DMFCs and MECs.

3.4.2. Catalyst for methanol oxidation reaction

In this study, which was carried out during the doctoral stay at the Università degli Studi di Palermo, Italy, electrodes with Ni, NiMo and NiCu catalysts have been prepared on different substrates, such as stainless steel mesh (SS), nickel foams (NF), titanium felts (TiFelt) and titanium foils with nanotubes (TiFoilNTs), in order to evaluate their properties against the methanol oxidation reaction (MOR) in alkaline medium, expressed in Eq. 3.54 (E. H. Yu et al., 2010):



During the study, the oxygen evolution reaction (OER) also took place when using solutions without the presence of methanol. The OER in alkaline medium can be expressed as (Deng et al., 2022; F. Liu et al., 2024):



The process of preparing the electrodes starts with the treatment of the substrates, followed by the deposition of the catalyst on them by means of an electrodeposition technique. Finally, the characterisation of the 1x1 cm² electrodes prepared is carried out using cyclovoltammetry (CV) and stability tests, where a current density is set and the voltage is recorded for a given time, recording the corresponding chronopotentiometry.

Each type of substrate receives a specific treatment before electrodeposition and subsequent characterisation. The nickel foam (NF) is washed with distilled water and immersed in acetone (C₃H₆O) for 5 min in an ultrasonic bath, followed by washing with distilled water and immersion in 5 M HCl solution in ultrasound for 10 min to complete the cleaning process. It is then left to dry at room temperature.

In the case of stainless steel mesh (SS), after washing with distilled water, it is immersed in acetone under ultrasound for 5 min. Then, it is immersed in a 0.5 M H₂SO₄ solution for 10 min with ultrasound.

The titanium felt anodized (TiFelt) preparation includes a wash with distilled water, followed by a 1 sec immersion in a HF:HNO₃:H₂O (1:1:3 by volume) solution and then in an acetone bath with ultrasound for 5 min. After this, the TiFelt is immersed in ethanol (C₂H₆O) for 5 min under ultrasound. After this process, the support is anodised to oxidise the surface by CV in a 0.1 M H₈B₄N₂O₇ solution, with a voltage range from Open Circuit Potential (OCP) to 1 V vs Ag/AgCl reference electrode with a 10 mV/s step.

For the generation of nanotubes in the Ti foil (TiFoilNTs), the following procedure is used: the Ti foils are etched for 15 seconds in a mixture of HF:HNO₃:H₂O (1:1:3 by volume). They are then cleaned by sonication in acetone and ethanol for 5 min each, rinsed with deionised water and air dried. TiO₂ nanotubes are formed in a solution of ethylene glycol with 0.25 wt% NH₄F and 0.75 wt% deionised water. The anodizing process is carried out in a two-electrode cell configuration, by using Al foil as the cathode and applying a constant voltage of 45 V for 10 min, followed by a heat treatment at 723 K for 3 h to induce crystallisation of the nanotubes (Pecoraro et al., 2024). After this process and before electrodeposition, the TiFoilNTs are again subjected to an ultrasonic wash in acetone for 5 min and another in ethanol for 10 min.

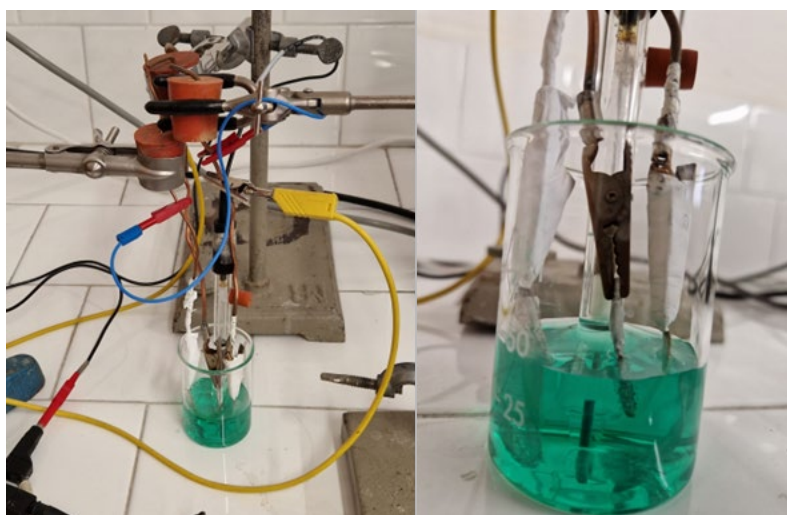


Figure 3.22: Three-electrode cell used for the electrodeposition of catalysts on different supports

Electrodes with these substrates are prepared by electrodeposition in a three-electrode cell, see Figure 3.22, with the substrate as working electrode, two platinum mesh as counter electrodes and a Ag/AgCl reference electrode. These electrodepositions are carried out using a VersaSTAT3 potentiostat-galvanostat. The cell electrolyte used is prepared by dissolving salts in distilled water. For Ni electrodeposition, a 0.5 M H₃BO₃ and 0.5 M NiSO₄·6H₂O solution is used. For NiMo, a solution of H₃BO₃ 0.5 M, NiSO₄·6H₂O 0.5 M and (NH₄)₆Mo₇O₂₄·4H₂O 0.021 M is used. And for NiCu, a solution of H₂BO₃ 0.5 M, NiSO₄·6H₂O 0.5 M and CuSO₄·5H₂O 0.0125 M is used. After preparing the solutions, the pH of each solution is adjusted by adding H₂SO₄ until a pH of 2.5 is reached. Then, the substrate is immersed in 50 ml of the solution corresponding to the desired catalyst

by assembling the three-electrode cell and a voltage of -2 V vs. Ag/AgCl reference electrode is applied for 10 min. After this process, the electrodes are cleaned with distilled water and left to air dry, and then subjected to characterisation by CV.

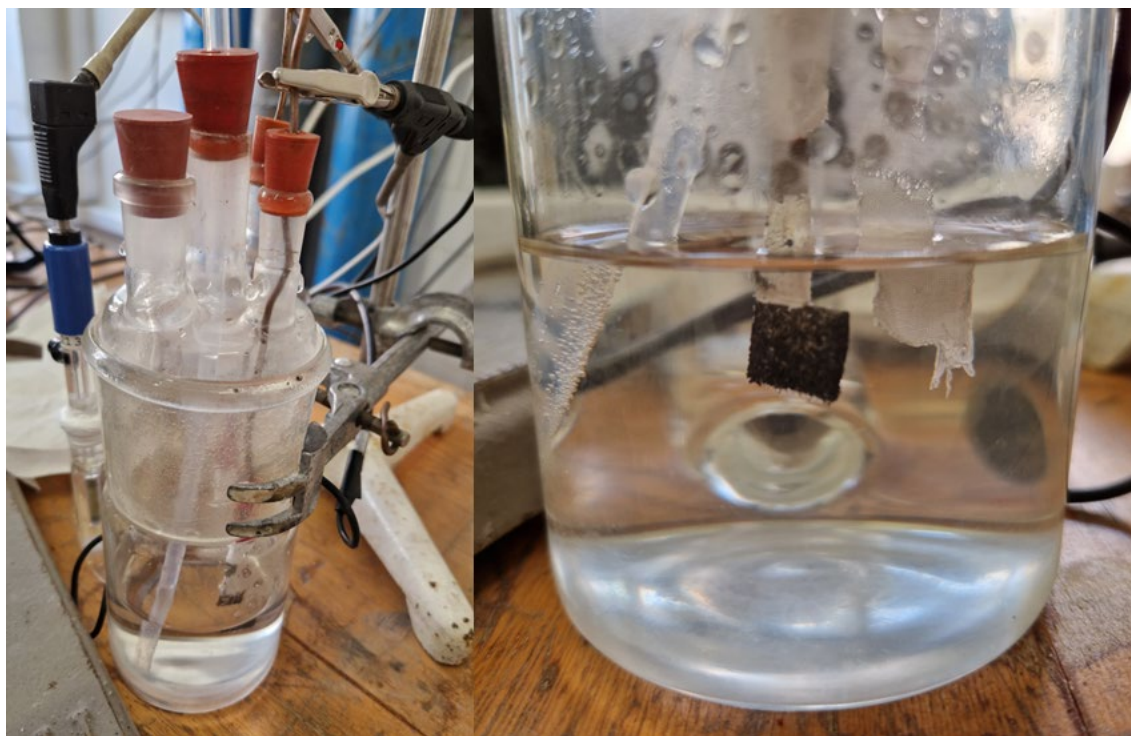


Figure 3.23: Three-electrode cell used for the cyclovoltammetries and stability tests of the different electrodes studied

For the CVs, a new three-electrode cell is established, see Figure 3.23, modifying the electrolyte and using as reference electrode one of Hg/HgO. These CVs are performed using a PARSTAT 4000 potentiostat-galvanostat. The electrolyte used is a solution of 50 ml of KOH 1M or KOH 1M + CH₃OH 1M. Cyclovoltammetry is performed in a voltage range of 0.1 to 0.9 V vs Hg/HgO with a step of 100 mV/s using a platinum mesh electrode as counter electrode, see Figure 3.23, and the prepared electrode as working electrode. This setting allows a comparison of the electrode behaviour for the oxygen evolution reaction (OER) when using KOH alone and the response to the methanol oxidation reaction (MOR) when using KOH 1M + CH₃OH 1M.

Initially, two electrodes of each catalyst-support combination are prepared and characterised using SS mesh and NF as supports. Subsequently, two additional electrodes of each NiCu-support combination are prepared using all available substrates (SS mesh, NF, TiFelt and TiFoilNTs).

In both electrolytes (KOH 1M and KOH 1M + CH₃OH 1M), a different electrode of the same catalyst-support combination is introduced, although both electrodes are prepared in the same way. This strategy avoids possible oxidation or deterioration of the electrode after the test in the 1M KOH solution.

The two best results obtained among all catalyst-support combinations are compared by means of a stability test, which consists of applying a current of 100 mA/cm² and recording the voltage for 8 hours. The same setup is used as for the cyclovoltammetries, but this time using a 200 ml solution of KOH 1M + CH₃OH 1M. This test is repeated three times with a new solution, for a total of 24 hours of electrode testing.

3.4.3. MEC working conditions

The working condition tests for the MEC single cells have been designed to match the characteristics of the tests performed on DMFC single cells, as specified in Table 3.4. This is because the temperature ranges in which the MECs operate typically vary within the range of 303 K to 353 K (Pethaiah et al., 2020; Take et al., 2007), while the methanol concentration ranges from 1 M to 10 M (Lamy et al., 2015; Sanchez et al., 2022; Take et al., 2007), with good results obtained by operating with a concentration below 4 M. These values therefore match the test parameters established for working conditions of DMFCs.

In the specific context of the MEC anode, a serpentine flow field plate with a channel width of 1.0 mm and a depth of 1.0 mm is used. The total channel surface is 4x4 cm², with 25 straight channel sections, implying an open ratio of 62.4 %. This geometry has been used because three channel depths, 0.5 mm, 1.0 mm and 1.5 mm, have been previously tested and the best experimental results have been obtained for a channel depth of 1.0 mm. In addition, both the open ratio and the channel width are intermediate values within the range of variation of these parameters in DMFC anode serpentine flow fields.

To plot the polarization curves of the MEC single cell and to obtain the power density at 300 mA/cm², which serves as the system response parameter, the following procedure is used. First, the MEC single cell is prepared and 4 polarization curves are plotted for each combination of parameters set out in Table 3.4. From these polarization curves, the power density curves are plotted and the power density at 300 mA/cm² is recorded. For each combination of parameters, the

average of the three lowest power densities at 300 mA/cm² among the 4 curves obtained is calculated and the average obtained is used as the system response.

Once these power density responses are obtained for each combination of parameters, a mathematical model is developed using the RSM methodology. From this model, the corresponding response surfaces are generated, and an ANOVA analysis is carried out to evaluate the model.

3.4.4. MEC flow field geometry

Currently, no studies have been found in the scientific literature that address the influence on the MEC performance of methanol volumetric flow rate and anode channel geometries of a MEC with a serpentine flow field. Therefore, it is of interest to investigate (in this study) the different serpentine geometries, similar to the approach used in DMFC single cells. For this purpose, the same geometries designed in DMFC have been selected, since the anodic reaction is analogous. However, it is imperative to consider that the boundary conditions vary when operating at higher current densities in a MEC and when not employing a pressure-controlled cathode. During MEC polarization curve tests, only the generated hydrogen, which is at ambient pressure, flows through the cathode channels without a forced gas current flow through this cathode.

To investigate the influence of the geometrical parameters of the serpentine flow field on the anode plate of a MEC single cell, the geometries specified in Table 3.5 have been adopted. Polarization curve tests are carried out to evaluate the performance of each geometry. A new MEA is prepared for each serpentine configuration on the anode plate, and a MEC single cell is assembled, generating 8 polarization curves for each assembled MEC. To obtain the MEC response for each geometry, i.e. the power density at 300 mA/cm², the average of the 3 lowest power densities at this current density, obtained from the 8 power density curves corresponding to the polarization curves plotted, is calculated. For this study, the polarization curves are plotted with the following MEC operating conditions: temperature of 333 K, methanol flow rate of 3 ml/min and methanol concentration of 1 M. These parameters were selected as they represent intermediate values within the specified ranges of these parameters found in the literature, and moreover, they have been commonly employed in previous publications.

Once this power density response is obtained for each anode plate, the RSM methodology is used to generate the corresponding quadratic model, type of model

used to observe the non-linear behaviour of the response in relation to the factors under study. From this model, the relevant response surfaces are derived and an ANOVA analysis is performed to assess the adequacy of the model obtained.

4. Results and discussion

The present Chapter focuses on the exposition and analysis of the results derived from the investigation conducted within the framework of the doctoral thesis. In the corresponding chapter, three fundamental aspects in the field of energy technology are addressed, centred on the exploration and comparison of different approaches and relevant technologies. Within the study of using methanol and hydrogen as energy vectors, a technoeconomic analysis is conducted comparing hydrogen and methanol as alternatives for energy transportation in ships. In the context of employing methanol as an energy vector, the utilization of Direct Methanol Fuel Cells (DMFCs) for electrical energy generation from methanol in the final stages of the fuel transportation chain is considered, thus conducting an experimental investigation within this thesis. Furthermore, in the utilization of methanol as a hydrogen vector, the production of hydrogen from methanol in the final stages of the chain is necessary, a process achievable through the employment of a Methanol Electrolysis Cell (MEC), thereby also conducting the experimental study of this device within this thesis.

In Section 4.1, it is presented a comparative technoeconomic study between the use of liquefied hydrogen and methanol as energy vectors. This analysis is based on the collection and evaluation of theoretical models and methodologies of economic costs evaluation, with the aim of providing a comprehensive understanding of the technical and economic aspects associated with both options.

In Section 4.2, the results obtained from the evaluation of the performance of a DMFC by modifying its operating conditions are detailed. This research is based on practical experimentation and data analysis to understand the behaviour of the fuel cell in various operational configurations, with direct implications for its performance. In this case methanol is used as a source of electrical energy.

Finally, in Section 4.3, the results of the comparative analysis between different non-noble metal catalyst electrodes are presented, as well as the evaluation of the influence on the performance of a MEC of its operating conditions and the geometry of the flow field serpentine-based in the anode plate. This part of the study delves into specific aspects of electrolysis technology, exploring new possibilities to improve its operation and performance in practical applications. In this case, methanol serves as a source of energy which will be contained in hydrogen.

Together, these sections provide a comprehensive view of the advances and discoveries made within the research framework, contributing to scientific and technological knowledge in the field of methanol as energy vector and its use as fuel in electrochemical devices to produce electricity or hydrogen.

4.1. Methanol as energy carrier

The following section presents and discusses the results of the comparison between liquefied hydrogen and methanol as energy vectors for large-scale energy transmission by sea. This comparison includes three alternatives as presented in Figure 4.1: the use of liquefied hydrogen with subsequent regasification, the transportation of methanol by ship with subsequent electrolysis for hydrogen production at the destination, and the utilization of methanol with subsequent reforming process to obtain hydrogen at the destination.

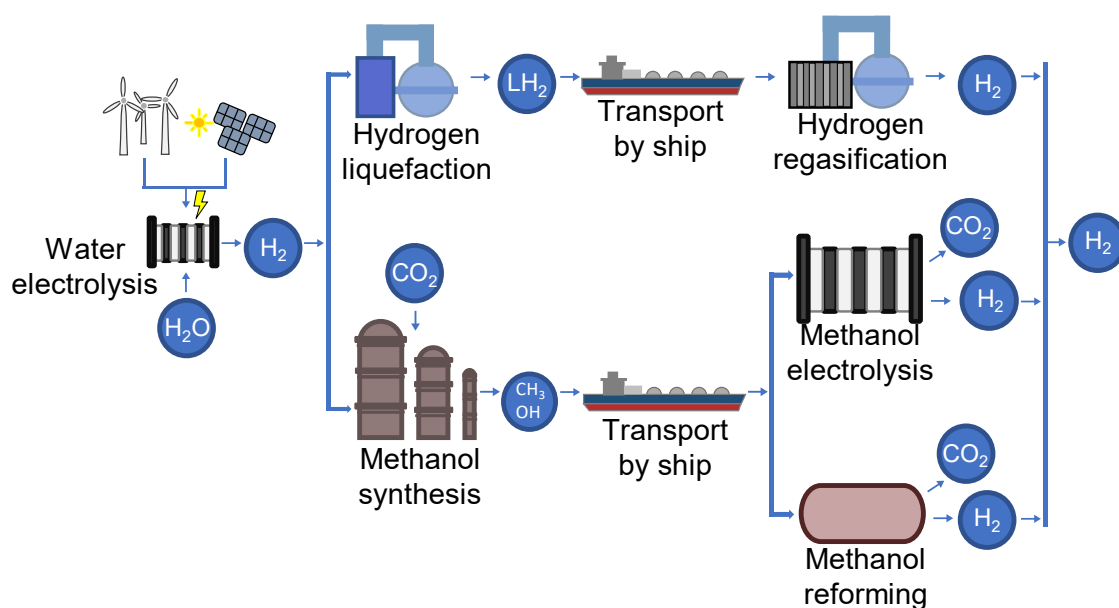


Figure 4.1: Diagram of alternatives used in this study for sea power transmission using liquefied hydrogen and methanol as energy vectors. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

Below are presented the assumptions made for each facility within each alternative to derive the associated costs for each facility. In this work, the values assigned to each parameter have been employed as input for the equations presented in the 3.1.2 Methodology Section, thereby deriving the results of this technoeconomic study. Thus, the outcomes obtained are dependent on these assumptions, which are subsequently detailed in following paragraphs.

Table 4.1 encompasses the fundamental assumptions utilized for the technoeconomic evaluations of the water treatment facility.

Table 4.1: Assumptions regarding the water treatment facility

Parameter	Value	Uncertainty	Reference
η_{HPP}	0.90	5 %	(El-Emam & Dincer, 2014)
η_{SWIP}	0.87	5 %	(El-Emam & Dincer, 2014)
η_{PT}	0.79	5 %	(El-Emam & Dincer, 2014)
f_1	0.9	5 %	(El-Emam & Dincer, 2014)
r_m	0.1	10 %	(El-Emam & Dincer, 2014)
C_{ch} (USD/m ³)	0.018	5 %	(El-Emam & Dincer, 2014)
p_{SWIP} (kPa)	650	5 %	(El-Emam & Dincer, 2014)
p_{HPP} (kPa)	5350	5 %	Assumption
p_{PT} (kPa)	5100	5 %	Assumption
CC_{RO} (USD/m ³)	0.01	5 %	(El-Emam & Dincer, 2014)
End of Life (%TCD)	10	5 %	Assumption

Table 4.2 outlines the foundational assumptions used in the technoeconomic assessments of the electrolysis plant.

Table 4.2: Assumptions regarding the water electrolysis plant

Parameter	Value	Uncertainty	Reference
j (A/cm ²)	1	5 %	(Carmo et al., 2019)
$\eta_{electrol}$	0.8	5 %	(Letcher, 2020)
Yearly O&M (% $C_{electrol}$)	1.5	5 %	(Godula-Jopek, 2015)
M-L refurbishment (% $C_{electrol}$)	200	5 %	(Godula-Jopek, 2015)
End of Life (% $C_{electrol}$)	10	5 %	(d'Amore-Domenech et al., 2021)
T^0 (°C)	25	1 %	Assumption
T_{O_2} (°C)	80	1 %	Assumption
T_{H_2} (°C)	80	1 %	Assumption
T_{H_2O} (°C)	25	1 %	Assumption
p^0 (kPa)	100	1 %	Assumption
p_{O_2} (kPa)	3000	1 %	Assumption
p_{H_2} (kPa)	3000	1 %	Assumption
p_{H_2O} (kPa)	3000	1 %	Assumption
$\Delta h_{f_{H_2}}^0$ (kJ/mol)	0	0 %	(Chase et al., 1986)
$\Delta h_{f_{O_2}}^0$ (kJ/mol)	0	0 %	(Chase et al., 1986)
$\Delta h_{f_{H_2O(l)}}^0$ (kJ/mol)	-285.830	0 %	(Chase et al., 1986)
HHV_{H_2} (MJ/kg)	141.88	0 %	(Godula-Jopek, 2015)

Table 4.3 presents the foundational assumptions utilized in the technoeconomic evaluations of the hydrogen liquefaction plant.

Table 4.3: Assumptions regarding the hydrogen liquefaction plant

Parameter	Value	Uncertainty	Reference
Yearly O&M (% C_{LP})	3	5 %	(Elgowainy & Reddi, 2015)
M-L refurbishment (% C_{LP})	40	5 %	(d'Amore-Domenech et al., 2021)
End of Life (% C_{LP})	10	5 %	(d'Amore-Domenech et al., 2021)
w_{liquef} (kWh/kg)	6.1	3 %	(Cardella, Decker, Sundberg, et al., 2017)
w_{liquef} (MJ/kg)	22.0	3 %	(Cardella, Decker, Sundberg, et al., 2017)

Table 4.4 provides an overview of the foundational assumptions used in the technoeconomic calculations of the liquid hydrogen tanks.

Table 4.4: Assumptions regarding the liquid hydrogen storage

Parameter	Value	Uncertainty	Reference
Yearly O&M (% C_{LHT})	3	5 %	(d'Amore-Domenech et al., 2021)
M-L refurbishment (% C_{LHT})	0	5 %	(d'Amore-Domenech et al., 2021)
End of Life (% C_{LHT})	10	10 %	(d'Amore-Domenech et al., 2021)

$w_{reliquef}$ (kWh/kg)	6.1	3 %	(Cardella, Decker, Sundberg, et al., 2017)
$w_{reliquef}$ (MJ/kg)	22.0	3 %	(Cardella, Decker, Sundberg, et al., 2017)
Daily boil-off (% average m_{H_2} stored)	0.1	5 %	(d'Amore-Domenech et al., 2021)
Average m_{H_2} stored (% m_{H_2} capacity)	50	0 %	(d'Amore-Domenech et al., 2021)
Number of tanks	3	0 %	Assumption
Capacity of each tank (% m_L)	33.33	0 %	Assumption

Table 4.5 provides the fundamental assumptions utilized for the technoeconomic calculations of the ships for hydrogen transportation. $\dot{W}_{nom}$ for sailing is estimated based on data from ships with similar characteristics (MAN, 2013; R. Faizal & M. Holmlund-Sund, 2015; Sinha & Mohd Norsani Wan Nik, 2012).

Table 4.5: Assumptions regarding the LH₂ fleet

Parameter	Value	Uncertainty	Reference
c_{TC} (kUSD/day)	90	10 %	(d'Amore-Domenech et al., 2021)
C_V (kUSD/round trip land terminal)	15	10 %	(d'Amore-Domenech et al., 2021)
Ship capacity (t _{H2})	12760	5 %	Assumption
V_H (m ³)	180000	5 %	Assumption

Nominal pressure (bar)	1	-	Assumption
Min. pressure (bar)	1	-	Assumption
$s_{V_{nom}}$ (kn)	20	10 %	Assumption
$s_{V_{nom}}$ (m/s)	10.29	10 %	Assumption
$\dot{W}_{nom}$ (sailing) (MW)	35	5 %	(MAN, 2013; R. Faizal & M. Holmlund-Sund, 2015; Sinha & Mohd Norsani Wan Nik, 2012)
$\dot{W}_{nom}$ (Loading and offloading) (MW)	2	10 %	Assumption
Power plant efficiency η_{FC} (based on LHV _{H2})	0.55	5 %	(Oh et al., 2023)
t_{LS} (s)	3600	5 %	Assumption
$\dot{V}_L$ (m ³ /h)	12000	5 %	Assumption
$\dot{V}_{OL}$ (m ³ /h)	12000	5 %	Assumption

Table 4.6 outlines the foundational assumptions utilized in the technoeconomic assessments of the hydrogen regasification plant.

Table 4.6: Assumptions regarding the regasification plant

Parameter	Value	Uncertainty	Reference
$f_{install}$	1.3	5 %	(Elgowainy & Reddi, 2015)
M-L refurbishment (% $C_{Regasif}$)	200	5 %	Assumption
End of Life (% $C_{Regasif}$)	5	5 %	Assumption

Table 4.7 outlines the foundational assumptions utilized for the technoeconomic assessments of the methanol synthesis plant.

Table 4.7: Assumptions regarding the methanol synthesis plant

Parameter	Value	Uncertainty	Reference
H ₂ usage (kgH ₂ /kgMeOH)	0.192	5 %	(Nyári et al., 2020)
CO ₂ usage (kgCO ₂ /kgMeOH)	1.397	5 %	(Nyári et al., 2020)
CO ₂ cost (USD/kg)	0.0229	5 %	(Nyári et al., 2020)
M-L refurbishment (% C_{Synth})	200	5 %	Assumption
Yearly Fixed O&M (% C_{Synth})	1.5	5 %	(Nyári et al., 2020)
End of Life (% C_{Synth})	10	5 %	Assumption

The baseline assumptions utilized for the technoeconomic evaluations of methanol storage facilities are outlined in Table 4.8.

Table 4.8: Assumptions regarding the methanol storage facilities

Parameter	Value	Uncertainty	Reference
M-L refurbishment (% C_{SMeOH})	100	5 %	Assumption
End of Life (% C_{SMeOH})	5	5 %	Assumption

Table 4.9 outlines the baseline assumptions utilized for the technoeconomic evaluations of methanol transport ships.

Table 4.9: Assumptions regarding the methanol fleet

Parameter	Value	Uncertainty	Reference
c_{TC} (kUSD/d)	19	10 %	(Clarkson Research Services Limited, 2021)
C_V (kUSD/round trip land terminal)	15	10 %	Assumption
Ship capacity (t_{MeOH})	95040	5 %	(Wärtsilä, 2024b)
V_{MeOH} (m ³)	120000	5 %	(Wärtsilä, 2024b)
Nominal pressure (bar)	1	-	Assumption
Min pressure (bar)	1	-	Assumption
$s_{V_{nom}}$ (kn)	15.4	5 %	(Wärtsilä, 2024b)
$s_{V_{nom}}$ (m/s)	7.92	5 %	(Wärtsilä, 2024b)
$\dot{W}_{nom}$ (sailing) (MW)	15	5 %	(Wärtsilä, 2024b)

$\dot{W}_{nom}$ (Loading and offloading) (MW)	2	5 %	Assumption
Power plant efficiency η_{engine} (based on LHV_{MeOH})	0.35	5 %	Assumption
t_{LS} (s)	3600	5 %	Assumption
$\dot{V}_L$ (m ³ /h)	12000	5 %	Assumption
$\dot{V}_{OL}$ (m ³ /h)	12000	5 %	Assumption

Table 4.10 presents the baseline assumptions used for the technoeconomic calculations of the methanol electrolysis plant.

Table 4.10: Assumptions regarding the methanol electrolysis plant

Parameter	Value	Uncertainty	Reference
j (A/cm ²)	0.150	5 %	(Sethu et al., 2014)
$\eta_{electrol}$	0.34	5 %	(Sethu et al., 2014)
Yearly O&M (% $C_{electrol}$)	0.2	5 %	(Schmidt et al., 2017)
M-L refurbishment (% $C_{electrol}$)	200	5 %	(Schmidt et al., 2017)
End of Life (% $C_{electrol}$)	10	5 %	Assumption
T^0 (°C)	25	1 %	Assumption
T_{CO_2} (°C)	80	1 %	Assumption
T_{H_2} (°C)	80	1 %	Assumption
T_{H_2O} (°C)	25	1 %	Assumption
T_{CH_3OH} (°C)	25	1 %	Assumption
p^0 (kPa)	100	1 %	Assumption

p_{O_2} (kPa)	5000	1 %	Assumption
p_{H_2} (kPa)	5000	1 %	Assumption
p_{H_2O} (kPa)	5000	1 %	Assumption
p_{CH_3OH} (kPa)	5000	1 %	Assumption
$\Delta h_{f_{H_2}}^0(T^0, p^0)$ (kJ/mol)	0	0 %	(Chase et al., 1986)
$\Delta h_{f_{CO_2}}^0(T^0, p^0)$ (kJ/mol)	-393.522	0 %	(Chase et al., 1986)
$\Delta h_{f_{H_2O(l)}}^0(T^0, p^0)$ (kJ/mol)	-285.830	0 %	(Chase et al., 1986)
$\Delta h_{f_{CH_3OH(l)}}^0(T^0, p^0)$ (kJ/mol)	-238.81	0 %	(Chase et al., 1986)
HHV_{H_2} (MJ/kg)	141.88	0 %	(Godula-Jopek, 2015)

Table 4.11 enumerates the baseline assumptions utilized for the technoeconomic calculations of the methanol steam reforming plant.

Table 4.11: Assumptions regarding the methanol steam reforming plant

Parameter	Value	Uncertainty	Reference
η_{reform} (%)	85	5 %	(Lian et al., 2019)
r_{conv} (kg _{H2} /kg _{MeOH})	0.189	5 %	(Byun et al., 2020)
M-L refurbishment (% C_{Reform})	200	5 %	Assumption
End of Life (% C_{Reform})	20	5 %	Assumption

The results obtained using the assumptions previously described in Table 4.1 to Table 4.11 are presented below.

Figure 4.2 illustrates the perceived Levelized Cost Of Hydrogen (LCOH) at the destination for the different options examined in this analysis: liquefied hydrogen (LH2), electrolysis-based methanol (MeOH+electrol), and steam reforming-based methanol (MeOH+reform). The LCOH is depicted for varying quantities of hydrogen generated at the source: 100 kt/y, 1 Mt/y, and 10 Mt/y, across three routes investigated: Pecem (Brazil) to Algeciras (Spain) [Bra-Sp 5629 km], Pecem (Brazil) to Rotterdam (the Netherlands) [Bra-Ned 7438 km], and Hastings (Australia) to Kobe (Japan) [Aus-Jpn 9082 km]. All LCOH values presented in Figure 4.2 assume an electricity price at the source of 40 USD/MWh and an electricity price at the destination of 150 USD/MWh. The breakdown of LCOH in Figure 4.2 includes production, packaging, transportation, and unpackaging costs. Notably, the LCOH of production differs among the LH2, MeOH+electrol, and MeOH+reform options, primarily due to variations in the delivered hydrogen quantity at the receiving end, as depicted in Figure 4.3. While production costs exhibit minimal sensitivity to changes in the mass of hydrogen produced, packaging and unpackaging costs are notably more sensitive as reported for methanol synthesis units (Schorn et al., 2021). In this work this sensitivity may be attributed to the definitions of packaging and unpackaging. Both packaging and unpackaging costs encompass the expenses associated with storing liquefied hydrogen or methanol at receiving terminals, which are diluted by the volume of delivered hydrogen. The net volume of storage facilities at each sending terminal aligns with the cargo volume accommodated by each cargo vessel, while the net volume of storage facilities at each receiving terminal corresponds to the cargo remaining unconsumed during the ship round trip. In Figure 4.2 the breakdown of the perceived LCOH at the receiving terminal encompasses production, packing, transport, and unpacking. Production solely entails the LCOH of hydrogen production. Packing encompasses all processes to enhance hydrogen density: liquefaction and storage for LH2, and methanol synthesis and storage for MeOH. Transport covers solely the cost of maritime transport for the "packed" hydrogen. Unpacking incorporates storage and costs to revert the "packed" hydrogen: regasification for LH2, electrolysis for MeOH+electrol, and steam reforming for MeOH+reform.

As stated above and as can be seen in Figure 4.3, the amount of hydrogen delivered at destination varies between the alternatives studied. This is because hydrogen and methanol are consumed during the transport process to use them as fuel for ships. Besides, methanol is employed as fuel to provide the thermal energy needed in the reforming process in the studied alternative that includes this process. This

difference in the amount of hydrogen delivered to the destination also explains the differences in the values associated with hydrogen production in the LCOH costs in Figure 4.2.

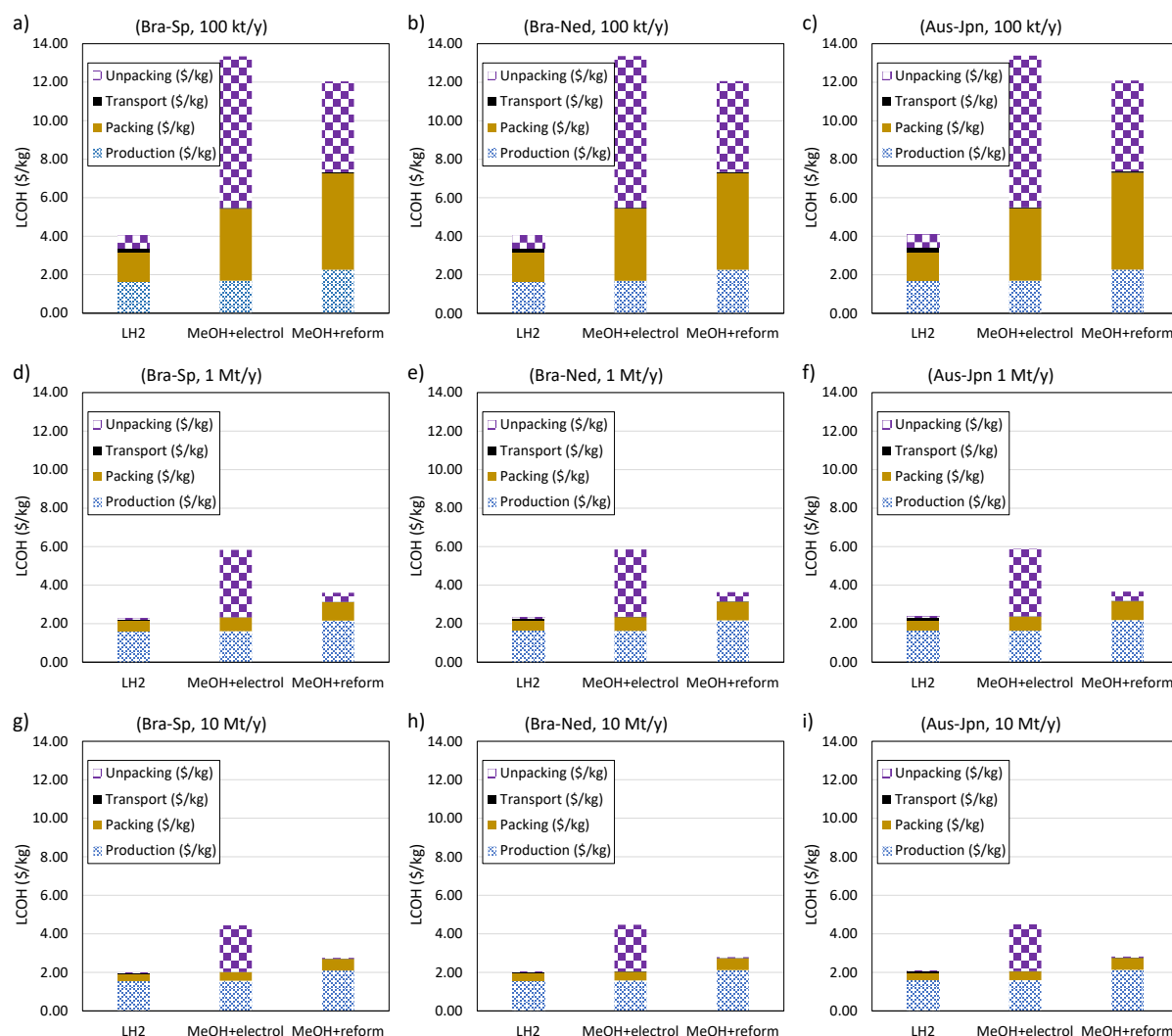


Figure 4.2: The breakdown of the perceived Levelized Cost Of Hydrogen (LCOH) at the receiving terminal predicated on an electricity price of 40 USD/MWh at the source and 150 USD/MWh at the destination. All cost items mentioned in the legend are depicted in the graphs; those not indicated are considered negligible. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

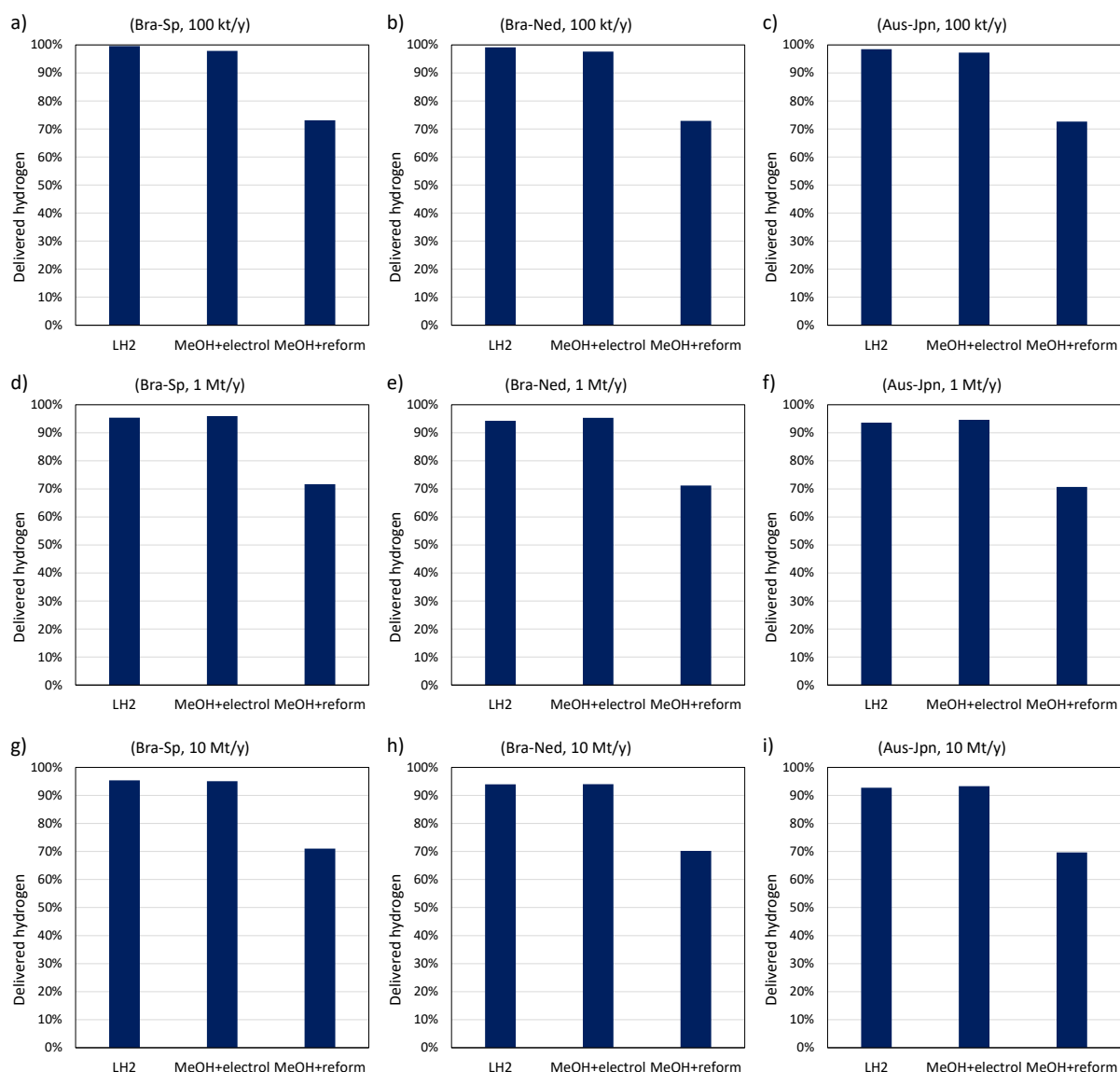


Figure 4.3: Ratio of delivered hydrogen obtained after unpacking process expressed as percentage over the produced hydrogen available at the source. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

Figure 4.4 illustrates the impact of destination electricity prices on the LCOH for the methanol transport and subsequent electrolysis alternative. It is imperative that electricity costs reflect current market rates and their inherent variability. To address this, three distinct destination electricity price points are examined: 100 USD/MWh (27.8 USD/GJ), 150 USD/MWh (41.7 USD/GJ), and 200 USD/MWh (55.6 USD/GJ). Analogous to Figure 4.2, Figure 4.4 depicts LCOH values across varying hydrogen mass flow rates originating from the source, encompassing the three scenarios scrutinized in this investigation.

Similarly to Figure 4.2, the LCOH depicted in Figure 4.4 is dissected into production, packing, transport and unpacking costs. It is discernible that alterations in destination electricity prices have a minor impact on the final LCOH, primarily influencing the unpacking stage. Later studies have shown that the variation in the electricity prices can have a greater effect on methanol production from hydrogen (Sollai et al., 2023). Besides, in this thesis the electricity consumption during e-methanol electrolysis per unit mass of produced hydrogen remains invariant with changes in hydrogen mass flow rates, owing to the assumption of constant efficiency in the electrolysis process. Consequently, no discernible economies of scale are observed concerning energy consumption in e-methanol electrolysis. Conversely, economies of scale are identifiable in the unpacking phase within storage facilities, as well as in the capital investment costs associated with methanol electrolysis facilities. Besides, in this Figure 4.4, no difference in the LCOH is observed due to the change of transport distances, as the cost associated to transport process is relatively small compared to the rest of the processes as reported in literature (Schorn et al., 2021), i. e. in this thesis production, packing and unpacking.

In industries where electrification poses challenges for decarbonization, particularly in high-temperature thermal processes and heavy-duty transport, the adoption of zero-emission or low-emissions fuels like green hydrogen or green methanol offers a viable pathway. The choice between these fuels becomes inconsequential when their costs per unit of energy are equivalent. Illustrated in Figure 4.5 is the Levelized Cost of Energy (LCOE) at the receiving terminal, delineated into production, packing, and transport components. This analysis considers an electricity price at the source of 40 USD/MWh, alongside the lower heating value of both fuels, across varying levels of hydrogen production at the source across three delineated routes. For lower hydrogen mass flow rates, employing LH2 proves to be more cost-effective than utilizing MeOH in processes such as those aforementioned. However, as the hydrogen mass flow rate at the source escalates, the discrepancy in LCOEs between LH2 and MeOH diminishes, indicating a convergence of economic viability. Notably, economies of scale in the MeOH alternative become increasingly apparent with rising hydrogen production rates. Indeed, at a production rate of 10 Mt/y of hydrogen at the source, there is a slight difference in the LCOE obtained with LH2 and MeOH alternatives. In such cases, opting for MeOH can become more pragmatic due to the methanol ease of handling and storage under ambient conditions and the lowering of this cost with

economies of scale, as obtained in other studies for the methanol synthesis process (Schorn et al., 2021), despite having obtained a slightly higher LCOE in this study for MeOH than for LH2 presented in Figure 4.5.

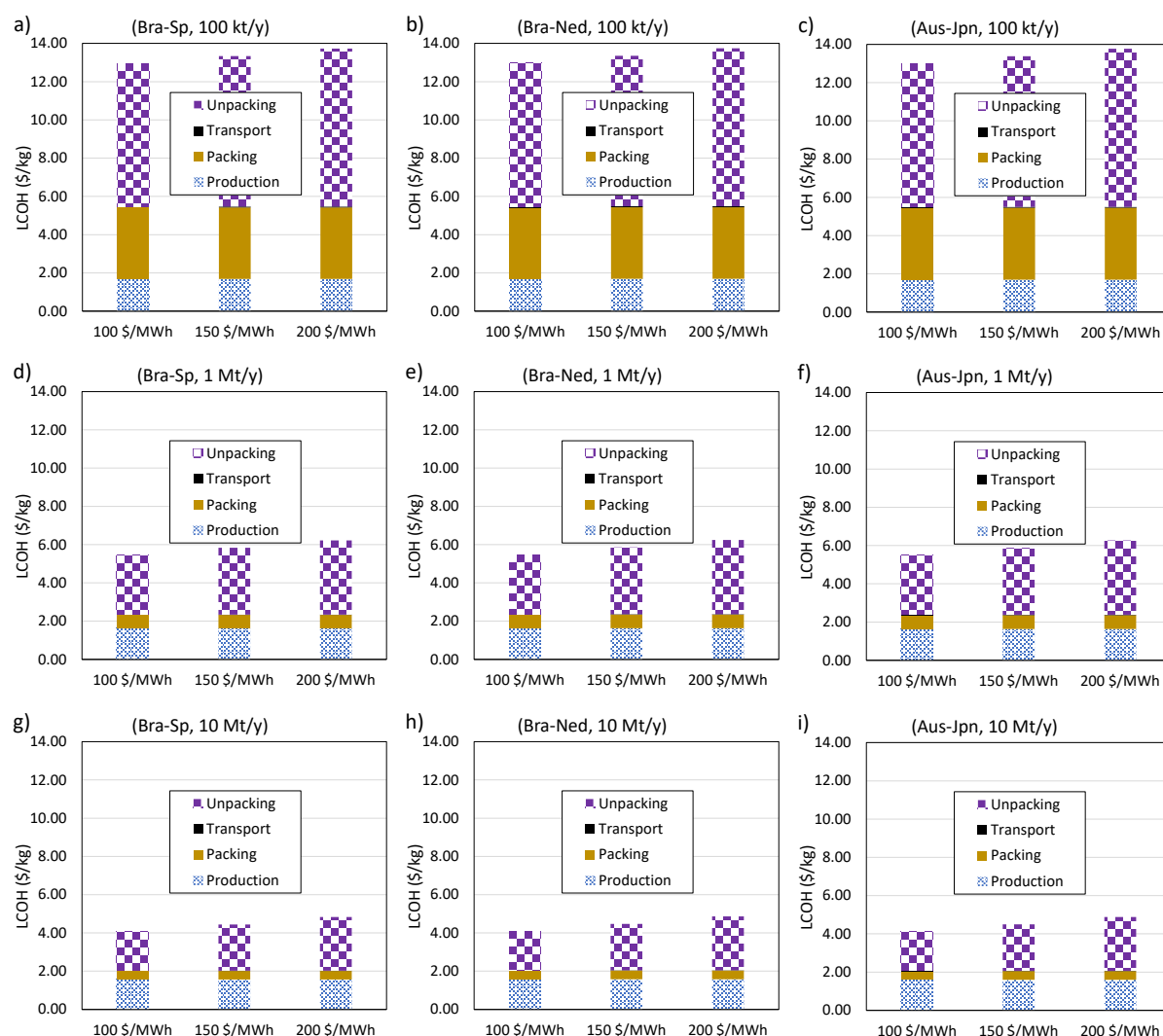


Figure 4.4: Levelized Cost Of Hydrogen (LCOH) as a function of the electricity price at destination in the alternative of methanol transport and electrolysis process. All cost items mentioned in the legend are depicted in the graphs; those not indicated are considered negligible. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

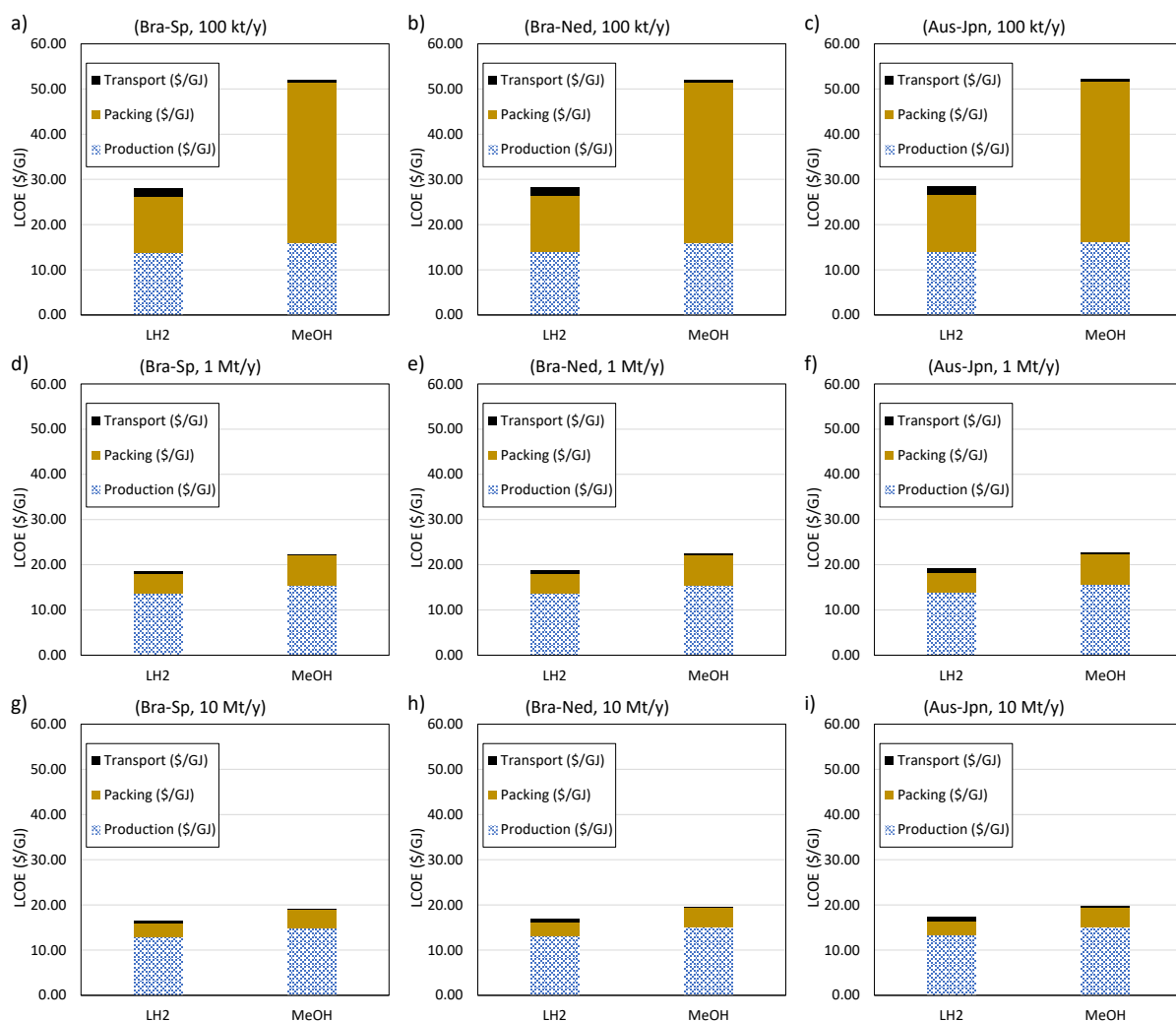


Figure 4.5: Levelized Cost Of Energy (LCOE) at the receiving terminal corresponding to the alternatives of using liquefied hydrogen or methanol as energy carriers. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

Figure 4.6 illustrates the LCOH at the receiving terminal, incorporating uncertainty bands, in relation to the hydrogen mass flow rate generated at the source. This analysis accounts for an electricity price of 40 USD/MWh at the source and 120 USD/MWh at the destination, encompassing the three routes examined in this investigation. Across all alternatives, the LCOH demonstrates a significant decrease as the annual volume of transported hydrogen escalates, coinciding well with the trend in the results presented in literature (Cui & Aziz, 2023), reaching in this work a plateau around 1 Mt/y presented in Figure 4.6. Beyond this threshold, the LCOH exhibits minimal fluctuations, indicating limited gains from economies of scale. Furthermore, there are no points on this graph where the cost between two alternatives appears to be equal.

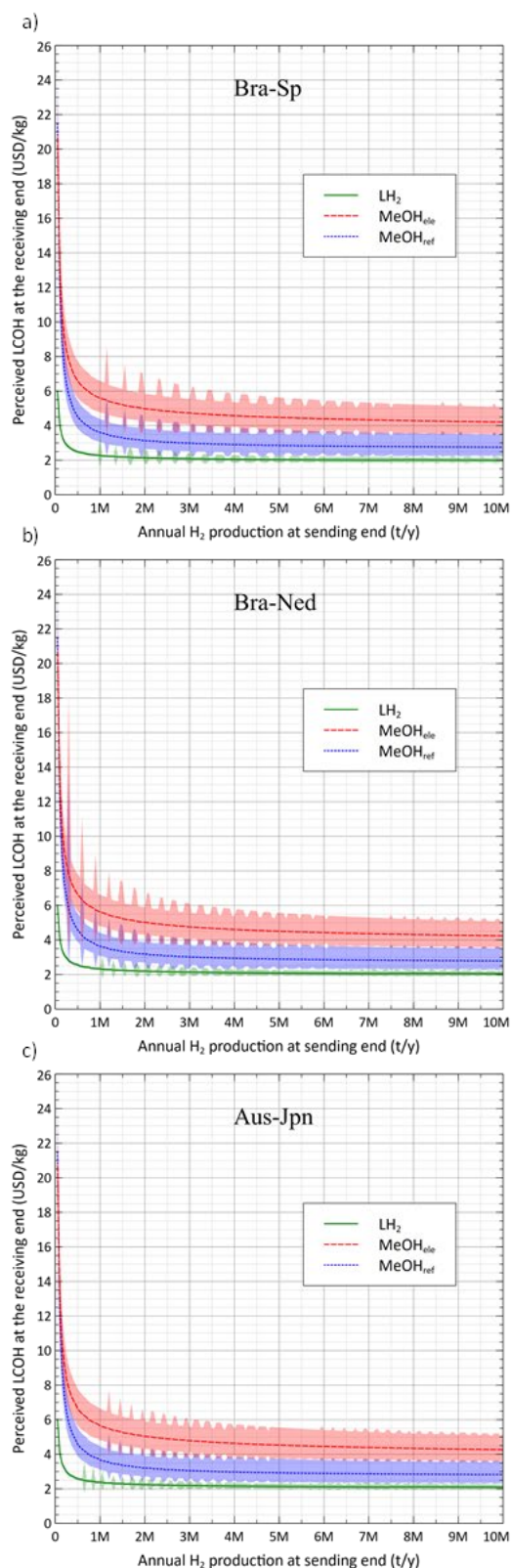


Figure 4.6: Levelized Cost Of Hydrogen (LCOH) perceived at the receiving terminal depicted alongside uncertainty margins, contingent upon the hydrogen mass flow rate originating from the source. This depiction takes into account electricity pricing, set at 40 USD/MWh at the source and 120 USD/MWh at the destination. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

Figure 4.6 illustrates that the levelized cost of hydrogen imported to Spain, the Netherlands, and Japan hovers around 2 USD/kg for the alternative of transporting LH₂ when the hydrogen production volume exceeds 1 Mt/y, assuming an electricity price of 40 USD/MWh at the source. Conversely, Table 4.12 indicates that if the source electricity price exceeds 50 USD/MWh, the local hydrogen production cost surpasses 2 USD/kg. Thus, under such circumstances, importing hydrogen from regions with renewable electricity rates below 40 USD/MWh proves advantageous. Given the prevailing electricity rates in Spain, the Netherlands, and Japan, bulk importation of hydrogen from regions enjoying wholesale renewable electricity rates below 40 USD/MWh emerges as a favourable strategy, provided the hydrogen production volume at the source exceeds 1 Mt/y.

Table 4.12: Levelized cost analysis of hydrogen produced (LCOH), contingent upon both hydrogen mass flow rate and electricity pricing. All costs associated with LCOH are denoted in the column tables in USD/kg_{H₂}. Reprinted with permission from (Meca et al., 2022). Copyright 2022 American Chemical Society

Electricity price (USD/MWh)	Hydrogen mass flow rate		
	100 (kt/y)	1 (Mt/y)	10 (Mt/y)
20	0.958±0.014	0.857±0.009	0.795±0.006
40	1.651±0.014	1.550±0.009	1.487±0.006
50	1.997±0.014	1.896±0.009	1.834±0.006
60	2.344±0.014	2.242±0.009	2.180±0.006
100	3.729±0.015	3.628±0.009	3.566±0.006
150	5.462±0.015	5.360±0.010	5.298±0.006
200	7.194±0.015	7.092±0.010	7.030±0.006

4.2. Direct Methanol Fuel Cell

This section presents the outcomes of the RSM methodology applied to the experimental findings from Direct Methanol Fuel Cell (DMFC) single cell tests. In Section 4.2.1, the results of exploring the influence of operational parameters on DMFC performance are detailed. Through systematic experimentation, a deeper understanding is gained regarding the intricate interplay between operational conditions and DMFC behaviour. Notably, the investigation identifies key parameters that significantly impact DMFC performance among those studied, elucidating how the interactions of these parameters further influence performance. In Section 4.2.2, the results obtained through the CCD design to determine combinations of parameters for the serpentine flow field geometry of the DMFC anode plate to be tested are presented. This analysis takes into account the geometric and technical constraints associated with this channel design, offering valuable insights into improving DMFC performance.

4.2.1. Working conditions

This section presents the results of an experimental study to determine the influence of operational conditions on the performance of a DMFC. The study focuses on three key parameters: DMFC temperature (T), concentration of the aqueous methanol solution (M) used as fuel, and volumetric flow rate of aqueous methanol ($\dot{V}$) supplied to the DMFC. By applying Response Surface Methodology (RSM), not only the individual effects of each parameter but also their combined impact on DMFC performance are explored.

The response variable chosen for this investigation is the peak power density of a DMFC single cell, $\dot{W}_{DMFC}$. By employing a Central Composite Design (CCD) within RSM, the interactions between these operational parameters and their effects on peak power density are systematically analysed.

For this study, factors ($\dot{V}$, M and T) have been selected and the CCD design has been applied to obtain combinations of factor values for DMFC experimentally testing, as presented in Table 4.13. These parameter combinations are used for conducting DMFC experiments, resulting in polarization curves for each factor combination. A total of 73 polarization curves as the one presented in Figure 4.7 were obtained during the DMFC tests for this study, listed in Annex B.

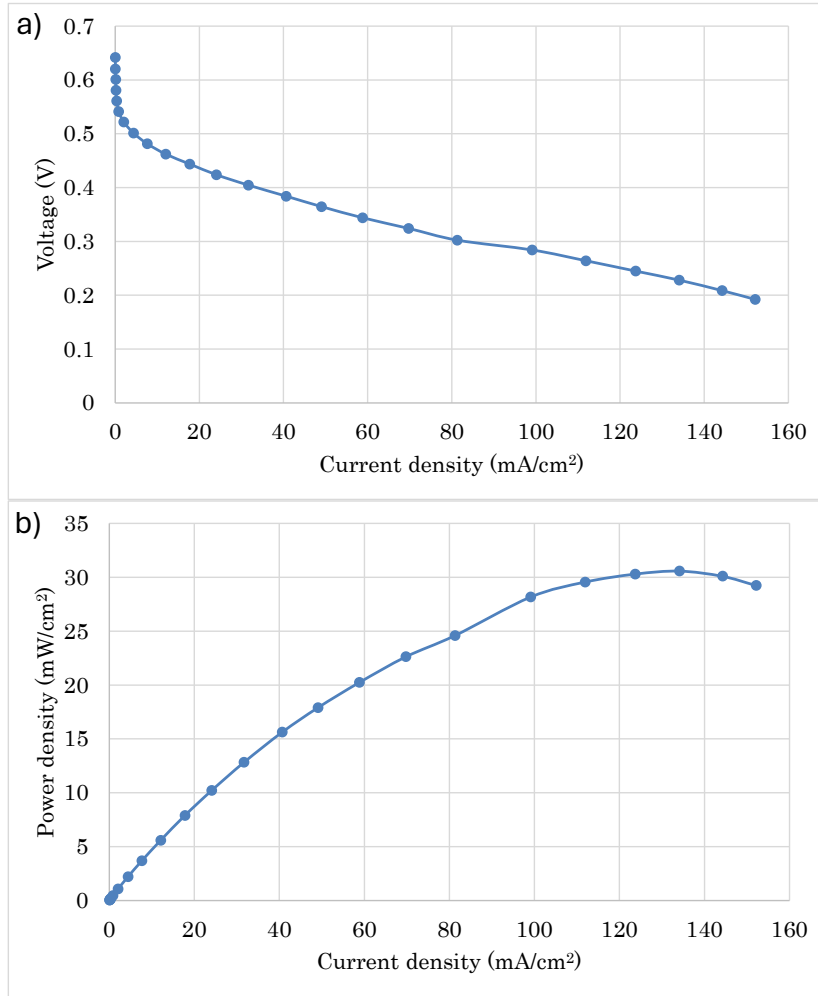


Figure 4.7: a) Polarization curve of the DMFC single cell of this study obtained at a temperature of 50 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2 M and methanol volumetric flow rate 4.5 ml/min. b) Power density curve obtained from the polarization curve

From the polarization curves obtained, power density curves are derived, and ultimately, peak power density values are obtained, also documented in Table 4.13. Thus, in Table 4.13, the parameter combinations derived from the CCD design are presented, along with the experimentally obtained peak power density ($\dot{W}_{DMFC}$) values from DMFC single cell tests.

Table 4.13: Parameter combinations of the Direct Methanol Fuel Cell (DMFC) working conditions obtained from Central Composite Design and corresponding peak power density $\dot{W}_{DMFC}$ values obtained from experimental DMFC tests. Here $\dot{V}$ signifies the methanol volumetric flow rate, M denotes methanol concentration and T indicates DMFC temperature

$\dot{V}$ (ml/min)	$10^8 \cdot \dot{V}$ (m ³ /s)	M (mol/l)	$10^3 \cdot T$ (mol/m ³)	T (°C)	T (K)	$\dot{W}_{DMFC}$ (mW/cm ²)
1.90	3.17	2.00	2.00	50.0	323.0	30.77
3.00	5.00	1.00	1.00	40.0	313.0	30.24
3.00	5.00	1.00	1.00	60.0	333.0	45.18
3.00	5.00	3.00	3.00	40.0	313.0	24.67
3.00	5.00	3.00	3.00	60.0	333.0	7.49
4.50	7.50	0.27	0.27	50.0	323.0	26.19
4.50	7.50	2.00	2.00	32.7	305.7	19.37
4.50	7.50	2.00	2.00	50.0	323.0	30.39
4.50	7.50	2.00	2.00	50.0	323.0	26.25
4.50	7.50	2.00	2.00	50.0	323.0	27.98
4.50	7.50	2.00	2.00	50.0	323.0	25.76
4.50	7.50	2.00	2.00	67.3	340.3	23.11
4.50	7.50	3.73	3.73	50.0	323.0	7.49
6.00	10.00	1.00	1.00	40.0	313.0	28.60
6.00	10.00	1.00	1.00	60.0	333.0	42.52
6.00	10.00	3.00	3.00	40.0	313.0	18.46
6.00	10.00	3.00	3.00	60.0	333.0	6.14
7.10	11.83	2.00	2.00	50.0	323.0	23.15

By employing the RSM methodology using the results presented in Table 4.13, Eq. 4.1 is derived. This mathematical expression enables the determination of peak power density resulting from the combination of the values of the three studied parameters.

$$\begin{aligned}\dot{W}_{DMFC} = & -62.1 - 4.2\dot{V} + 40.5M + 2.8T - 0.3\dot{V}M + 0.03\dot{V}T - 0.7MT \\ & + 0.2\dot{V}^2 - 2.9M^2 - 0.01T^2\end{aligned}\quad (4.1)$$

where $\dot{W}_{DMFC}$ represents the predicted power density in mW/cm², $\dot{V}$ signifies the volumetric flow rate in ml/min, M denotes methanol concentration in mol/l and T indicates DMFC temperature in °C.

Projecting the predicted peak power density values attainable using different methanol flow rates, concentrations, and DMFC temperatures can be facilitated using Eq. 4.1. These predicted peak power density values are discerned by holding one of the stipulated parameters constant while modifying the other two, thereby generating response surfaces as those depicted in Figure 4.8 to Figure 4.10.

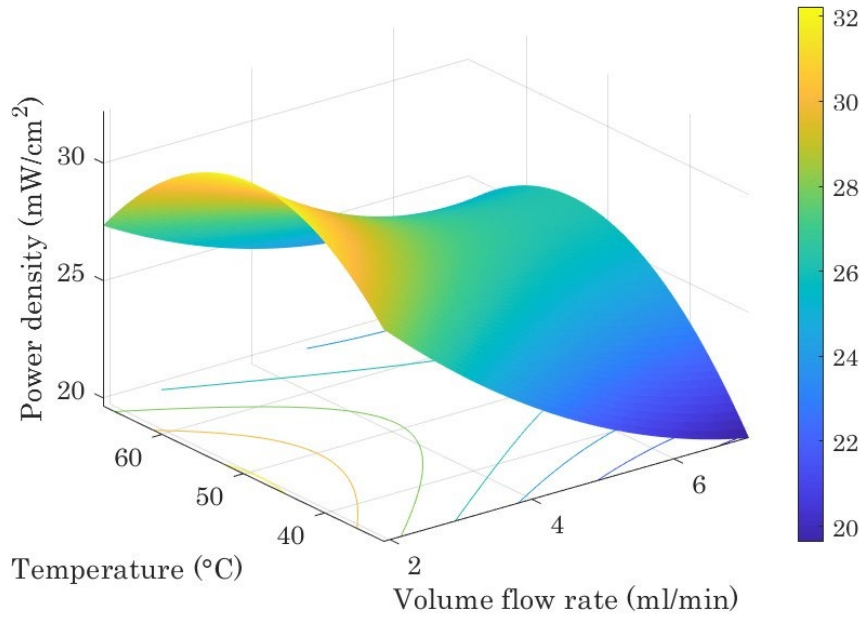


Figure 4.8: Predicted peak power density response surface obtained when setting the methanol concentration at 2M and modifying the methanol volumetric flow rate and temperature values of the Direct Methanol Fuel Cell

In Figure 4.8 it is observed that maintaining the methanol concentration at 2 M, the maximum predicted peak power density of the DMFC would be achieved at a temperature of around 50 °C and a low volumetric flow rate. This phenomenon can be attributed to the enhancement of reaction kinetics at both the anode and cathode with increasing temperature (Alizadeh et al., 2013). However, excessively high temperatures may exacerbate methanol crossover due to enhanced methanol diffusion through the polymer membrane (Raso García et al., 2017). Moreover, an increase in the volumetric flow rate of methanol can also facilitate crossover, along

with a reduction in the temperature of the catalytic layer due to the introduction of methanol at a higher flow rate and lower temperature than the operating temperature of the DMFC (Z. Zhao et al., 2023).

Figure 4.9 shows a maximum DMFC predicted peak power density achieved at a methanol concentration below 2M when operating at 50°C. In this case, the peak power density appears to be more independent of the methanol volumetric flow rate in line with the results reported in the literature (Charoen et al., 2017; Silva & Rouboa, 2012), although it slightly increases for lower volumetric flow rates. The behaviour of the power density related to methanol concentration may be attributed to the fact that higher methanol concentrations can lead to increased methanol crossover, thereby reducing the voltage of the DMFC and consequently its power density (Liao et al., 2007).

As observed in Figure 4.8 and Figure 4.9, and demonstrated now in Figure 4.10, maintaining the volumetric flow rate of methanol at 4.5 ml/min, an increase in temperature and a low methanol concentration result in an increase in the predicted power density.

Observations from Figure 4.9 and Figure 4.10 reveal that diminished methanol concentration corresponds to augmented power density values, in accordance with the behaviour of DMFCs reported in literature (Charoen et al., 2017). Likewise, in Figure 4.8 it can be seen that decreased methanol flow rate leads to heightened power density values when concentration remains fixed, albeit with reduced significance when temperature is stabilized, see Figure 4.9. Additionally, elevated temperature settings in Figure 4.10 are observed to bolster higher power density values when methanol volumetric flow rate is held constant, yet this effect is not evident in Figure 4.8 when concentration is fixed as a too high temperature with 2 M methanol concentration leads to higher methanol crossover.

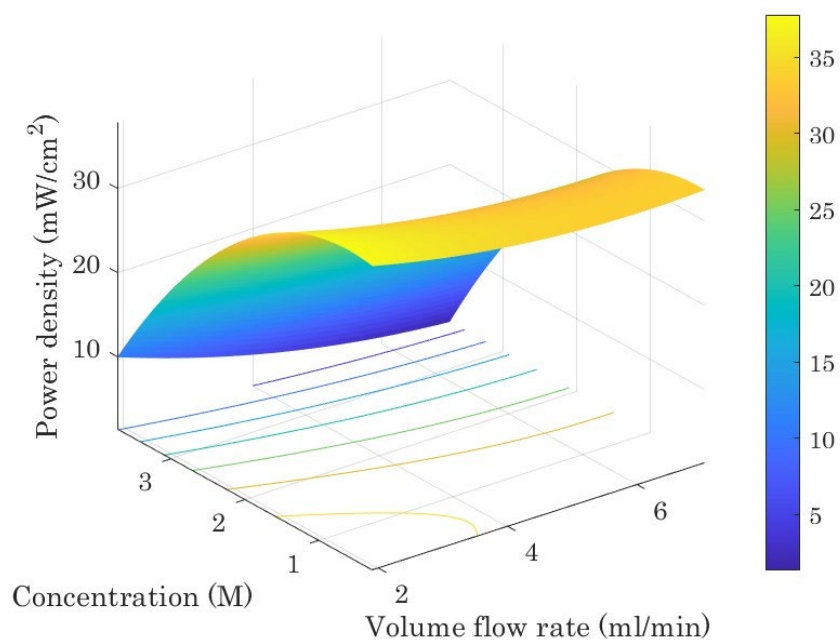


Figure 4.9: Predicted peak power density response surface obtained when setting the Direct Methanol Fuel Cell temperature at 50 °C and modifying the methanol concentration and volumetric flow rate

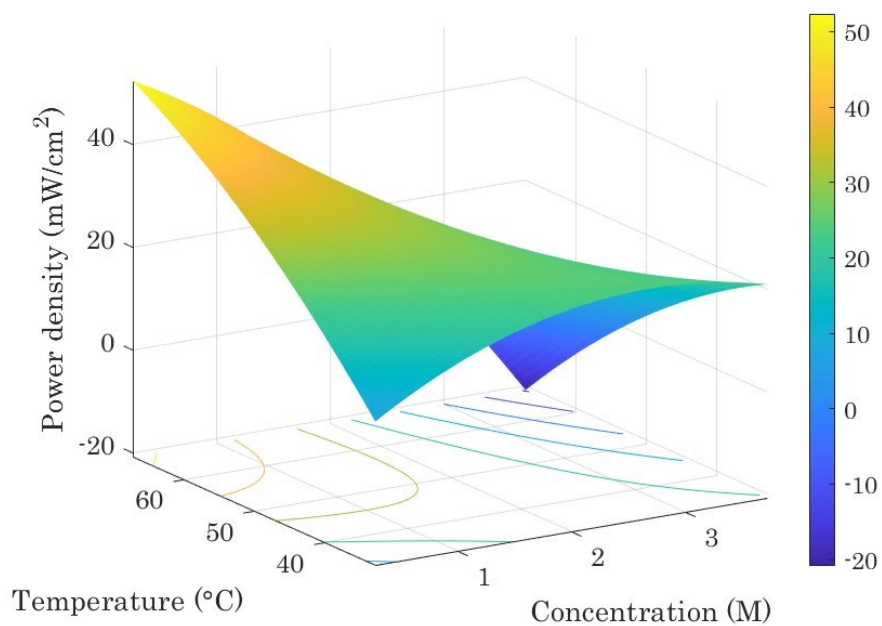


Figure 4.10: Predicted peak power density response surface obtained when setting the methanol volumetric flow rate at 4.5 ml/min and modifying the temperature of the Direct Methanol Fuel Cell and the methanol concentration values

To comprehensively explore the interplay among the parameters studied and verify the reliability of the findings, an analysis of variance (ANOVA) is conducted. The synopsis of this assessment is delineated in Table 4.14.

Table 4.14: Results of the analysis of variance (ANOVA) performed on the mathematical model obtained by applying the response surface methodology to study the effect of operating conditions on the performance of a Direct Methanol Fuel Cell

Variable	Estimate	Standard Error	tStat	p-Value
Volumetric flow rate ($\dot{V}$)	-4.243	8.122	-0.522	0.616
Concentration (M)	40.485	11.354	3.566	0.007
Temperature (T)	2.764	1.452	1.904	0.093
$\dot{V}M$	-0.273	1.143	-0.239	0.817
$\dot{V}T$	0.032	0.114	0.280	0.787
MT	-0.730	0.171	-4.257	0.003
$\dot{V}^2$	0.222	0.581	0.382	0.713
M^2	-2.875	1.308	-2.198	0.059
T^2	-0.014	0.013	-1.076	0.313

The ANOVA examination detailed in Table 4.14 serves to pinpoint the parameters that exert substantial influence on DMFC peak power density outcomes. Regarding the volumetric flow rate, the p-value exceeds the threshold of 0.05, rendering it statistically non-significant. Conversely, both concentration and temperature demonstrate notable effects, with the former exhibiting a p-value below 0.05, indicative of significance, and the latter approaching this threshold. Furthermore, the interaction term between concentration and temperature also yields a statistically significant effect.

The adequacy of the model fit can be evaluated through the R^2 and adjusted R^2 metrics. The R^2 value, denoting the proportion of variance elucidated by the model, stands at 0.90. Complementarily, the adjusted R^2 , which adjusts for the number of predictors and degrees of freedom, is calculated as 0.79. In summary, the analysis

underscores the significant influence of methanol concentration (M) and the concentration-temperature interaction term (MT) on the response variable, DMFC peak power density, W_{DMFC} . Notably, the model exhibits a robust fit, explaining 90 % of the variability observed. These results underscore the perceptible impact of methanol concentration variations on power density, as well as the combined influence of concentration and temperature on the response variable. Such insights underscore the imperative nature of considering and regulating these factors during response optimization.

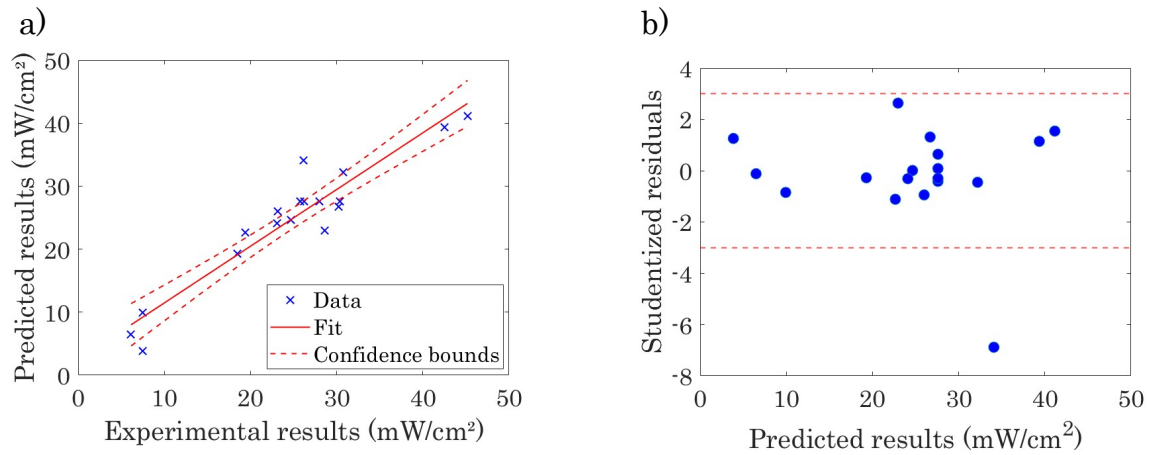


Figure 4.11: a) Evaluation of Direct Methanol Fuel Cell peak power density acquired through experimentation versus projections from the model obtained when varying its working conditions. b) Examination of studentized residuals for peak power density in contrast to predicted values

Figure 4.11 compares the predicted peak power density derived from the quadratic model of Eq. 4.1 with the experimental results. Examination of the graph unveils a discernible linear relationship between the predicted and experimental values, indicative of a favourable concordance between the model and the actual experimental data. Most projected values are situated within the confines of the confidence intervals, bolstering the reliability of the model and indicating a satisfactory fit of the quadratic model. Nevertheless, it is imperative to remark the presence of one distinct outlier in Figure 4.11a that markedly deviates from the established linear trend, lying beyond the bounds of the confidence intervals. This outlier necessitates further scrutiny, potentially warranting model refinement or additional experimental data acquisition to enhance the precision and prognostic capacity of the model.

Figure 4.11b illustrates the correlation between standardized residuals and predicted outcomes. This depiction facilitates the assessment of deviations

between observed and anticipated values. Upon visual scrutiny, no overt patterns are discernible, suggesting that the model adequately encompasses the dataset variability. Nonetheless, a singular data point, as detected in Figure 4.11a, registers a residual value exceeding the acceptable range, hinting at a possible outlier. Subsequent inquiry is warranted to elucidate the characteristics of this observation.

4.2.2. Flow field geometry

In this section, the outcomes of the serpentine flow field geometries for DMFC single cell anode plates are presented, derived from the application of the Central Composite Design (CCD) considering the geometric and technical constraints outlined in Section 3.3.3 DMFC flow field geometry. By employing the CCD design, combinations of parameter values are obtained, encompassing the open ratio (O_R), channel width (e), and channel depth (d), alongside the corresponding values for the number of straight channel sections (N_c) and rib width (l), as detailed in Table 3.5, information already provided in the methodology in order to explain the process of obtaining these results. These results establish a fundamental framework for both the manufacturing process and the empirical evaluation of anode geometries within DMFCs.

The plates designed according to the geometries specified in Table 4.15 have been successfully fabricated. The result of this process is shown in Figure 4.12. Experimental testing of DMFC single cells with these new plates has begun and results will be incorporated in future scientific publications.

Table 4.15: Combination of geometrical parameters defining the serpentine flow field of DMFC anode plates obtained by applying a Central Composite Design considering geometrical and technical constraints. Here O_R is the open ratio, e is the channel width, d represents the channel depth, N_c is the number of straight channel sections and l is the rib width

O_R (%)	e (mm)	d (mm)	N_c	l (mm)
19.2	0.98	1.30	7	5.52
30.3	0.83	0.90	14	2.19
30.3	0.83	1.70	14	2.19
30.3	1.13	0.90	10	3.19
30.3	1.13	1.70	10	3.19
45.4	0.71	1.30	25	0.92
45.4	0.98	0.61	18	1.32
45.4	0.98	1.30	18	1.32
45.4	0.98	1.99	18	1.32
45.4	1.25	1.30	14	1.74
60.6	0.83	0.90	29	0.57
60.6	0.83	1.70	29	0.57
60.6	1.13	0.90	21	0.81
60.6	1.13	1.70	21	0.81
71.7	0.98	1.30	29	0.41

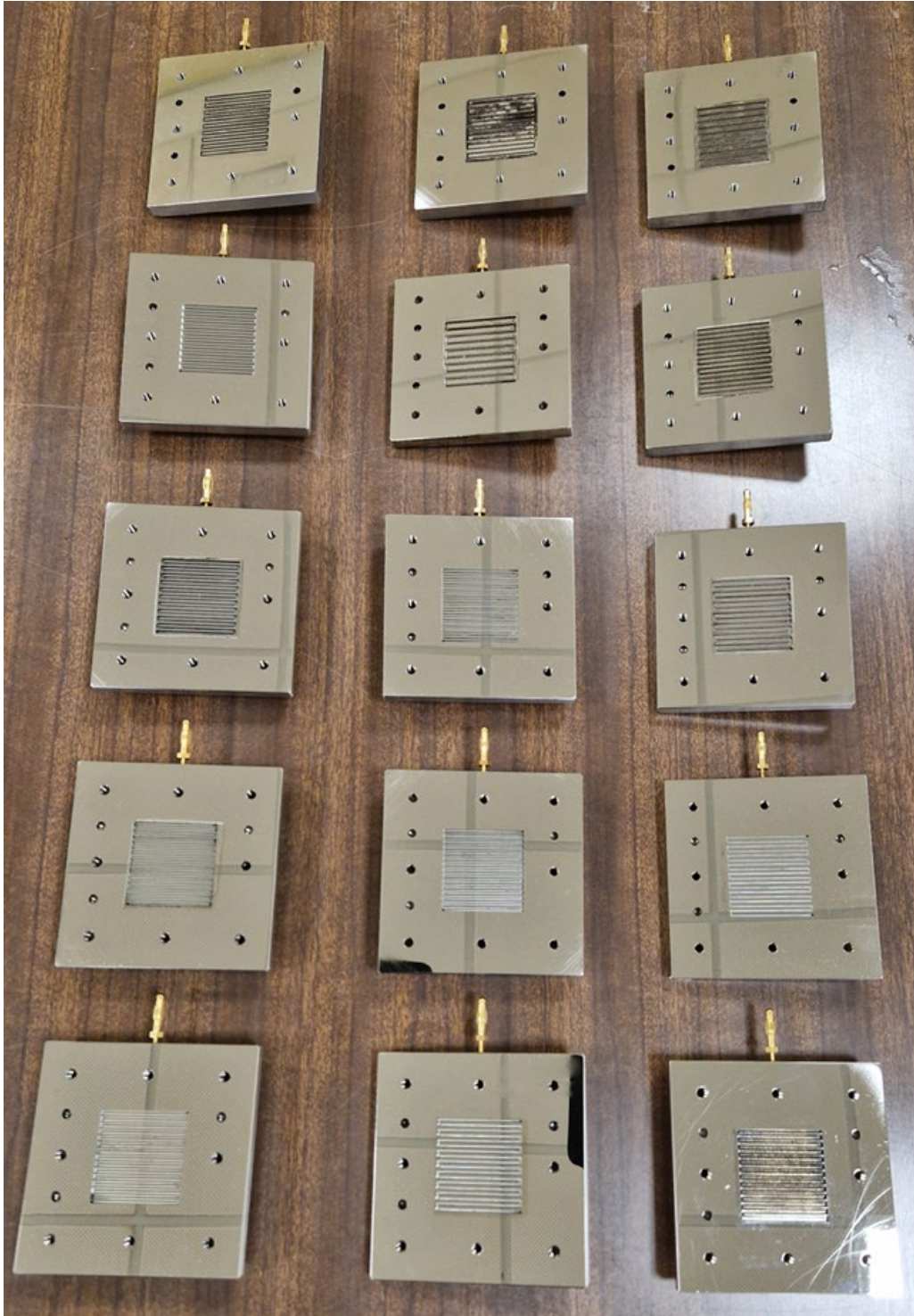


Figure 4.12: Photograph of the anode plates designed and manufactured according to the geometrical parameter of the serpentine flow field obtained by applying the CCD design

4.3. Methanol Electrolysis Cell

This section provides a comprehensive overview of experimental findings related to methanol electrolysis for hydrogen production. The results presented herein encapsulate investigations conducted across various facets of this electrochemical process.

In Section 4.3.1, particular emphasis is placed on comparing different supports and catalysts for electrodes prepared via electrodeposition for the methanol oxidation reaction, utilizing non-noble catalysts. The outcomes shed light on the comparative effectiveness of these supports in facilitating the desired electrochemical transformations.

Furthermore, Section 4.3.2 delves into the application of Response Surface Methodology to explore the influence of operational parameters on the performance of Methanol Electrolysis Cells. Through systematic experimentation, insights are gained into the intricate interplay between operational conditions and MEC behaviour, identifying which parameters most affect the MEC performance of all those studied and how the interactions of these parameters also affect this performance.

Additionally, in the subsequent Section, 4.3.3, the results obtained from employing RSM methodology to examine the impact of geometric parameters of a flow field serpentine-based anode plate configuration for MECs are outlined. This exploration provides valuable insights into optimizing the design and configuration of flow fields to enhance the effectiveness of MECs.

Together, these sections offer valuable insights into the experimental studies conducted to elucidate the intricacies of methanol electrolysis and its potential as a viable pathway for hydrogen production. Through comparative studies on electrode supports, exploration of operational parameters influence on MEC performance and examination of geometric parameters impact on flow field design, a comprehensive understanding of methanol electrolysis is attained.

4.3.1. Catalyst for methanol oxidation reaction in alkaline medium

This section presents the outcomes of a study investigating electrodes produced via electrodeposition using different catalysts (Ni, NiMo, and NiCu) and varied supports (stainless steel mesh (SS), nickel foam (NF), titanium felt (TiFelt), and titanium foil with nanotubes (TiFoilNTs)). The performance of these electrodes has

been assessed for the methanol oxidation reaction in an alkaline medium. This alkaline medium has been used as it is the most widely used in the literature for the study of catalysts for methanol electrolyser anodes, this study being a preliminary step for the future study of these catalysts in an acidic medium.

The Figure 4.13 displays cyclic voltammetry (CV) analyses carried out using 1M KOH and 1M KOH + 1M CH₃OH solutions for Ni and NiMo catalysts on SS. This figure reveals that the inclusion of Mo leads to an increase in current density at identical voltages compared to electrodes comprising solely Ni. Notably, the introduction of Mo into the Ni catalyst, particularly in conjunction with the KOH solution, unveils redox peaks absent in the case of Ni alone.

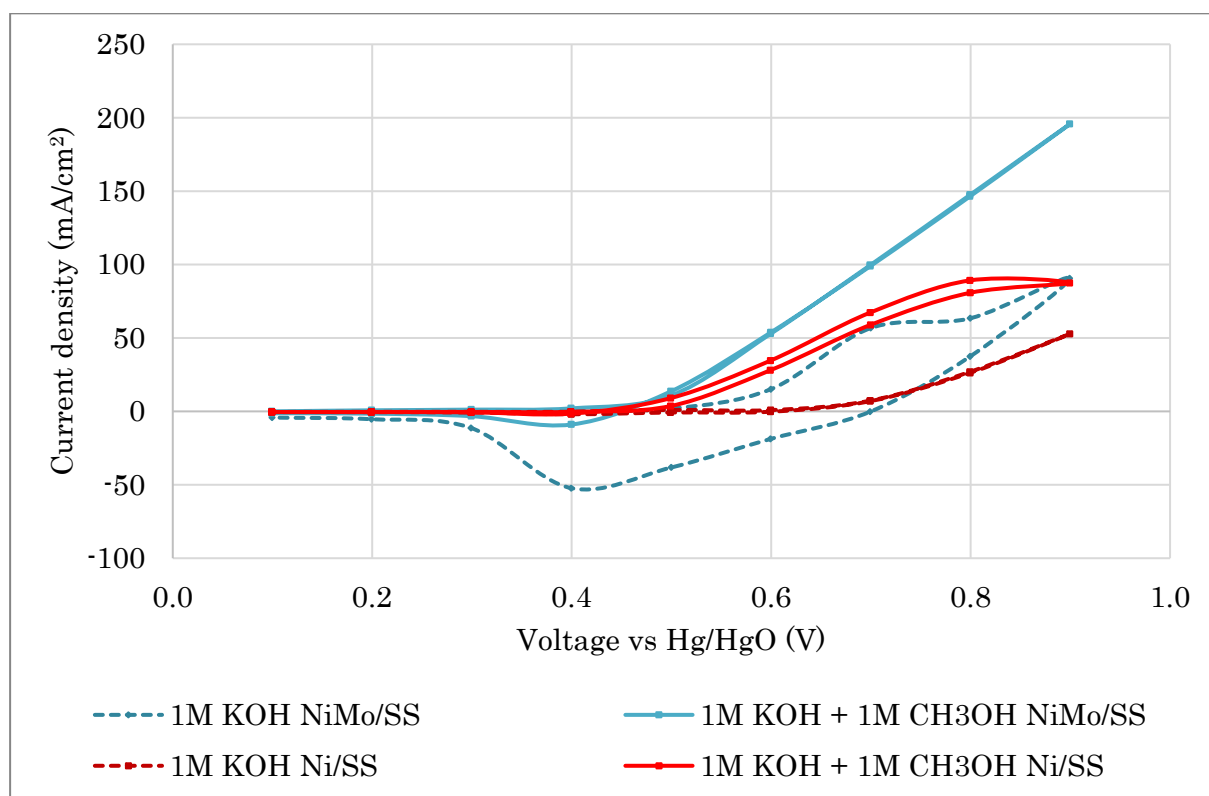


Figure 4.13: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing Ni and NiMo catalysts on stainless steel mesh (SS), employing 1 M KOH and 1 M KOH + 1 M CH₃OH solutions

The CVs depicted in Figure 4.14 showcase the performance of NiMo and NiCu catalysts on SS in 1M KOH and 1M KOH + 1M CH₃OH solutions. Notably, the figure illustrates that when using only KOH, the NiMo electrode exhibits superior activity compared to NiCu. However, upon the addition of CH₃OH, the activity of

NiCu significantly enhances, evidenced by a notable increase in current density, albeit similar to that of NiMo.

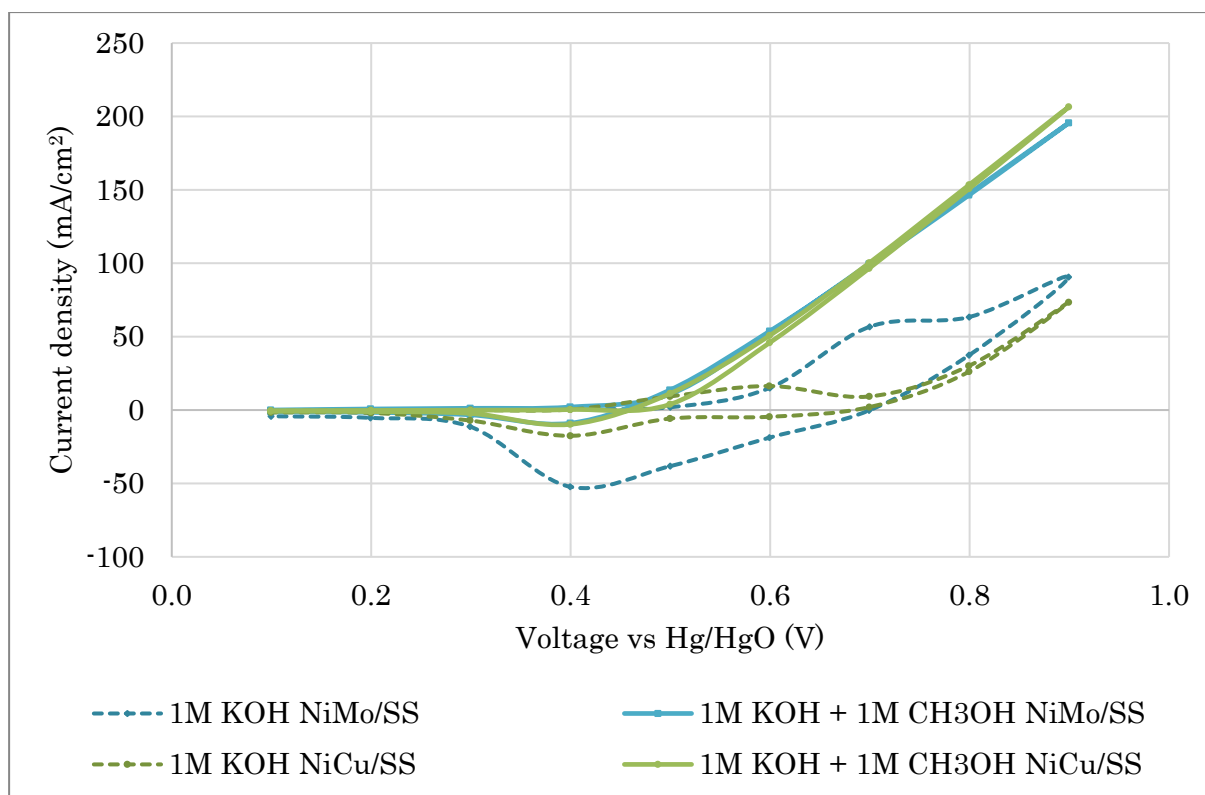


Figure 4.14: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing NiMo and NiCu catalysts on stainless steel mesh (SS), employing 1 M KOH and 1 M KOH + 1 M CH₃OH solutions

In Figure 4.15, CVs are presented for Ni and NiMo catalysts on NF in 1M KOH and 1M KOH + 1M CH₃OH solutions. Similar to the observations on SS, the addition of Mo to the catalyst enhances the electrode activity, both in the absence and presence of CH₃OH.

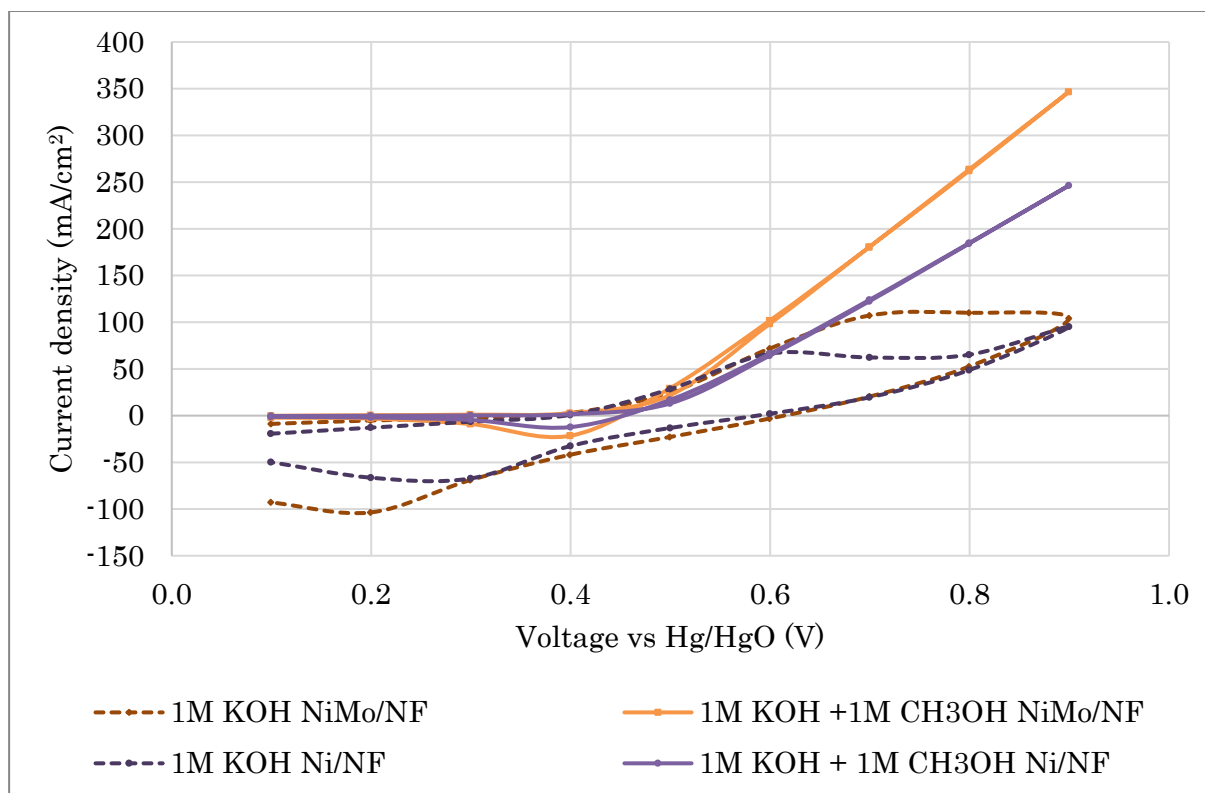


Figure 4.15: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing Ni and NiMo catalysts on nickel foam (NF), employing 1 M KOH and 1 M KOH + 1 M CH₃OH solutions

In Figure 4.16 CVs are displayed for NiMo and NiCu catalysts on NF in 1M KOH and 1M KOH + 1M CH₃OH solutions. Similar to the observations on SS, when using only KOH, NiMo may exhibit higher activity. However, upon adding CH₃OH to the solution, the NiCu electrode demonstrates higher current densities at the same voltage compared to NiMo, as observed in the SS case in Figure 4.14.

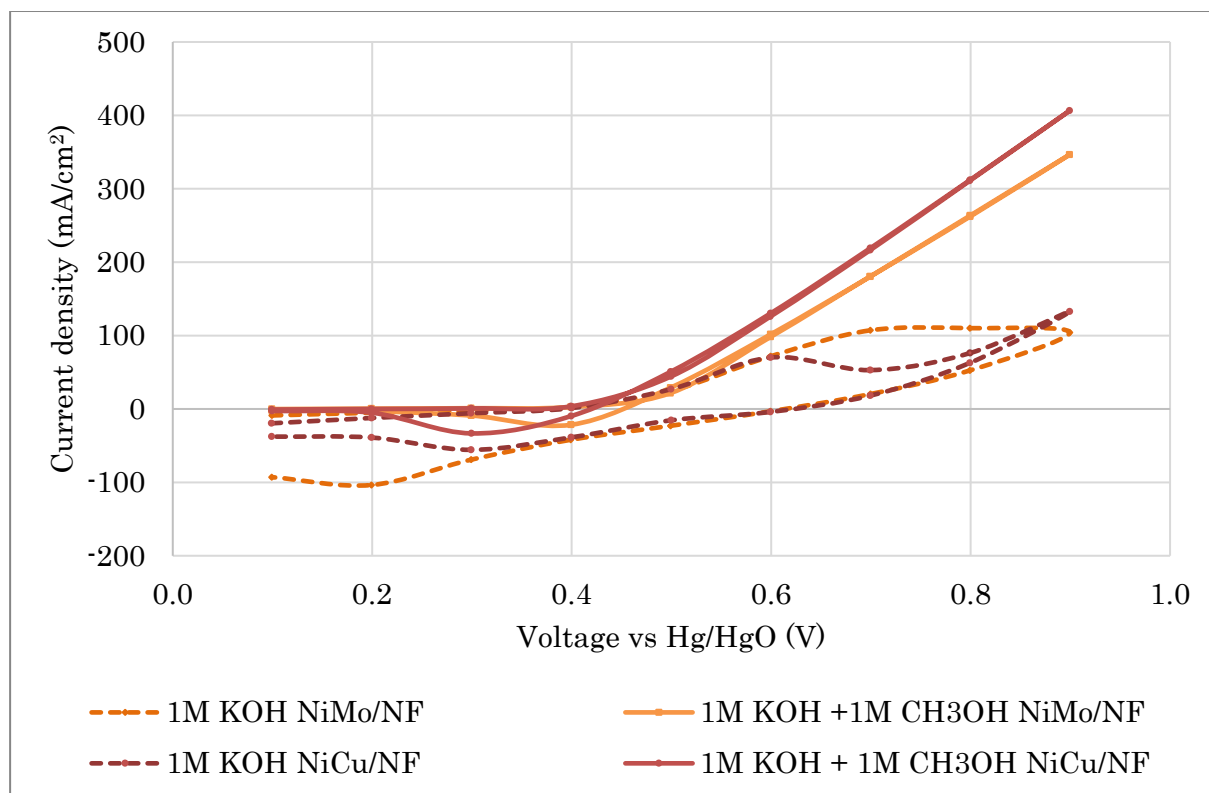


Figure 4.16: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing NiMo and NiCu catalysts on nickel foam (NF), employing 1 M KOH and 1 M KOH + 1 M CH₃OH solutions

The redox peak area progressively increases with the addition of Cu²⁺, as observed in Figure 4.14 and Figure 4.16. This phenomenon could be ascribed to the transformation of the deposited layer from granular to dendritic morphology induced by the presence of Cu²⁺ (Mei et al., 2023). This transformation leads to an augmentation in the specific surface area of the electrode, thereby offering more active sites for the electrochemical reaction (Mei et al., 2023).

Furthermore, when evaluating the electrode by adding CH₃OH to the solution, the improvement in catalytic performance is evident. This improvement depends not only on the alteration in the microstructure of the deposited layer induced by the addition of Cu²⁺ but also on the activation of partial charge transfer around the Ni²⁺ sites due to Cu doping. This phenomenon significantly increases the number of Ni³⁺ active sites. Hence, electrodes with NiCu may exhibit superior results in Figure 4.14 to Figure 4.16, especially in the case of NF, where the support itself serves as a catalyst.

In summary, when utilizing NiCu, both on SS mesh and Ni foam in KOH solution, a slight increase in electrode activity is observed, which becomes much more

pronounced in the presence of methanol. Conversely, the incorporation of Mo leads to an enhancement in activity compared to using only Ni in KOH solution, surpassing even the activity observed with NiCu. However, the activity with NiCu catalyst outweighs that of NiMo in the presence of KOH when adding CH₃OH.

Having established that the catalyst exhibiting the highest activity towards MOR is NiCu, both on SS and NF substrates, new electrodes are prepared using this catalyst on various supports, namely SS, NF, TiFelt, and TiFoilNTs.

In Figure 4.17, the CVs conducted in 1M KOH solution for electrodes prepared with NiCu on different substrates are presented. Figure 4.18 displays the CVs for the same electrodes in 1M KOH + 1M CH₃OH solution. Both in the case of 1M KOH alone and in 1M KOH + 1M CH₃OH, it is evident that the activity is higher with the NF support. This could be attributed to NF being a foam, providing a larger active electrode area. Additionally, NF consists of Ni, an active catalyst in this reaction, which, with the presence of Cu, exhibits enhanced activity towards MOR. This can be observed in the difference between the peaks of TiFelt and NF without CH₃OH, with an even greater disparity between these two peaks when CH₃OH is added. The next most active material is TiFelt, likely due to its active area as a felt material, as it does not show much difference compared to NF but does compared to TiFoilNTs.

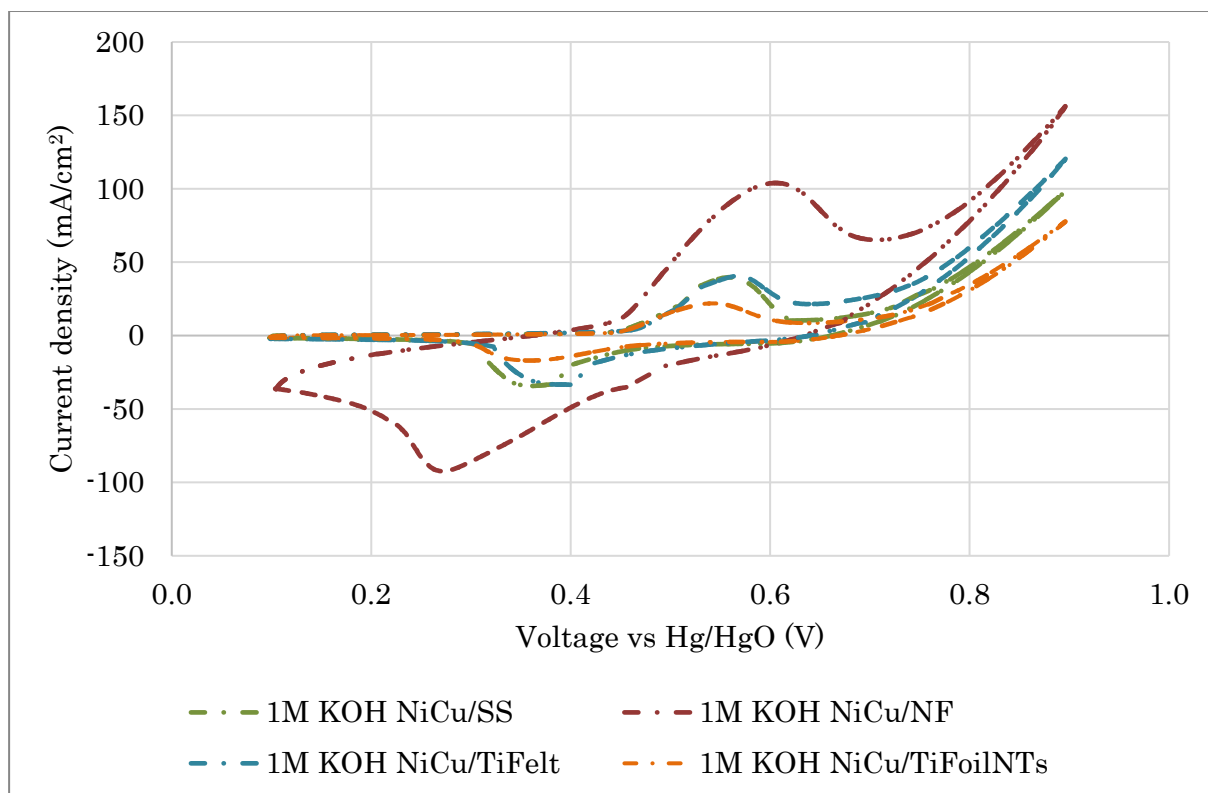


Figure 4.17: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing NiCu catalyst on stainless steel mesh (SS), nickel foam (NF), titanium felt anodized (TiFelt) and titanium foil with nanotubes (TiFoilNTs), employing 1 M KOH solution

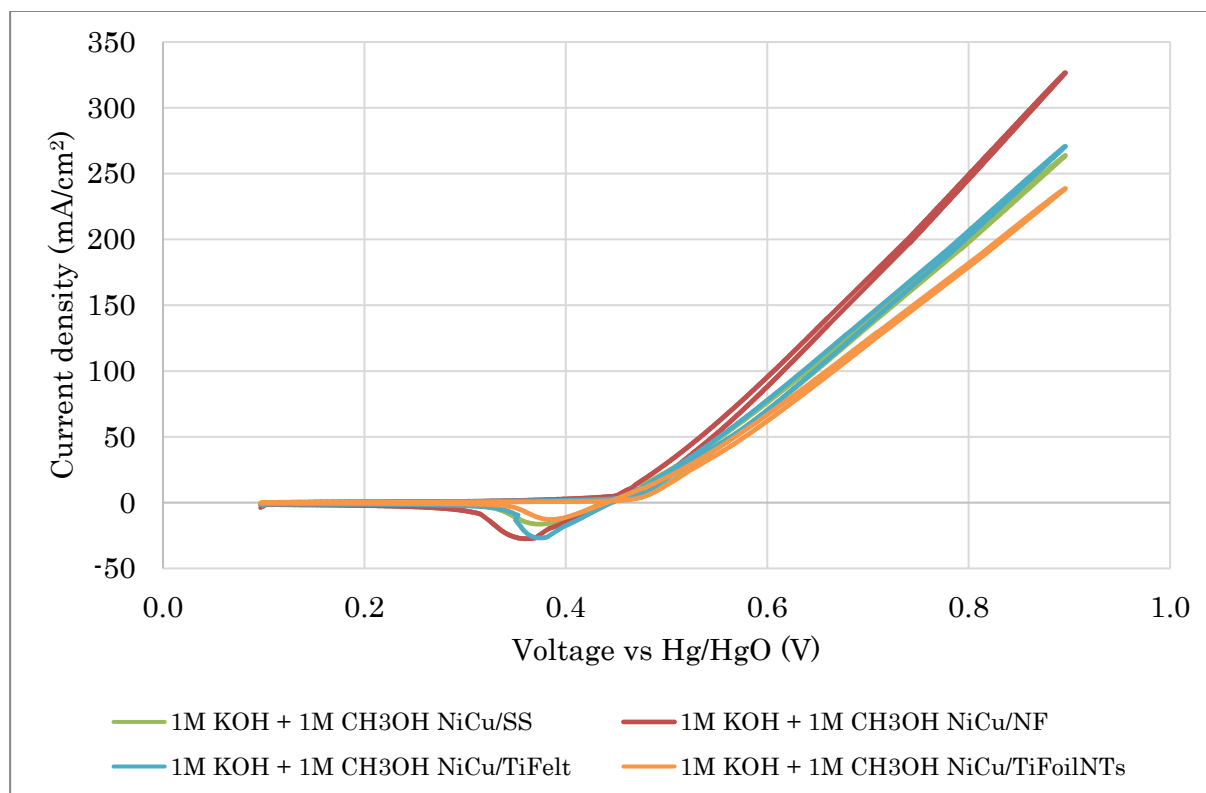


Figure 4.18: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing NiCu catalyst on stainless steel mesh (SS), nickel foam (NF), titanium felt anodized (TiFelt) and titanium foil with nanotubes (TiFoilNTs), employing 1 M KOH + 1M CH₃OH solution

Figure 4.19 presents the combined results from Figure 4.17 and Figure 4.18 to illustrate the difference in voltage at which electrode activity is observed for the oxygen evolution reaction (OER) in the presence of KOH alone, and the methanol oxidation reaction (MOR) upon adding CH₃OH to the solution. In this figure, the disparity between the voltages for OER, around 0.75 V, and MOR, around 0.45 V, is shown. This implies a lower required potential for the methanol oxidation reaction, indicating that this process is less energetically demanding than the oxygen evolution reaction (L. Li et al., 2023).

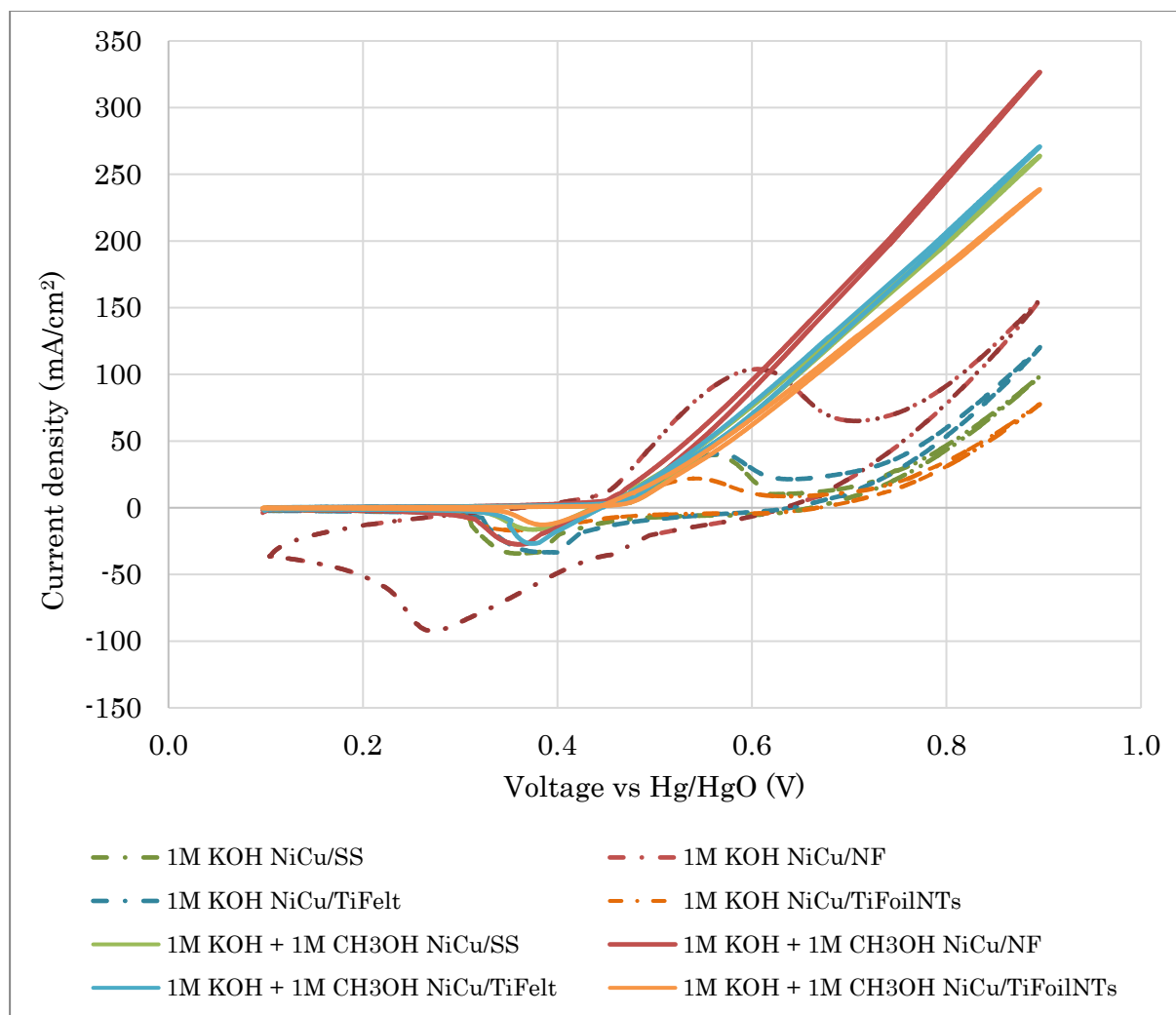


Figure 4.19: Cyclic voltammetry curves with a scan rate of 100 mV/s for electrodes containing NiCu catalyst on stainless steel mesh (SS), nickel foam (NF), titanium felt anodized (TiFelt) and titanium foil with nanotubes (TiFoilNTs), employing 1 M KOH and 1 M KOH + 1 M CH₃OH solutions

In Figure 4.20 the results of chronopotentiometry tests are presented for the two electrodes exhibiting the highest activity towards MOR, comprised of NiCu catalyst on NF and TiFelt. This figure illustrates the change of solution every 8 hours, with the complete replacement of the previous 1M KOH + 1M CH₃OH solution with a fresh one. Additionally, a series of peaks can be observed in the first 8-hour segment, corresponding to the sampling of the solution performed every hour to analyse its composition via HPLC. Unfortunately, a portion of the samples evaporated during storage, as they had to be stored until the HPLC equipment could be set up, which was not available during these experiments, thereby hindering the composition analysis. This analysis was expected to detect

formic acid, a product of methanol oxidation, in line with previous results reported in literature (Liang et al., 2021; Xiang et al., 2020).

By comparing the voltage values at the beginning and end of each of the three 8 h periods, as depicted in Figure 4.20, the percentage increase in voltage for each electrode during each 8 h period is obtained. For NF, the percentage increases are 15.7 %, 6.7 %, and 7.8 %, while for TiFelt, they are 13.7 %, 13.0 %, and 10.8 %, corresponding to each of the 8 h test periods. These results indicate that for NF, fixing the current leads to a gradual increase in voltage over time, and consequently, an increase in the power supplied to promote the oxidation reaction. However, this increase is less pronounced compared to using TiFelt as the support material.

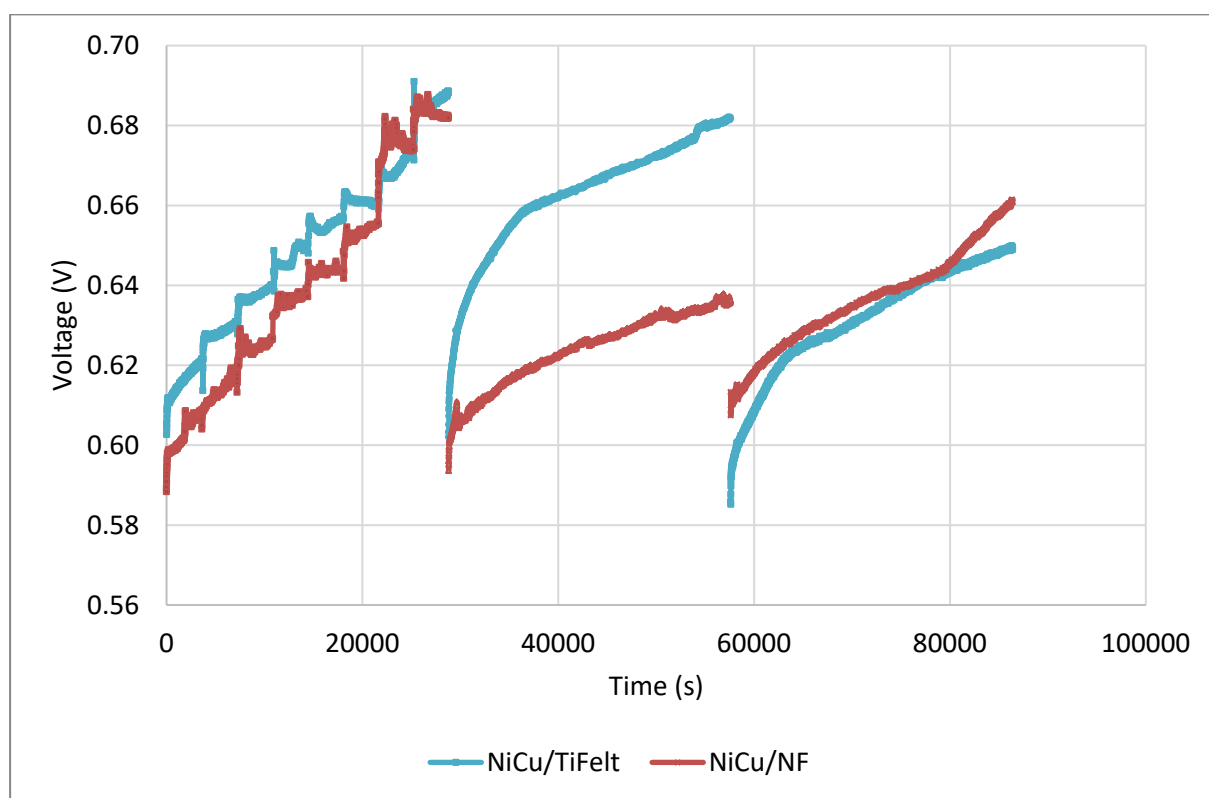


Figure 4.20: Chronopotentiometry curves at 100 mA/cm² for electrodes containing NiCu catalyst on nickel foam (NF) and titanium felt anodized (TiFelt), employing 1 M KOH + 1M CH₃OH solution replaced every 8 h

Based on the results obtained from the various electrodes analysed, it is concluded that there is an increase in activity when using NiCu as a catalyst on different supports such as SS, NF, TiFelt, and TiFoilNTs for the methanol oxidation reaction in an alkaline environment. However, further testing is required to determine the

durability and degradation over time of the two best electrodes obtained, utilizing NiCu catalyst with NF and TiFelt supports. Although NF shows slightly lower voltage increase results, they are comparable to those of TiFelt, indicating the need for additional tests to ascertain their long-term performance. SEM analysis of the electrodes prepared before and after the durability tests could show changes in the electrode surface (H. Liu et al., 2020; Q. Sun et al., 2018), giving information on the evolution of the structures on the electrode surface due to the processes and materials used (Anantharaj et al., 2022; J. Li et al., 2021).

4.3.2. Working conditions

In this section the collective impact of working conditions on MEC performance is studied. For this purpose, the RSM methodology is used, employing as experimental response the MEC power density ($\dot{W}_{MEC}$) consumed at 300 mA/cm². This specific current density is selected due to its positioning within the ohmic region of the polarization curve, representing a high current density and occurring prior to the zone predominantly influenced by concentration overpotential. For each set of methanol volumetric flow rate ($\dot{V}$) methanol concentration (M) and MEC temperature (T) combinations delineated in Table 4.16, derived through application of the CCD design, the corresponding power density of the MEC at 300 mA/cm² is determined from the polarization curves and power density curves experimentally obtained. A total of 76 polarization curves and derived power density curves as the ones presented in Figure 4.21 were obtained during the MEC tests for this study, listed in Annex C.

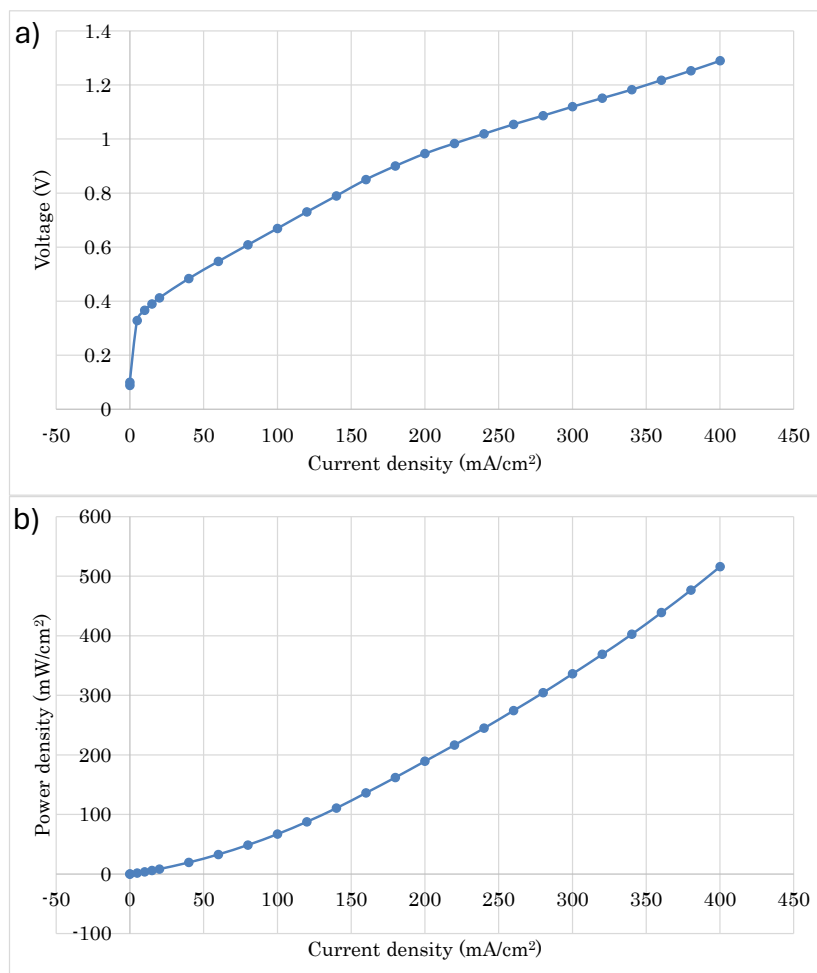


Figure 4.21: a) Polarization curve of the MEC single cell of this study obtained at a temperature of 50 °C, methanol concentration of 2 M and methanol volumetric flow rate 4.5 ml/min. b) Power density curve obtained from the polarization curve

Table 4.16: Parameter combinations of the Methanol Electrolysis Cell (MEC) working conditions obtained from Central Composite Design and corresponding power density, $\dot{W}_{MEC}$, values at 300 mA/cm² obtained from experimental MEC tests. Here $\dot{V}$ signifies the methanol volumetric flow rate, M denotes methanol concentration and T indicates MEC temperature

$\dot{V}$ (ml/min)	$10^8 \dot{V}$ (m ³ /s)	M (mol/l)	$10^3 M$ (mol/dm ³)	T (°C)	T (K)	$\dot{W}_{MEC}$ (mW/cm ²)
1.90	3.17	2.00	2.00	50.0	323.0	377.9
3.00	5.00	1.00	1.00	40.0	313.0	405.5
3.00	5.00	1.00	1.00	60.0	333.0	375.1
3.00	5.00	3.00	3.00	40.0	313.0	399.8
3.00	5.00	3.00	3.00	60.0	333.0	340.3
4.50	7.50	0.27	0.27	50.0	323.0	618.1
4.50	7.50	2.00	2.00	32.7	305.7	431.6
4.50	7.50	2.00	2.00	50.0	323.0	375.4
4.50	7.50	2.00	2.00	50.0	323.0	375.7
4.50	7.50	2.00	2.00	50.0	323.0	377.0
4.50	7.50	2.00	2.00	50.0	323.0	374.7
4.50	7.50	2.00	2.00	67.3	340.3	348.0
4.50	7.50	3.73	3.73	50.0	323.0	360.4
6.00	10.00	1.00	1.00	40.0	313.0	526.0
6.00	10.00	1.00	1.00	60.0	333.0	374.2
6.00	10.00	3.00	3.00	40.0	313.0	437.9
6.00	10.00	3.00	3.00	60.0	333.0	318.5
7.10	11.83	2.00	2.00	50.0	323.0	403.8

Using the data from Table 4.16, the RSM methodology is applied, resulting in Eq. 4.2, which mathematically describes the relationship among the three parameters studied and the anticipated response from the MEC:

$$\begin{aligned} \dot{W}_{MEC} = & 319.6 + 101.1\dot{V} - 139.8M + 3.4T - 8.6\dot{V}M - 1.5VT + 4 \cdot 10^{-2}MT \\ & + 4 \cdot 10^{-2}\dot{V}^2 + 32.9M^2 - 3 \cdot 10^{-3}T^2 \end{aligned} \quad (4.2)$$

where W_{MEC} denotes the predicted MEC power density at 300 mA/cm² expressed in mW/cm², $\dot{V}$ represents the methanol volumetric flow rate in ml/min, M signifies the methanol concentration in mol/l, and T indicates the MEC temperature in °C.

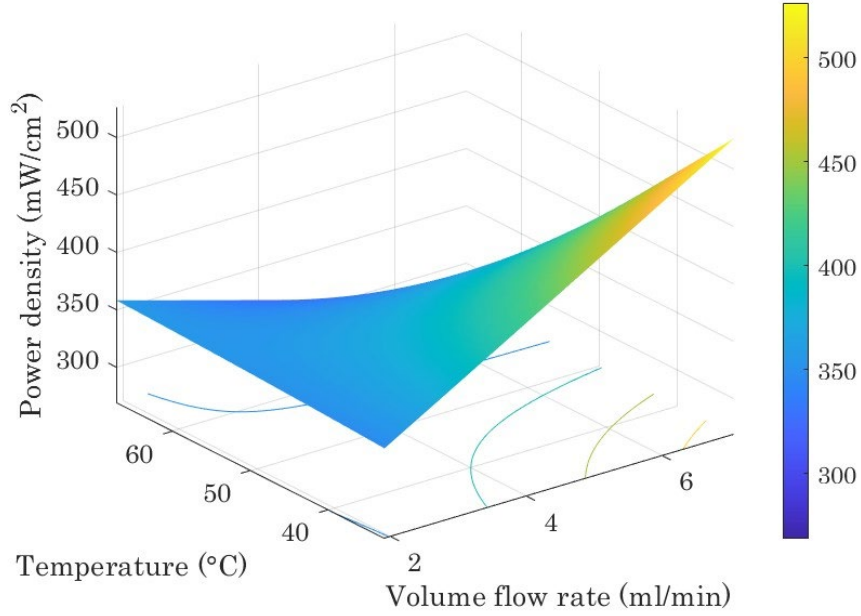


Figure 4.22: Predicted power density at 300 mA/cm² response surface obtained when setting the methanol concentration at 2M and modifying the methanol volumetric flow rate and temperature values of the Methanol Electrolysis Cell

Figure 4.22 illustrates the impact of MEC temperature and methanol volumetric flow rate on the power density of the tested device. When maintaining the methanol concentration at 2M and a temperature below 55 °C, increasing the volumetric flow rate results in elevated electrical power consumption. This phenomenon may stem from the reduced residence time of methanol in the diffusion layer, hindering proper reaction and diminishing fuel utilization efficiency (Ramasamy et al., 2022). Additionally, it could be attributed to a decrease in the temperature of the catalytic layer caused by introducing a liquid solution at room temperature into a system operating at temperatures exceeding 40 °C (Z. Zhao et al., 2023).

Figure 4.23 depicts the response surface obtained plotting Eq. 4.2 with the temperature set at 50 °C while adjusting methanol concentration and volumetric flow rate values to derive the power density response. As illustrated in Figure 4.23, at 50 °C a higher methanol flow rate correlates with an increase in the power required for methanol electrolysis, particularly at low concentrations. This

phenomenon is attributed to limited methanol availability due to low concentration (H. K. Ju et al., 2017) and diminished catalyst temperature due to increased methanol volumetric flow rate at a lower temperature than the methanol electrolyser, necessitating increased power support for methanol electrolysis.

The interactive impact of temperature and methanol concentration is depicted in the response surface of Figure 4.24 when the volumetric flow rate is fixed at 4.5 ml/min. Notably, low temperatures and concentrations correspond to increased electrical energy demand in the MEC, attributed to decreased reaction kinetics at lower temperatures and reduced methanol availability for oxidation reactions at lower fuel concentrations (Lamy et al., 2015). Conversely, MEC power density starts to increase at elevated methanol concentrations, attributable to methanol hygroscopic properties, which can block water molecules interactions on the proton exchange membrane, thereby decreasing ionic conductivity (Uhm et al., 2012).

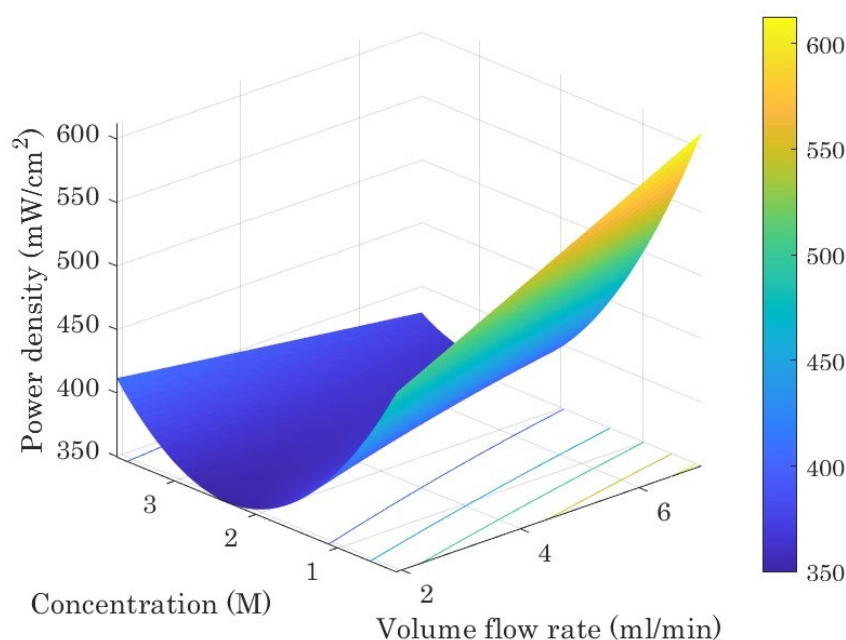


Figure 4.23: Predicted power density at 300 mA/cm² response surface obtained when setting the Methanol Electrolysis Cell temperature at 50 °C and modifying the methanol concentration and volumetric flow rate

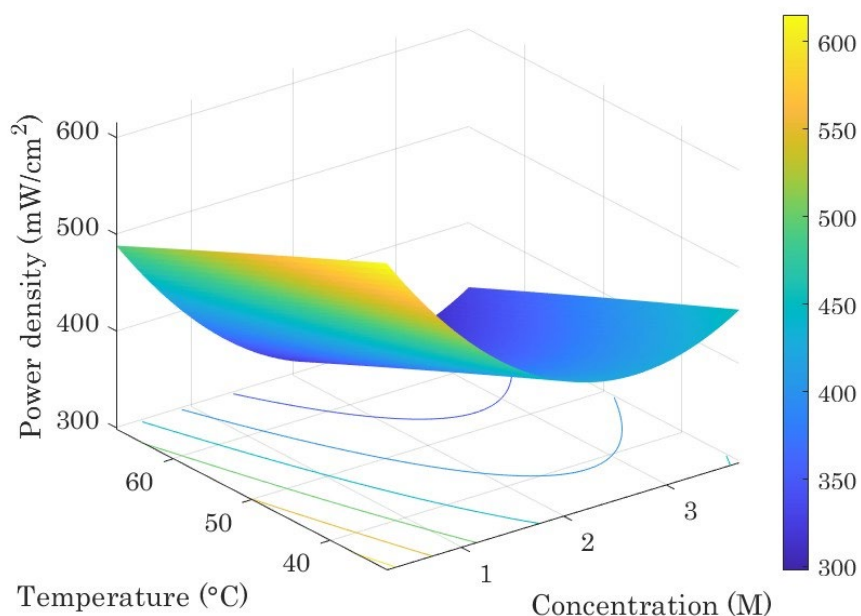


Figure 4.24: Predicted power density at 300 mA/cm² response surface obtained when setting the methanol volumetric flow rate at 4.5 ml/min and modifying the temperature of the Methanol Electrolysis Cell and the methanol concentration values

Table 4.17: Results of the analysis of variance (ANOVA) performed on the mathematical model obtained by applying the Response Surface Methodology to study the effect of operating conditions on the performance of a Methanol Electrolysis Cell

Variable	Estimate	Standard Error	tStat	p-Value
Volumetric flow rate ($\dot{V}$)	101.057	69.278	1.459	0.183
Concentration (M)	-139.834	96.848	-1.444	0.187
Temperature (T)	3.383	12.386	0.273	0.792
$\dot{V}M$	-8.607	9.746	-0.883	0.403
$\dot{V}T$	-1.512	0.975	-1.551	0.160
MT	0.041	1.462	0.028	0.978
$\dot{V}^2$	0.037	4.957	0.007	0.994
M^2	32.867	11.153	2.947	0.019
T^2	-0.003	0.112	-0.025	0.981

To analyse the significance of each of the parameters of the mathematical model introduced in Eq 4.2, an ANOVA analysis is carried out. In the findings of this analysis presented in Table 4.17, a notable influence of the investigated parameters on MEC power density response is not readily apparent, except for the quadratic term of methanol concentration, exhibiting a p-value lower than 0.05. Nevertheless, insights gleaned from Table 4.16 and Figure 4.22 to Figure 4.24 reveal a correlation between all the parameters studied and the energy consumption in the electrolyser. This underscores the necessity for refining the obtained model to elucidate the previously observed relationships between parameters and MEC power density.

Moreover, catalyst degradation can occur due to methanol presence, stemming from catalytic surface poisoning via species adsorption, such as CO, or platinum and ruthenium dissolution during electrolysis in the presence of methanol (Becker et al., 2023). Consequently, after numerous tests, the catalytic layer may lose efficacy, necessitating increased electrical energy for methanol electrolysis. This could skew results for certain test conditions, potentially leading to increased power density under the same test conditions due to MEA degradation after multiple tests.

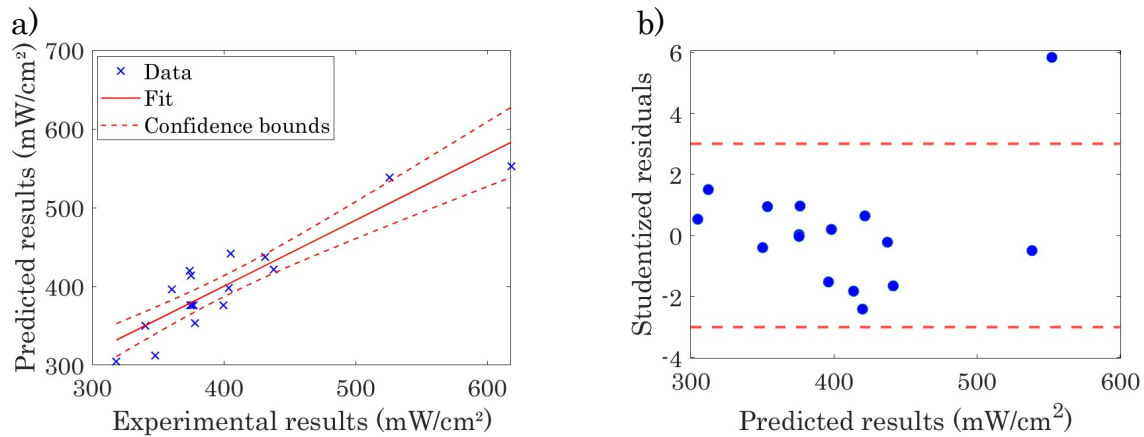


Figure 4.25: a) Evaluation of Methanol Electrolysis Cell power density at 300 mA/cm² acquired through experimentation versus projections from the model obtained when varying its working conditions. b) Examination of studentized residuals for power density at 300 mA/cm² in contrast to predicted values

Despite the lack of pronounced influence in the ANOVA test, Figure 4.25a illustrates the linear trend of power density observed during tests and predicted by the model, elucidating over 80 % of the experimental response. Furthermore, the residuals in Figure 4.25b do not exhibit a discernible pattern, with all but one

presenting acceptable values. This outlier is associated with a test conducted under almost extreme working conditions for the evaluated MEA (4.5 ml/min, 0.27 M, 50 °C; see Table 4.16), resulting in a substantial increase in required power density, 618.1 mW/cm², due to insufficient methanol for the oxidation reaction and potential water electrolysis occurrence (Lamy et al., 2015). This particular test, owing to the high voltage and power density attained, could exert significant influence on catalytic layer degradation and subsequent result alterations.

4.3.3. Flow field geometry

In this section, the focus is on the experimentally derived results regarding the influence of geometric parameters of a serpentine anode flow field on the behaviour of MECs. The methodology employed for obtaining these outcomes involves RSM methodology alongside a CCD design. Geometric parameters, i.e. the open ratio (O_R), channel width (e) and channel depth (d), are individually and collectively assessed for their impact on the power density required for MEC operation at a current density of 300 mA/cm². The parameter combinations obtained through the application of the CCD design, along with the corresponding experimental power density ($\dot{W}_{\text{MEC}}$) obtained for each combination, are outlined in Table 4.18. The power density for each geometrical combination is obtained from the polarization curve and derived power density curve of the MEC single cell tests with the corresponding anode plate for each geometry. A total of 120 polarization curves and corresponding power density curves as the ones presented in Figure 4.26 were obtained during the MEC tests for this study, listed in Annex C.

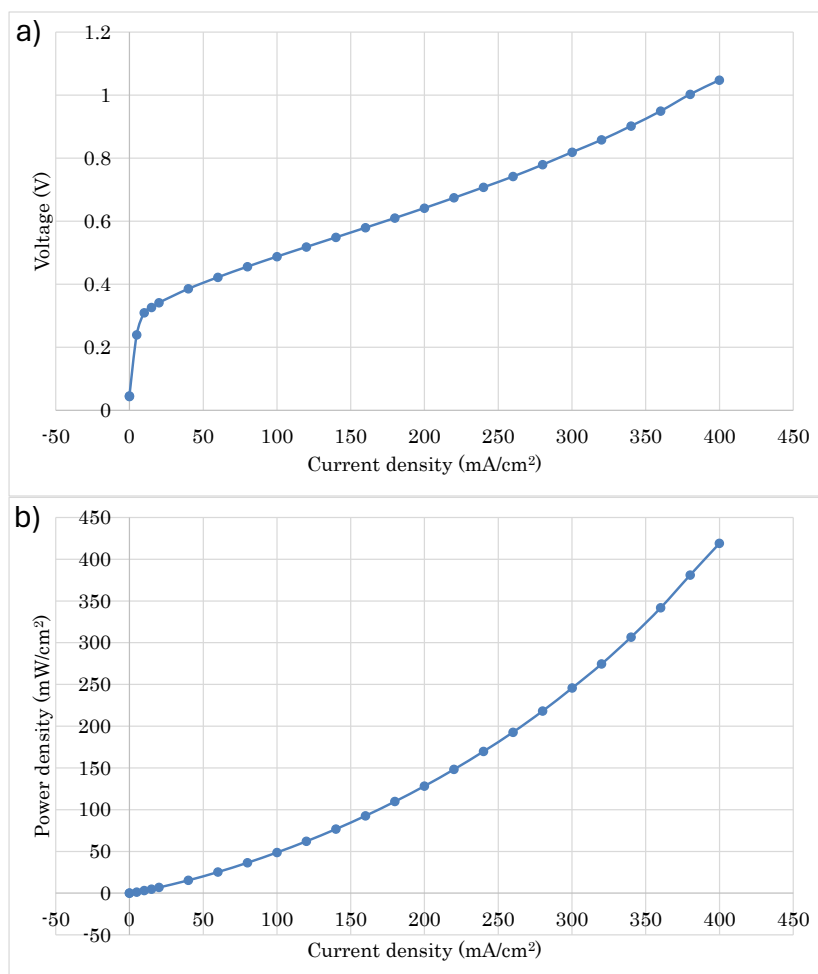


Figure 4.26: a) Polarization curve of the MEC single cell of this study obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm. b) Power density curve obtained from the polarization curve

Table 4.18: Geometric parameter combinations of the Methanol Electrolysis Cell (MEC) anode serpentine-based flow field obtained from Central Composite Design and corresponding MEC power density, $\dot{W}_{MEC}$, values at 300 mA/cm² obtained from MEC experimental tests. O_R is the open ratio, e is the channel width and d represents the channel depth

O_R (%)	e (mm)	d (mm)	$\dot{W}_{MEC}$ (mW/cm ²)
19.2	0.98	1.30	607.5
30.3	0.83	0.90	546.0
30.3	0.83	1.70	362.0
30.3	1.13	0.90	489.4
30.3	1.13	1.70	432.2
45.4	0.71	1.30	241.0
45.4	0.98	0.61	267.7
45.4	0.98	1.30	244.6
45.4	0.98	1.30	245.7
45.4	0.98	1.30	247.9
45.4	0.98	1.30	257.1
45.4	0.98	1.99	266.1
45.4	1.25	1.30	300.8
60.6	0.83	0.90	244.9
60.6	0.83	1.70	298.6
60.6	1.13	0.90	248.0
60.6	1.13	1.70	262.0
71.7	0.98	1.30	254.4

Based on the experimental tests conducted with various anode channel geometries and the corresponding power density obtained at 300 mA/cm², results collected in Table 4.18, the RSM methodology is applied to derive Eq. 4.3. This equation establishes a relationship between the predicted power density ($\dot{W}_{MEC}$) and the values of the open ratio (O_R), channel width (e) and channel thickness (d):

$$\begin{aligned} \dot{W}_{\text{MEC}} = & 2369.6 - 3902.7O_R - 1273.3e - 707.3d - 252.0O_Re + 635.2O_Rd \\ & + 176.8ed + 2935.9\dot{O}_R^2 + 611.3e^2 + 82.2d^2 \end{aligned} \quad (4.3)$$

This equation elucidates the interplay of these geometric parameters in determining MEC performance. Subsequently, the surface response plots depicted in Figure 4.27 to Figure 4.29 are generated based on Eq. 4.3, offering insights into the predicted MEC power density while fixing one of the three analysed geometric parameters and varying the others. Analysis of these plots reveals the significant influence of channel design on MEC performance, particularly concerning the open ratio, channel width and channel depth.

In Figure 4.27, when the channel depth is fixed at 1.30 mm and the open ratio and channel width are varied, it is observed that the open ratio predominantly affects the MEC power density response. Operating with an open ratio between 50 % and 60 % results in lower MEC power consumption, while intermediate values of channel width, between 0.90 and 1.10 mm, yield better outcomes for a channel depth of 1.30 mm. This observation suggests that low open ratios and channel widths impede methanol mass transfer (H. Yang & Zhao, 2005), while excessively high values of both parameters slow down the fluid velocity through the channels, worsening the removal of CO₂ bubbles that form on the anode (Park et al., 2012), particularly with a channel depth of 1.30 mm.

Similarly, in Figure 4.28 it can be observed that fixing the channel width at 0.98 mm a higher open ratio, around 60 %, and a lower channel depth, between 0.80 mm and 1.00 mm, decrease electrical MEC energy consumption. A higher open ratio with a moderate channel width of 0.98 mm allows for improved methanol mass transfer by increasing the number of channels and thus the channel area directly exposed to methanol (H. Yang & Zhao, 2005). However, excessively high open ratios, nearing 70 %, may compromise MEC performance by impeding convective flow and reaction product evacuation. Adjusting the channel depth in this case enhances CO₂ bubble removal and methanol mass transfer, thereby reducing power consumption during hydrogen generation from methanol electrolysis.

Moreover, Figure 4.29 demonstrates that fixing the open ratio at 45.4 % yields better results with a channel width around 0.9 mm and a depth between 1.5 and 1.6 mm. In this case very low values of channel width and depth make the serpentine channel long and narrow, so that due to the high current density the CO₂ production can cause bubbles to cover the channel and clog it (Kianimanesh

et al., 2012), limiting methanol transfer both in the exposed area of the GDL to the channel and below the ribs. Whereas high values of channel width and depth lead to a channel that is too short, limiting methanol transfer below the ribs due to the increased rib width and thus leading to a non-uniform distribution of methanol throughout the active area (H. Yang & Zhao, 2005), making higher power consumption necessary for the MEC operation.

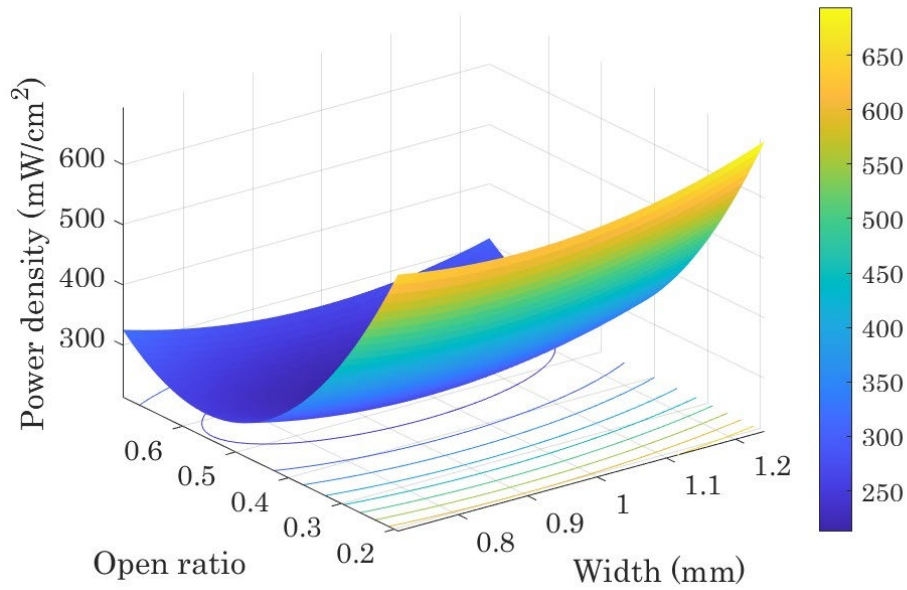


Figure 4.27: Predicted power density at 300 mA/cm² response surface obtained when setting the channel depth of the serpentine flow field anode plate of Methanol Electrolysis Cell at 1.30 mm and modifying the open ratio and channel width

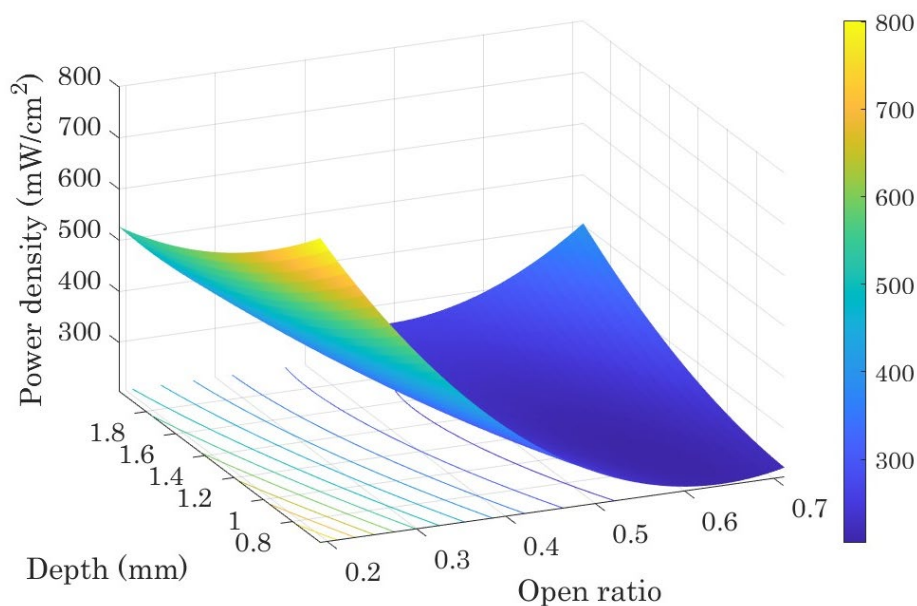


Figure 4.28: Predicted power density at 300 mA/cm² response surface obtained when setting the channel width of the serpentine flow field anode plate of Methanol Electrolysis Cell at 0.98 mm and modifying the open ratio and channel depth

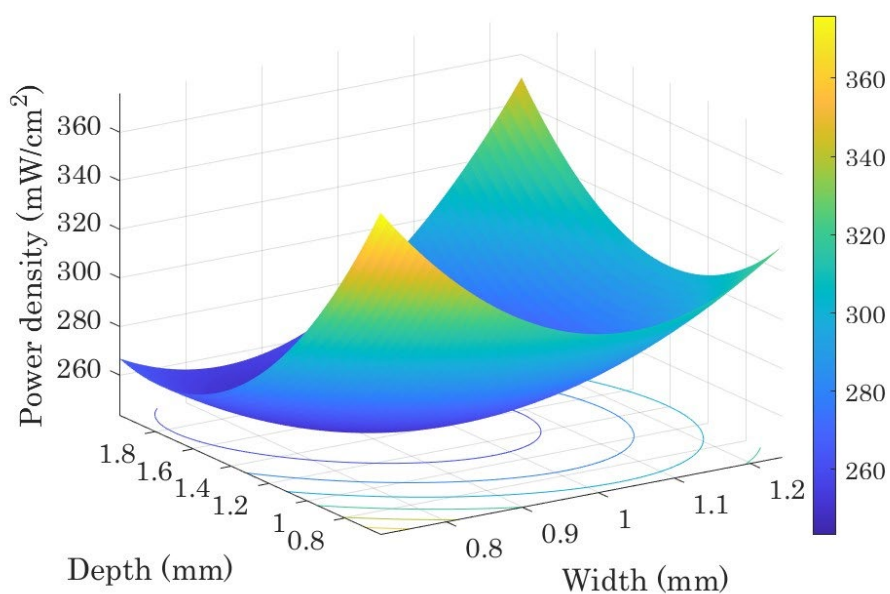


Figure 4.29: Predicted power density at 300 mA/cm² response surface obtained when setting the open ratio of the serpentine flow field anode plate of Methanol Electrolysis Cell at 45.4 % and modifying the channel width and channel depth

To ascertain the significance of each geometric parameter studied, an ANOVA of the mathematical model presented in Eq. 4.3 is conducted, with results detailed in Table 4.19. Both the open ratio and channel depth exhibit substantial influence on MEC power density, with the channel width exerting a comparatively lesser impact. The p-values associated with open ratio and channel depth parameters and the quadratic term of the open ratio indicate their statistical significance in explaining MEC performance variation. This implies that an adequate open ratio and channel depth can explain most of the observed MEC response, as the distribution of reagents along the active area and the evacuation of CO₂ bubbles are closely related in this case study to these two parameters.

Table 4.19: Results of the analysis of variance (ANOVA) performed on the mathematical model obtained by applying the Response Surface Methodology to study the effect of flow field serpentine-based geometries of the anode plate on the performance of a Methanol Electrolysis Cell

Variable	Estimate	Standard Error	tStat	p-Value
Open ratio (O_R)	-3902.7	745.4	-5.236	0.0008
Channel width (e)	-1273.3	923.9	-1.378	0.2054
Channel depth (d)	-707.3	287.4	-2.461	0.0392
$O_R e$	-252.0	568.8	-0.443	0.6694
$O_R d$	635.2	219.0	2.900	0.0199
ed	176.8	216.1	0.818	0.4371
O_R^2	2935.9	439.7	6.678	0.0002
e^2	611.3	428.3	1.427	0.1914
d^2	82.2	63.5	1.295	0.2314

Figure 4.30a illustrates the correlation between predicted and experimental power density values at 300 mA/cm², indicating a strong agreement between the model predictions and experimental observations. It can be seen that most of the values are within the confidence interval and follow a linear trend. In this case, the model

is able to explain more than 90 % of the experimental response obtained, with an R^2 of 0.95 and an adjusted R^2 of 0.89.

In Figure 4.30b, an outlier is observed, deviating from the trend exhibited by the rest of the results. This outlier corresponds to trials conducted with the serpentine geometry, featuring an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm. Further investigation is warranted to understand the underlying factors contributing to this anomalous behaviour. It is recommended to replicate the trial using this specific geometry to evaluate the reasons behind this deviation. Comparing the power density obtained with this configuration, which is 489.4 mW/cm², see Table 4.18, with that observed for the same open ratio and channel width but with a channel depth of 1.70 mm, yielding 432.2 mW/cm², see Table 4.18, suggests that repeating the test with a channel depth of 0.90 mm may reduce the MEC power consumption below these two power density values. This anticipated improvement is attributed to enhanced bubble removal facilitated by a reduction in channel depth, leading to an improved operation of the MEC.

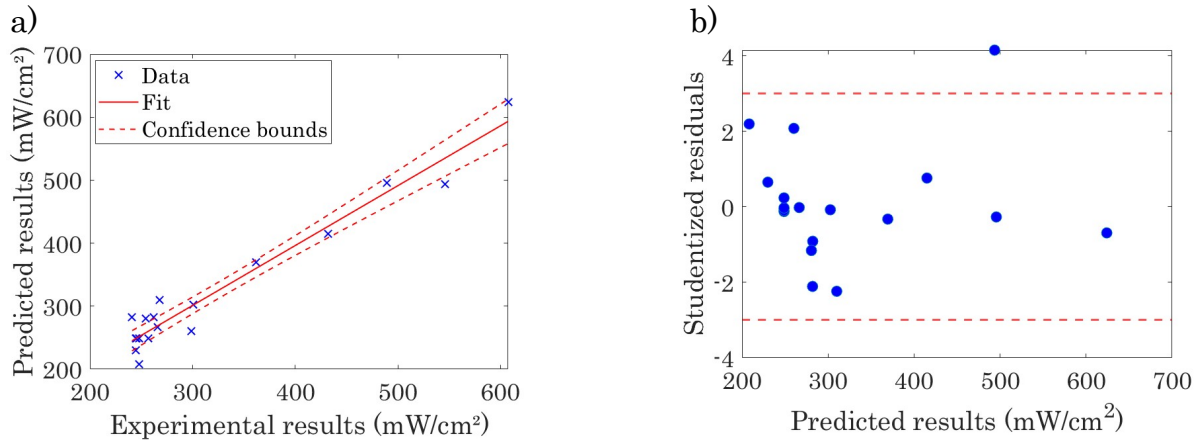


Figure 4.30: a) Evaluation of Methanol Electrolysis Cell power density at 300 mA/cm² acquired through experimentation versus projections from the model obtained when varying the geometry of the serpentine-based anode flow field. b) Examination of studentized residuals for power density at 300 mA/cm² in contrast to predicted values

Summarizing, to optimize anode channel geometry is crucial for enhancing MEC performance as evidenced by the analysis of geometric parameters of a serpentine flow field and their effects on MEC power density response. These findings provide valuable insights for the design and improvement of MEC systems.

5. Conclusions and future work

In this section, the conclusions drawn from each of the studies conducted within the framework of this doctoral thesis are presented. The first section focuses on conclusions arising from the technoeconomic analysis of using methanol as an energy carrier. The second section presents conclusions derived from experimental study of direct methanol fuel cells, devices employed to generate electrical energy from methanol and represent the final stages of methanol utilization as an energy carrier. The third section summarizes the conclusions of experimental studies on a methanol electrolysis cells, used to produce hydrogen from methanol, thereby constituting the latter stages of methanol utilization as a hydrogen carrier. Lastly, future research directions are outlined to advance studies on methanol as an energy carrier, delving into the design and improvement of new direct methanol fuel cells and methanol electrolyzers, whether through operational conditions or component modification.

5.1. Methanol as energy carrier

This study presents the analysis of three different energy transmission alternatives: one utilizing hydrogen as an energy carrier and other two utilizing e-methanol. The first method involves the transport of bulk liquefied hydrogen by ship, while the e-methanol options include utilizing e-methanol as a hydrogen carrier and differs in the process for obtaining hydrogen at destination, either through methanol electrolysis or through a reforming process. Upon comparing the results of these alternatives considering the assumptions made in this work, it has been noted that the most cost-effective option for most cases is the transportation of liquefied hydrogen. Following closely is the use of e-methanol as a hydrogen carrier, particularly when employing the reforming process to generate hydrogen. This is because, when considering the electricity cost for methanol electrolysis and the high initial investment in this facility compared to methanol reformers, the difference in cost currently favours the reforming approach.

Even when prioritizing the amount of hydrogen delivered to the destination, the transportation of liquid hydrogen remains the favoured choice for a hydrogen mass flow rate of 100 kt/y and navigation distances ranging from 5000 km to 7000 km. Nonetheless, considering only the amount of hydrogen delivered at destination, for longer distances and larger hydrogen mass flow rates, the economic perspective

favours the utilization of e-methanol as a carrier due to economies of scale and easier handling and storage, followed by an electrolysis process.

The main conclusions drawn from this study are:

- Considering situations where the arrival of energy is the focal point, regardless of the fuel used for its transport, liquefied hydrogen emerges as the best choice. However, for a hydrogen mass flow rate of 10 Mt/y, e-methanol presents an interesting alternative, with its levelized energy cost closely aligned with that of hydrogen transport.
- This study has found a near independence of destination hydrogen cost from the hydrogen mass transported once it surpasses 6 Mt/y. For hydrogen volumetric flow rates below 1 Mt/y, the storage cost in proportion to the destination hydrogen mass escalates, constituting a significant portion of the total cost within this mass range. A reduction in this expense would yield a substantial decrease in Levelized Cost Of Hydrogen, particularly for hydrogen mass flow rates below 1 Mt/y.
- Levelized cost values for imported hydrogen have been determined to be approximately 2 USD/kg for the designated destinations (Spain, the Netherlands, and Japan) for quantities exceeding 1 Mt/y, assuming an electricity price at the source of 40 USD/MWh. If the electricity price at the destination remains above 50 USD/MWh, importing hydrogen is deemed preferable to local production.
- The least cost-effective alternative involves methanol transport followed by electrolysis. Research focused on methanol electrolysis could enhance its efficiency and lead to a reduction in associated costs. This could potentially align the cost of this alternative more closely with that of transporting liquid hydrogen.
- This study primarily emphasizes economic considerations, aiming to pinpoint costly components within the logistics chain, such as hydrogen liquefaction, methanol synthesis and methanol electrolyzers. Technical improvements in these areas could significantly impact the levelized cost of hydrogen. Additionally, identifying inefficient elements within the logistics chain would be valuable. Therefore, it is necessary to conduct a more detailed exploration of energy comparisons among alternative options.

5.2. Direct Methanol Fuel Cell

This study investigated the impact of operational parameters on the performance of a Direct Methanol Fuel Cell (DMFC) through experimental analysis. The parameters examined included DMFC temperature, the concentration of aqueous methanol and the volumetric flow rate of methanol supplied to the DMFC. Applying Response Surface Methodology (RSM) and a Central Composite Design (CCD), the study systematically analysed the interactions between these parameters and their effects on DMFC peak power density. The principal findings derived from this investigation are:

- Temperature and volumetric flow rate have a combined influence on DMFC peak power density when methanol concentration is held constant, indicating that the temperature of the catalytic layer is affected by the methanol volumetric flow rate introduced at a temperature lower than that of DMFC operation.
- The study demonstrates the significant combined effect of temperature and methanol concentration on DMFC performance, with both parameters exerting substantial influence individually and in combination. Increasing DMFC temperature while reducing methanol concentration to approximately 1 M, under suitable methanol volumetric flow rate conditions, can enhance reaction kinetics and reduce methanol crossover, resulting in increased peak power density.
- The obtained model exhibits a robust fit, and comparison of predicted peak power density with experimental results reveals a favourable agreement between the model and actual data.
- This study offers valuable insights into optimizing operational parameters for DMFC performance, underscoring the importance of considering and regulating methanol concentration and temperature to maximize power density.

5.3. Methanol Electrolysis Cell

The study carried out for Methanol Electrolysis Cells presents a comprehensive synthesis of the experimental findings from three distinct studies focused on methanol electrolysis for hydrogen production. The investigations covered various aspects of this electrochemical process, including electrode evaluation, operational

parameters influence on Methanol Electrolysis Cell (MEC) performance and the influence of geometrical parameters of serpentine flow field configurations in MEC electrical energy consumption.

Firstly, the study on electrode evaluation highlighted the effectiveness of different catalysts (Ni, NiMo, and NiCu) and several supports for the methanol oxidation reaction in an alkaline media. The supports used are: stainless steel mesh (SS), Ni foam (NF), Ti felt anodized (TiFelt), and Ti foil with nanotubes (TiFoilNTs).

Secondly, the application of RSM provided insights into the influence of operational parameters (methanol concentration, volumetric flow rate, and MEC temperature) on MEC performance.

Lastly, the analysis of geometric parameters (open ratio, channel width and channel depth) of serpentine anode flow fields elucidated their impact on MEC performance.

The key insights obtained from this study are:

- The incorporation of Mo and Cu into the Ni catalysts demonstrated enhanced electrode activity, particularly in the presence of methanol. The morphological changes induced by Cu presence led to increased specific surface area, facilitating more active sites for the electrochemical reaction.
- The results showed the superior performance of NiCu catalysts, particularly on NF and secondly on TiFelt, for methanol oxidation.
- The results of MEC working conditions highlighted complex interactions among methanol concentration and temperature, significantly affecting MEC power density. Lower temperatures and concentrations resulted in increased electrical energy consumption, while higher concentrations led to enhanced MEC power consumption.
- Similar to the DMFC results, in MEC studies a combined influence of methanol volumetric flow rate and temperature can be observed, leading to a possible reduction in the temperature of the catalytic layer as the volumetric flow rate increases.
- The parameter exerting the most significant influence on MEC performance is methanol concentration. This outcome may stem from MEA degradation due to exposure to extreme operating conditions.

- The results of MEC anode channel serpentine flow fields revealed that an adequate open ratio and channel depth are crucial for optimizing MEC power density, with the channel width exerting a comparatively lesser influence.
- The model for MEC anode geometry effectively reveals more than 90 % of the experimental response achieved, with open ratio and channel depth significantly influencing both the distribution of reagents across the active area and the evacuation of CO₂ bubbles.
- The collective findings underscore the importance of optimizing electrode materials, operational parameters and geometric configurations to enhance the performance and viability of methanol electrolysis for hydrogen production. These insights contribute to the advancement of sustainable hydrogen production technologies and provide guidance for the design and operation of MEC systems.

5.4. Future work

Research activities aim to address inquiries and solve problems, driving progress for humanity. However, as new discoveries emerge, they often lead to further questions, fuelling the perpetual curiosity of the scientific community to seek better or more comprehensive solutions. Research work is inherently iterative, and this doctoral thesis is no exception. Therefore, forthcoming studies and enhancements applicable to the work conducted herein are proposed:

- Design, fabrication, assembly, improving and implementation of the cathode air treatment line based on the preliminary setup presented in this thesis.
- Theoretical examination of the feasibility of utilizing CO₂ produced during the operation of Direct Methanol Fuel Cells (DMFCs) and Methanol Electrolysis Cells (MECs) as a commodity in the methanol synthesis process. This entails capturing and storing the generated CO₂ after using methanol as an energy vector or hydrogen vector, and transporting this CO₂ to the methanol synthesis facility.
- Preparation of non-noble metal electrodes for methanol oxidation reaction in acidic environments and further characterization experiments compared to those conducted in alkaline environments. Further testing is necessary also to assess the long-term durability and degradation of the top-

performing electrodes, employing NiCu catalysts with NF and TiFelt supports.

- Completion of experiments based on the CCD design implemented in this thesis, employing response surface methodology to determine the geometric parameters of the anode serpentine flow field that exert the most influence on the performance of a DMFC.
- Improvements in test benches to mitigate the temperature decrease effect on catalyst layers resulting from increased methanol volumetric flow rate.
- Determine optimal theoretical parameter combinations, derived from mathematical models based on experimental results from both DMFC and MEC, that maximize device responses. Subsequently, conduct experiments using these combinations to enhance the performance of these devices.
- Study of Membrane Electrode Assembly (MEA) degradation in a MEC to assess the influence of operational conditions over extended periods and a larger number of experiments.
- Design, assembly, and experimental testing of stacks for both devices, DMFC and MEC, to determine the influence of operational conditions with an increased number of cells.
- Development of test protocols to not only collect current and voltage data from both devices but also to analyse the composition of the products expelled (both liquid and gaseous) during operation under several conditions.
- Assessment of MEC operational conditions effect on MEC performance at current densities lower than 300 mA/cm².
- Assessment of the influence of operational conditions on the formation and evacuation of CO₂ bubbles from the DMFC and MEC anodes, as well as the geometrical parameters of the serpentine flow field.

These future research directions aim to deepen understanding, improve performance and advance the practical application of methanol-based fuel cell and electrolysis technologies. They represent ongoing efforts to address challenges and refine methodologies in pursuit of sustainable energy solutions.

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Annexes

Annex A Ships powered with methanol

Table A.1: Companies with ships powered with methanol under design, construction or in service (Methanol Institute, 2023b)

Company	Ship status	Type of ship	Country	Year
Stena Line	In service	RoPax	Sweden	2015
Methanex Waterfront Shipping	In service	Chemical tanker	Canada	2016
Abeking & Rasmussen	Under design	Cruise	Germany	2019
Damen Shipyard	Under design	Offshore Support Vessel	Netherlands	2020
Liberty One	Under construction	Multipurpose	Germany	2020
Pa-X-ell2 Project	Under design	Cruise	Germany	2021
Maersk	Under construction	Container	Denmark	2021
Sumitomo Heavy	Under design	Tanker	Japan	2021
Van Oord	Under design	Subsea rock installation vessel	Netherlands	2021
Danube Shipping Company	Under construction	River pusher	Ukraine	2021
Port of Emden	Under construction	Harbor boat	Germany	2021
Mitsui OSK Lines	Under design	Chemical tanker	Japan	2021
Robert Allan Ltd	Under design	Crew transfer vessel	Canada	2021

Proman Stena Bulk	Under construction	Tanker	China	2021
Svitzer, AP Moller	Under design	Tug boat	Denmark	2021
X-Press Feeders Group	Under construction	Container	Singapore	2021
K Shipbuilding	Under design	Tanker	Korea	2021
MENENS	Under construction	Survey vessel	Netherlands	2021
Lürssen Yachts	Under design	Yacht	Germany	2021
Swedish Maritime Administration	In service	Pilot boat	Sweden	2021
E1 Marine	Under design	Towboat	United States	2022
Damen Shipyards	Under construction	Tug vessel	Netherlands	2022
ABS, SDTR Marine, SDARI	Under design	Bulk carrier	Singapore	2022
Balearia	Under construction	RoPax	Spain	2022
Van Oord	Under construction	Offshore installation vessel	Netherlands	2022
COSCO SHIPPING, CSSC Dalian Shipbuilding	Under design	VLCC	China	2022
Damen Shipyards	In service	Tug vessel	Netherlands	2022
AAL Shipping	Under construction	Multipurpose	Singapore	2022
Danaos	Under construction	Container	Greece	2022
Mitsui O. S. K. Lines	Under design	Tanker	Japan	2022

Læsø Municipality	Under construction	Ferry	Denmark	2022
Ørsted teams, Esvagt	Under construction	Service operation vessel	Denmark	2022
Uzmar, Robert Allan	Under design	Tug vessel	Canada	2022
Ocean Network Express	Under construction	Container	Japan	2022
Blue World Technologies, Tuco Marine	Under design	Workboats	Denmark	2022
CMA CGM	Under construction	Containership	France	2022
Ocean Yield	Under construction	Containership	Norway	2022
Proman Stena Bulk	In service	Tanker	China	2022
MPC Container Ships	Under construction	Container	Norway	2022
Topeka	Under construction	Container	Norway	2022
CSSC Qingdao Beihai, CSDC	Under design	Bulk carrier	China	2022
Sanlorenzo	Under design	Superyacht	Italy	2022
MOVE Logistics Goup	Under construction	RoRo	New Zealand	2022
Glosten, ABB	Under design	Tug vessel	USA	2022
Med Marine	Under design	Tug vessel	Turkey	2022
COSCO SHIPPING	Under construction	Container	China	2022
Euronav	Under construction	Tanker	Belgium	2022
Hengyu Energy	In service	Tanker	China	2022

Maersk	Under construction	Container	Denmark	2022
Orient Overseas Container Line	Under construction	Container	China	2022
Global Energy Trading, Stellar Ship Management Services	Under construction	Bunkering ship	Singapore	2022
Proman Stena Bulk	In service	Tanker	China	2022
OLjOla	Under design	Tanker	Sweden	2022
CMA CGM	Under construction	Container	France	2022
Alfred Wegner Institute	In service	Research vessel	Germany	2022
Cecon Contracting	Under construction	Cable installation vessel	Norway	2022
Disney Cruise Line	Under construction	Cruise	USA	2022
Proman Stena Bulk	In service	Tanker	China	2022
Zephyr & Boree	Under construction	Container	France	2022
<i>AP Møller-Maersk</i> , COSCO Shipping, OOCL.	Under construction	Ultra-large container	China-S.Korea	2022
Maersk	Under construction	Container	S. Korea	2023
<i>Hyundai Samho Heavy Industries</i> , HJ Heavy	Under construction	Container	S. Korea	2023
Algoma Central Corporation, The CSL Group	Under construction	Bulk carrier	Canada	2023

CMA CGM	Under construction	Container	France	2023
Vertom Goup	Under construction	Dry cargo vessel	Netherlands	2023
OCI, Unibarge	Under construction	Bunker barge	Netherlands	2023

Annex B Polarization and Power Density curves of Direct Methanol Fuel Cell

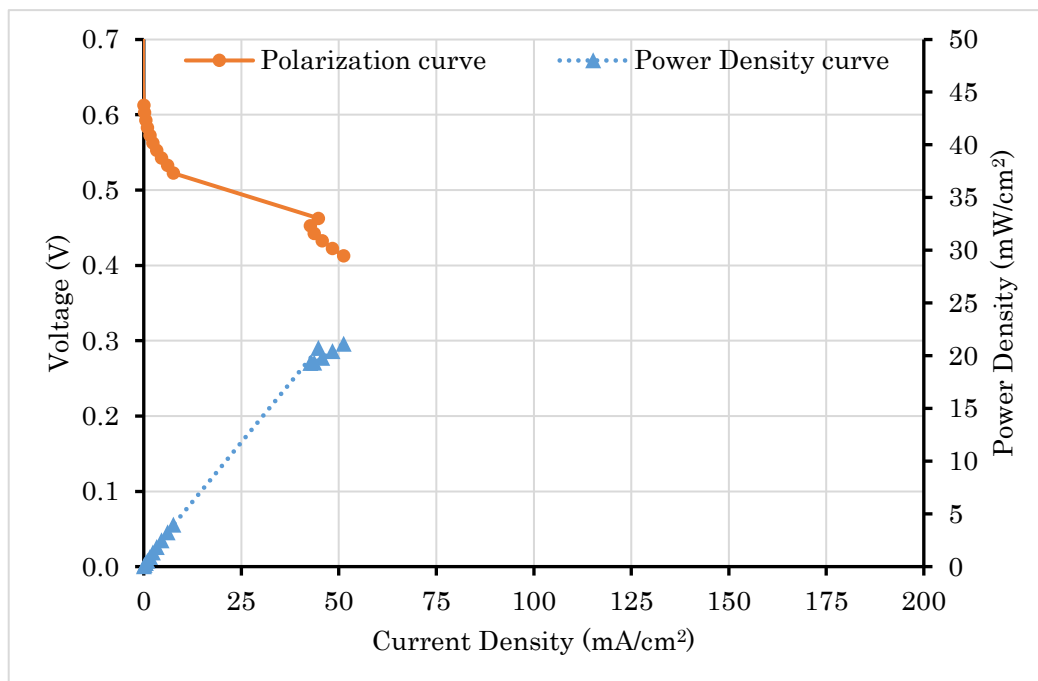


Figure B.1: Activation Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

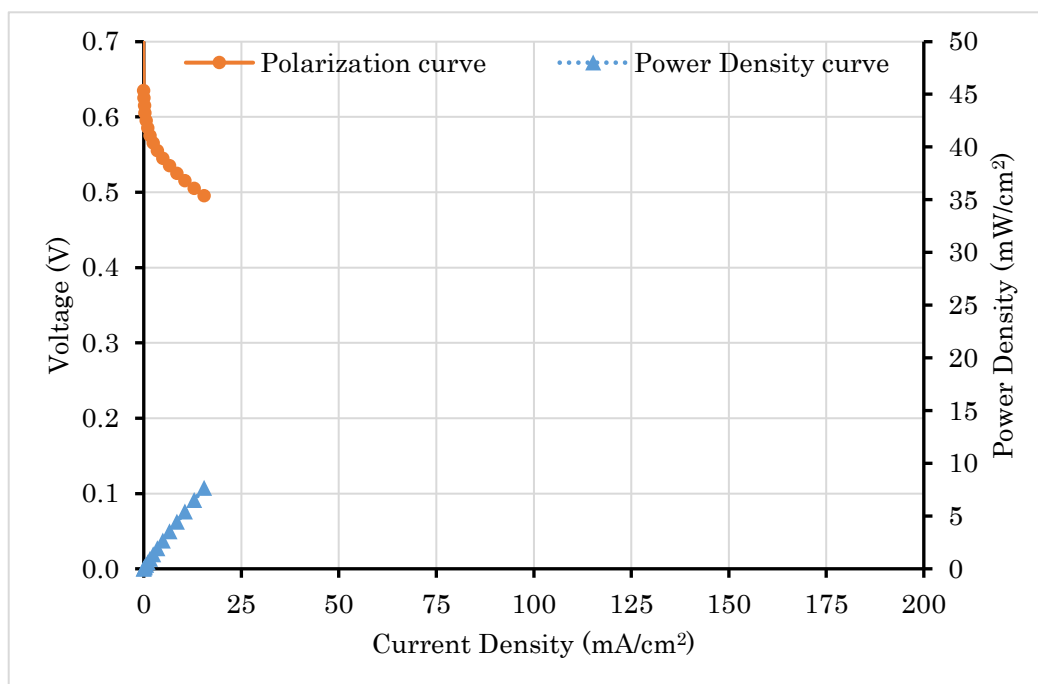


Figure B.2: Activation Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

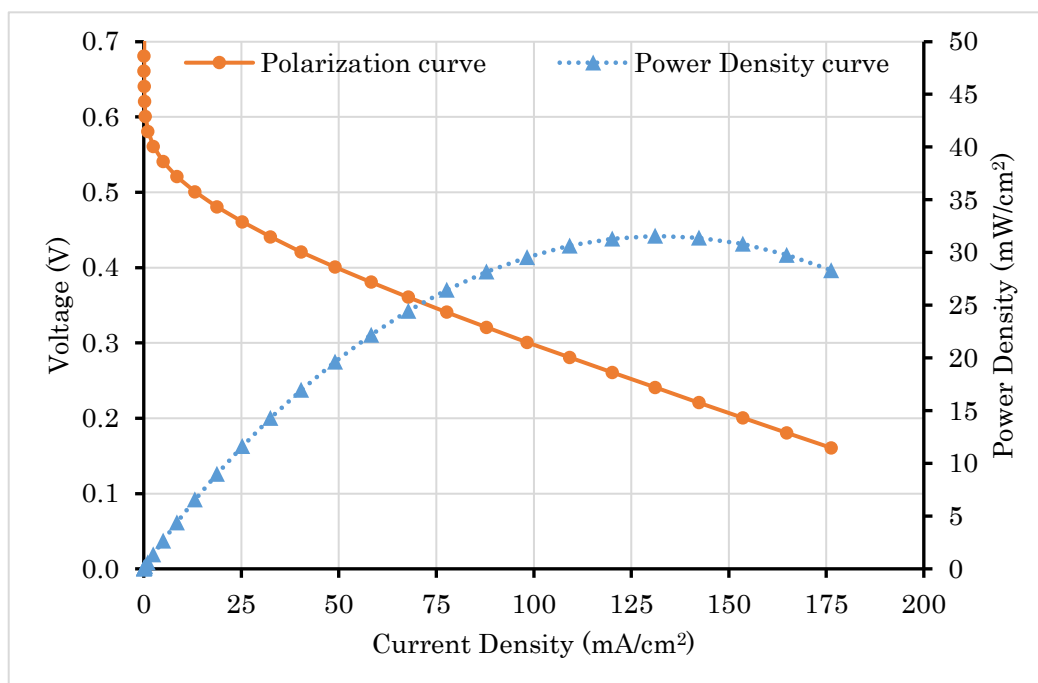


Figure B.3: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

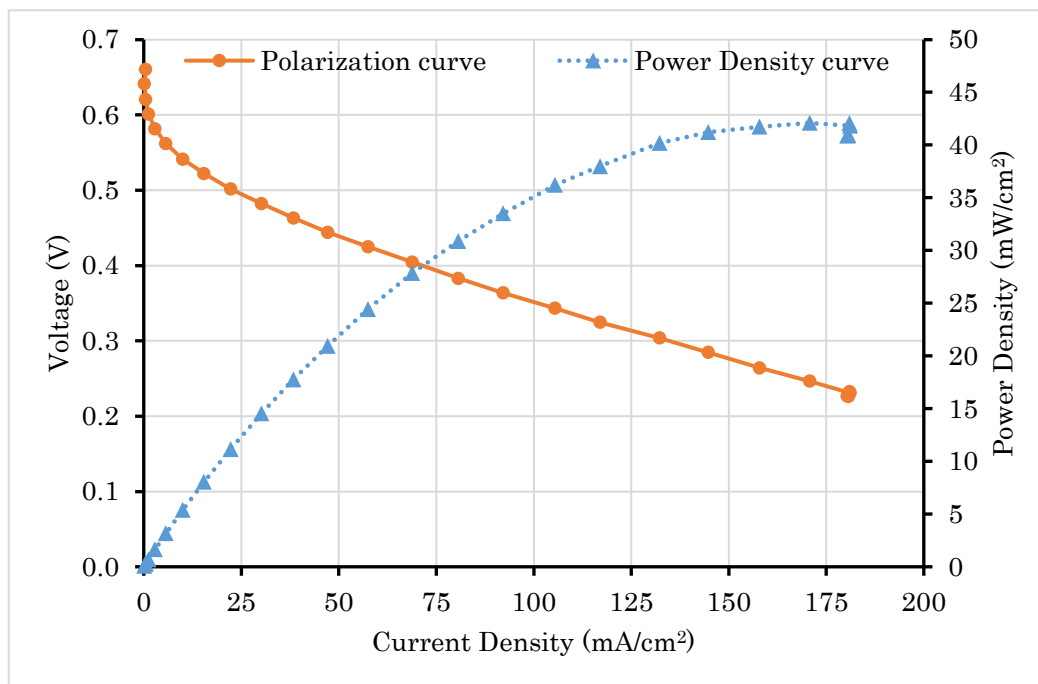


Figure B.4: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

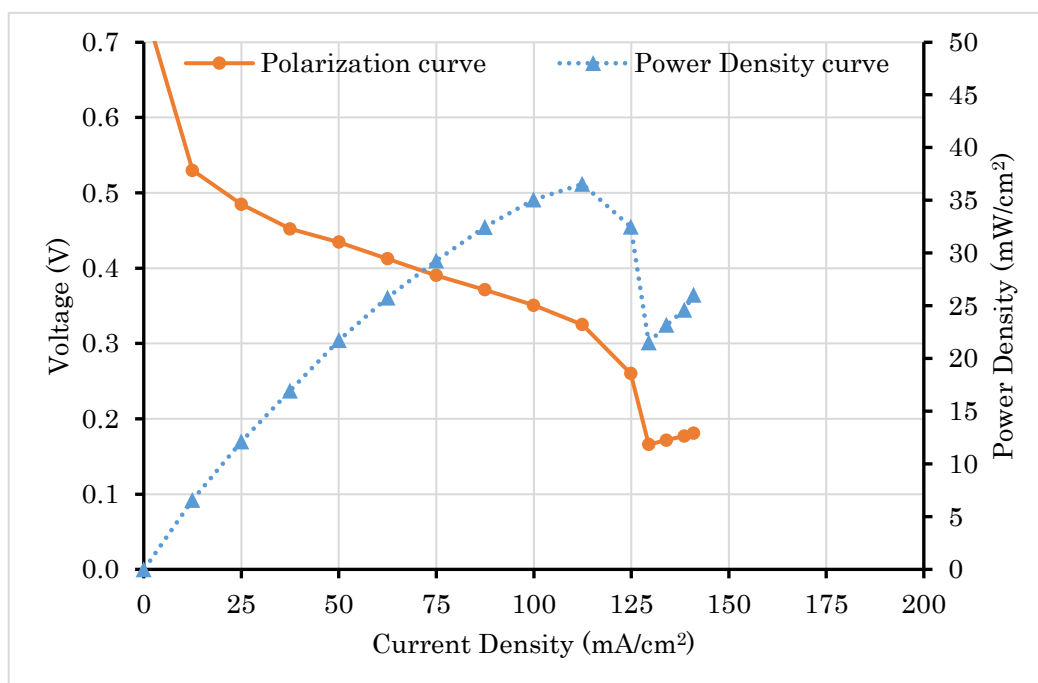


Figure B.5: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

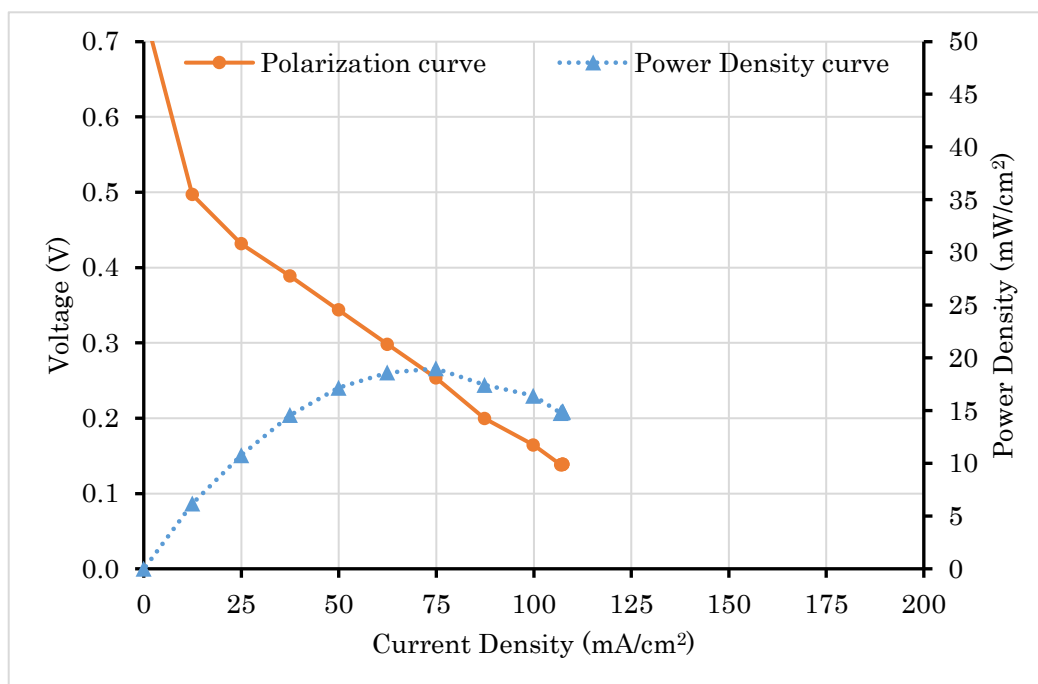


Figure B.6: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

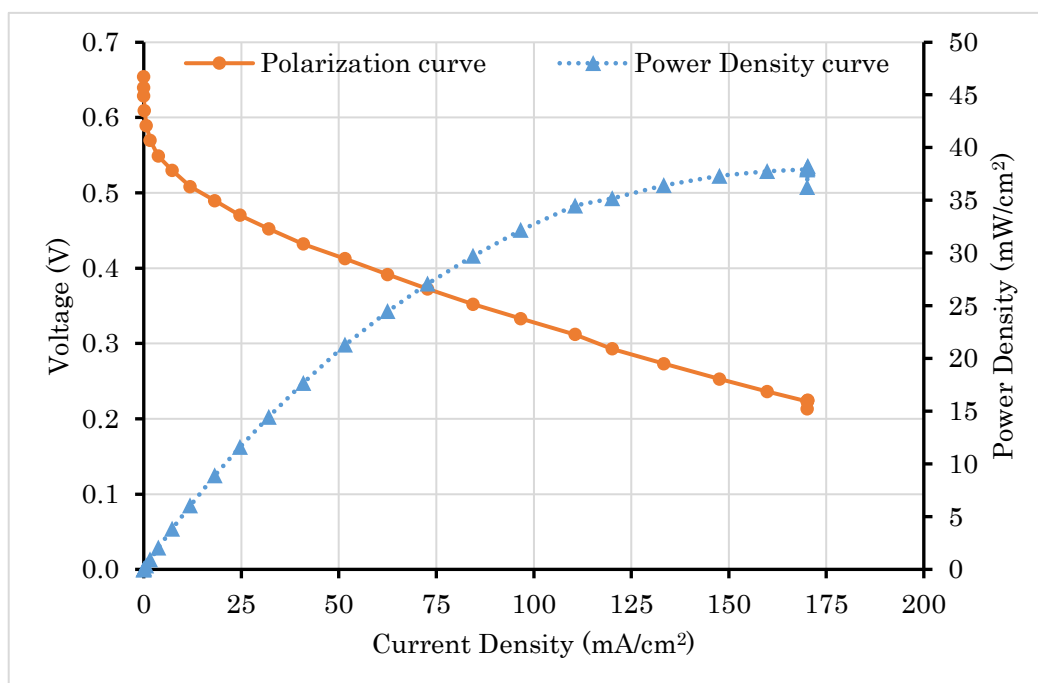


Figure B.7: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

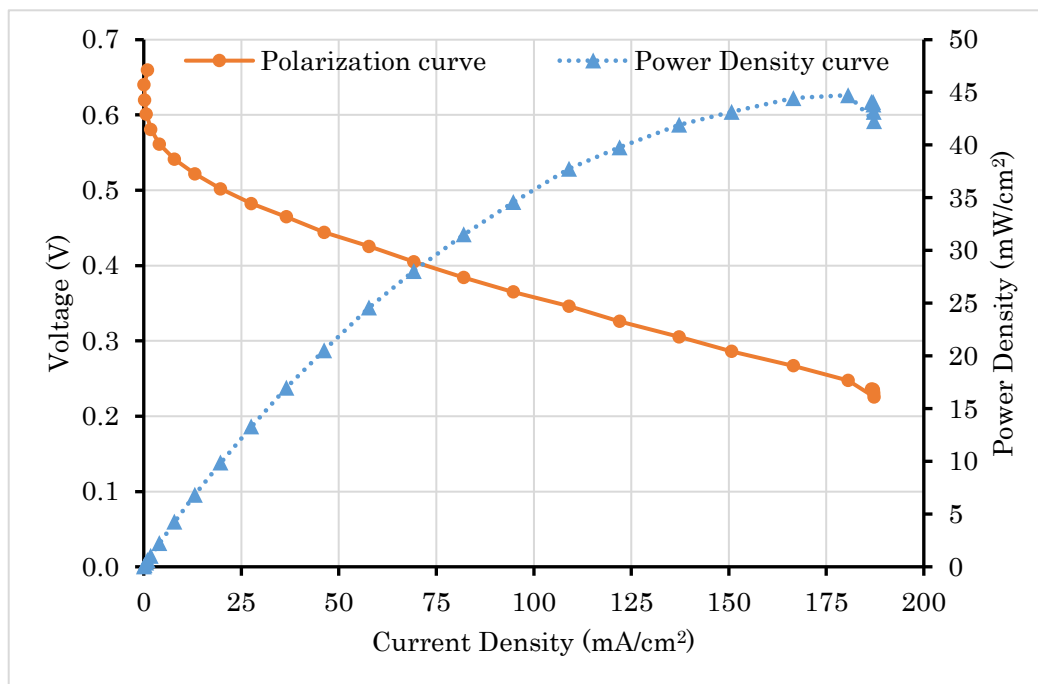


Figure B.8: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

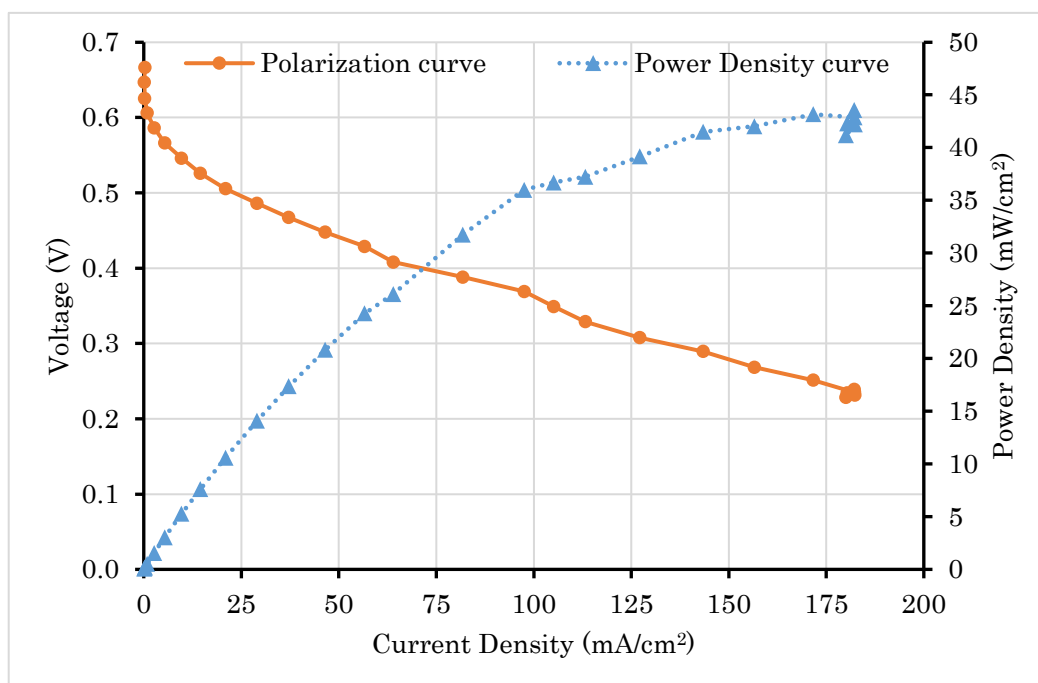


Figure B.9: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

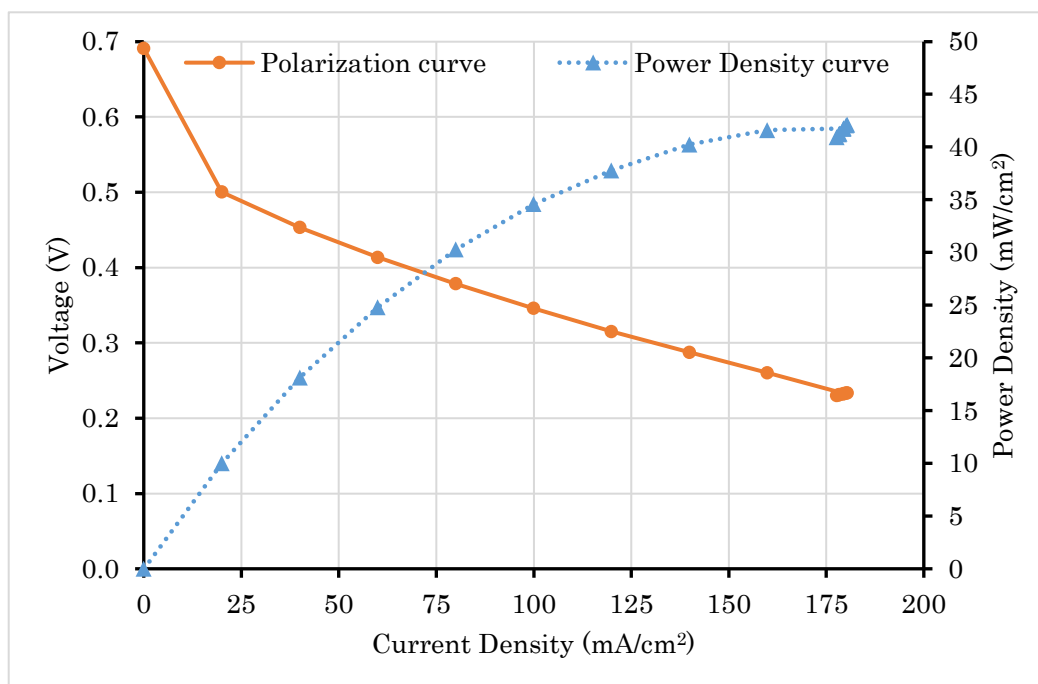


Figure B.10: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

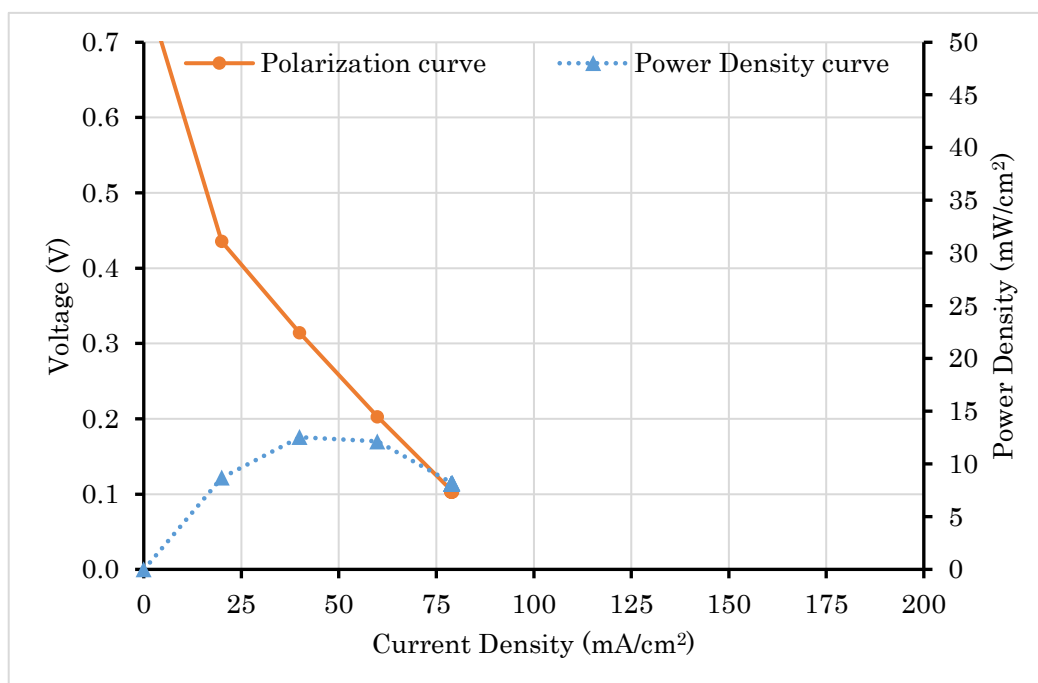


Figure B.11: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

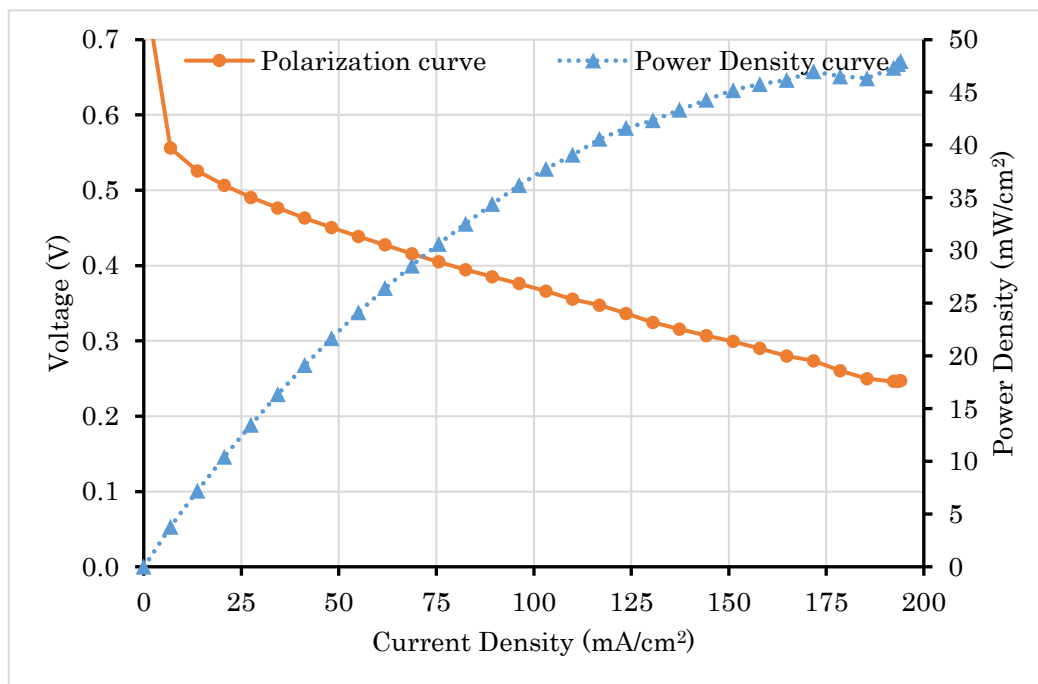


Figure B.12: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

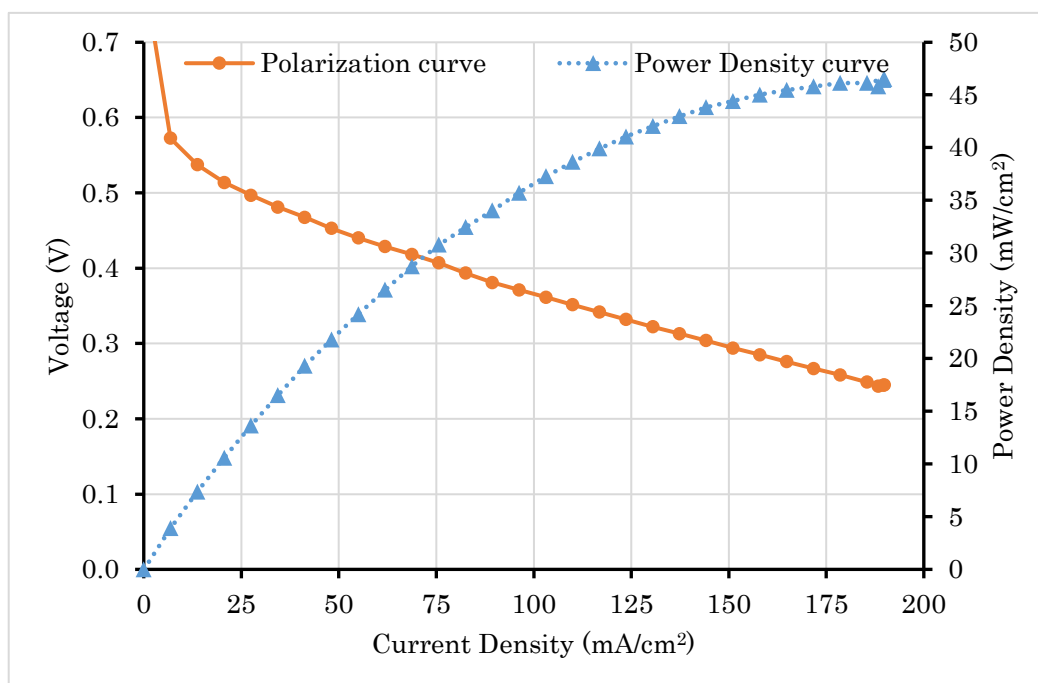


Figure B.13: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

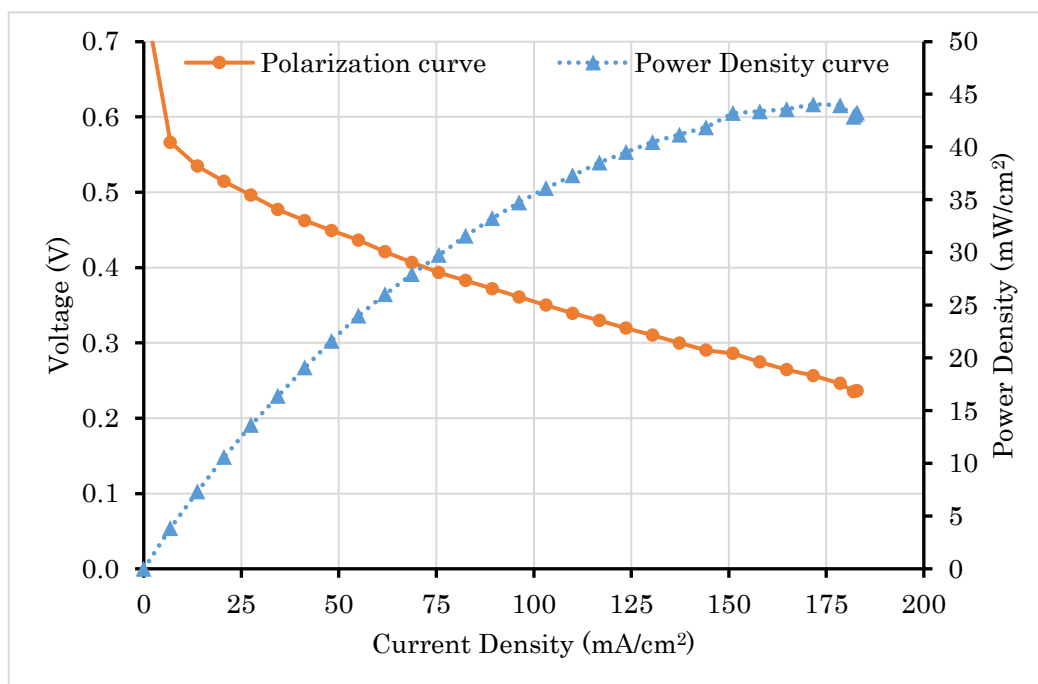


Figure B.14: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

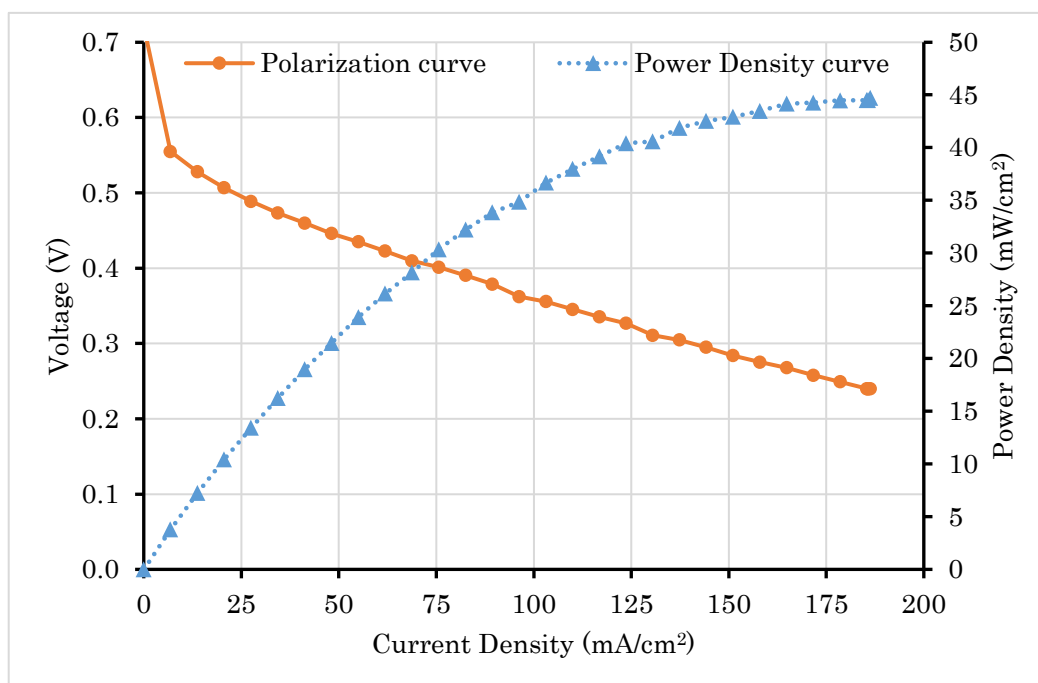


Figure B.15: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

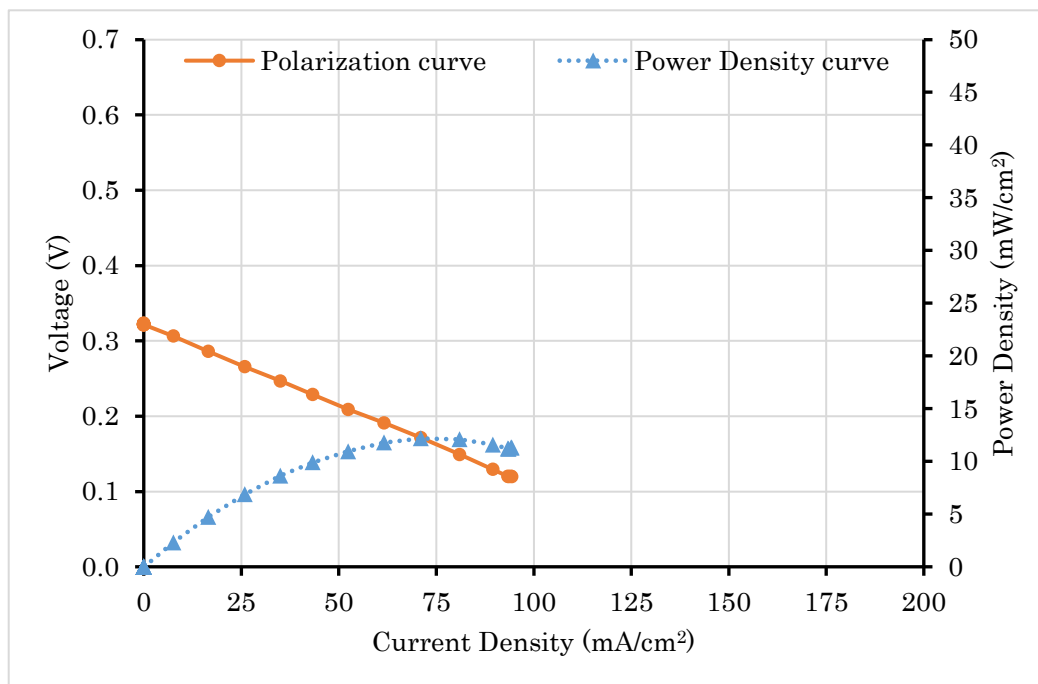


Figure B.16: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

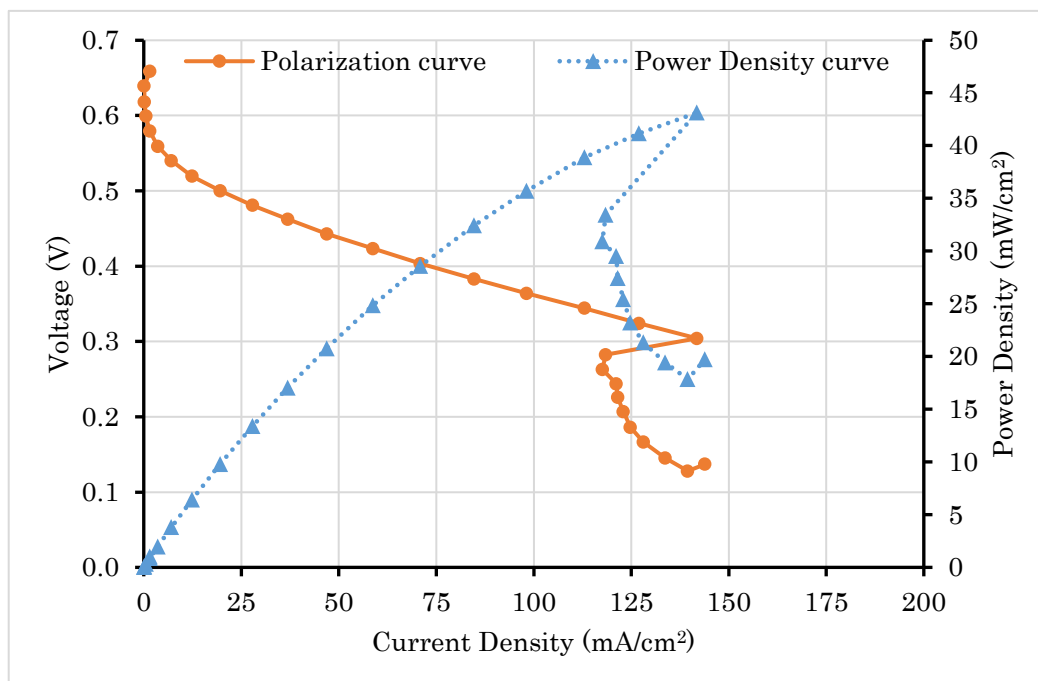


Figure B.17: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

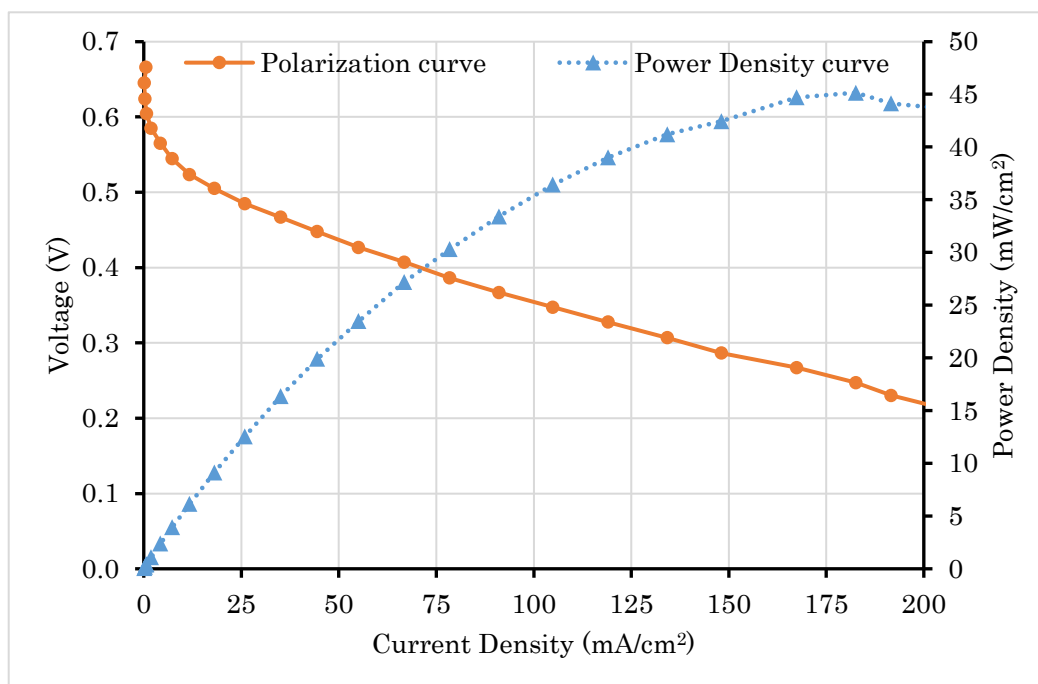


Figure B.18: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

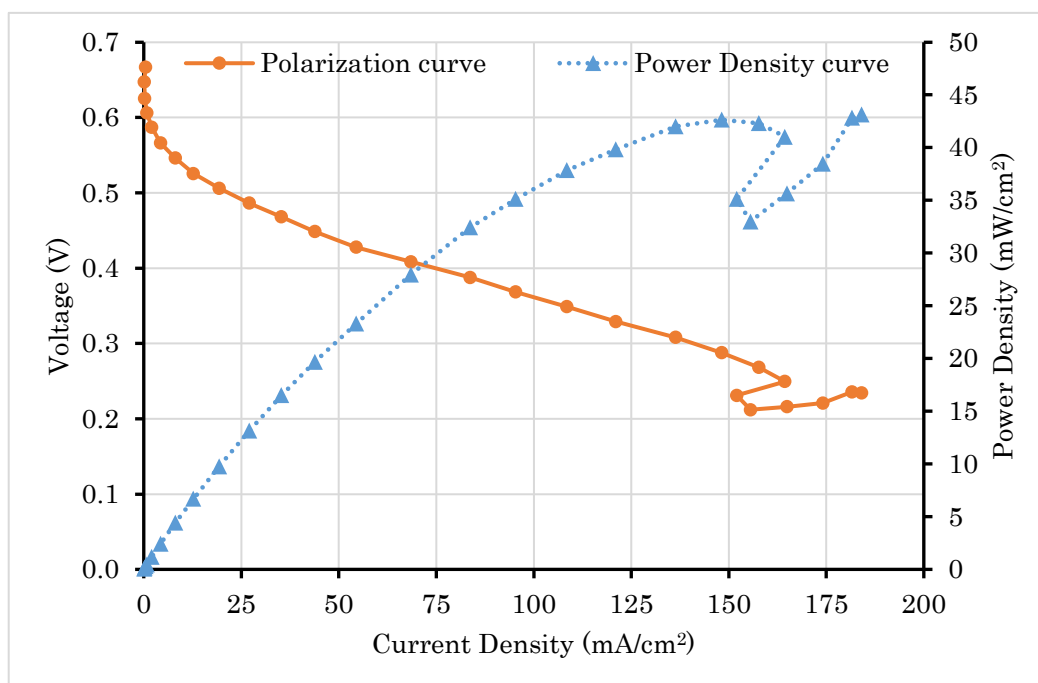


Figure B.19: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

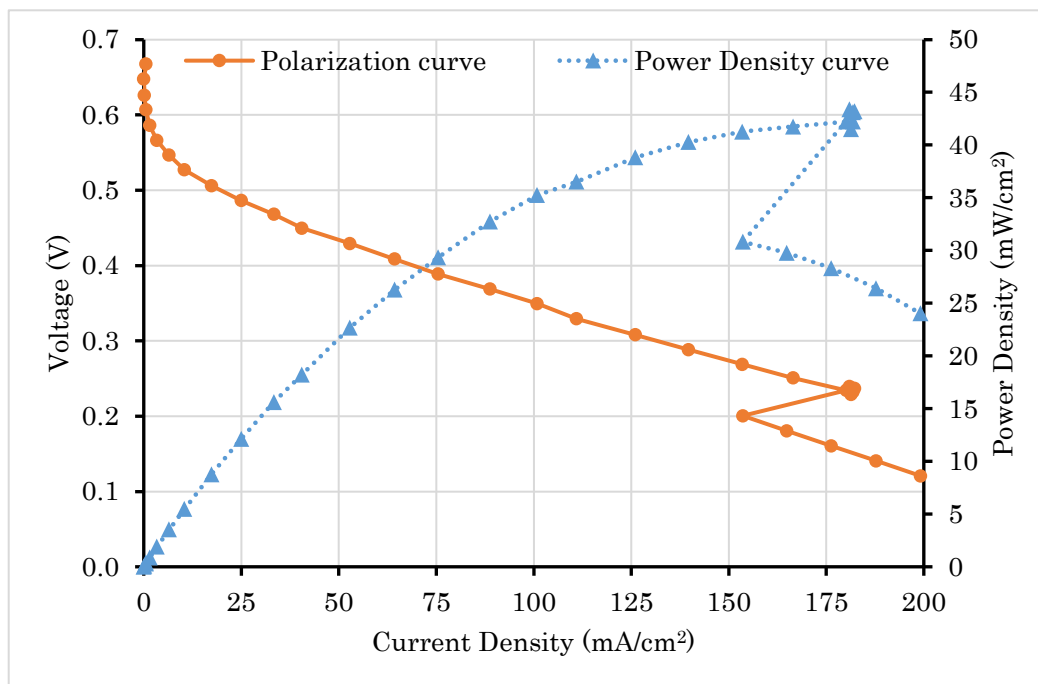


Figure B.20: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

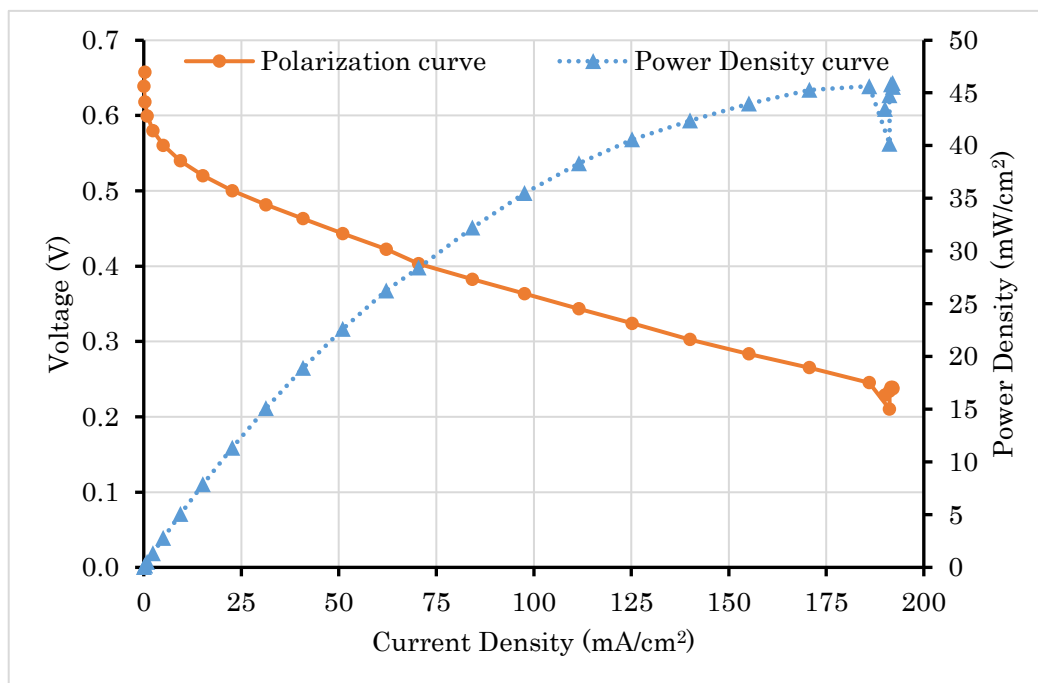


Figure B.21: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

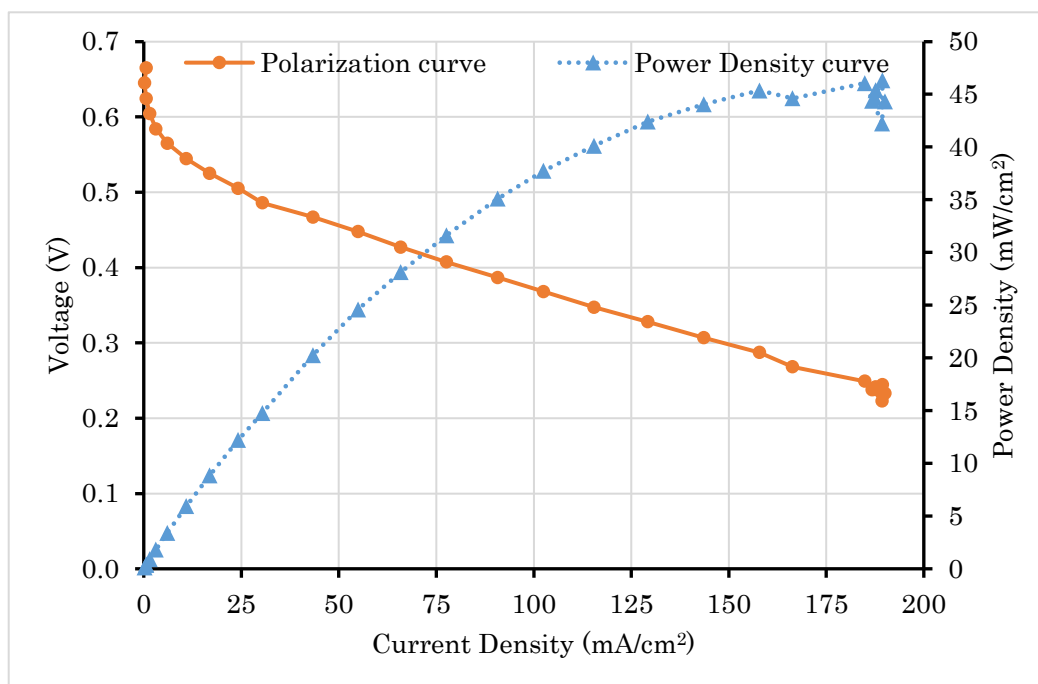


Figure B.22: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

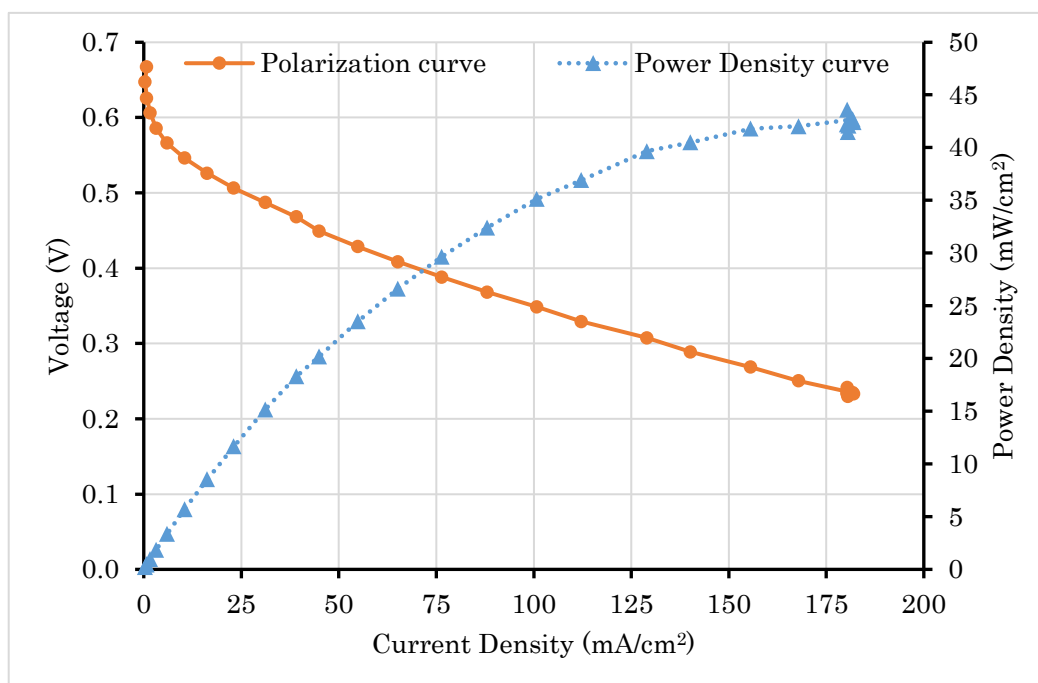


Figure B.23: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

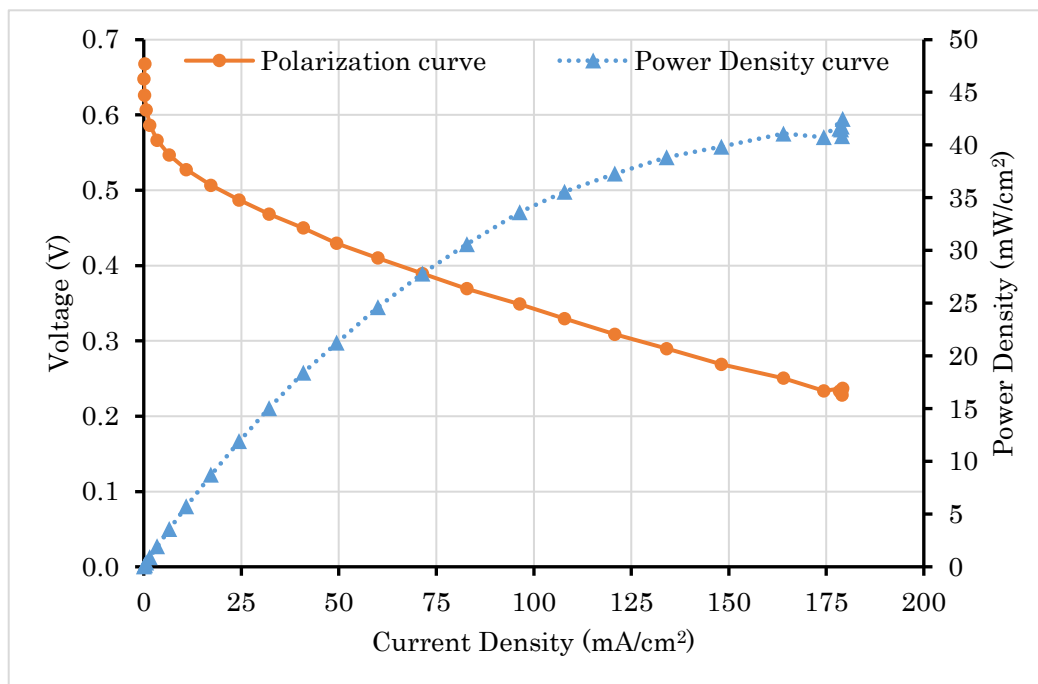


Figure B.24: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

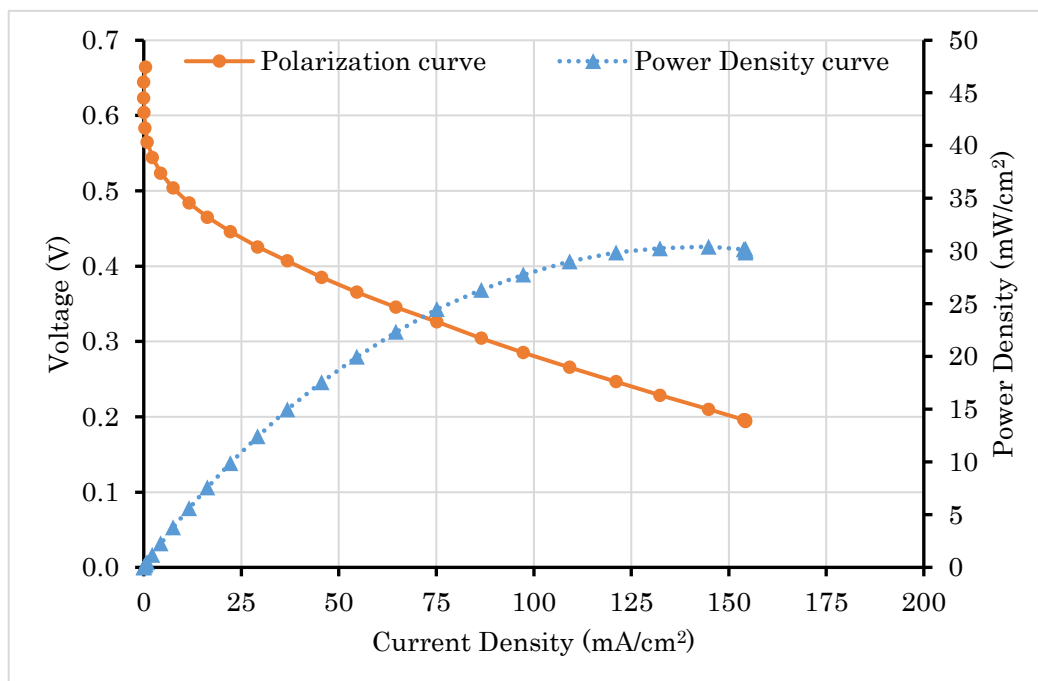


Figure B.25: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

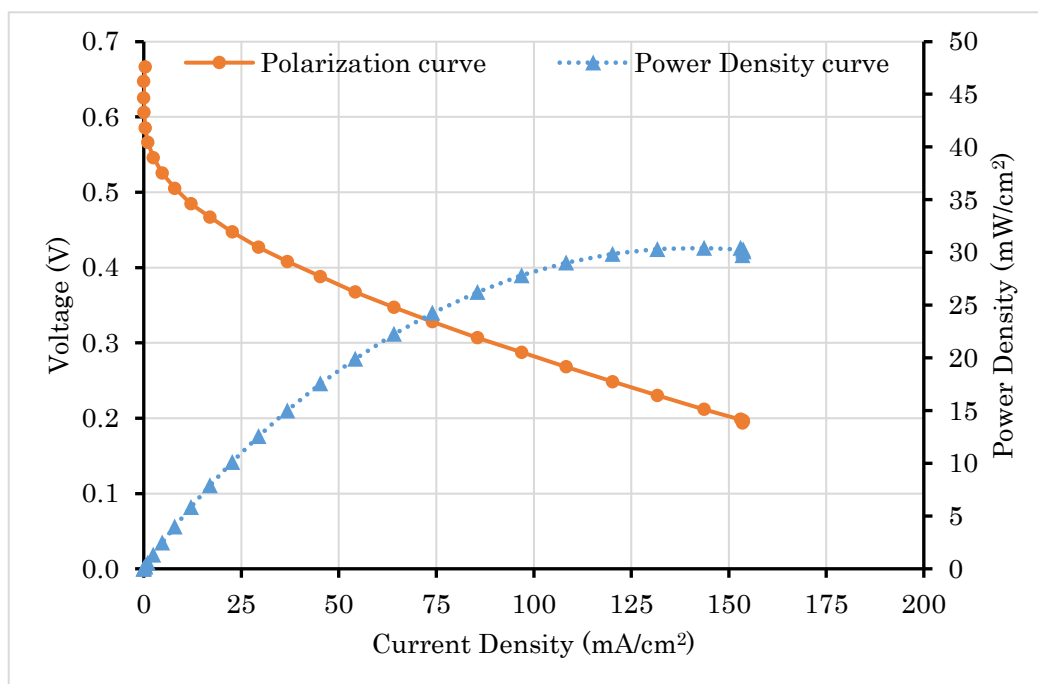


Figure B.26: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

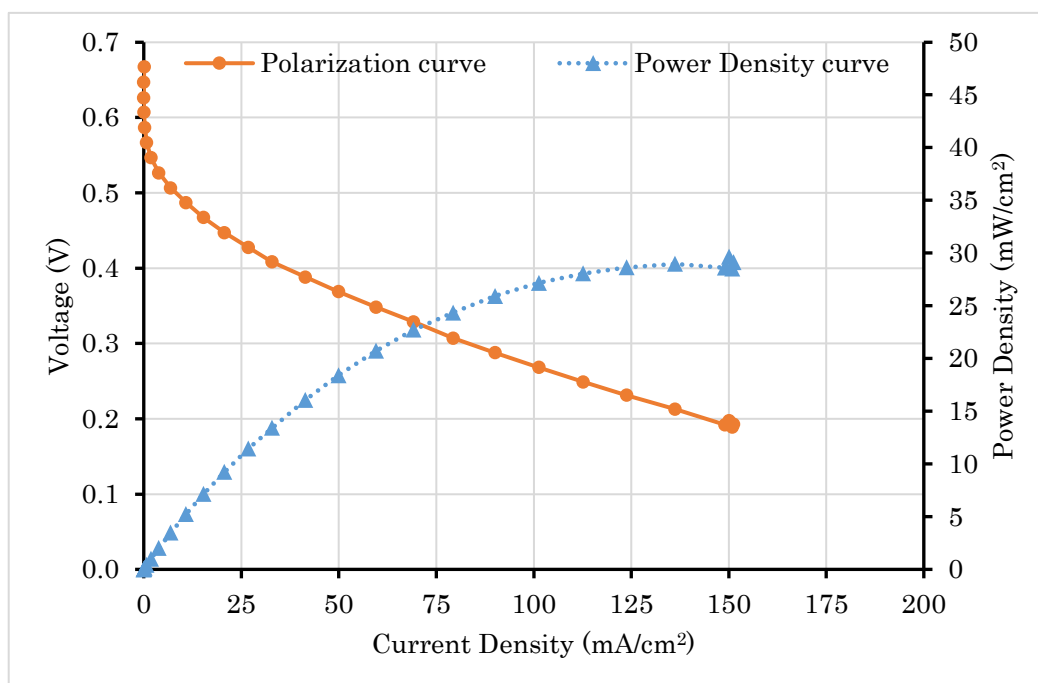


Figure B.27: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

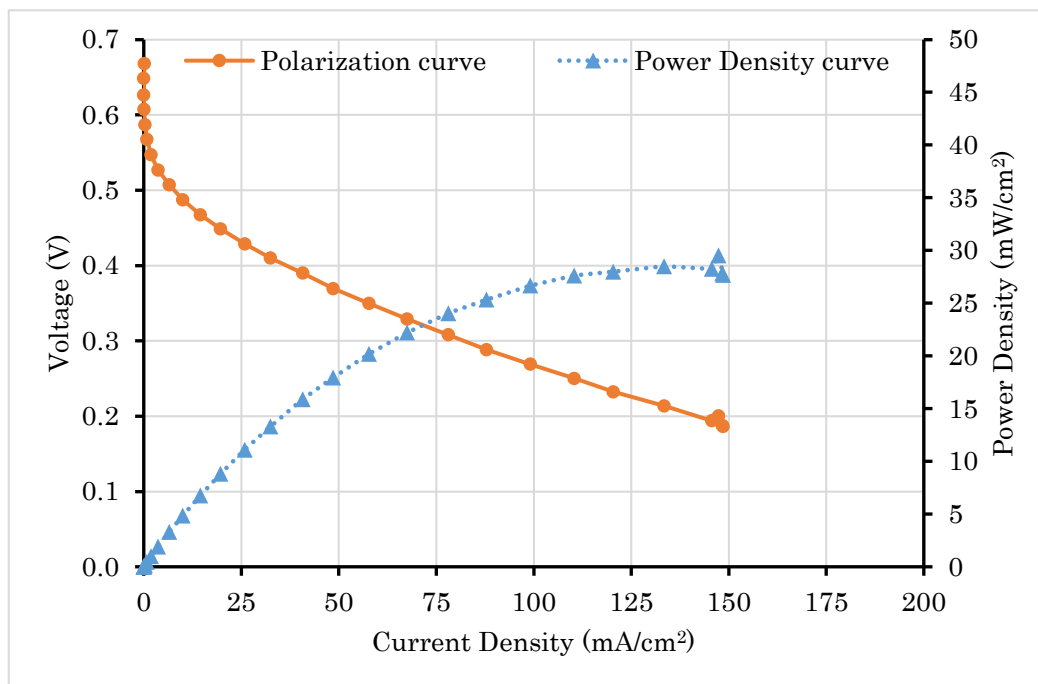


Figure B.28: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

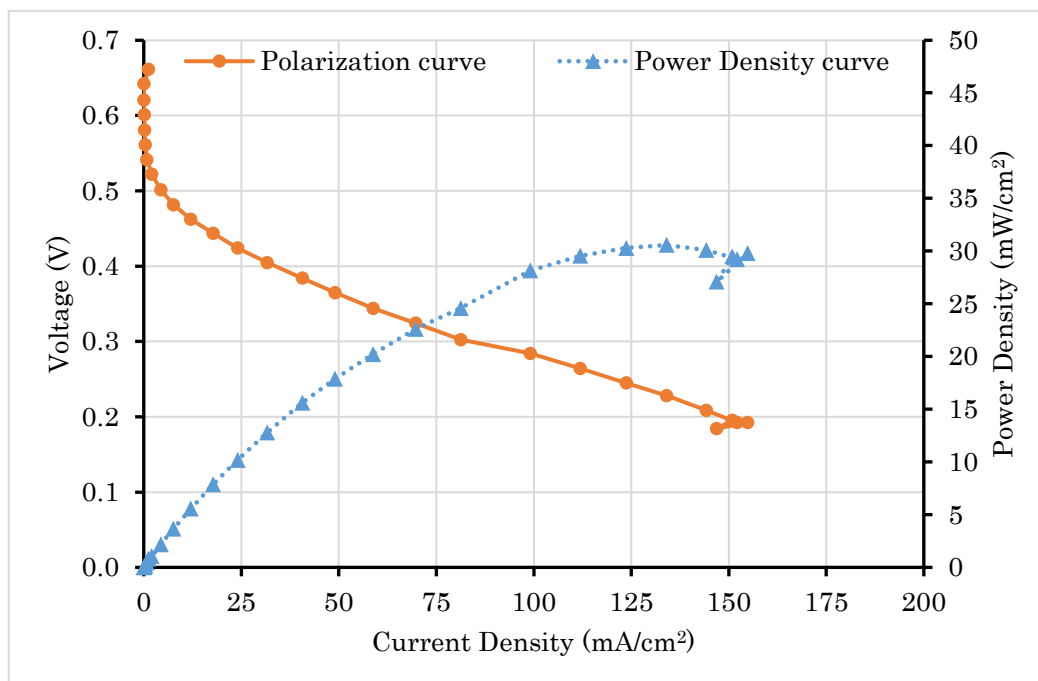


Figure B.29: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

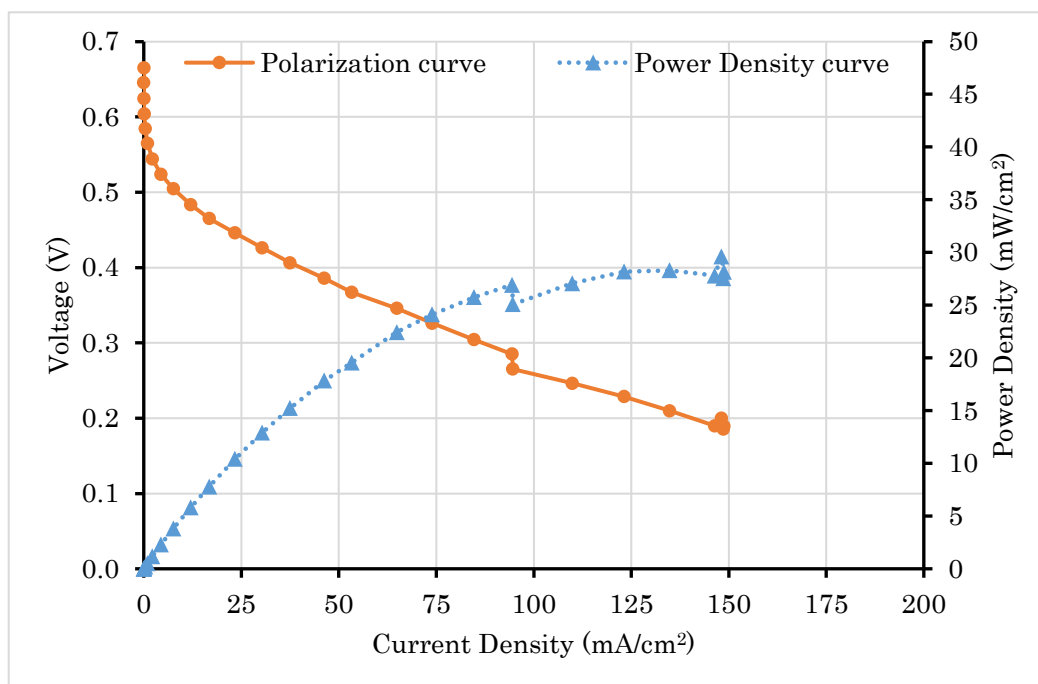


Figure B.30: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

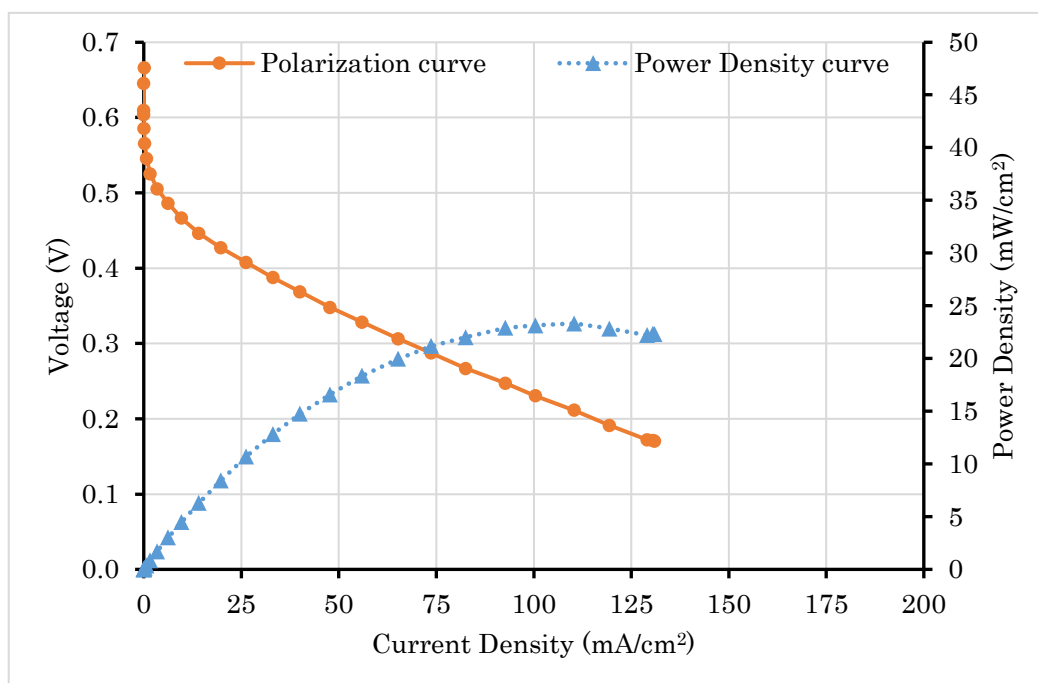


Figure B.31: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

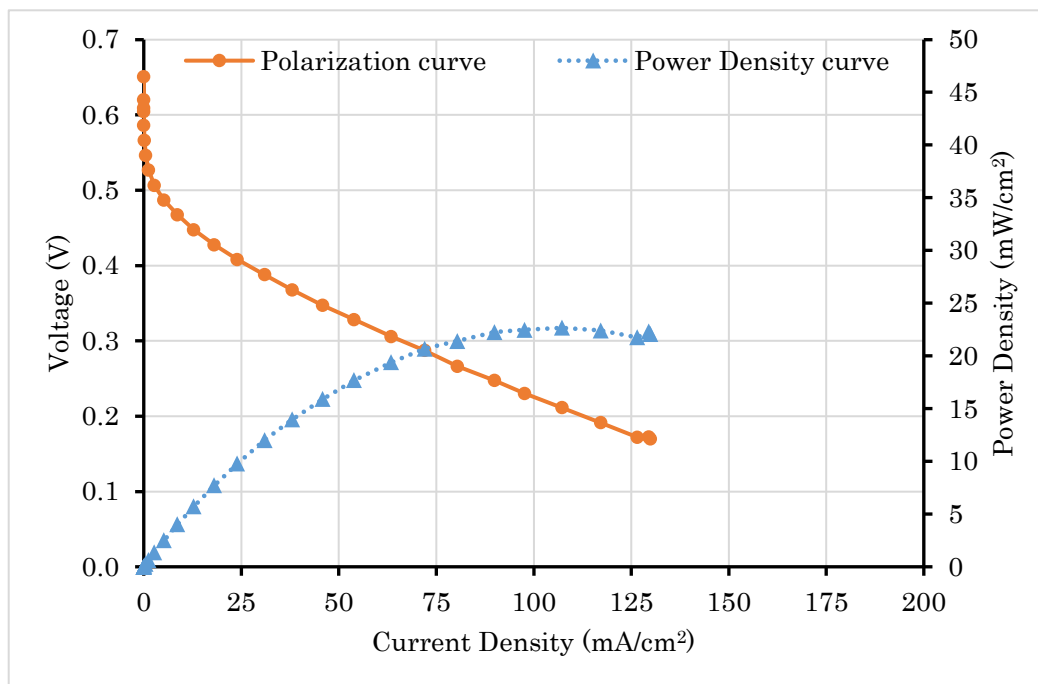


Figure B.32: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

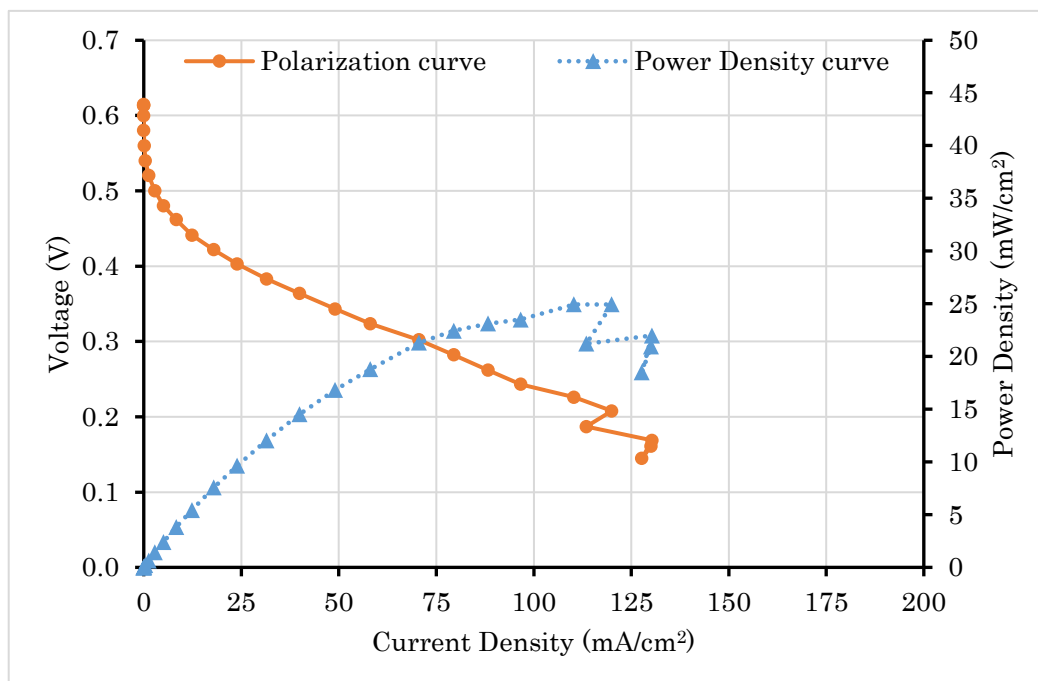


Figure B.33: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

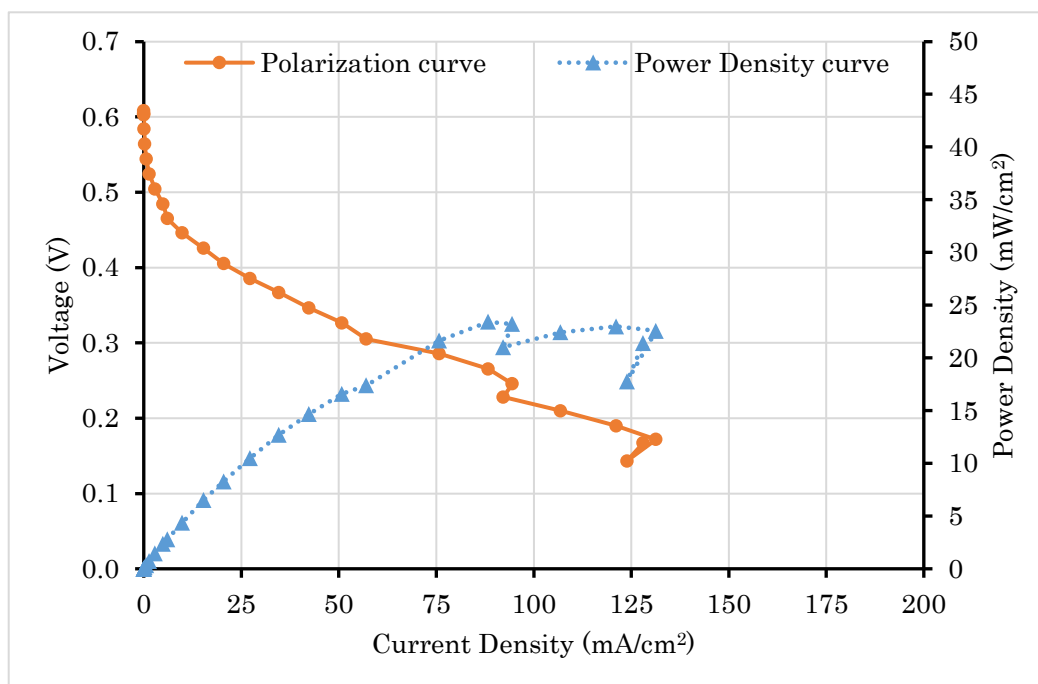


Figure B.34: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

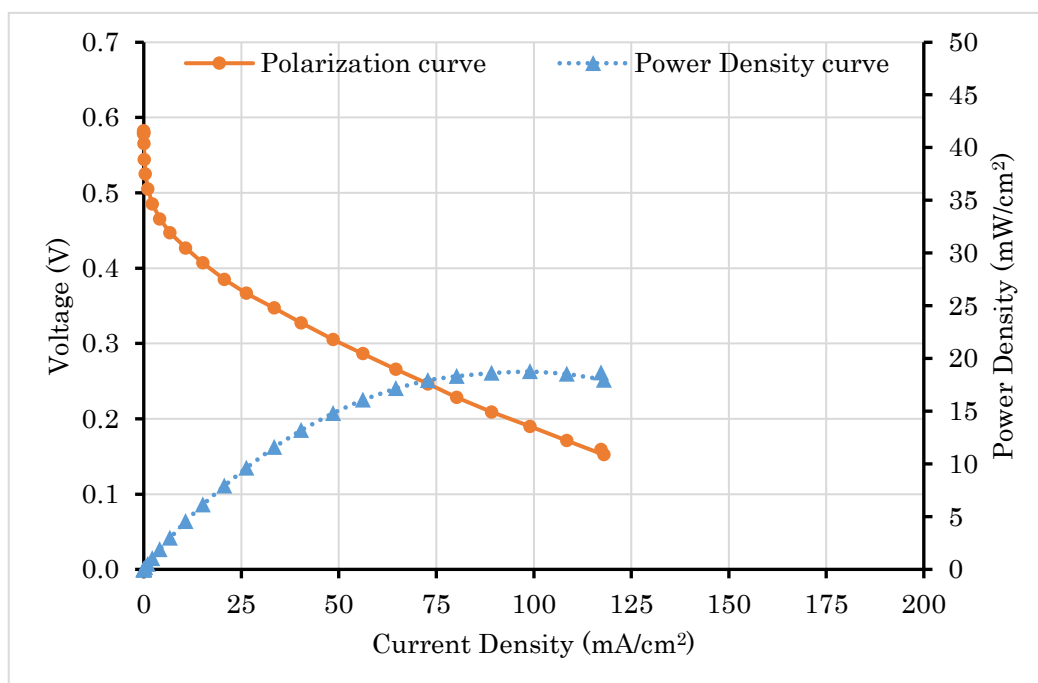


Figure B.35: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

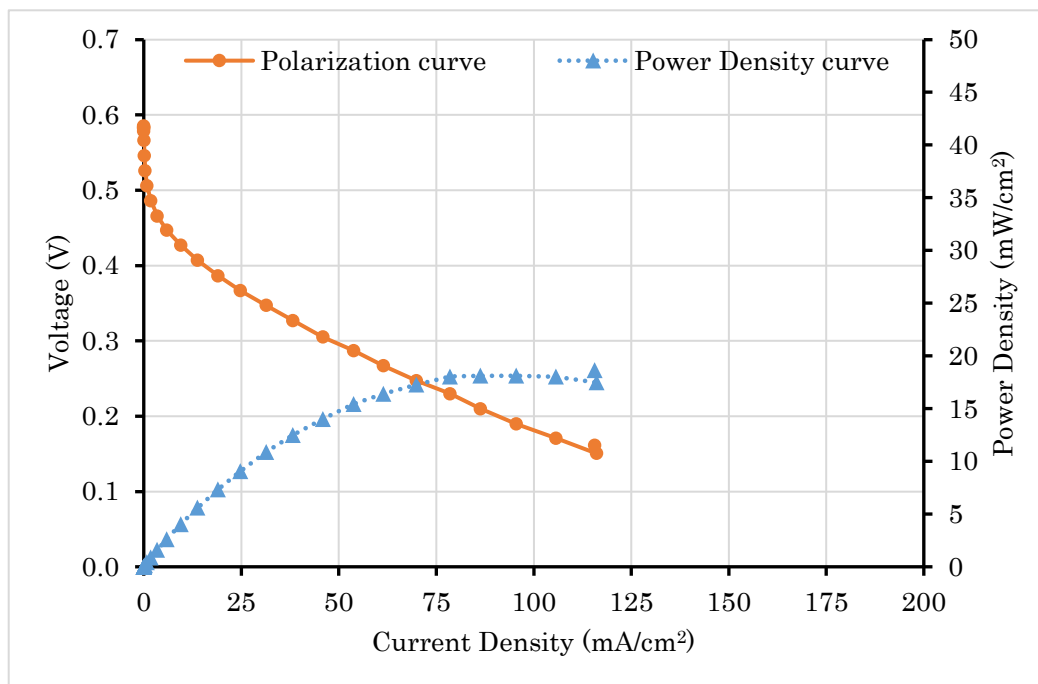


Figure B.36: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 40.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

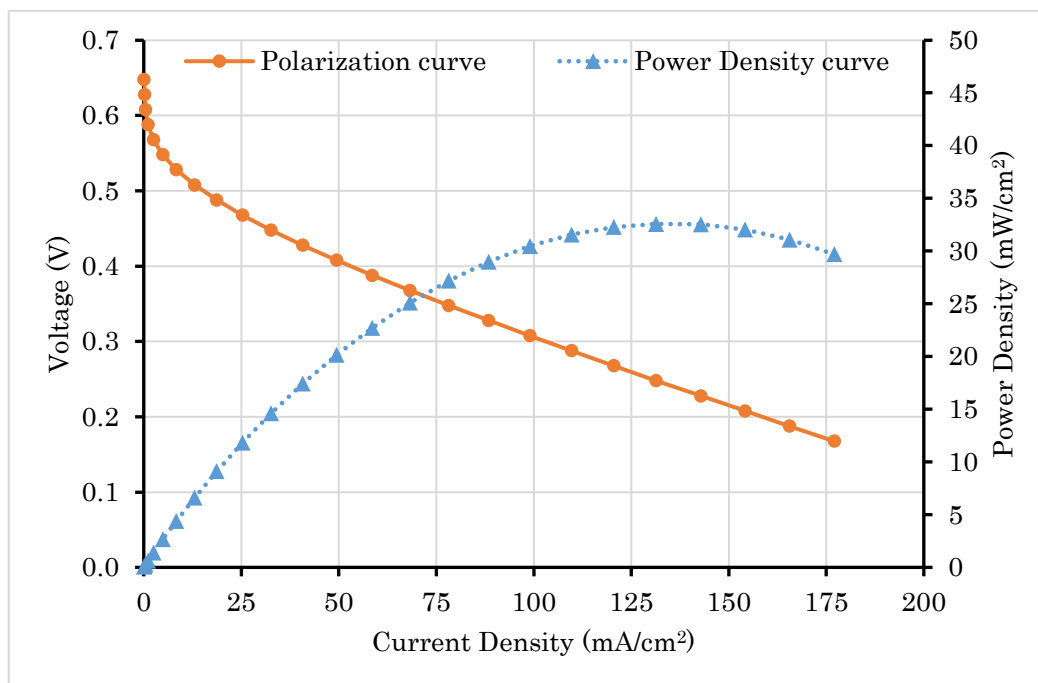


Figure B.37: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

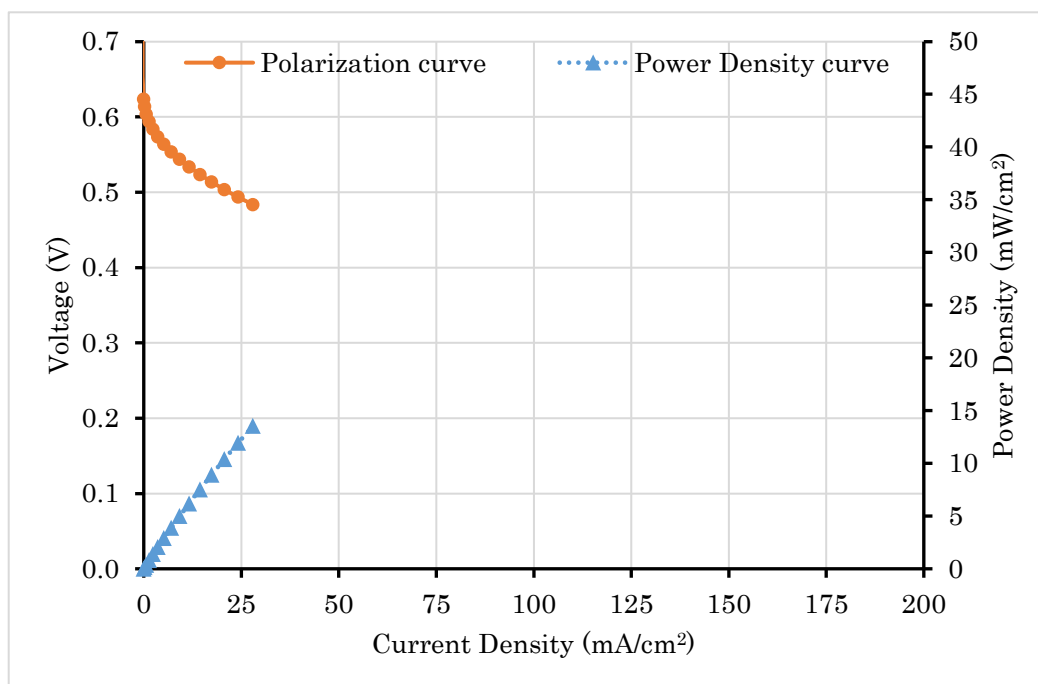


Figure B.38: Activation Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

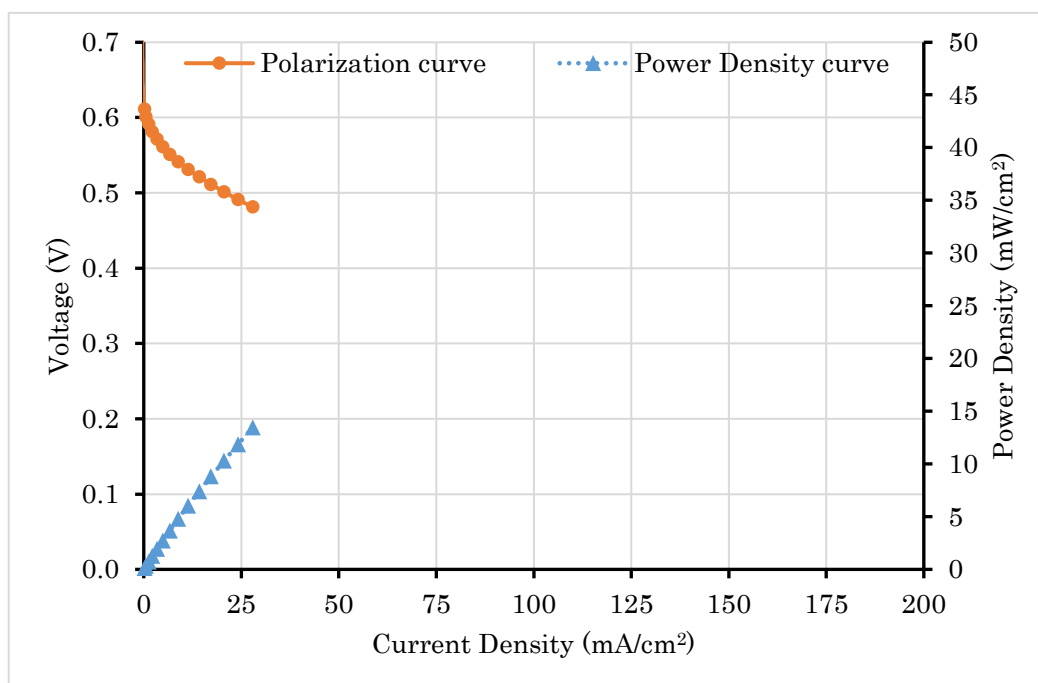


Figure B.39: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

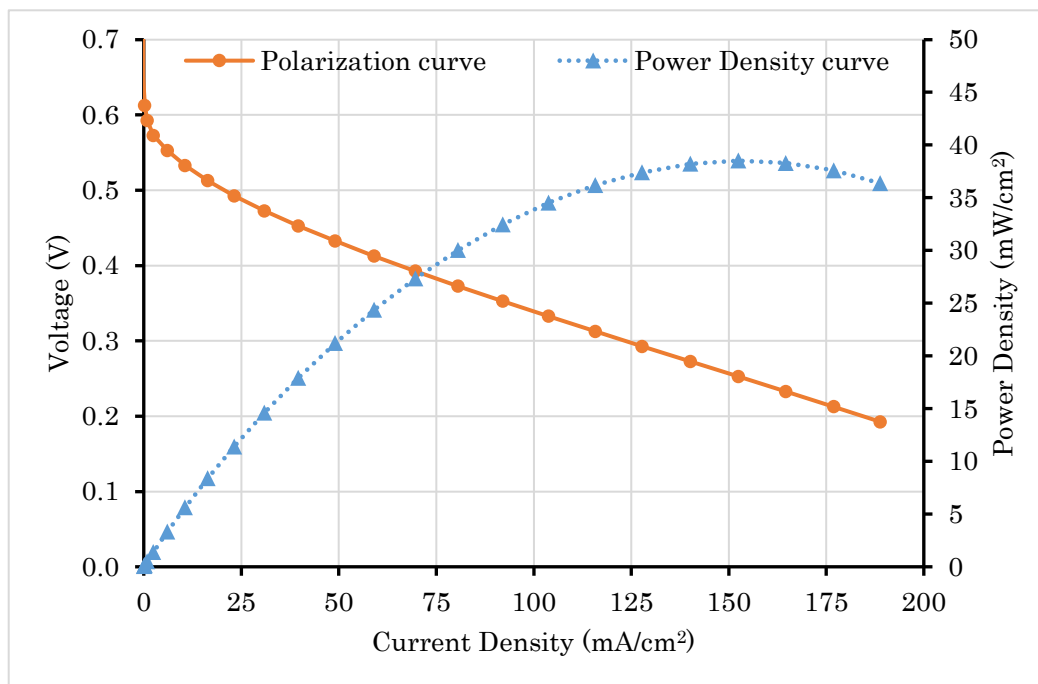


Figure B.40: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

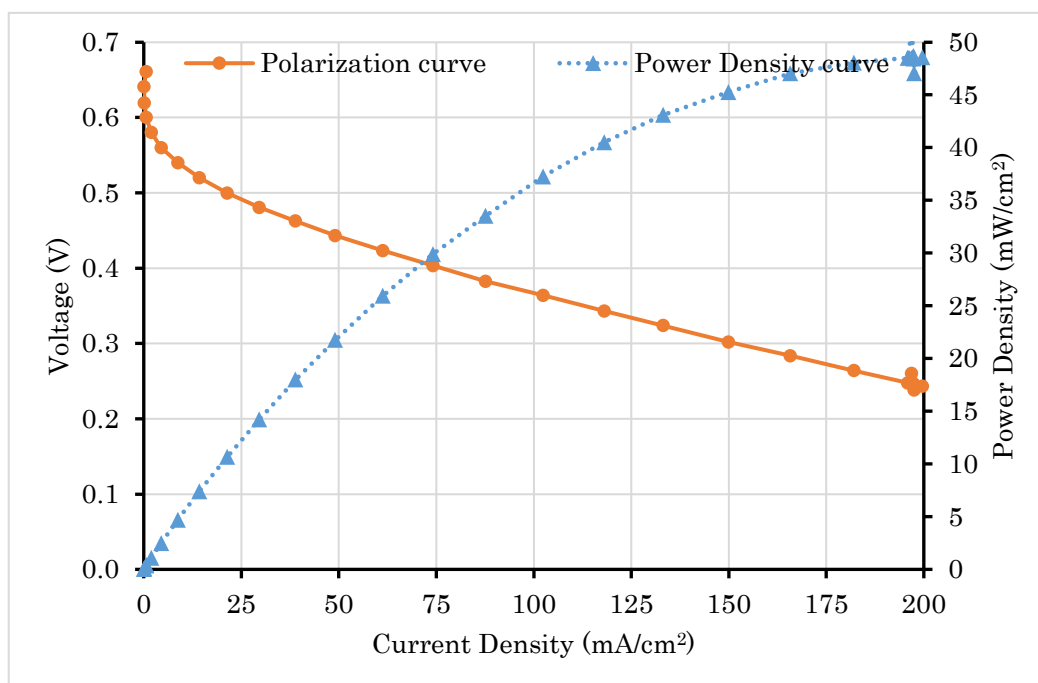


Figure B.41: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

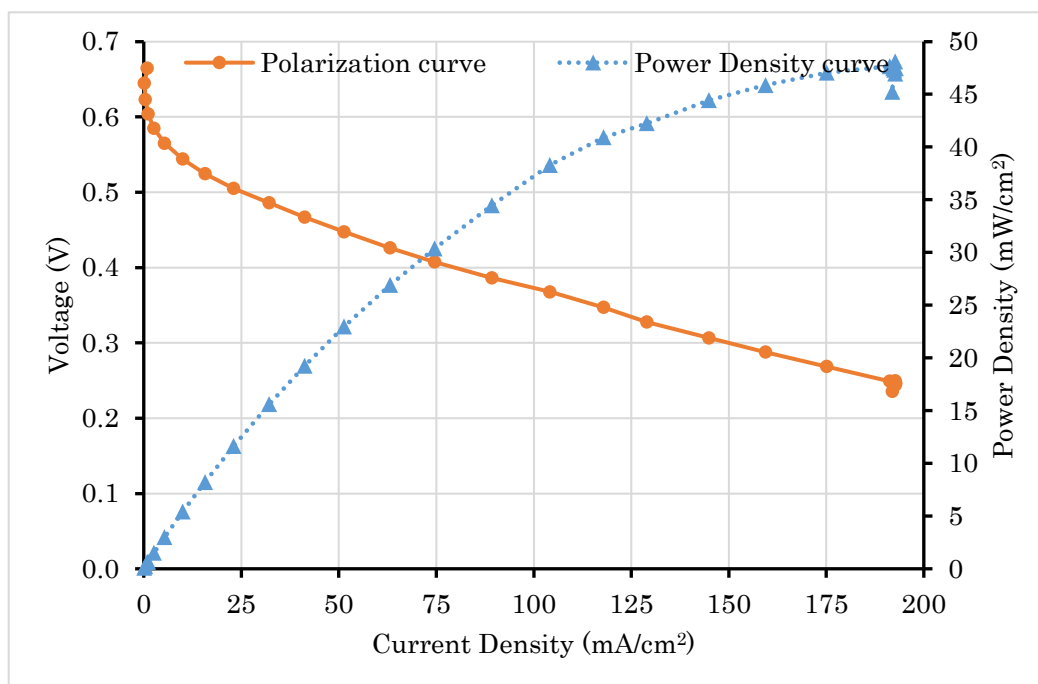


Figure B.42: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

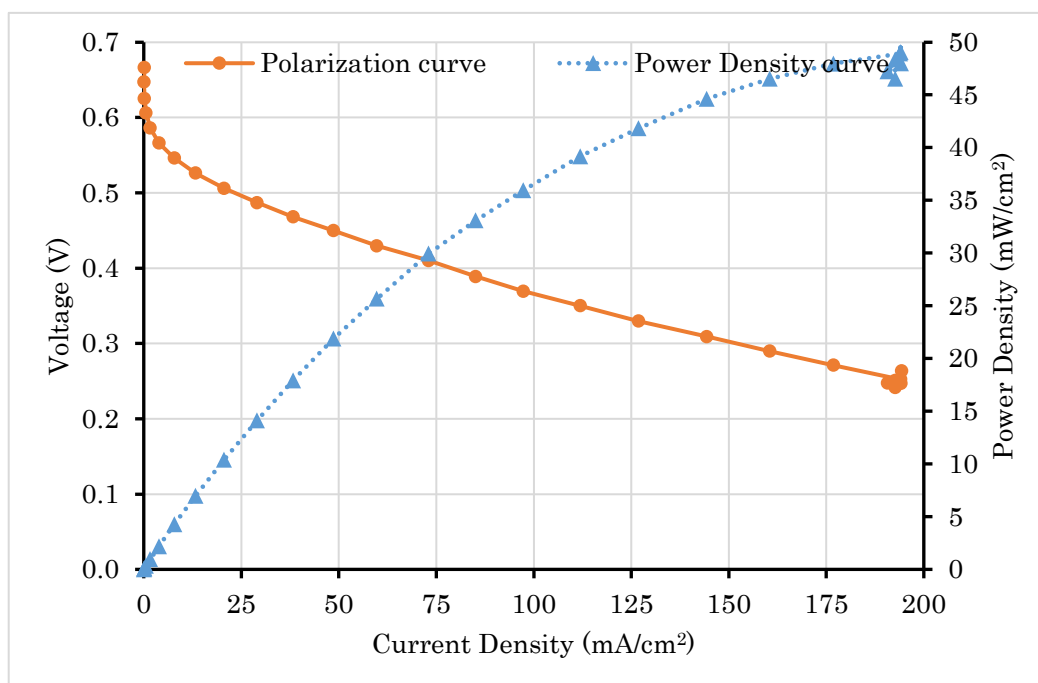


Figure B.43: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

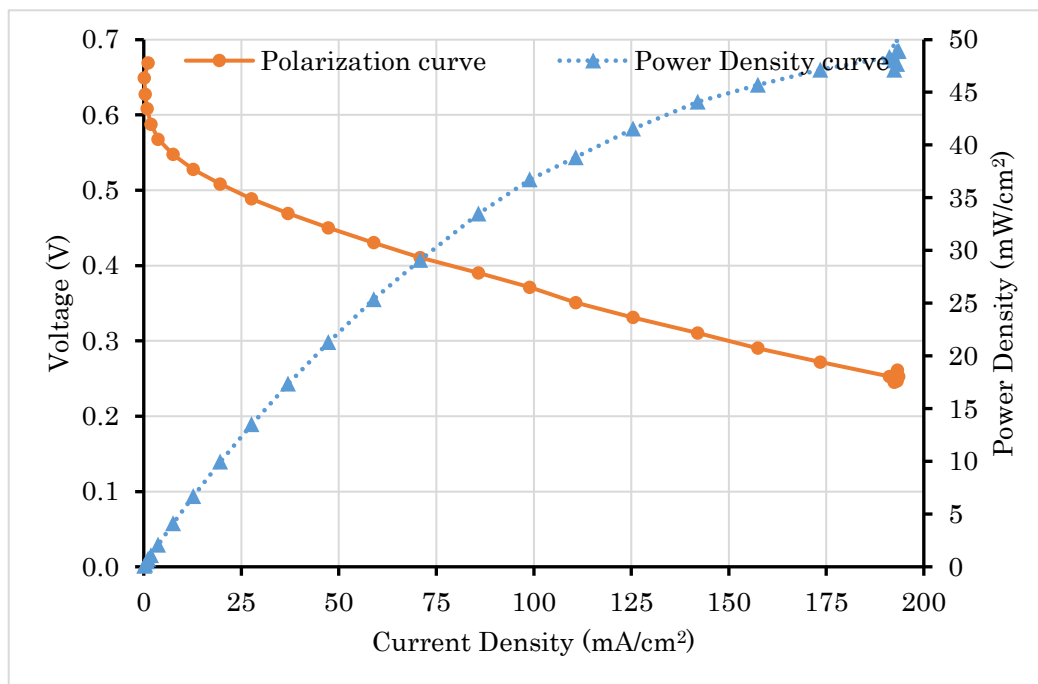


Figure B.44: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

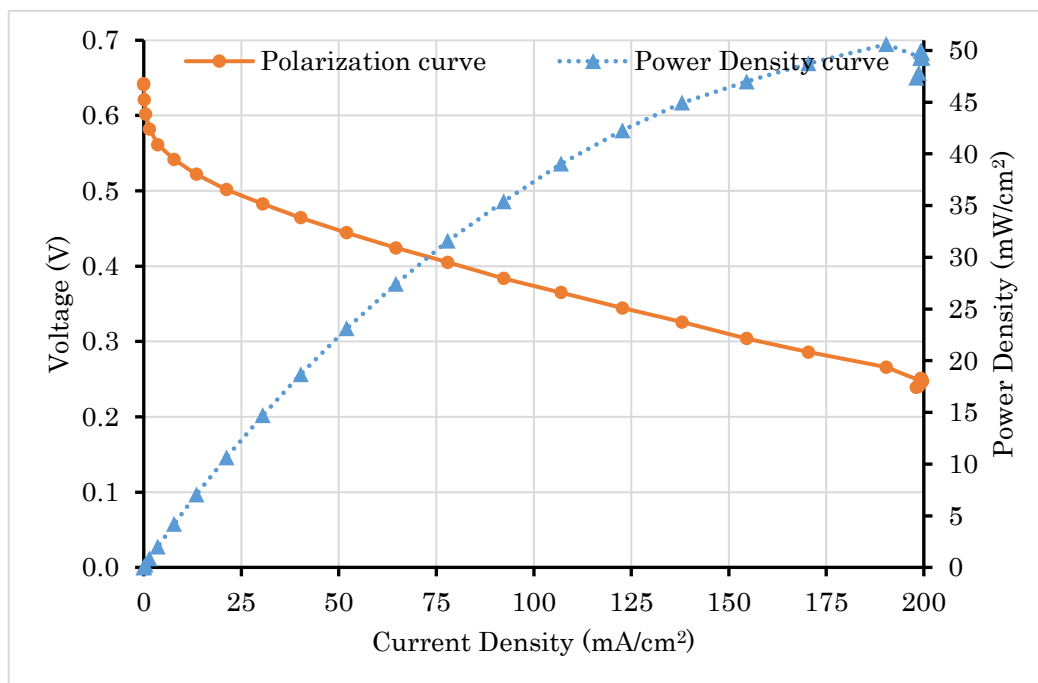


Figure B.45: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

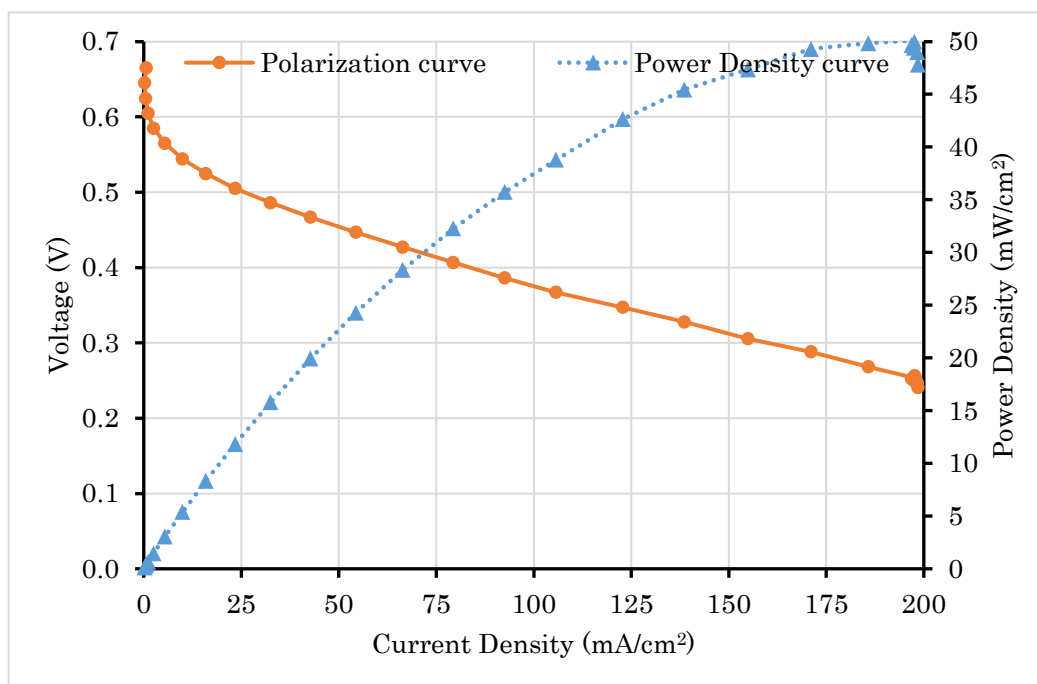


Figure B.46: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

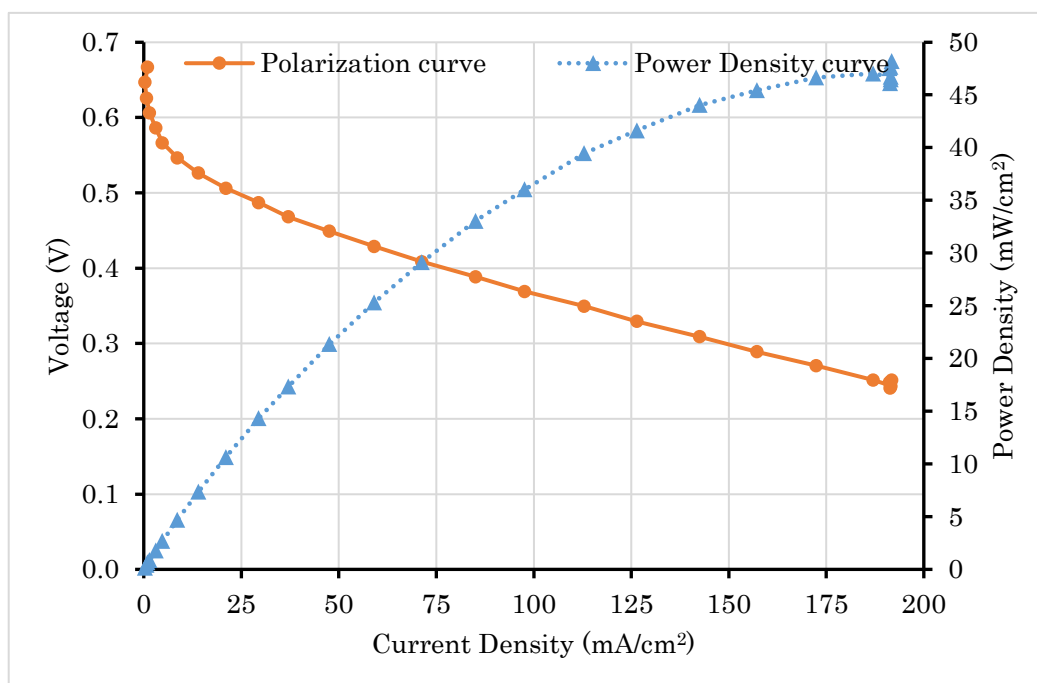


Figure B.47: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

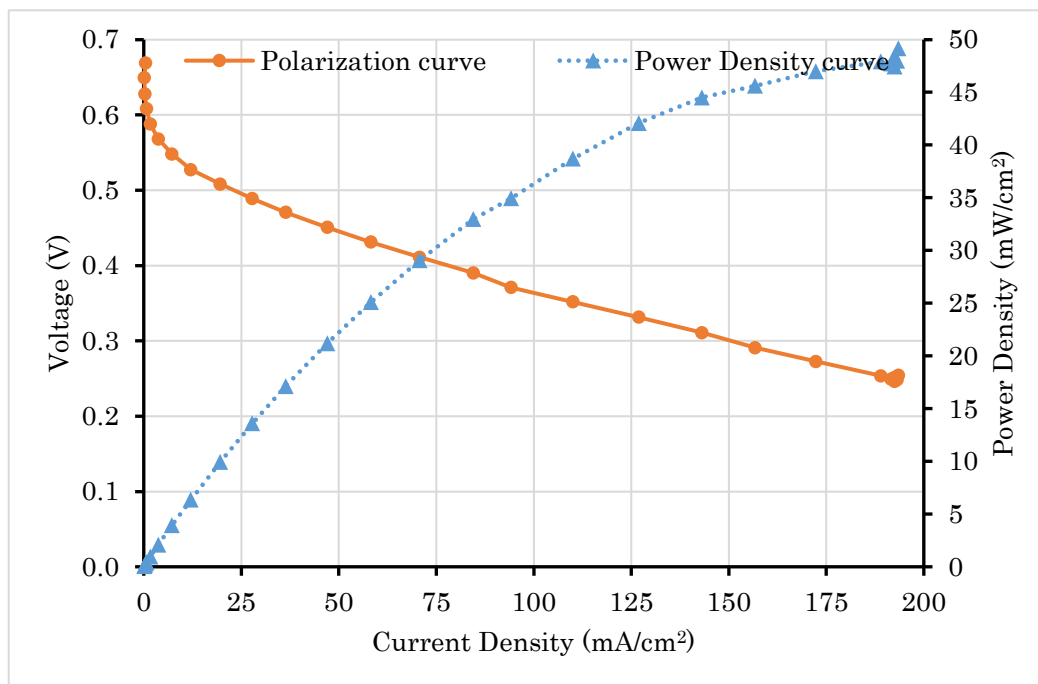


Figure B.48: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

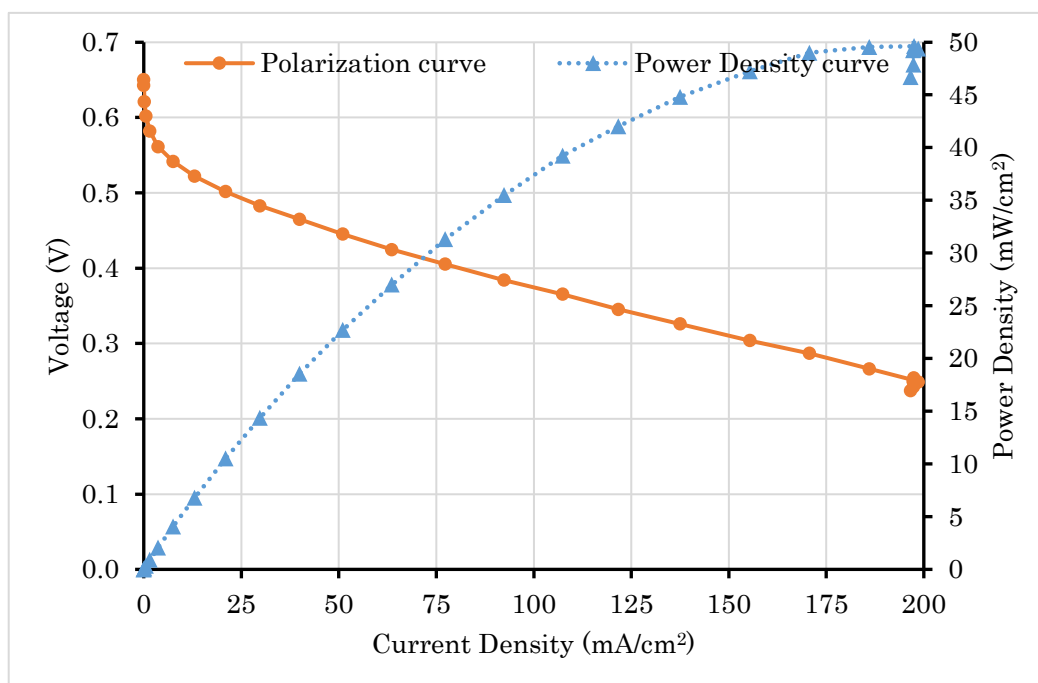


Figure B.49: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

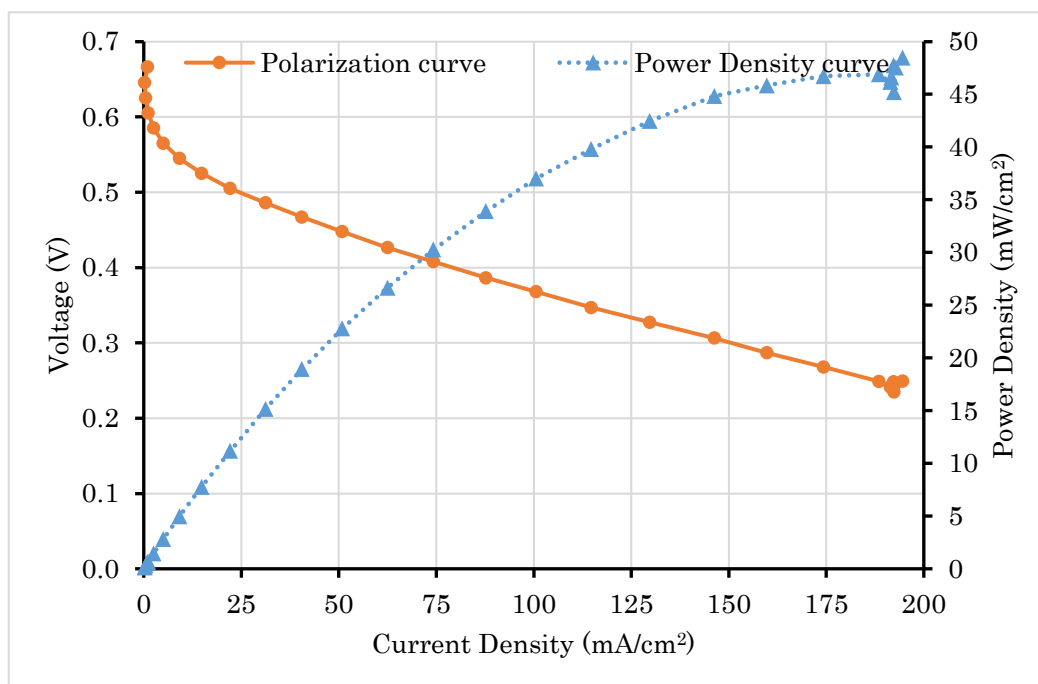


Figure B.50: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

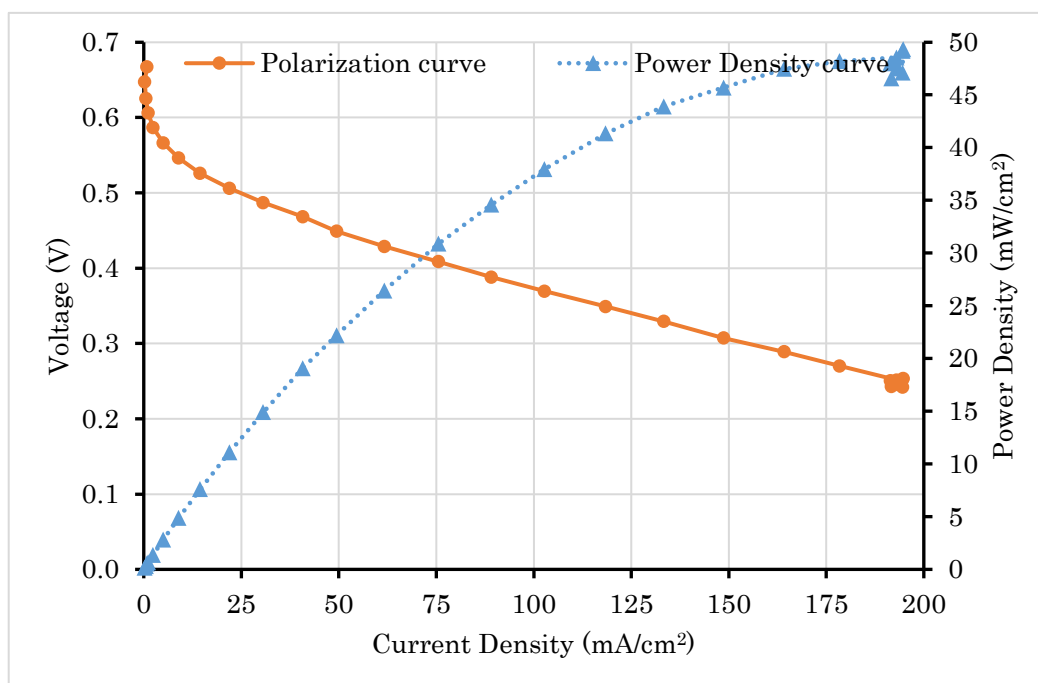


Figure B.51: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

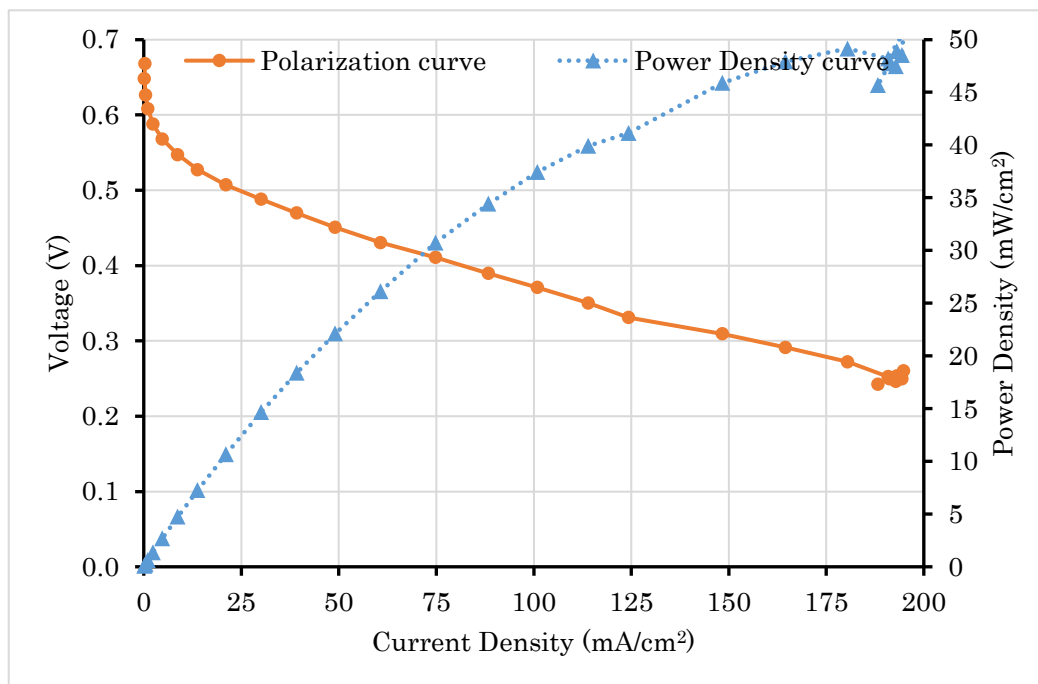


Figure B.52: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

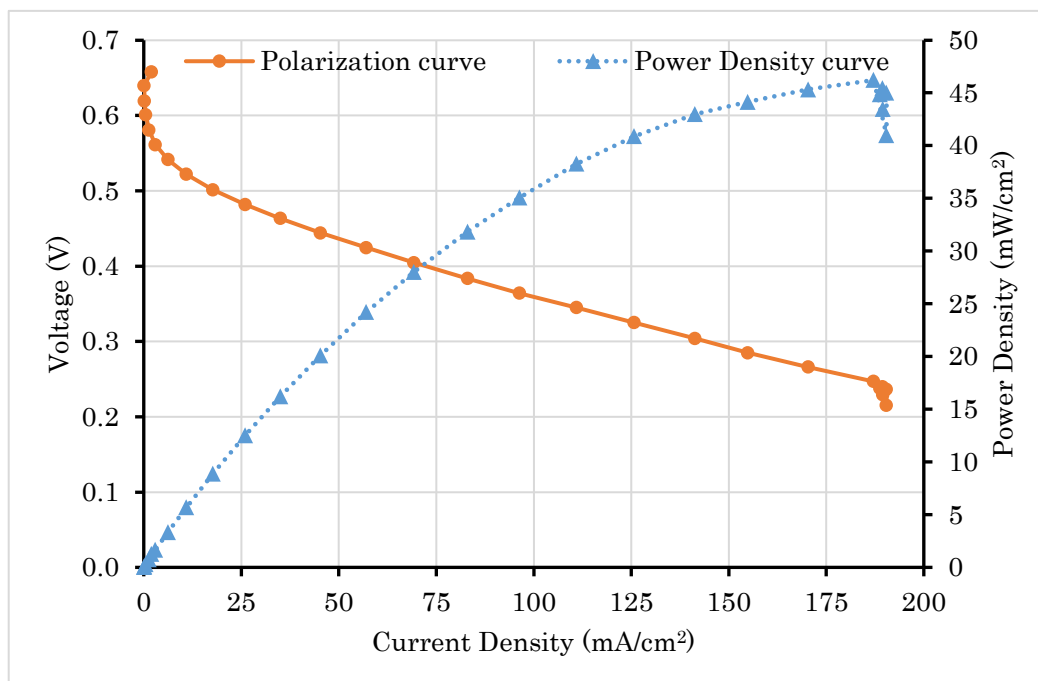


Figure B.53: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

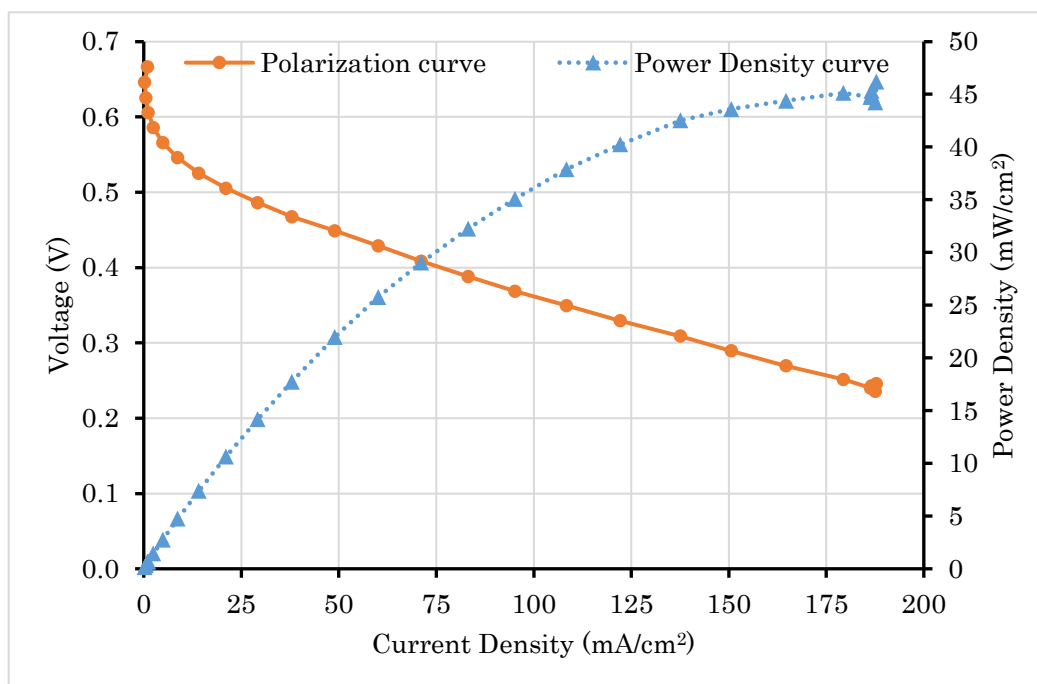


Figure B.54: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

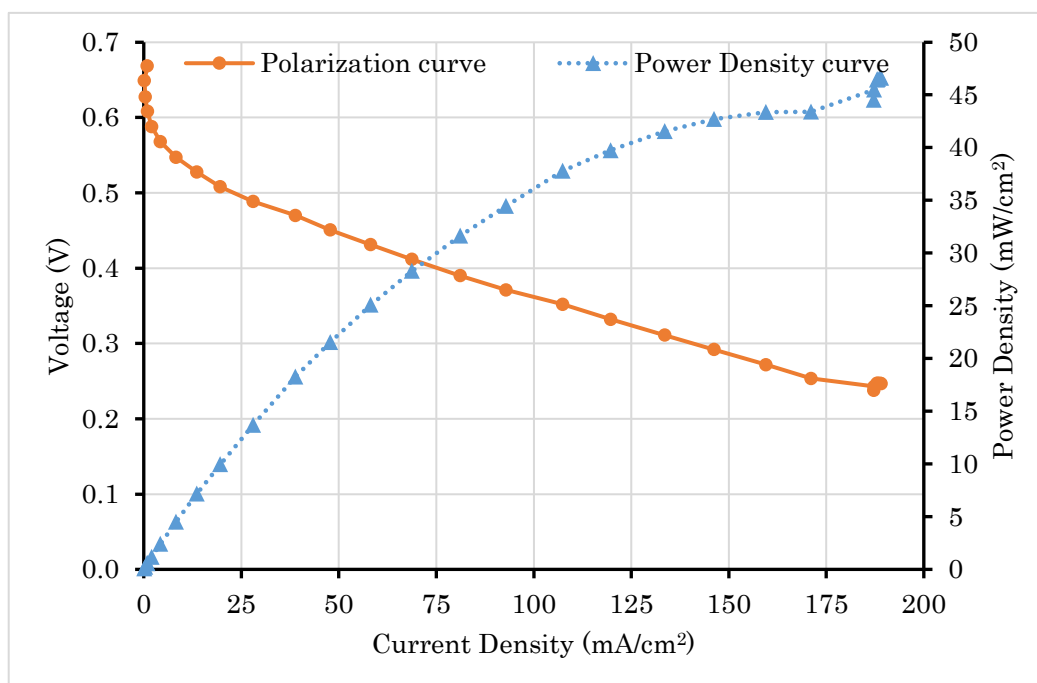


Figure B.55: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

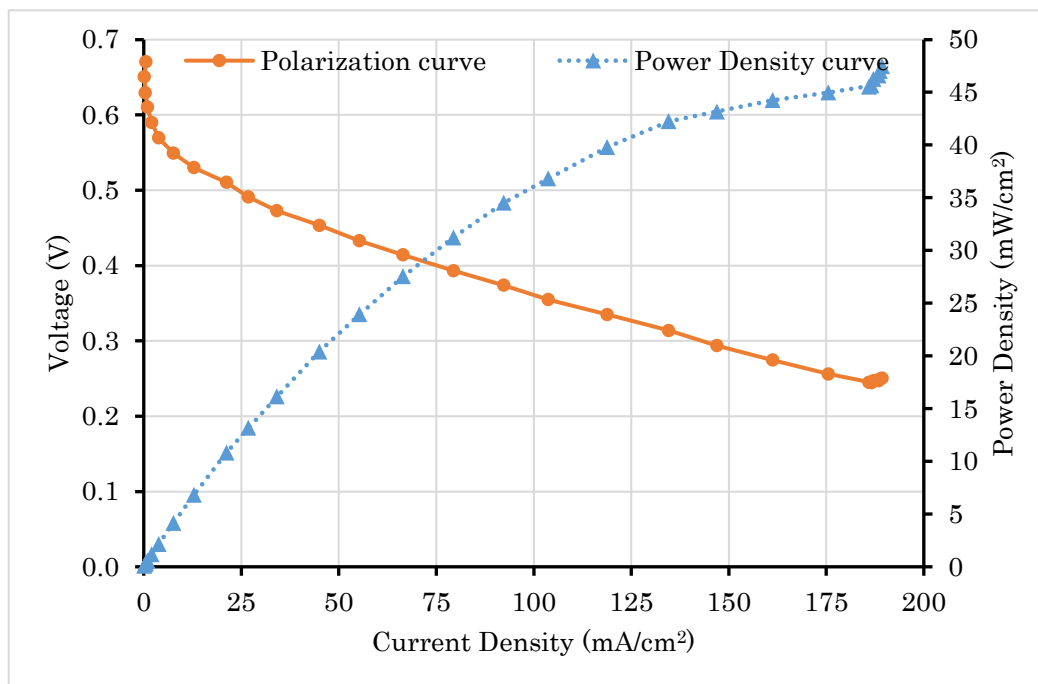


Figure B.56: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

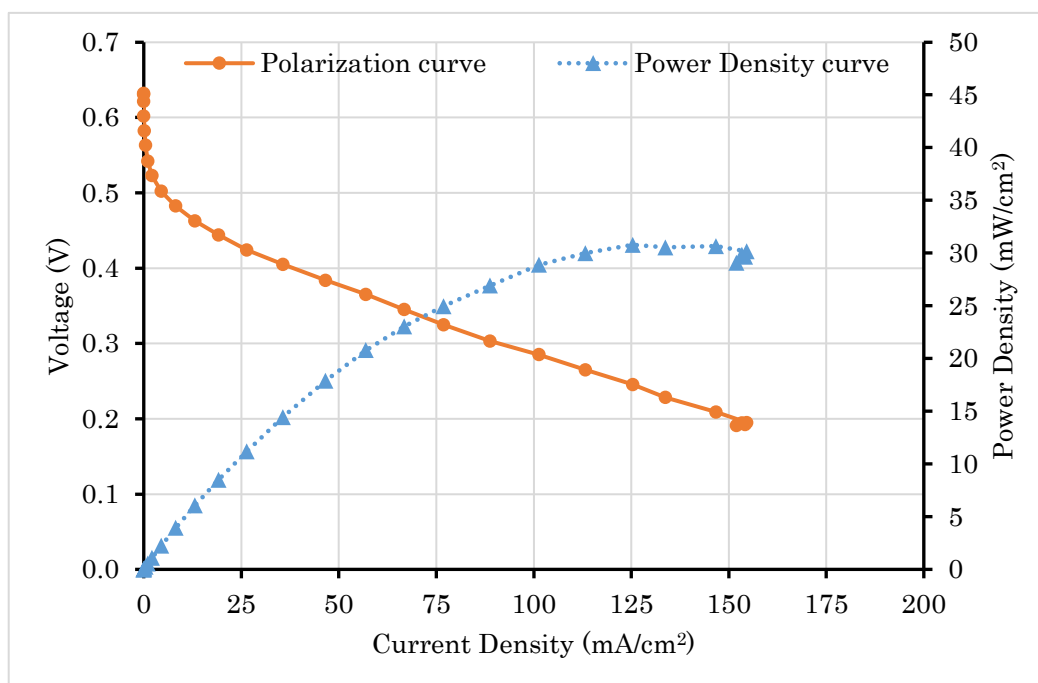


Figure B.57: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

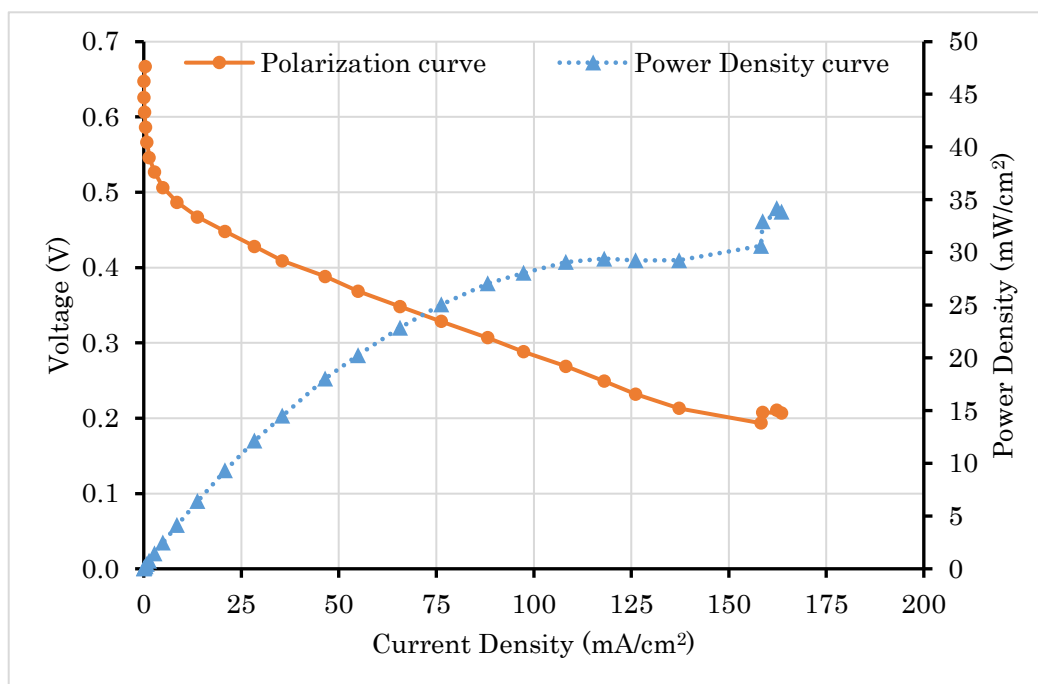


Figure B.58: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

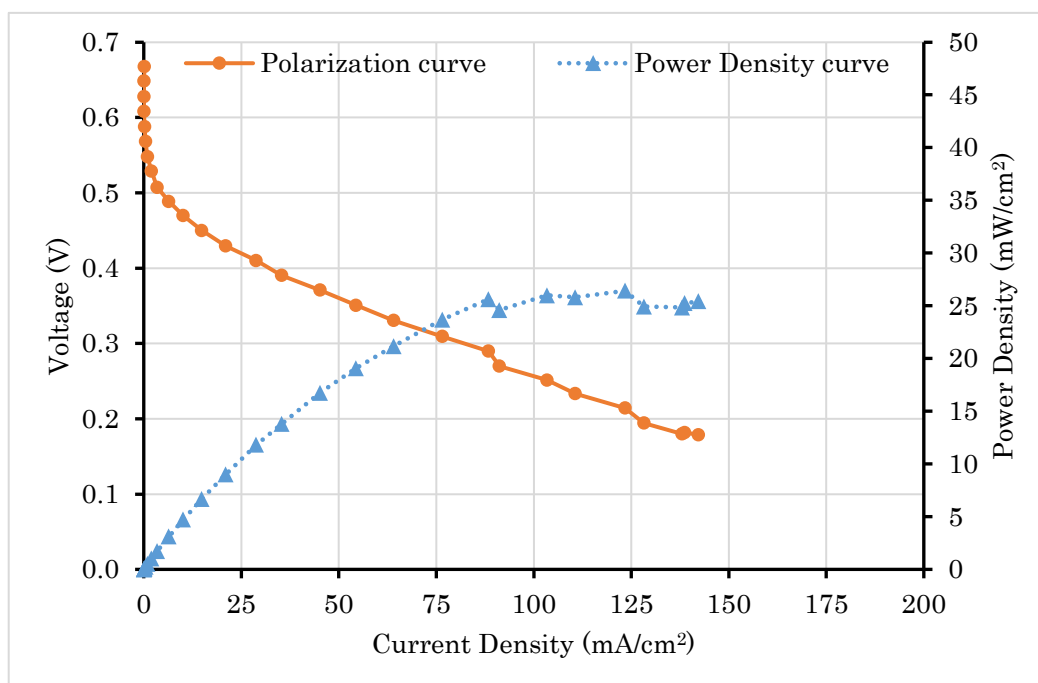


Figure B.59: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

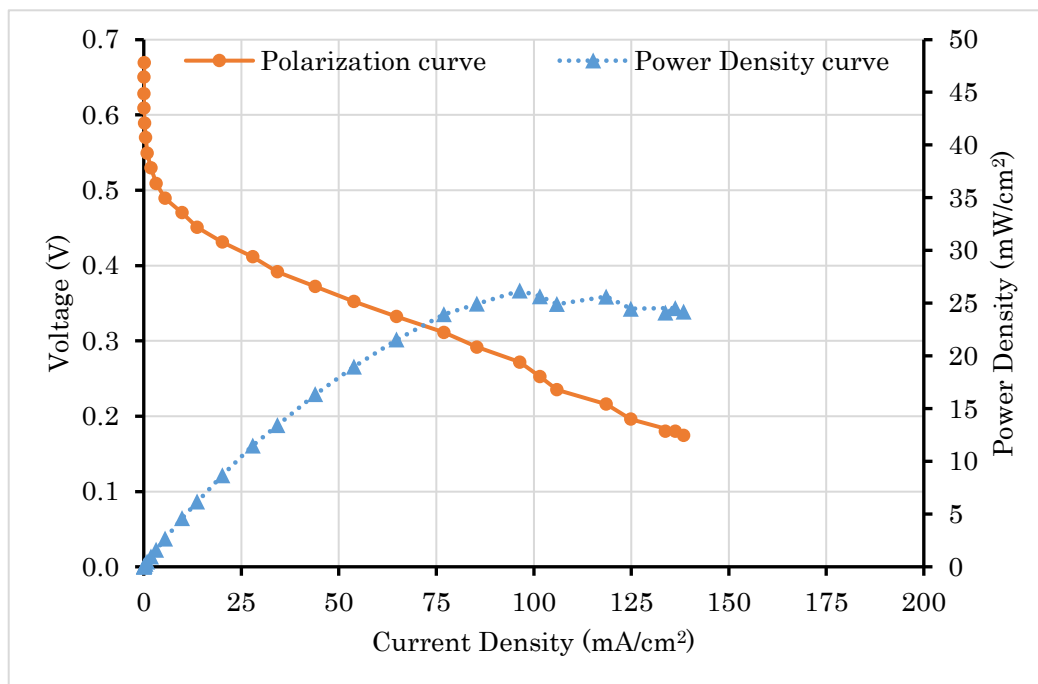


Figure B.60: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

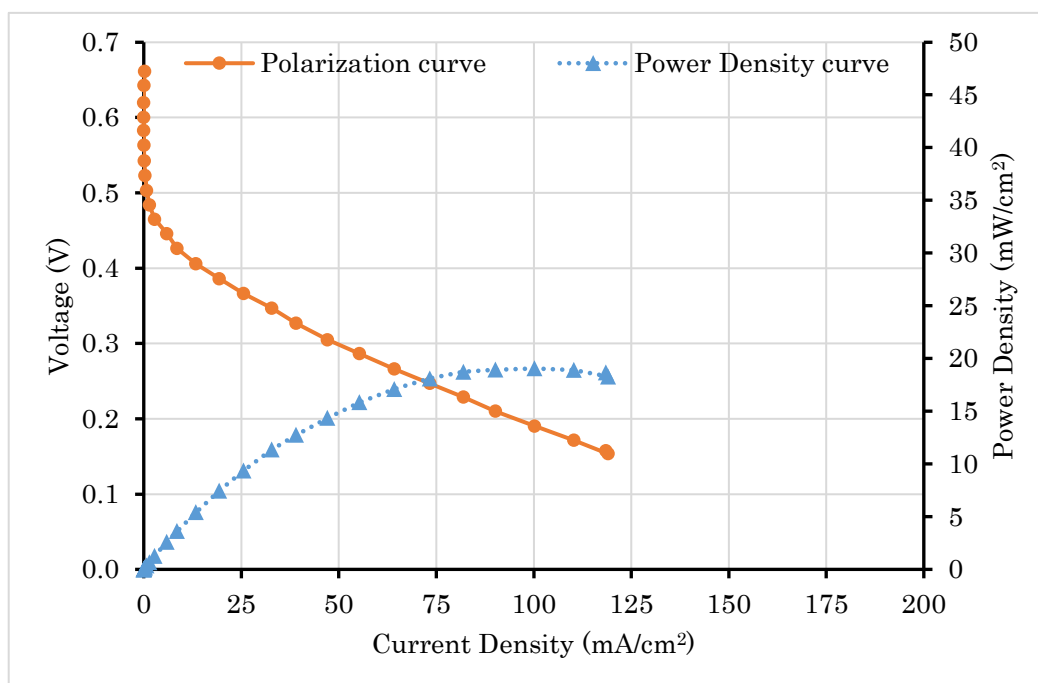


Figure B.61: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 32.7 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

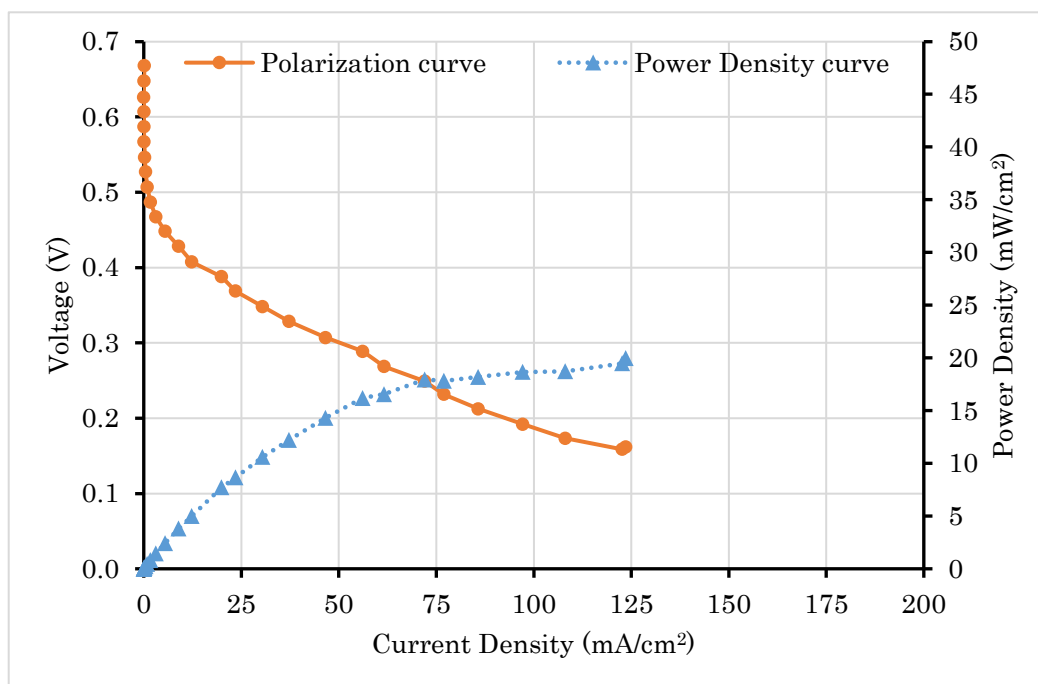


Figure B.62: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 32.7 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

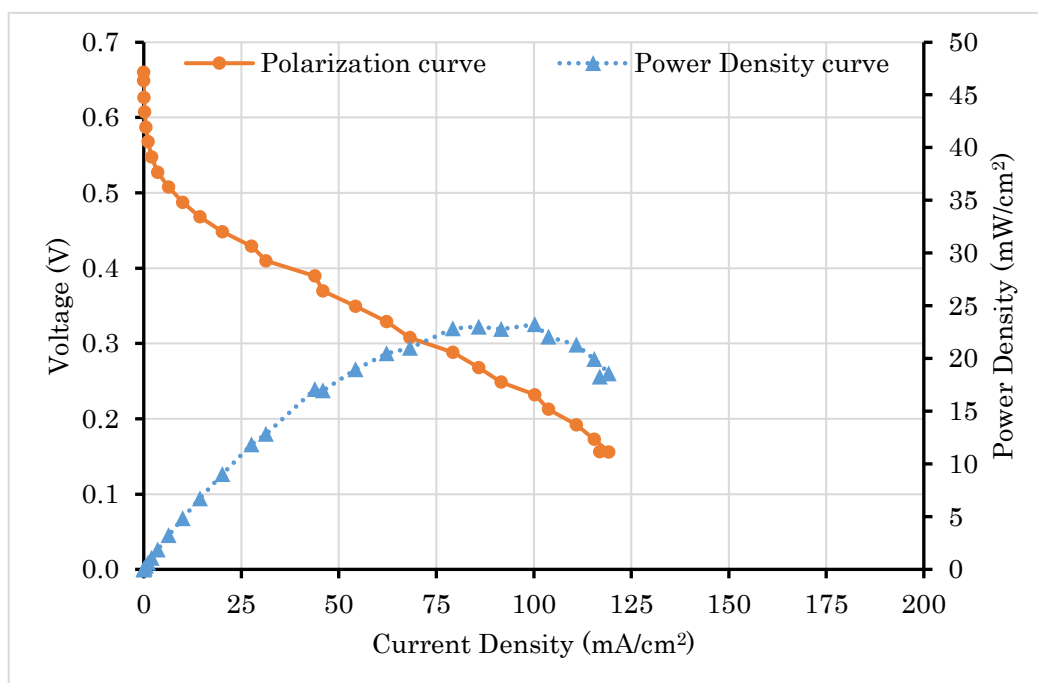


Figure B.63: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 67.3 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

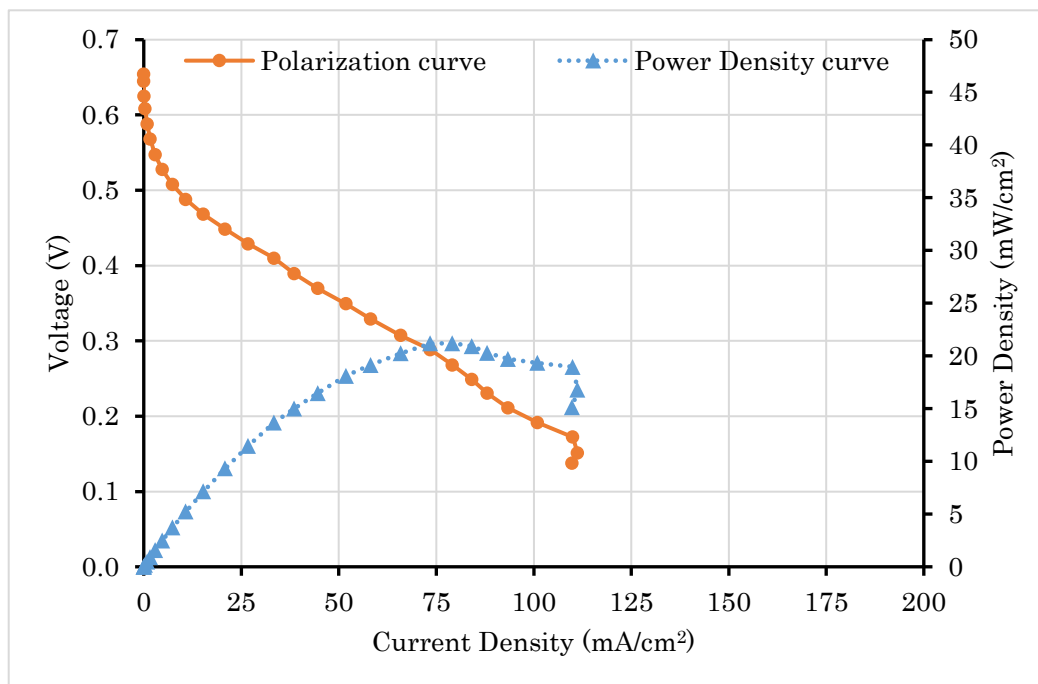


Figure B.64: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 67.3 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

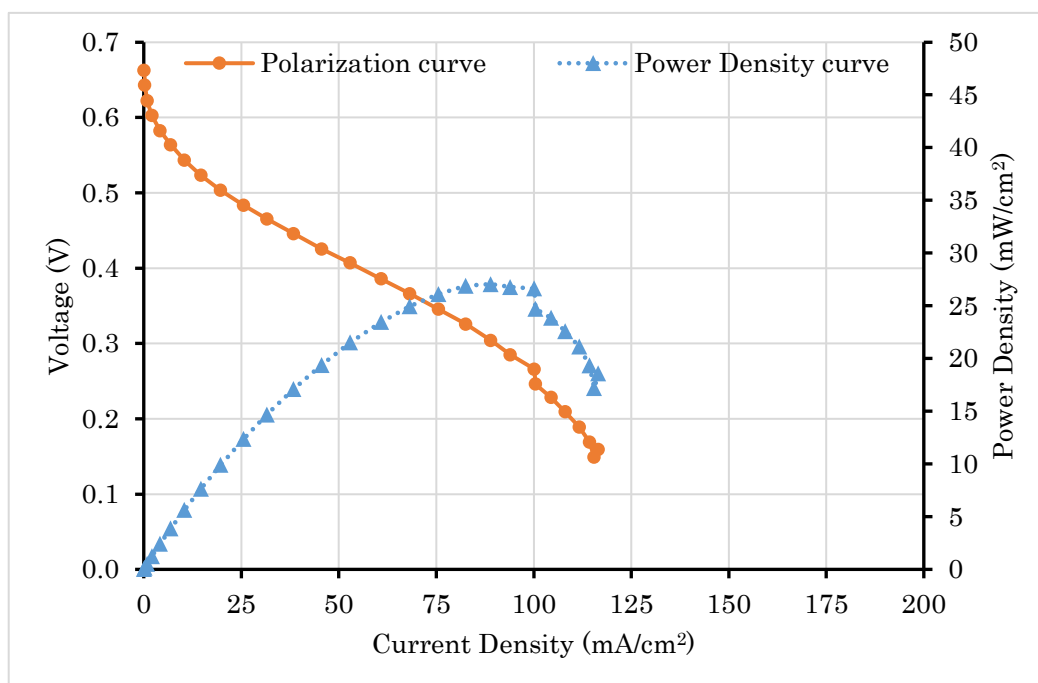


Figure B.65: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

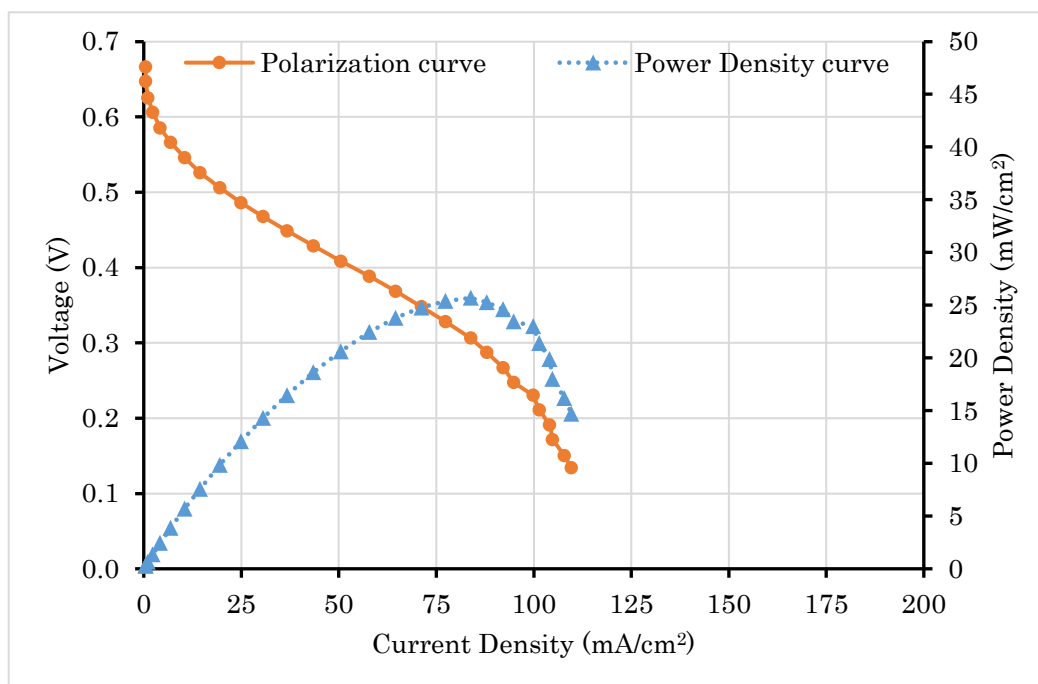


Figure B.66: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

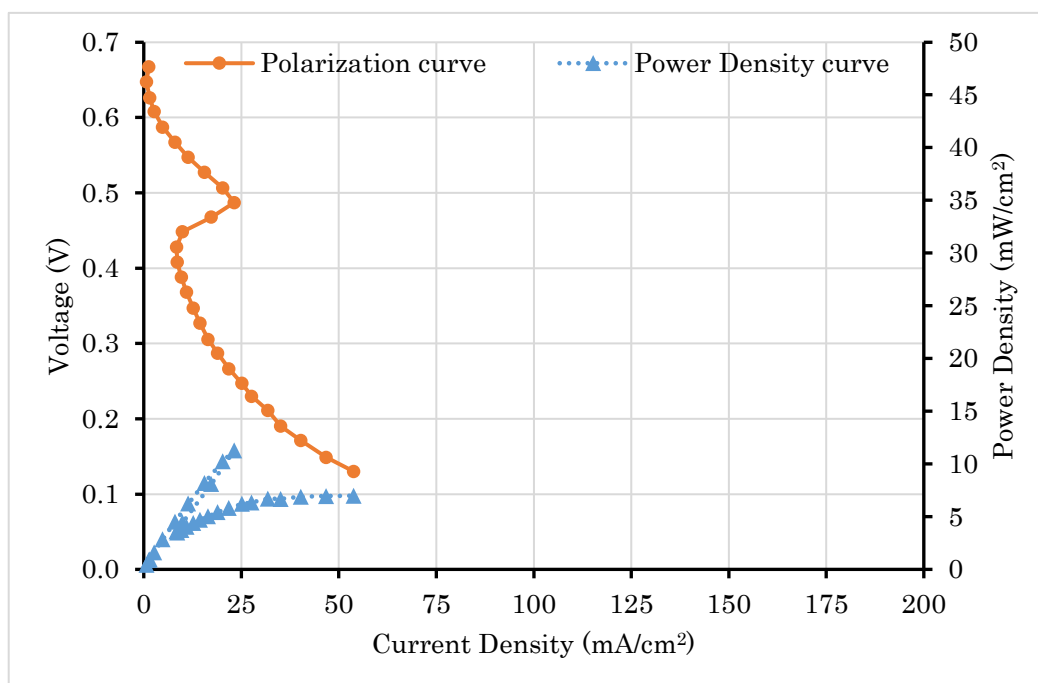


Figure B.67: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

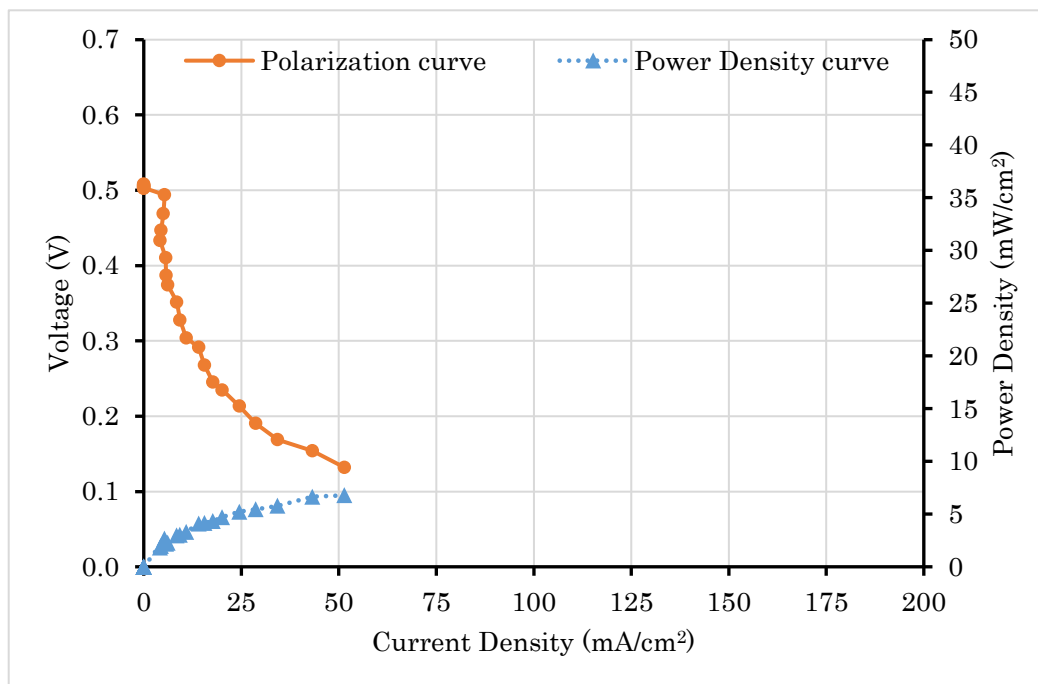


Figure B.68: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 50.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

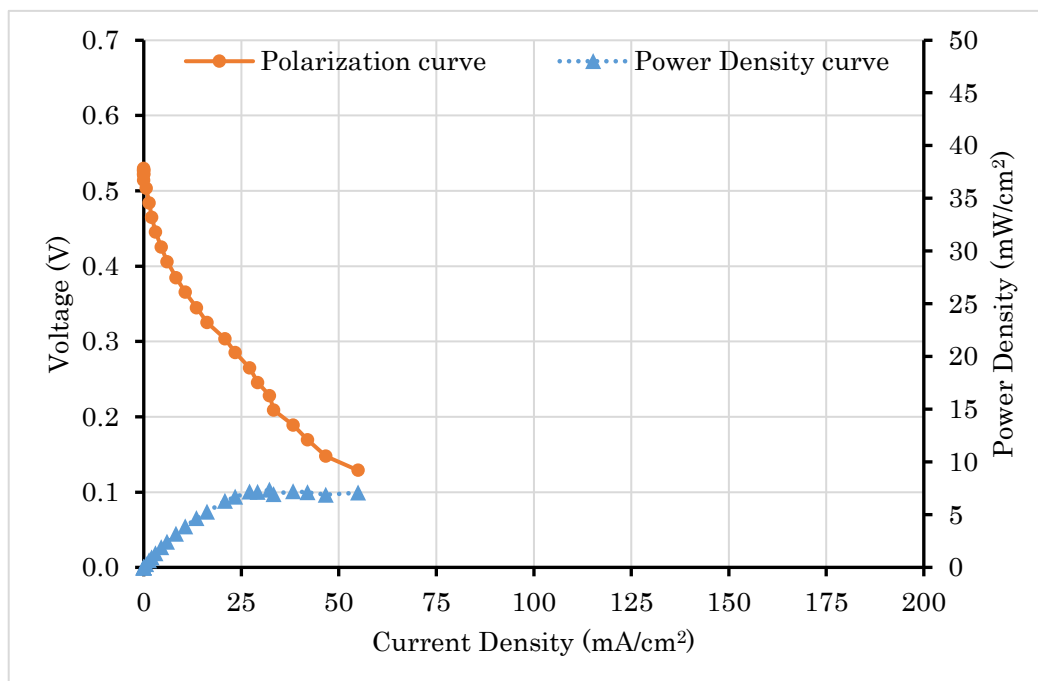


Figure B.69: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

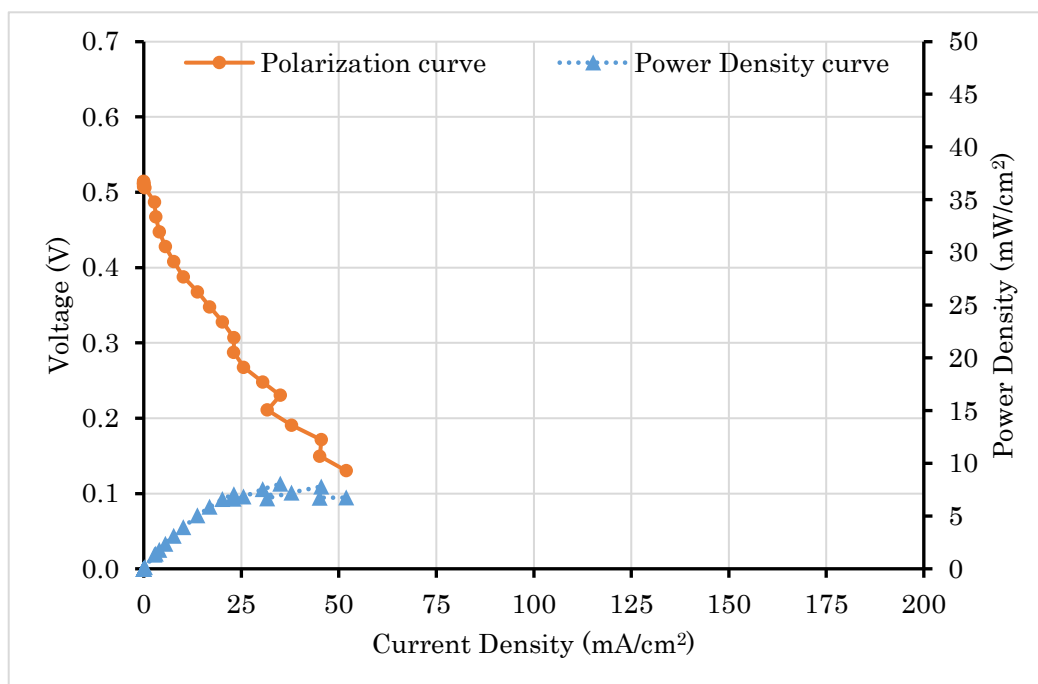


Figure B.70: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

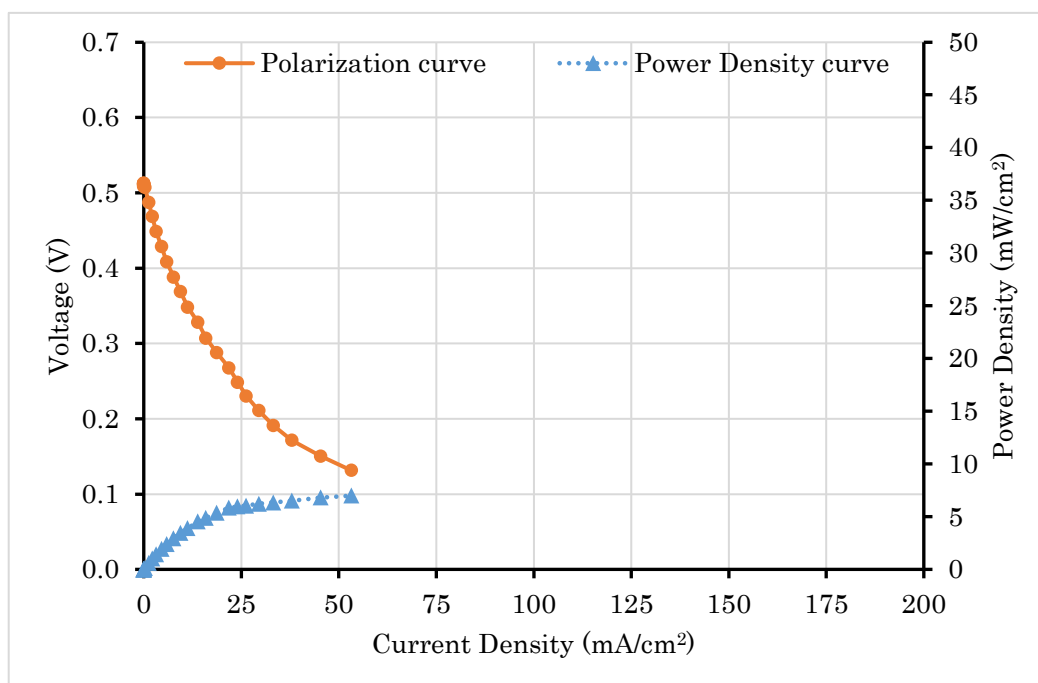


Figure B.71: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

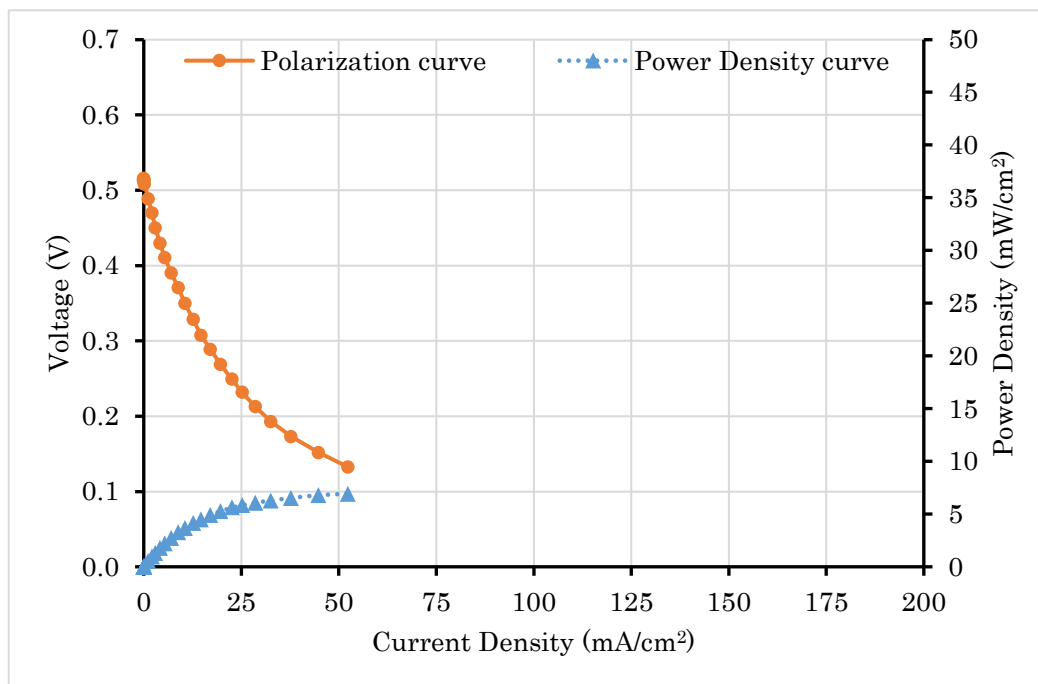


Figure B.72: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

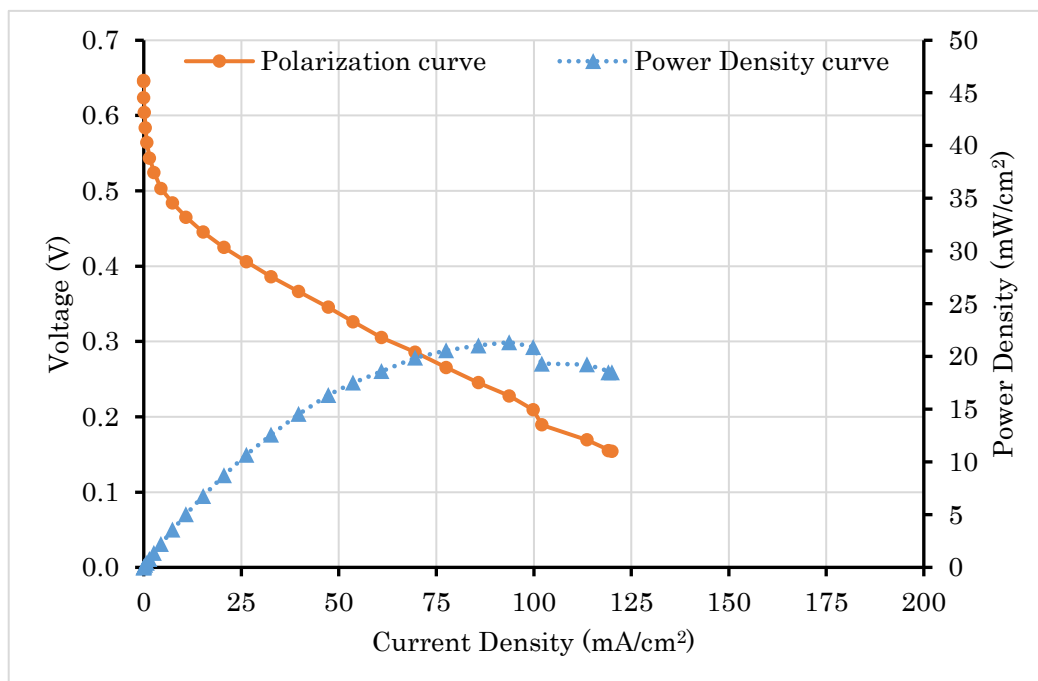


Figure B.73: Polarization curve and Power Density curve of the Direct Methanol Fuel Cell (DMFC) single cell obtained at a temperature of 60.0 °C, cathode pressure 1 bar, oxygen flow rate 110 ml/min, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

Annex C Polarization and Power Density curves of Methanol Electrolysis Cell

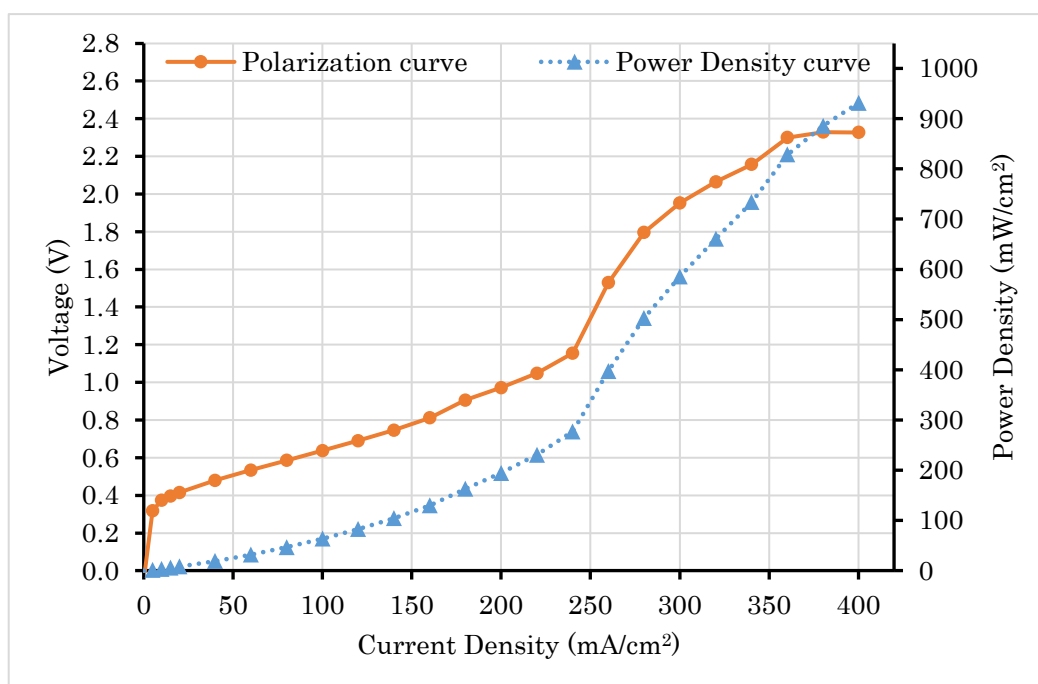


Figure C.1: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

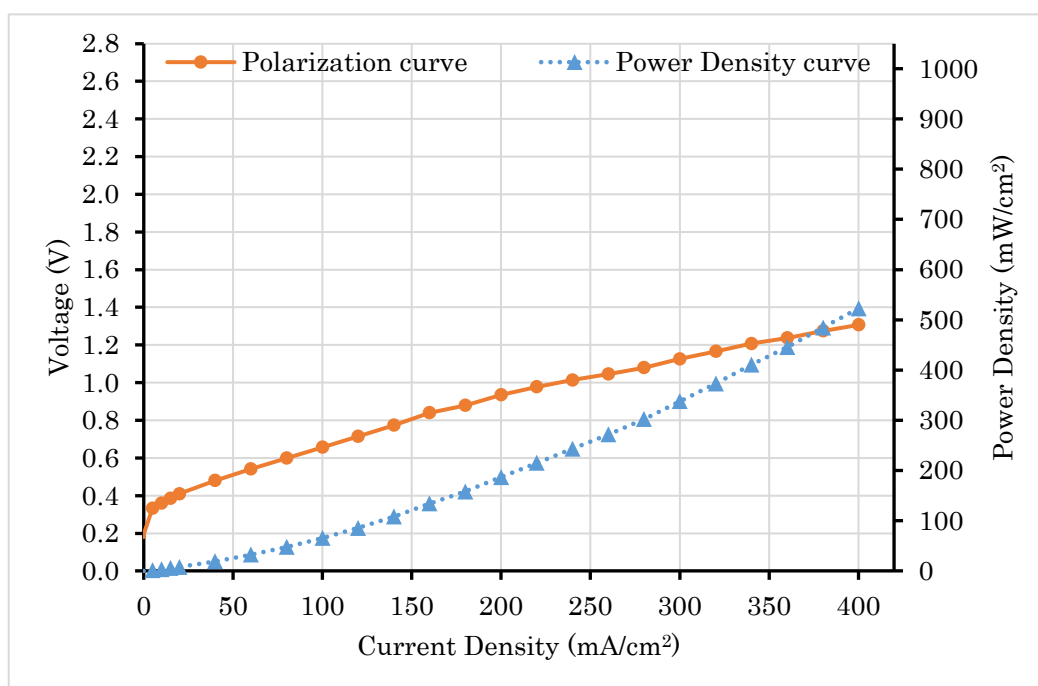


Figure C.2: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

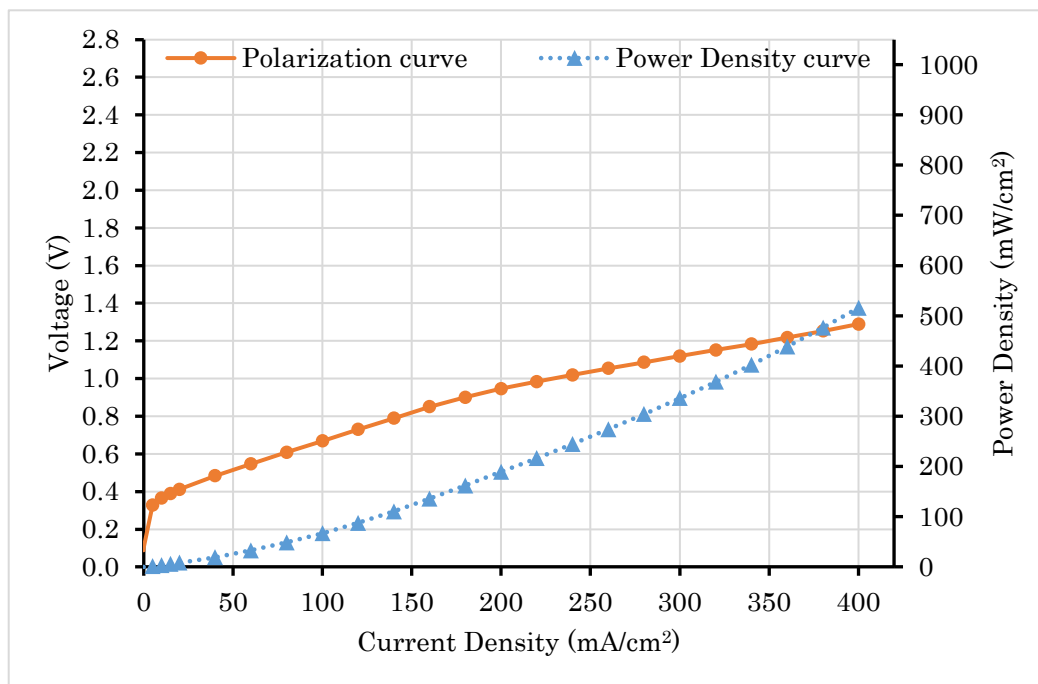


Figure C.3: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

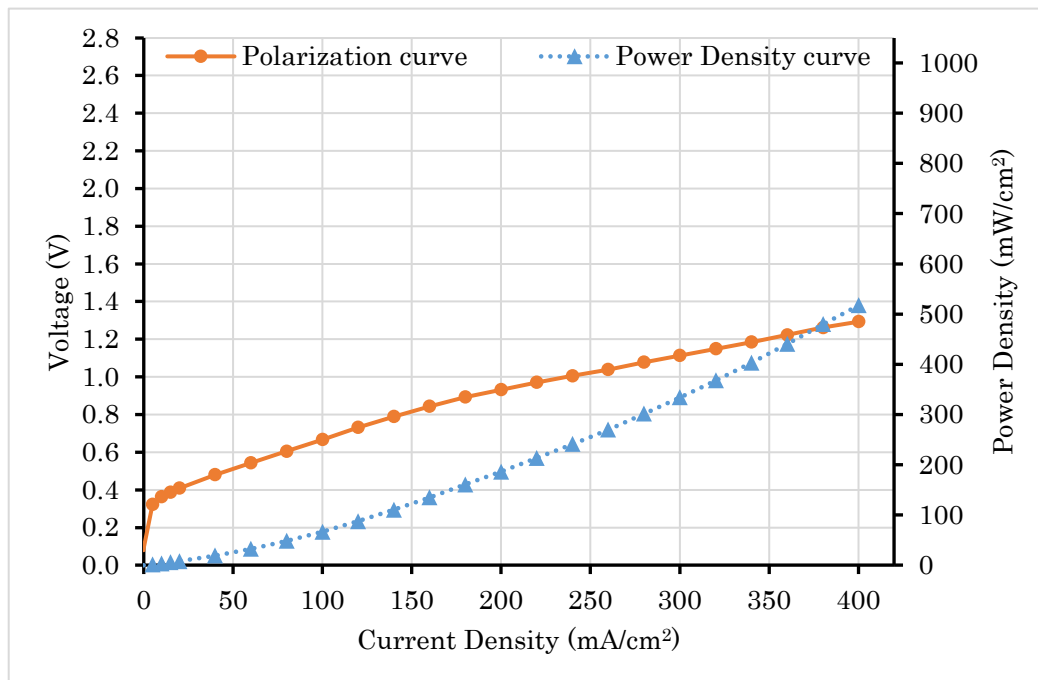


Figure C.4: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

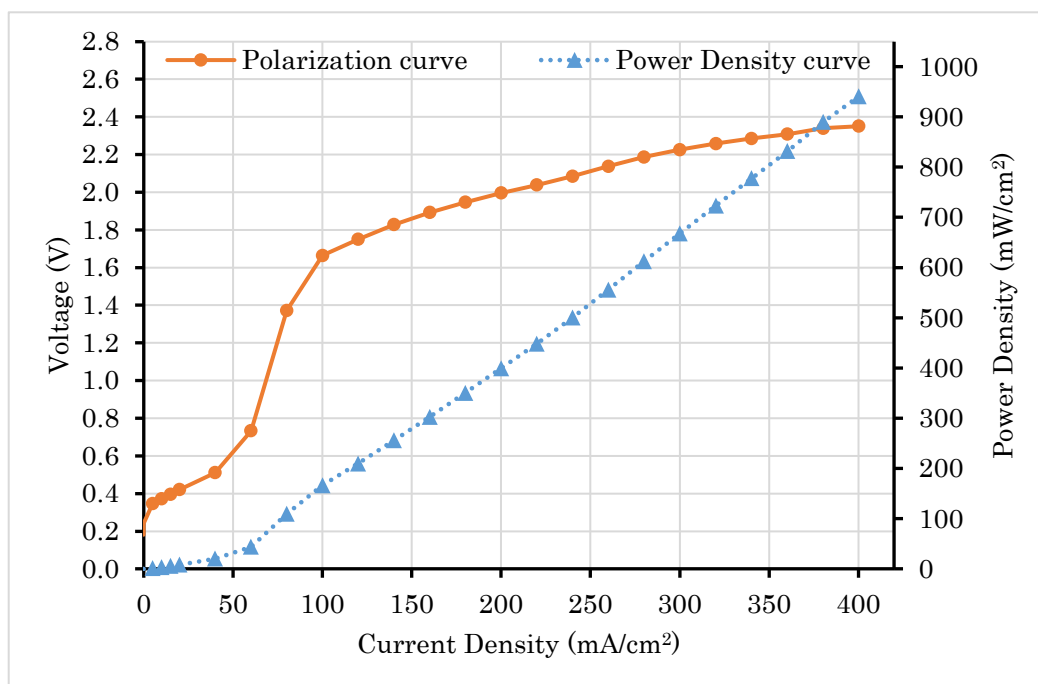


Figure C.5: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

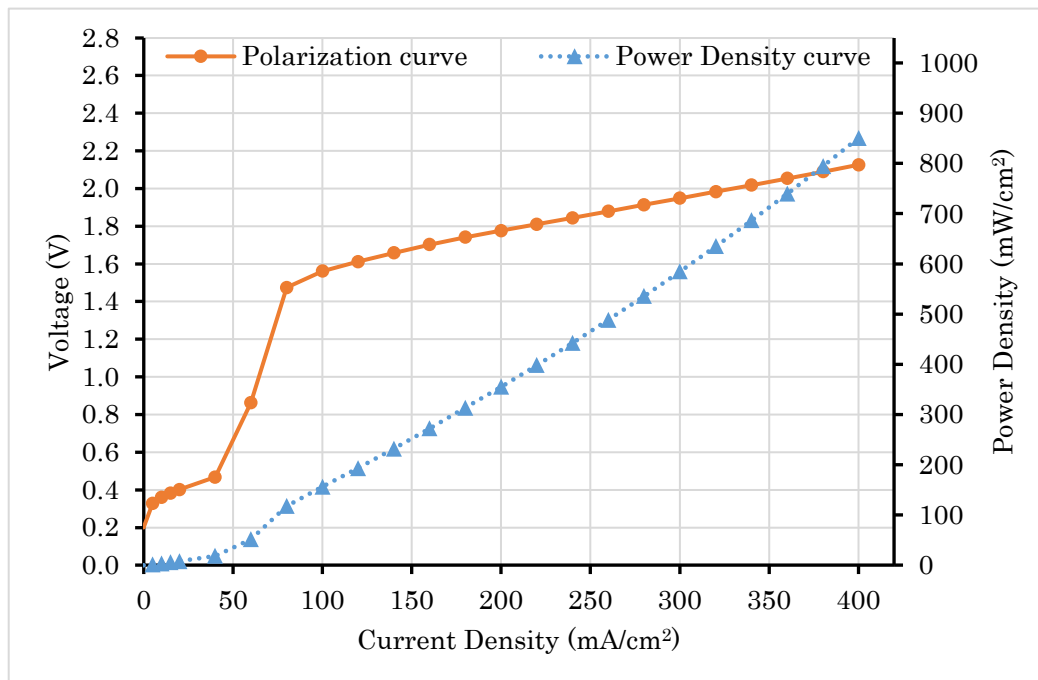


Figure C.6: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

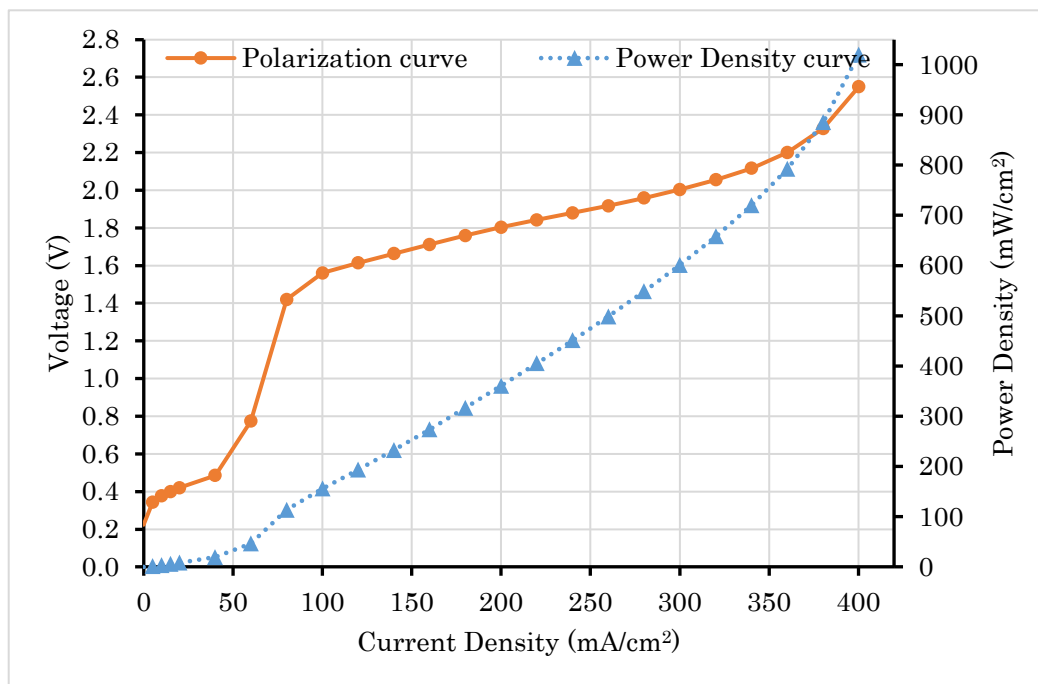


Figure C.7: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

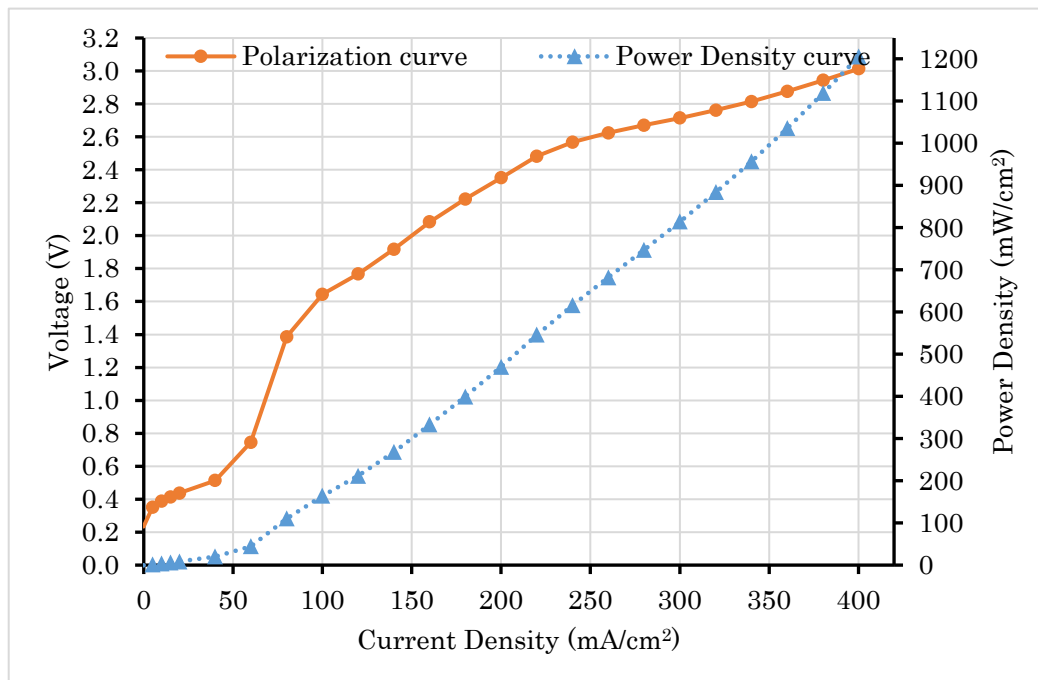


Figure C.8: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 0.27 M and methanol volumetric flow rate 4.50 ml/min.

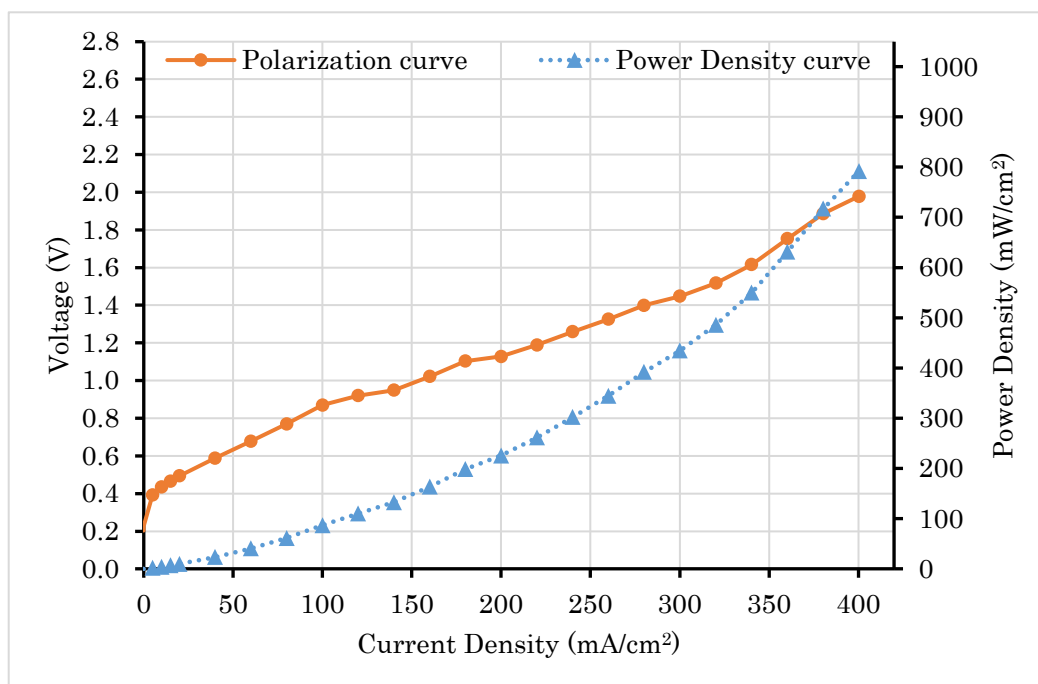


Figure C.9: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

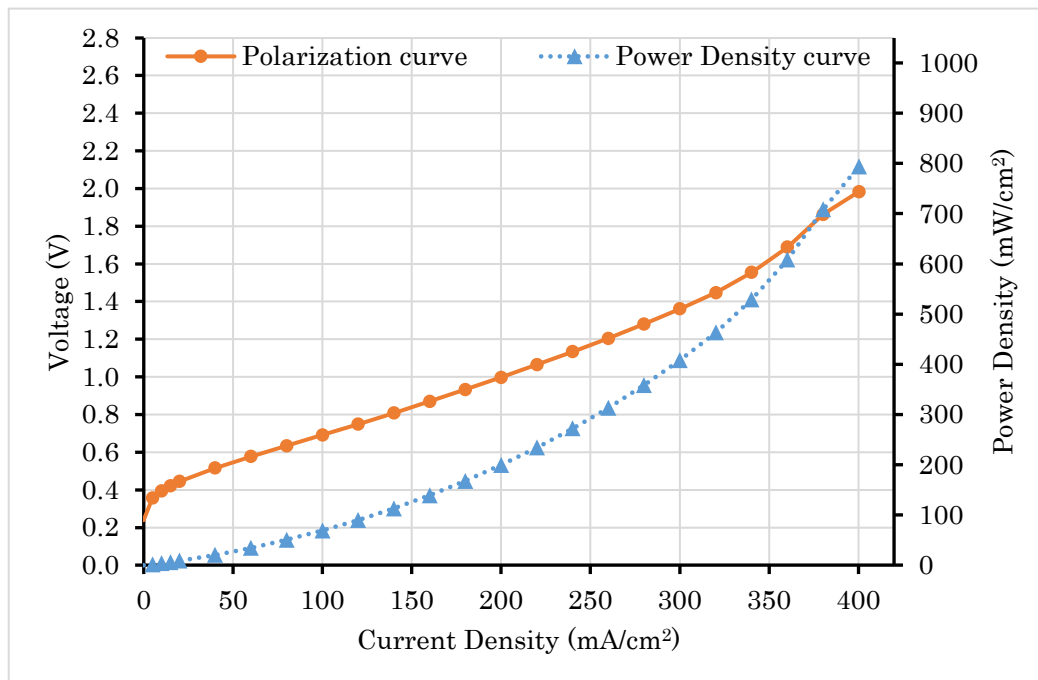


Figure C.10: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

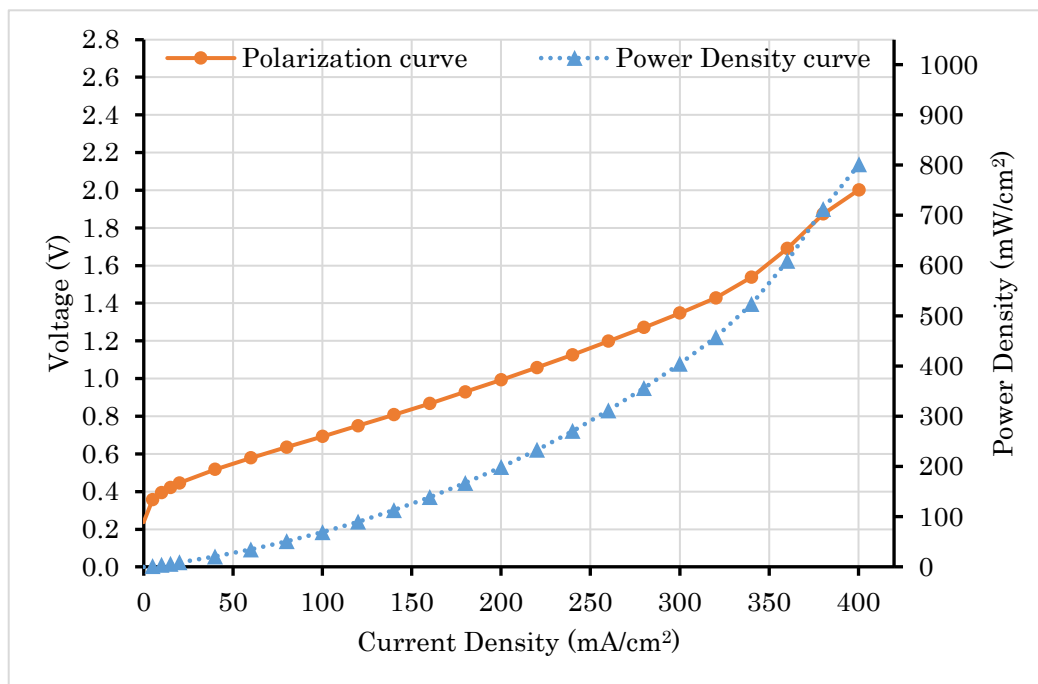


Figure C.11: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

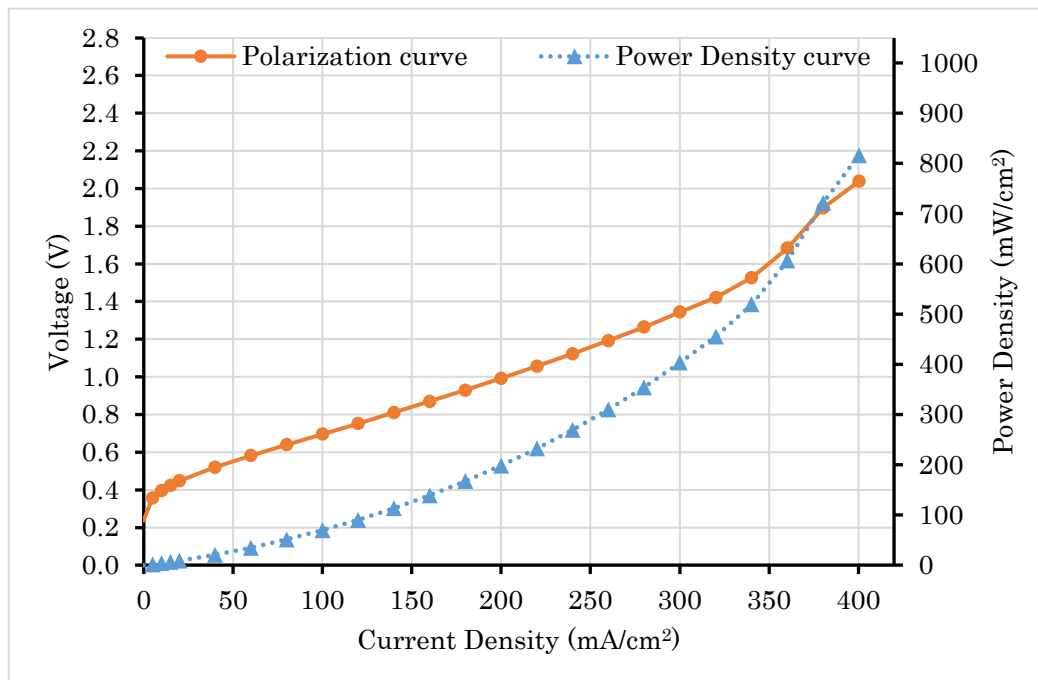


Figure C.12: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

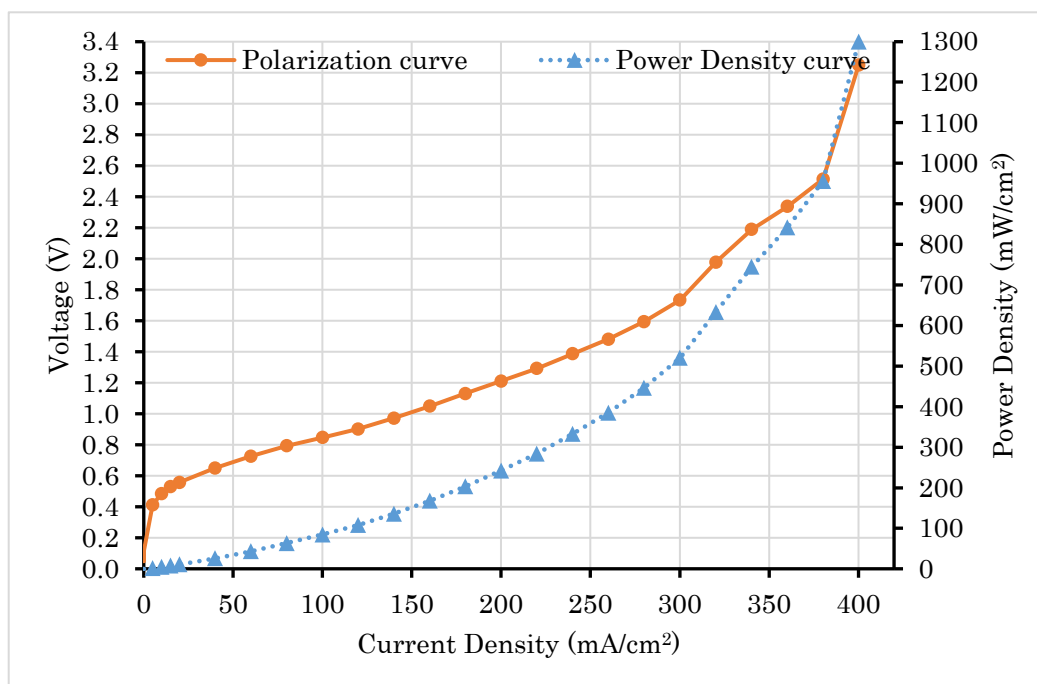


Figure C.13: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

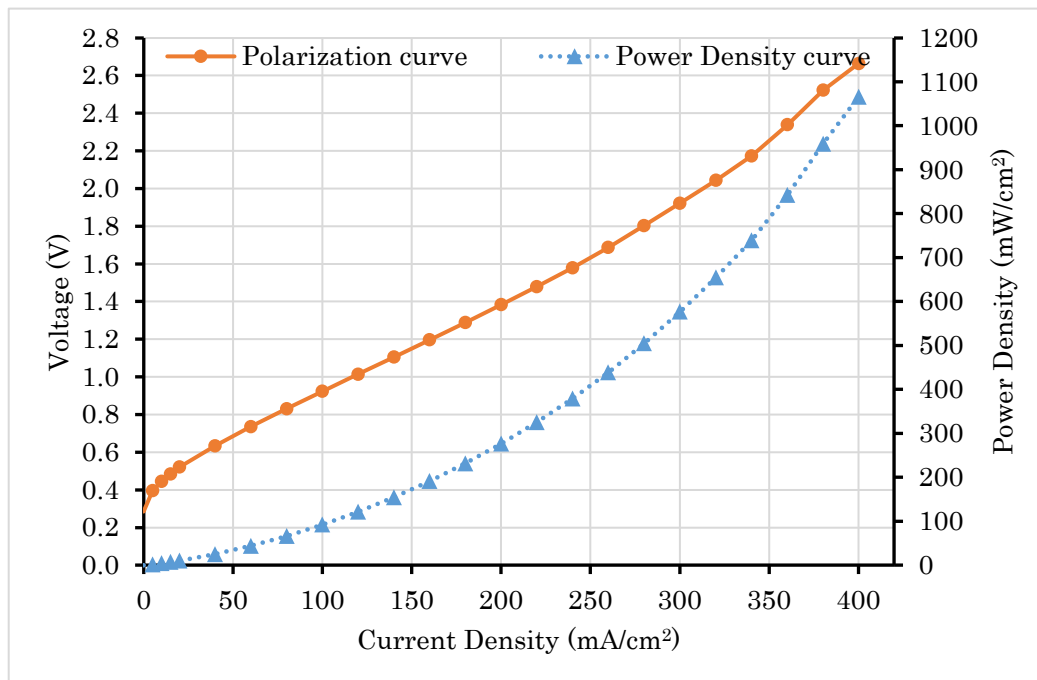


Figure C.14: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

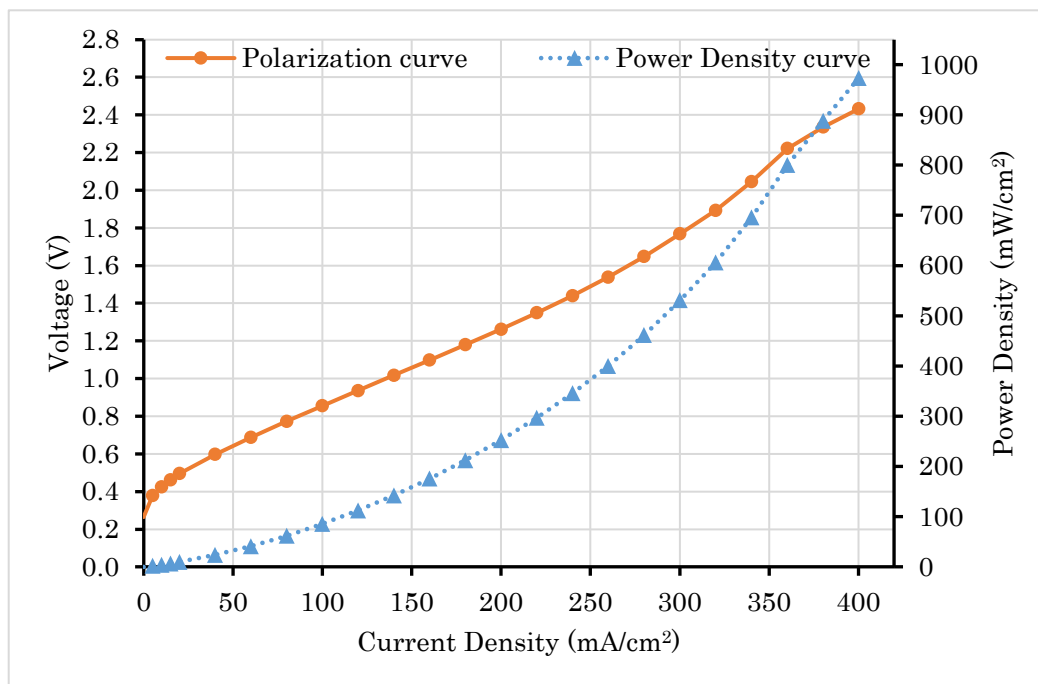


Figure C.15: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

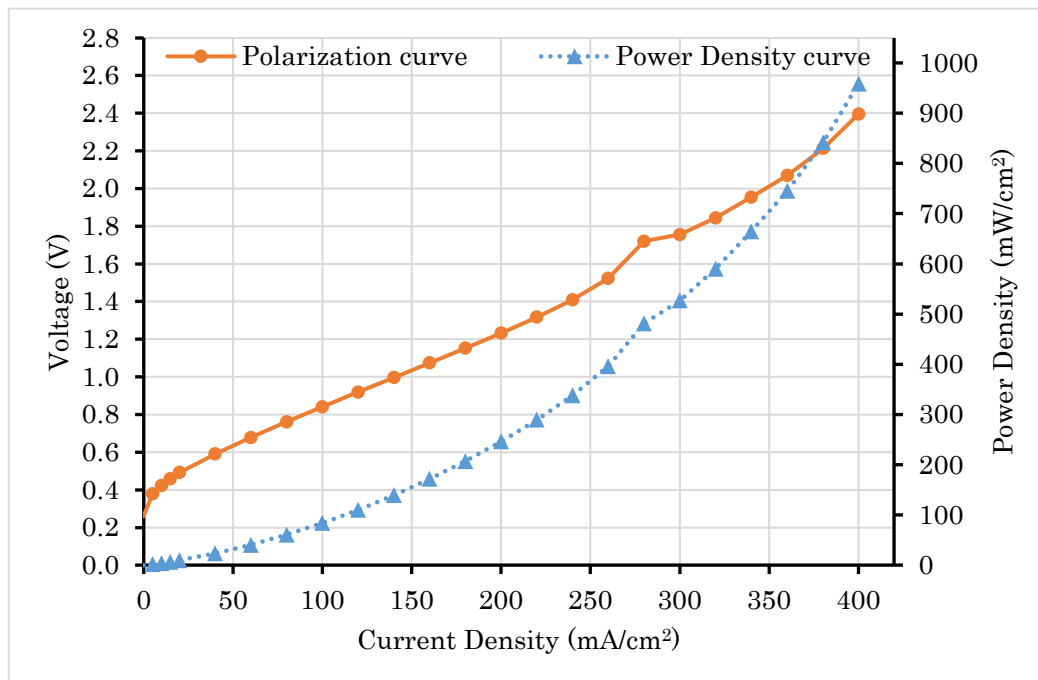


Figure C.16: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

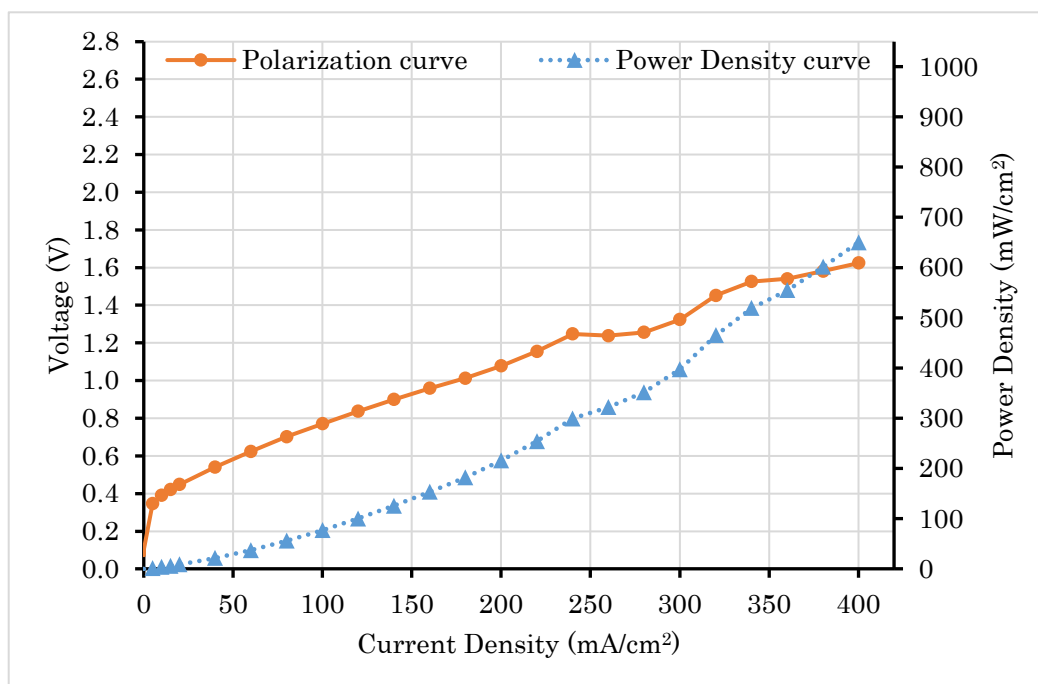


Figure C.17: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

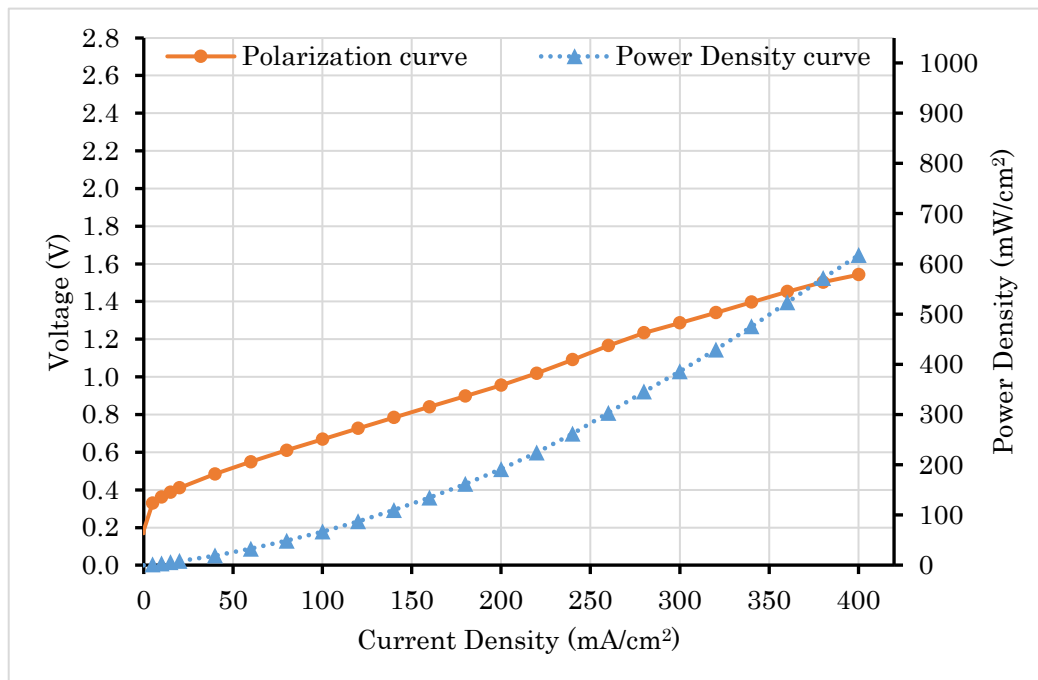


Figure C.18: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

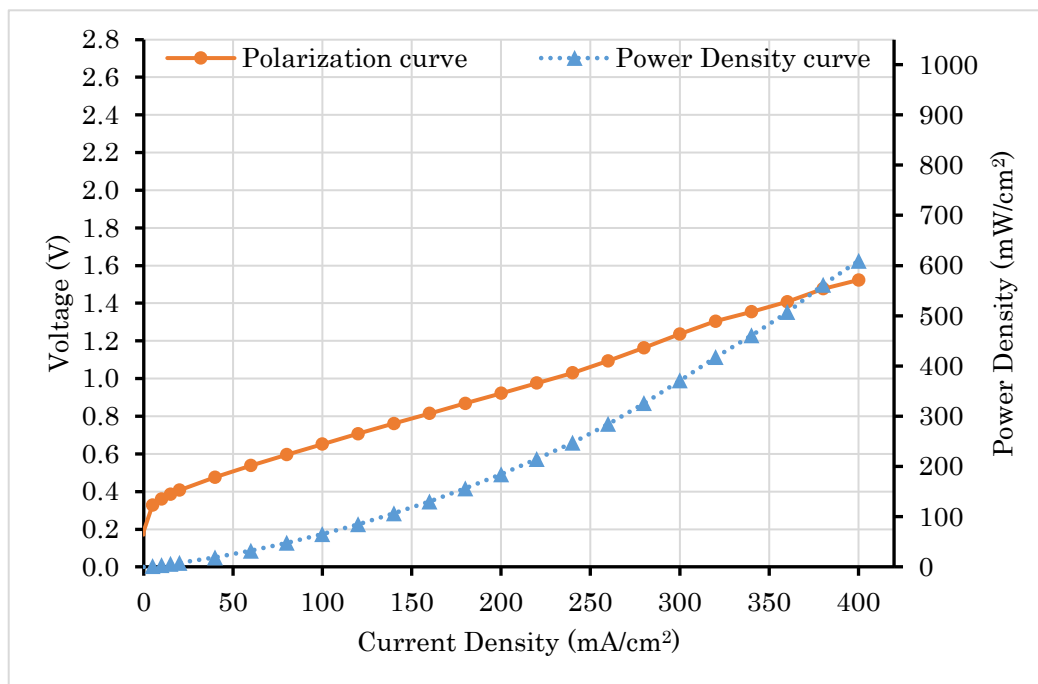


Figure C.19: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

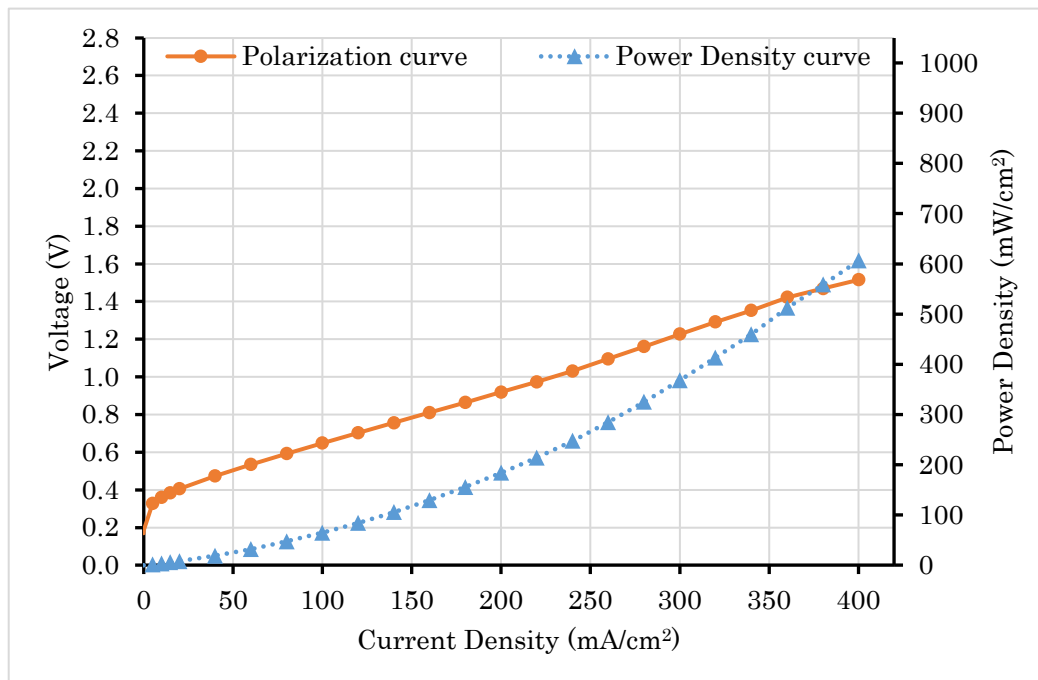


Figure C.20: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

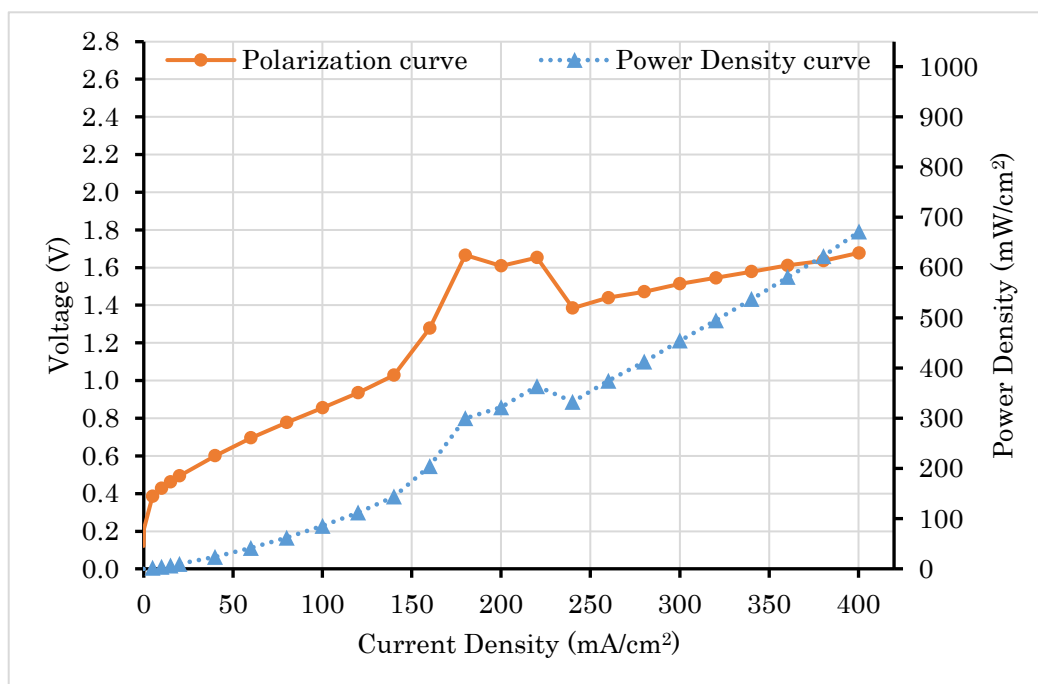


Figure C.21: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

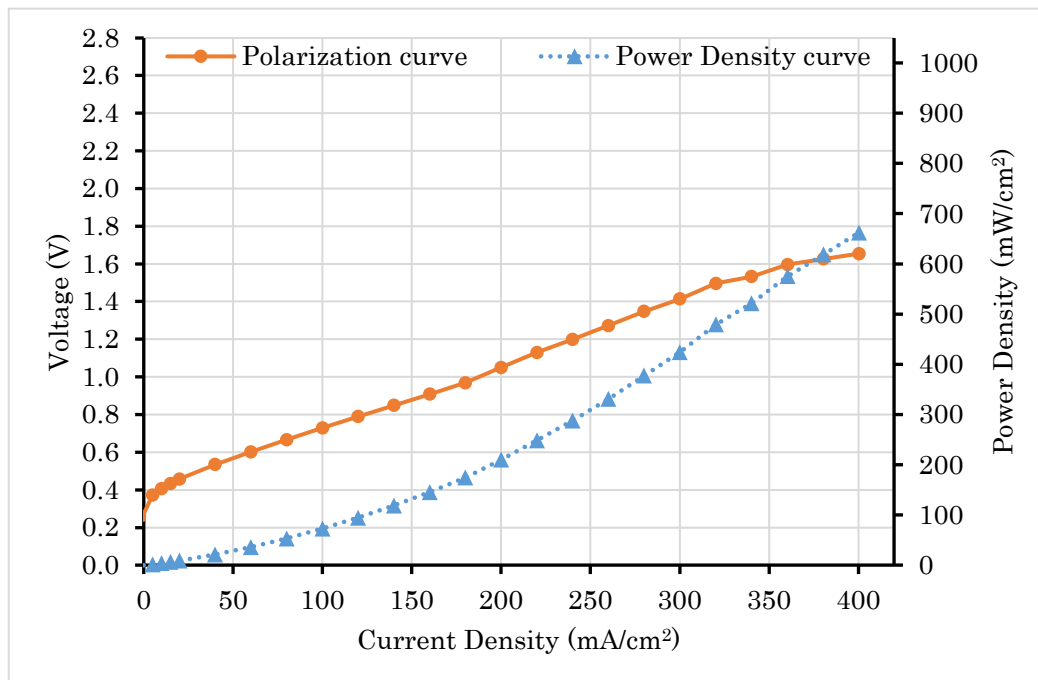


Figure C.22: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

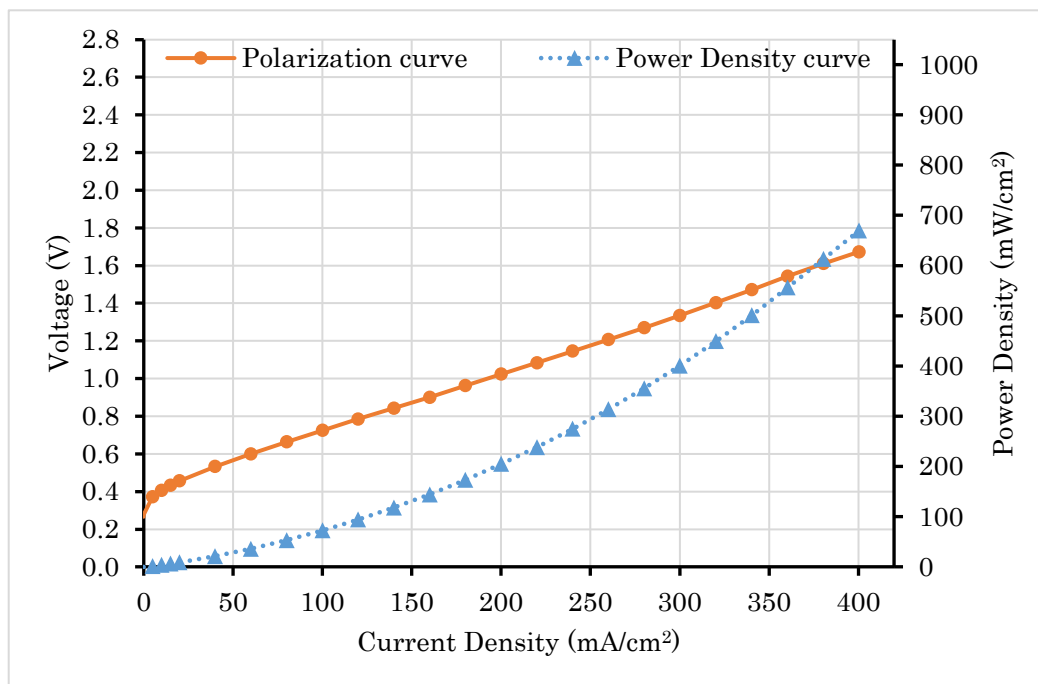


Figure C.23: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

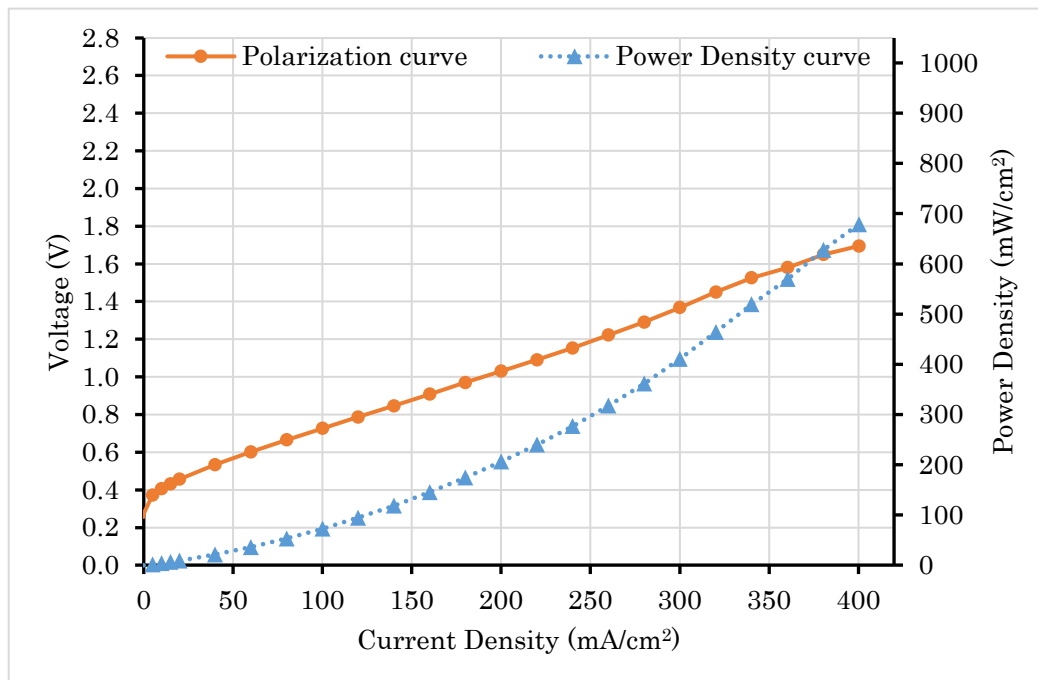


Figure C.24: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

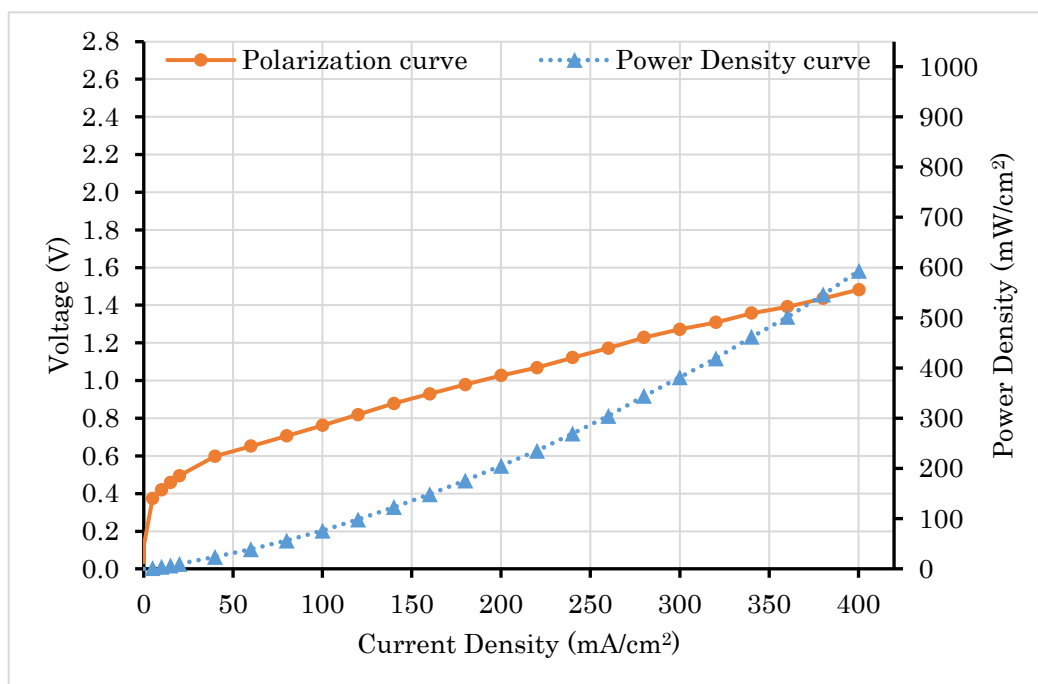


Figure C.25: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

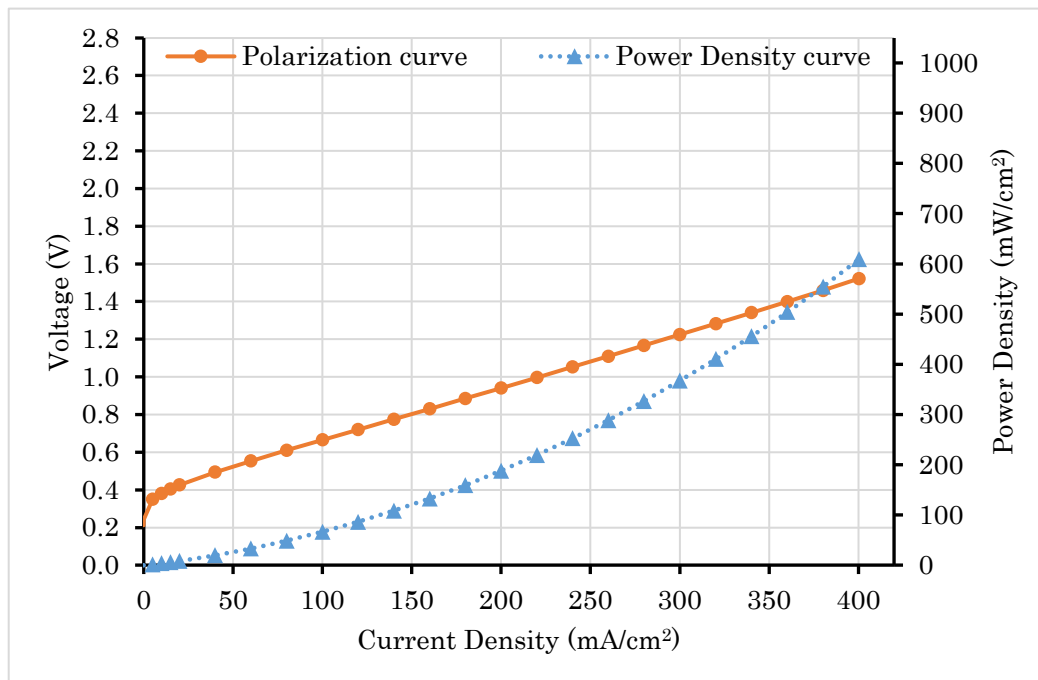


Figure C.26: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

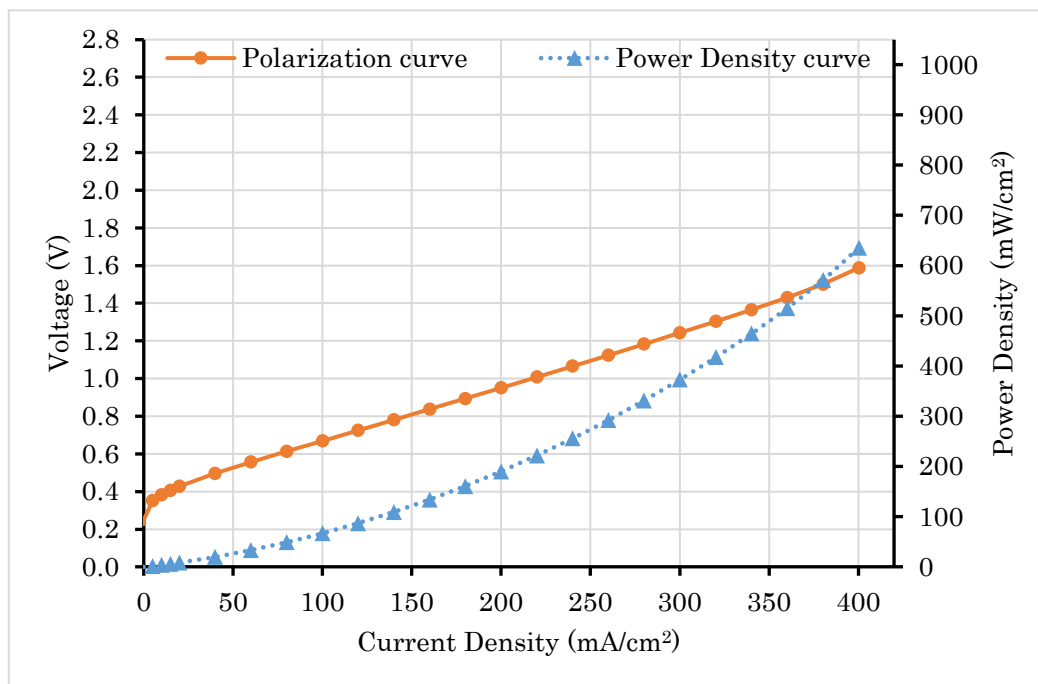


Figure C.27: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

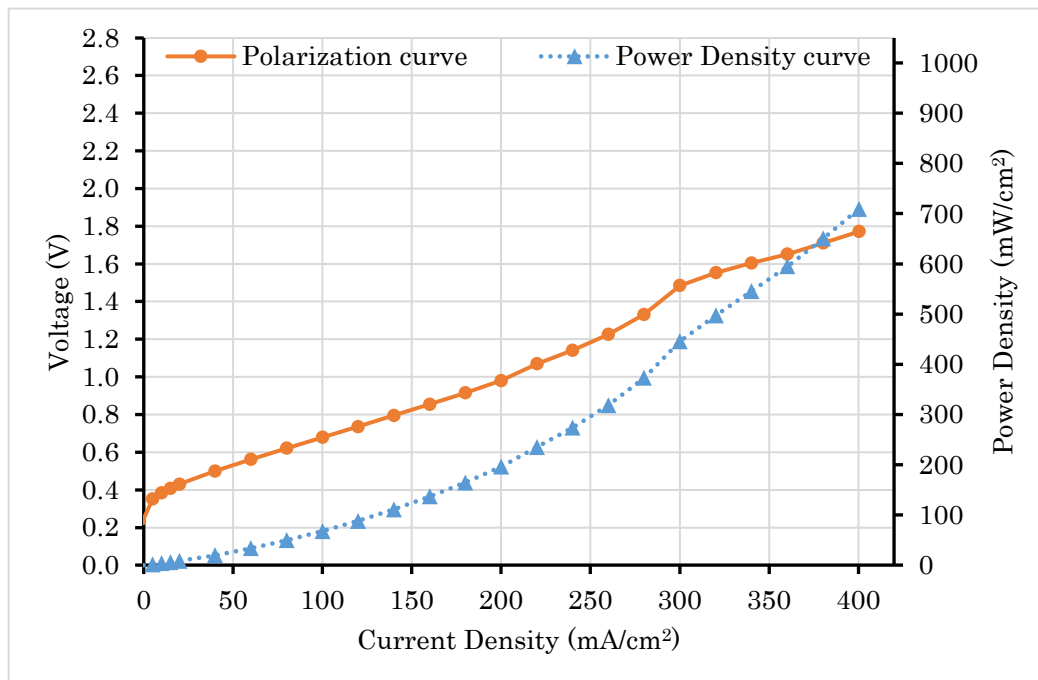


Figure C.28: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 6.00 ml/min.

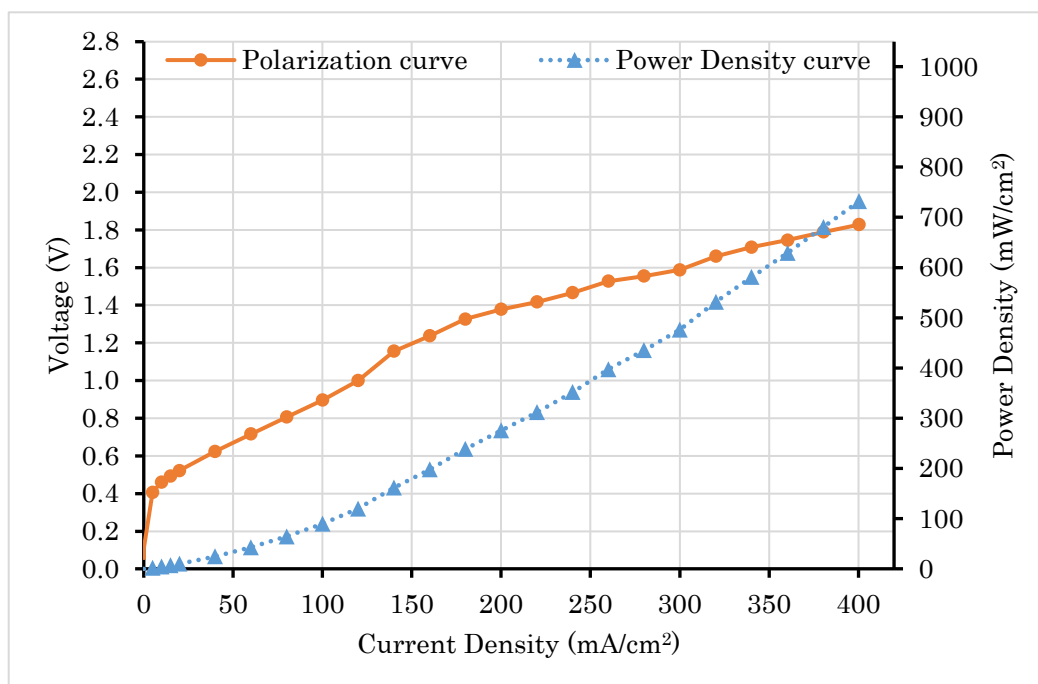


Figure C.29: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 32.7 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

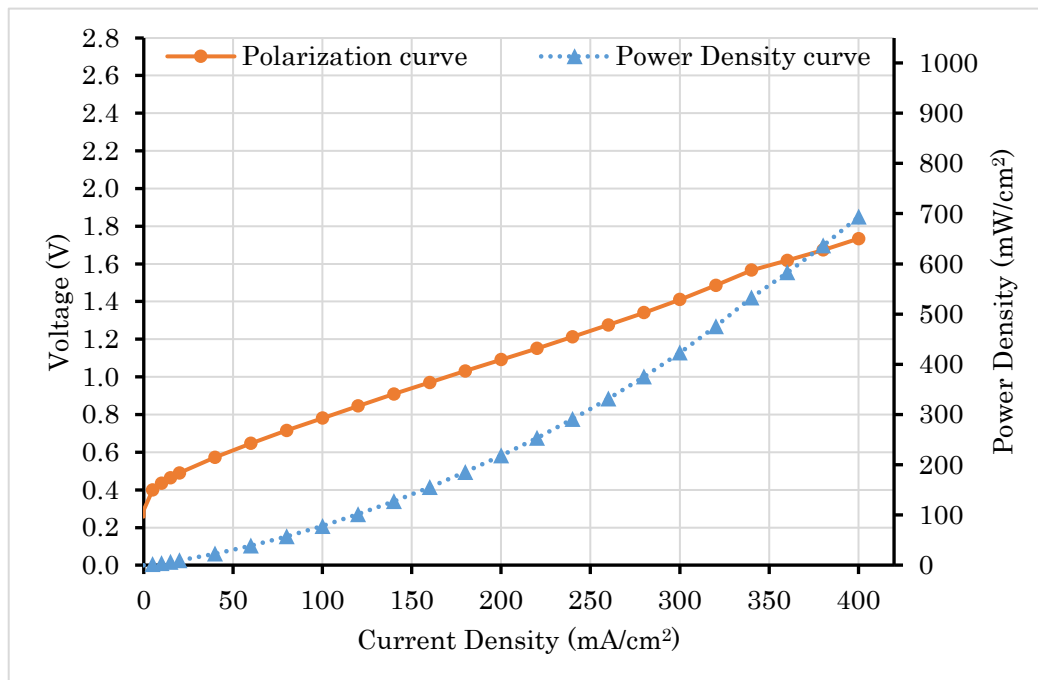


Figure C.30: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 32.7 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

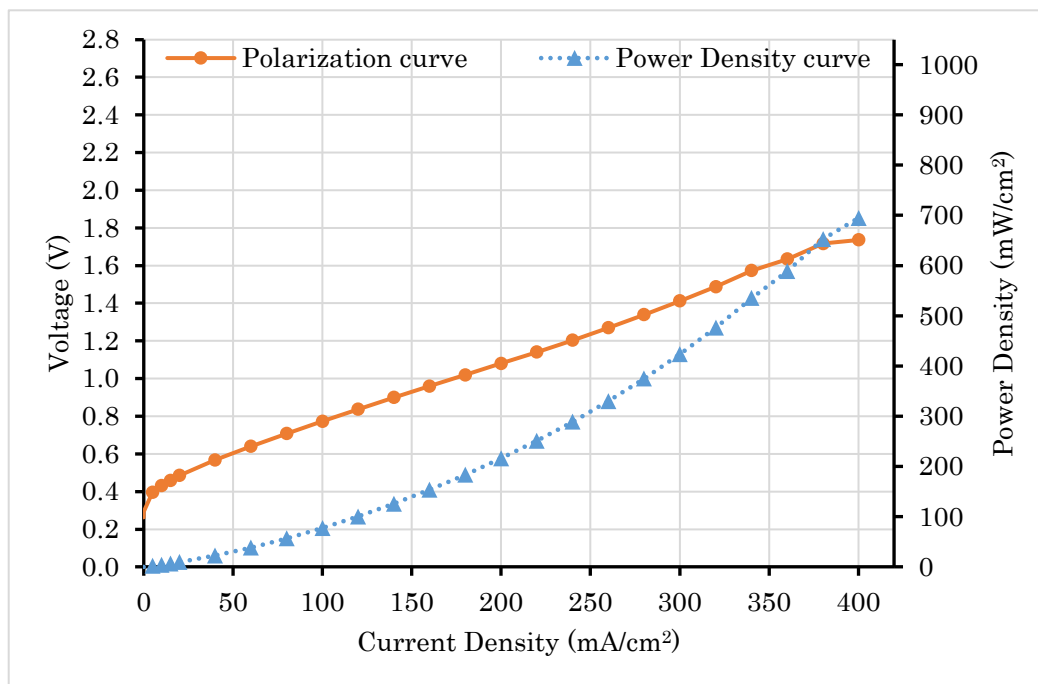


Figure C.31: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 32.7 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

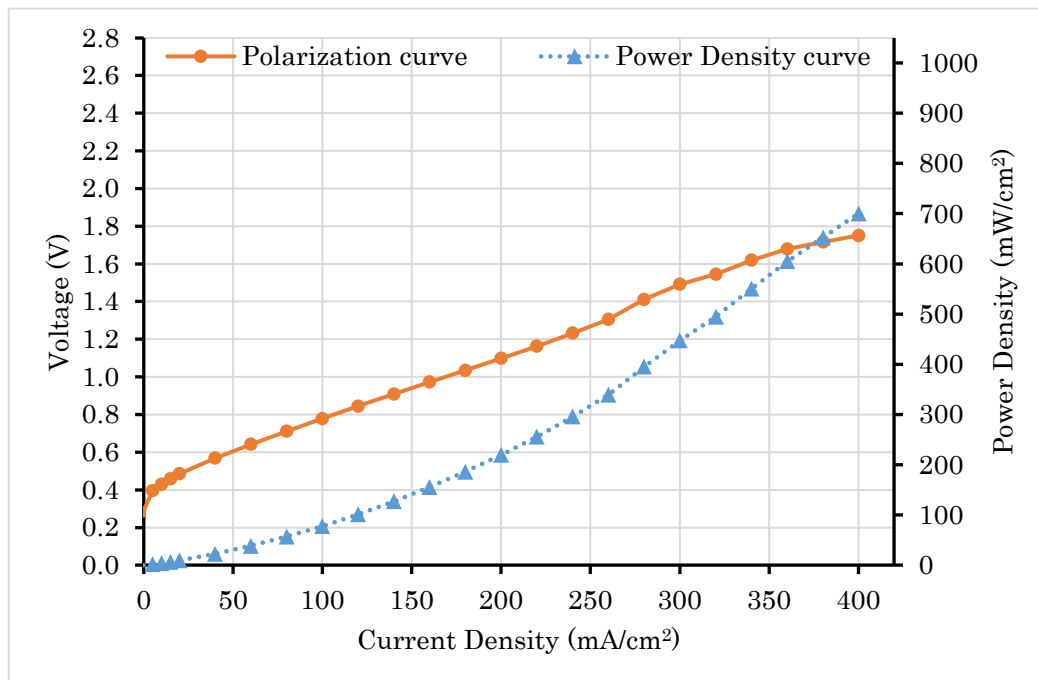


Figure C.32: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 32.7 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

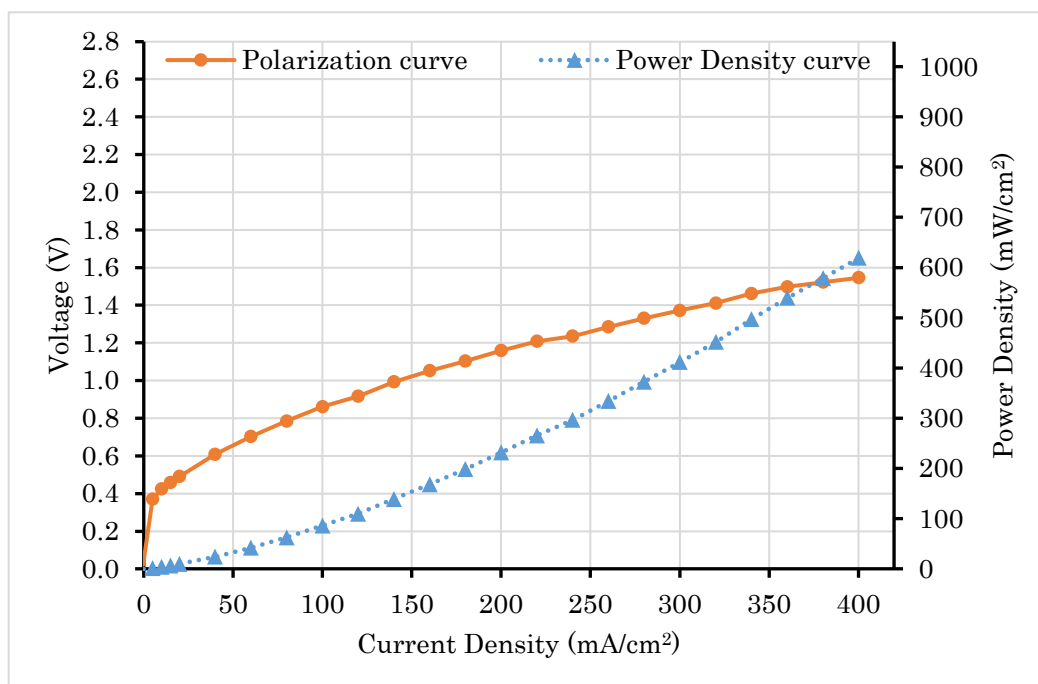


Figure C.33: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

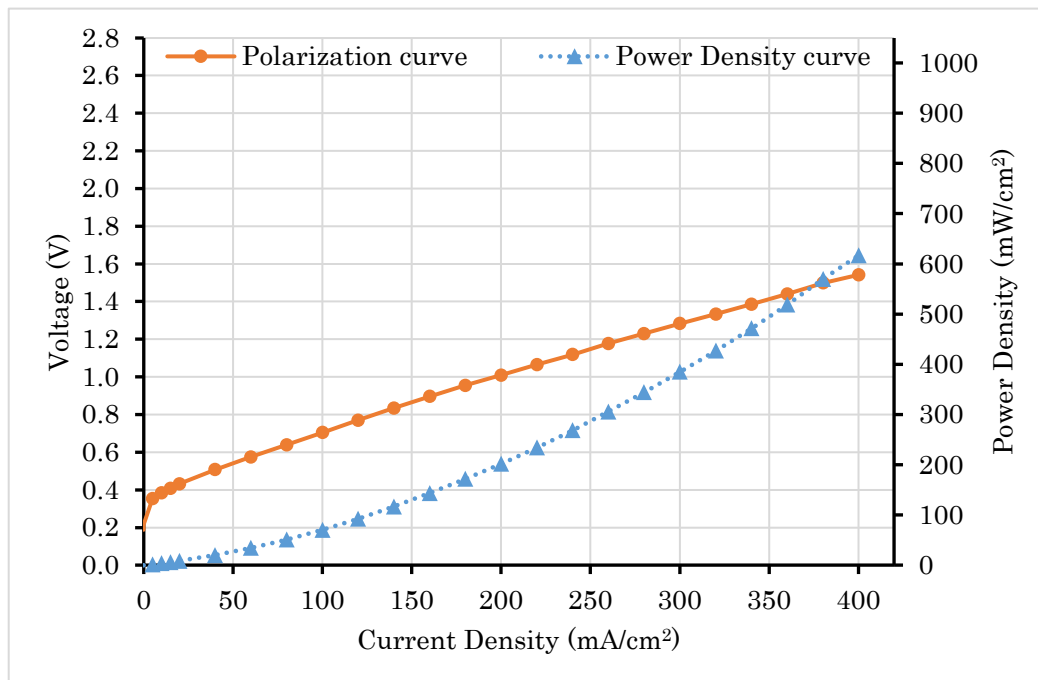


Figure C.34: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

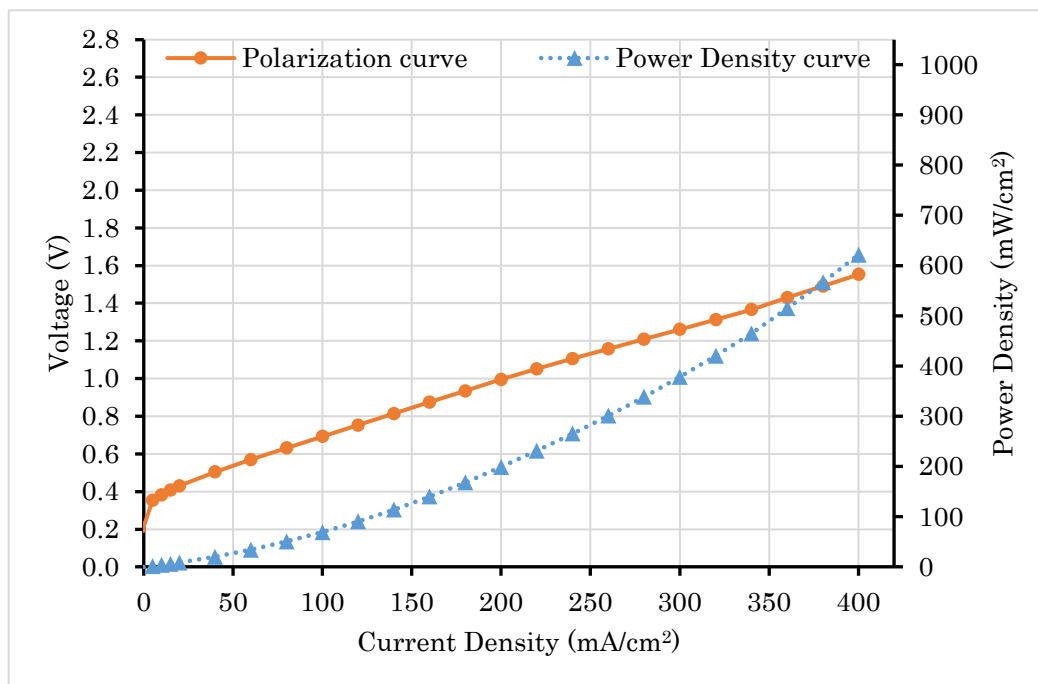


Figure C.35: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

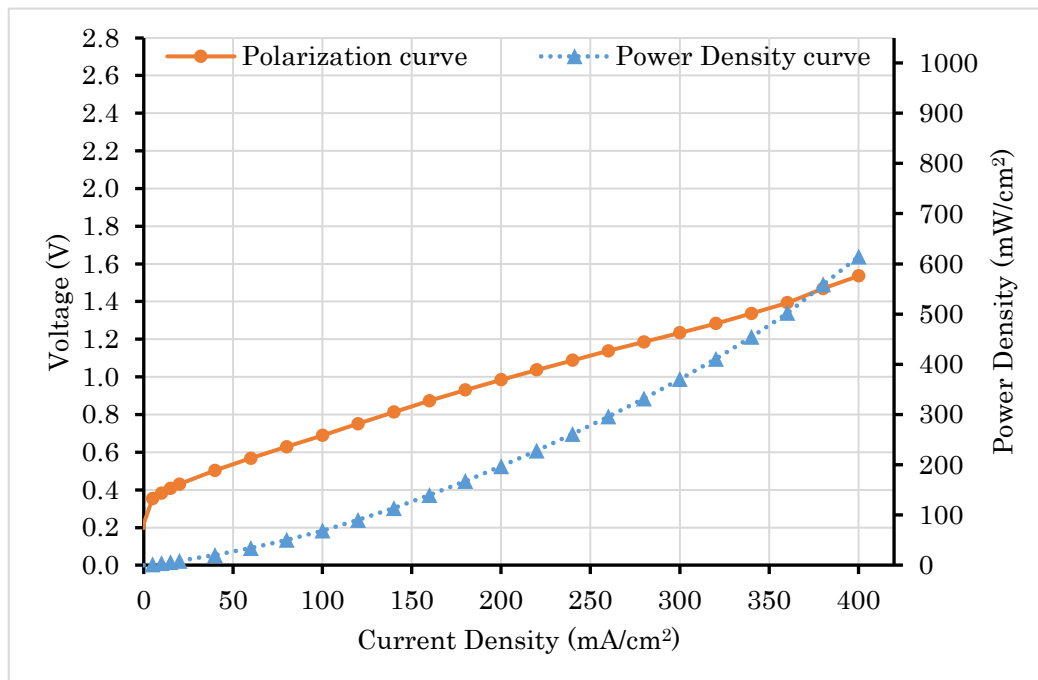


Figure C.36: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 1.90 ml/min.

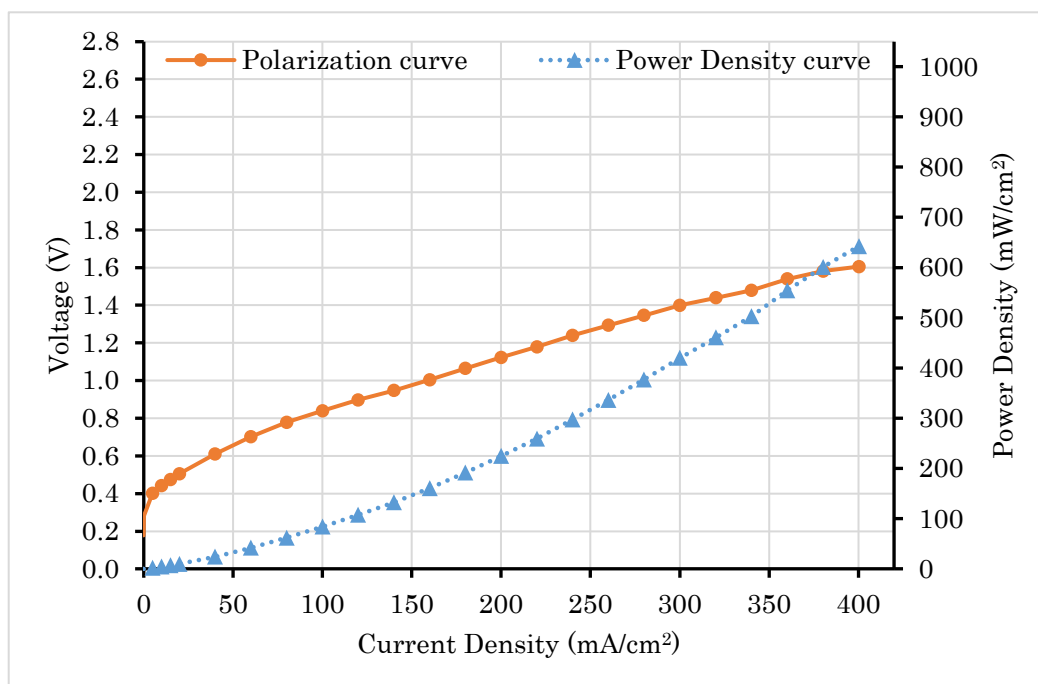


Figure C.37: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

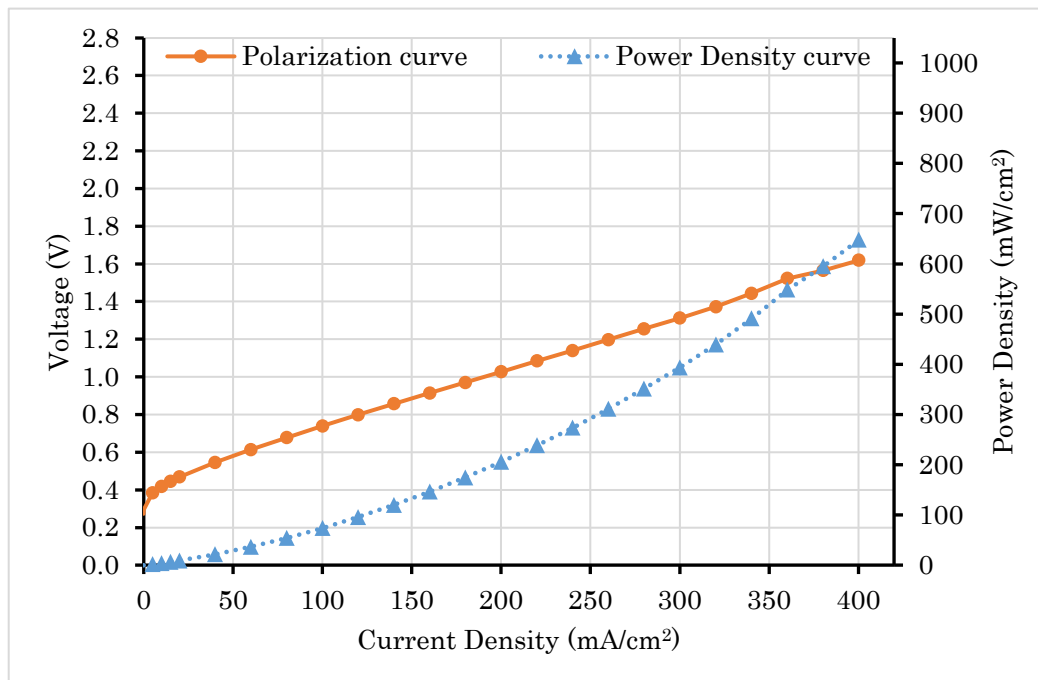


Figure C.38: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

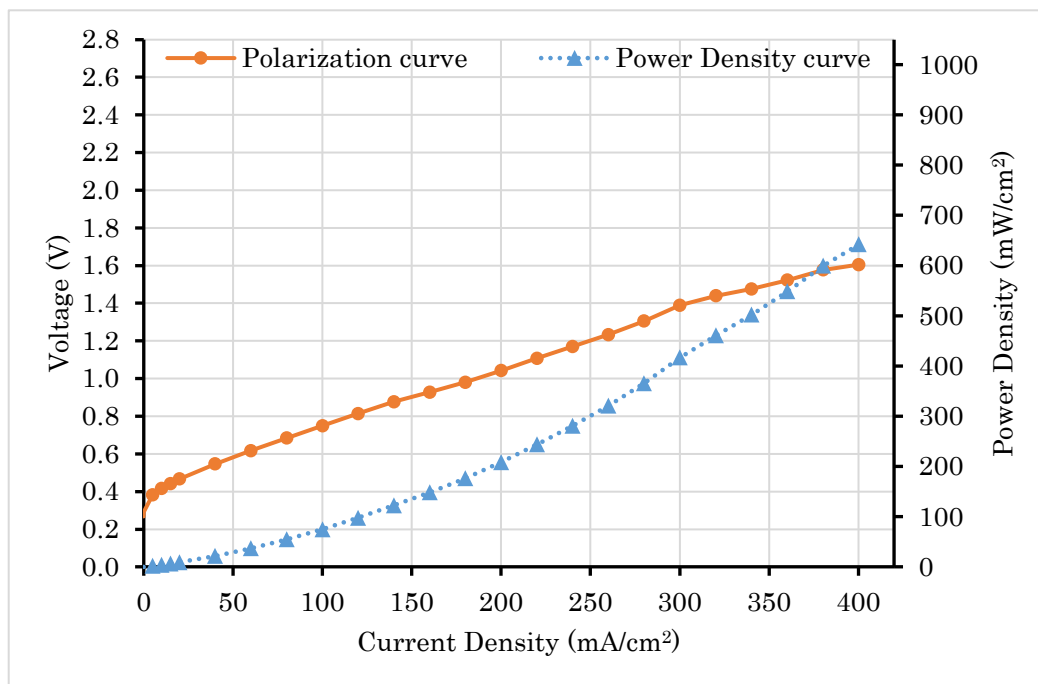


Figure C.39: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

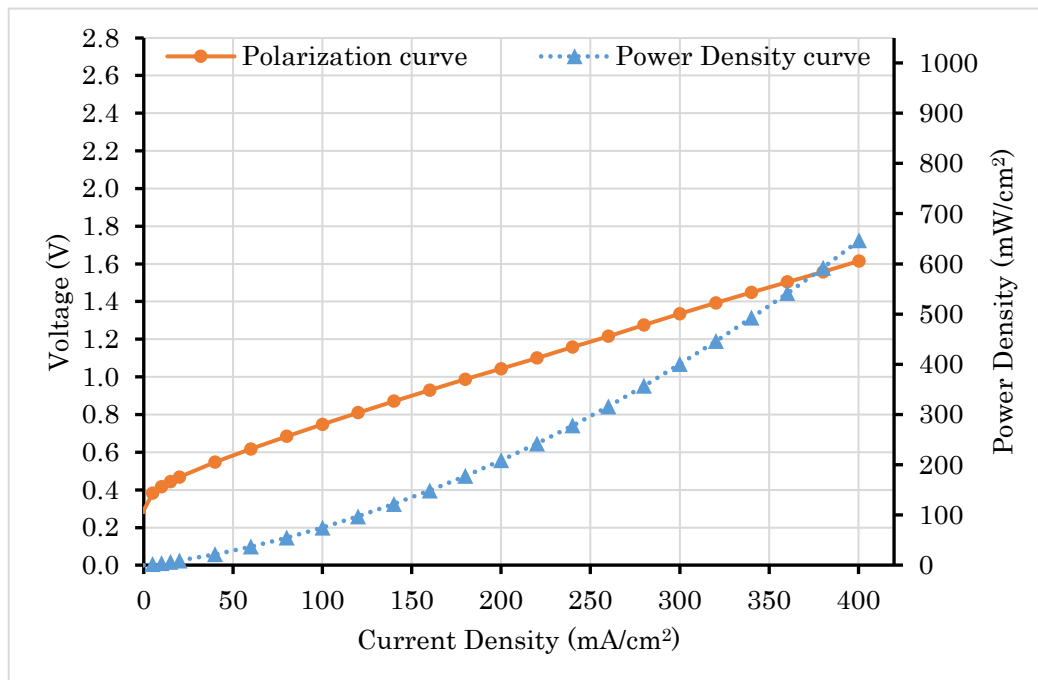


Figure C.40: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 7.10 ml/min.

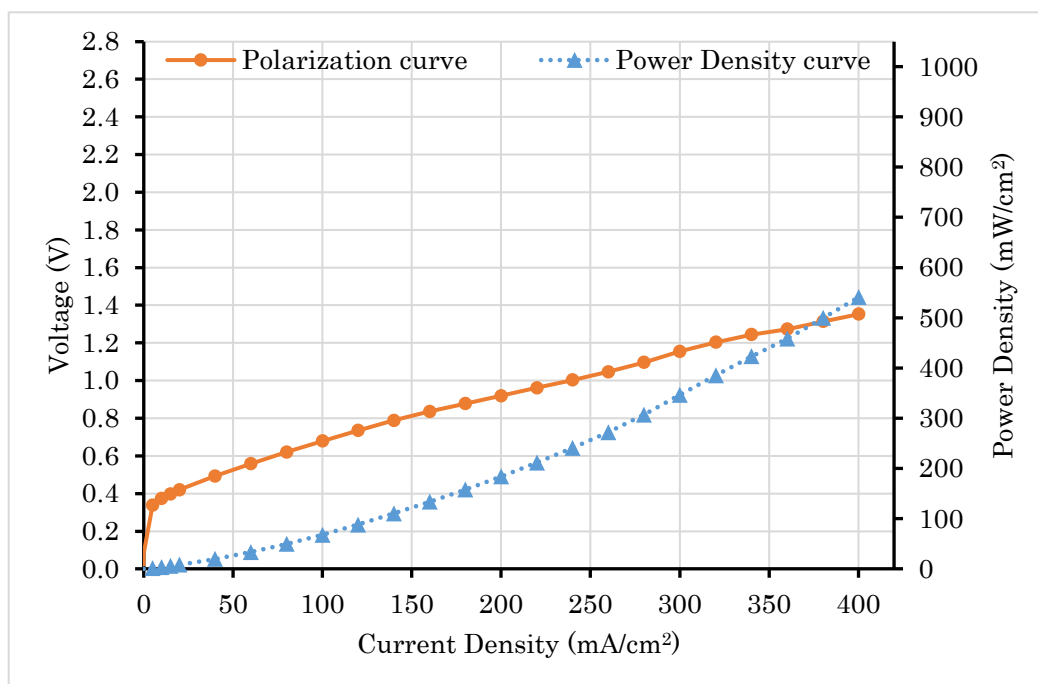


Figure C.41: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 67.3 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

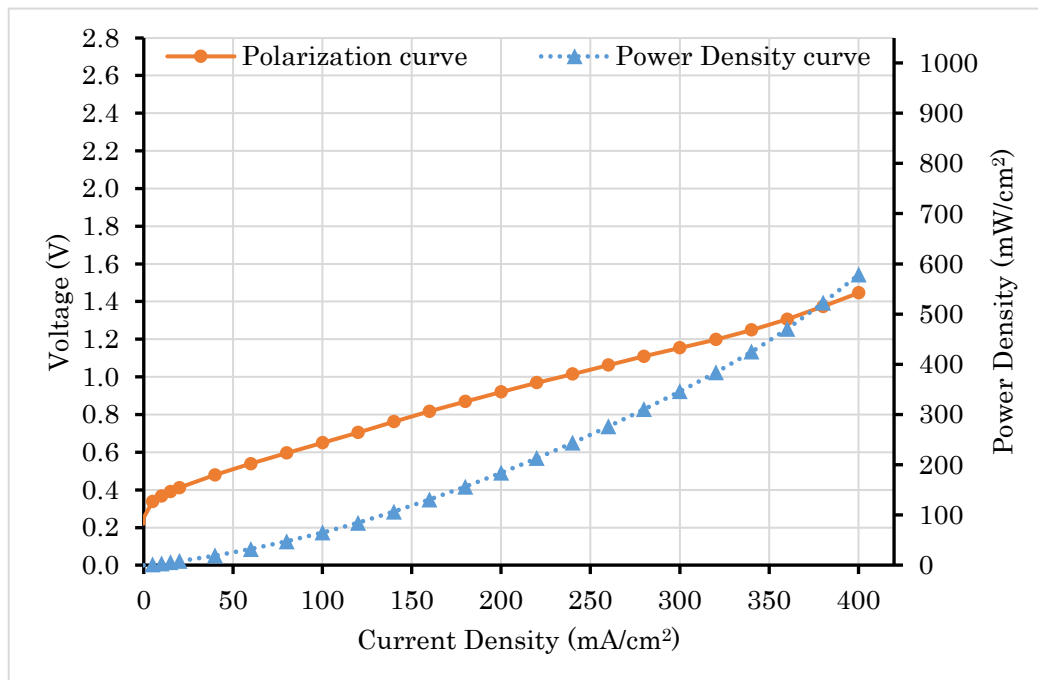


Figure C.42: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 67.3 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

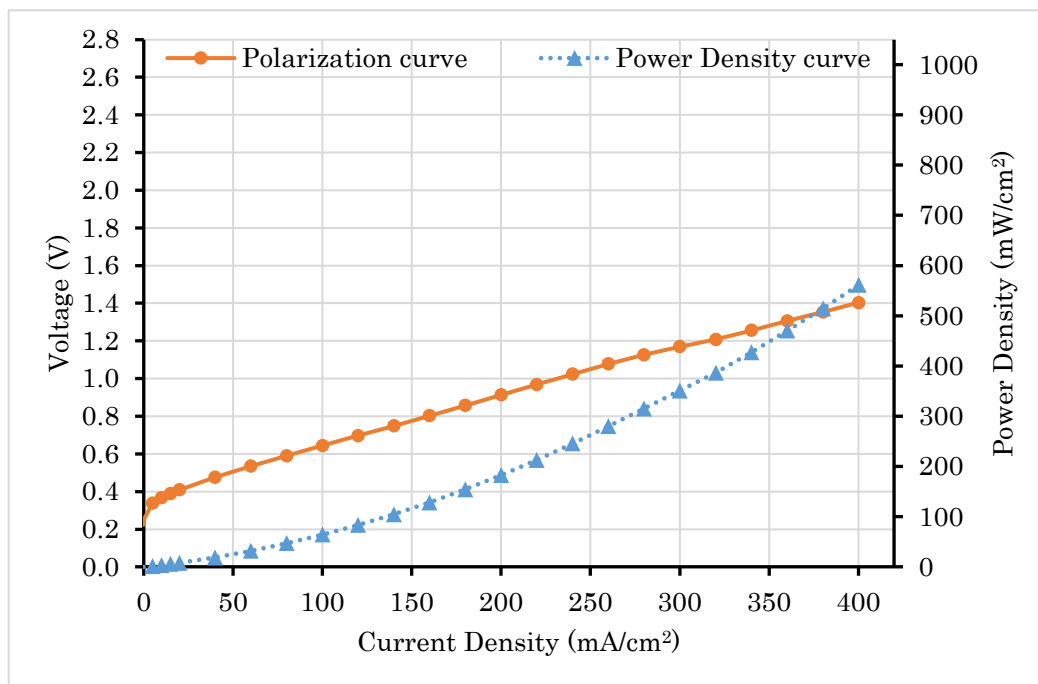


Figure C.43: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 67.3 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

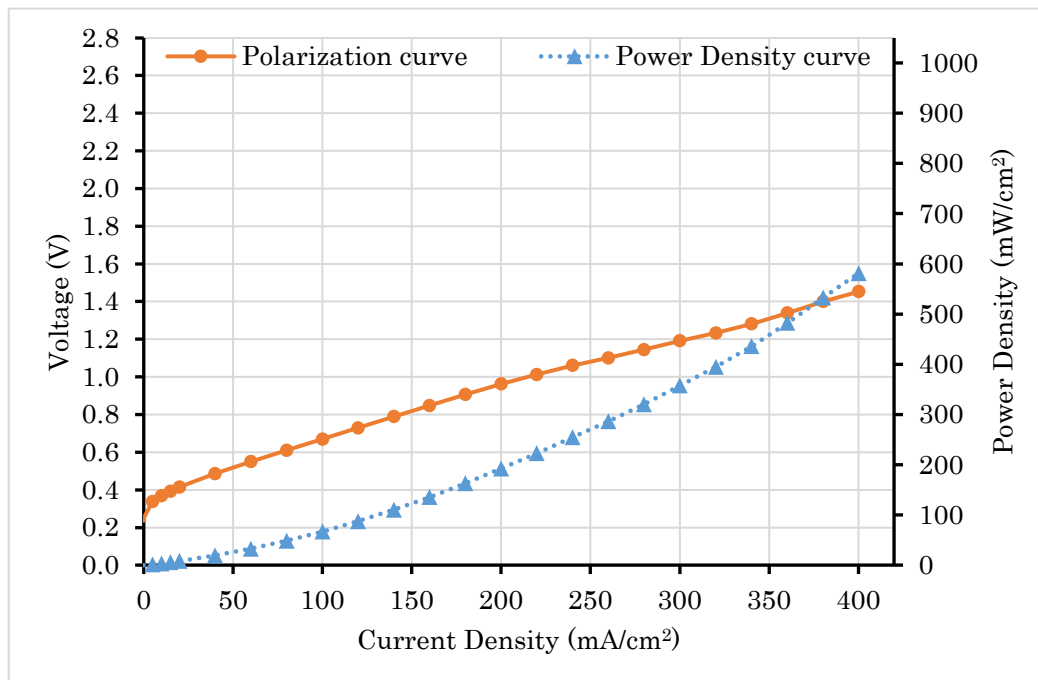


Figure C.44: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 67.3 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

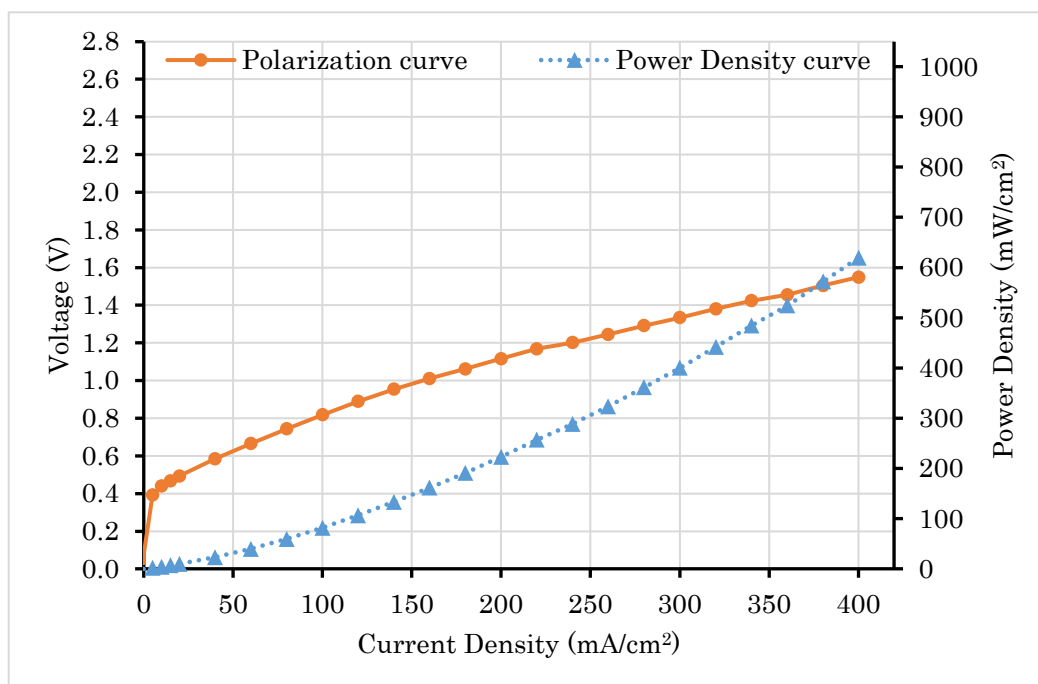


Figure C.45: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.50 ml/min.

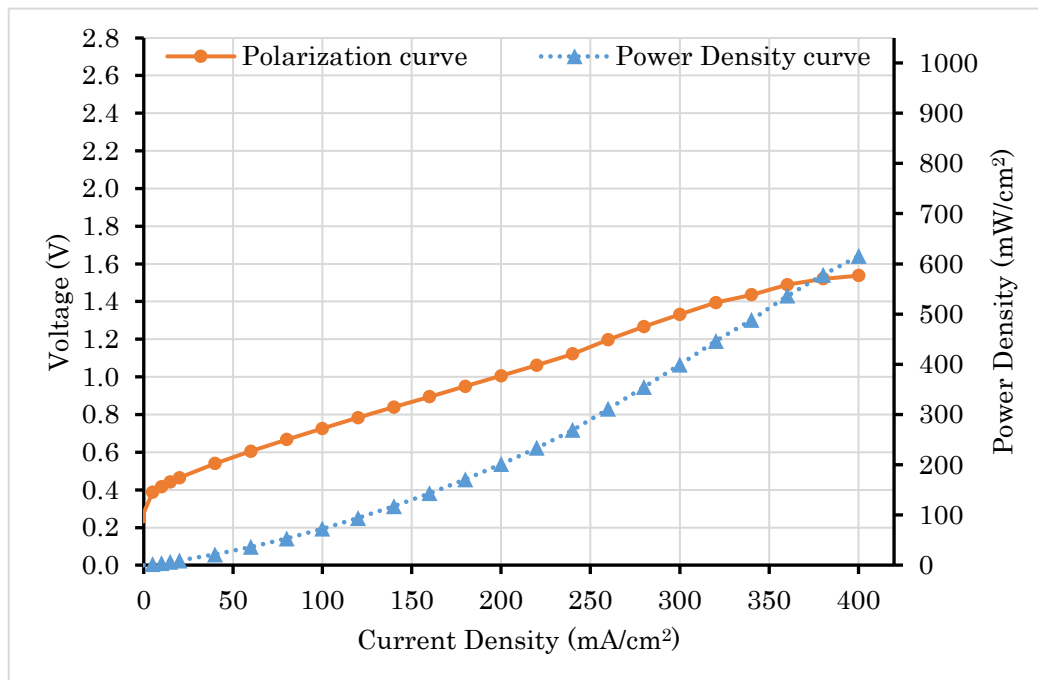


Figure C.46: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

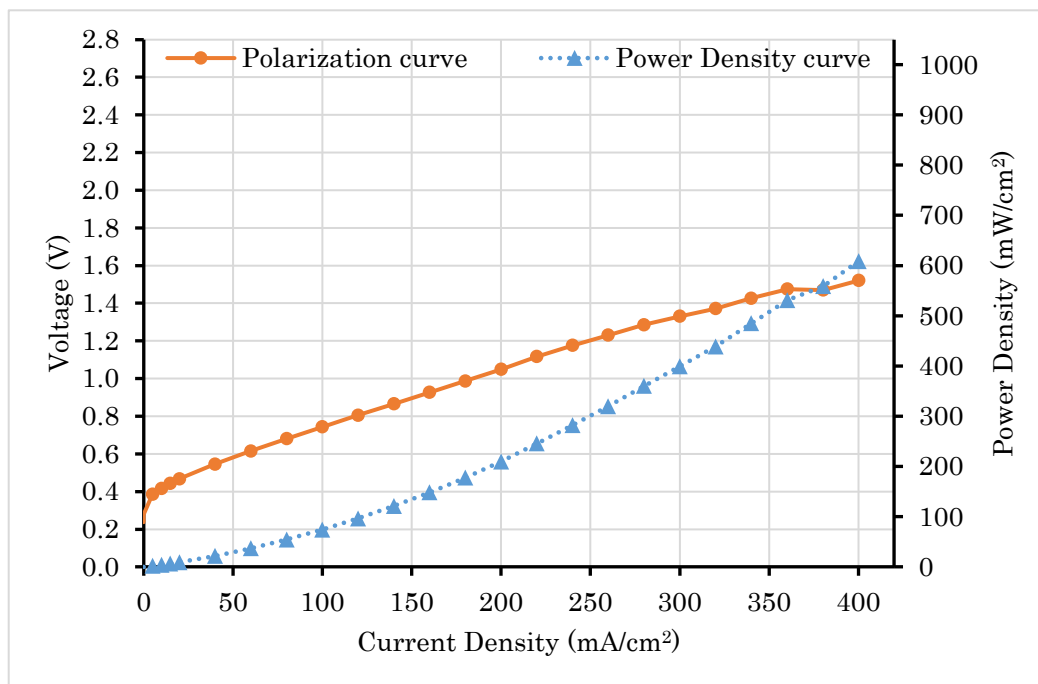


Figure C.47: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

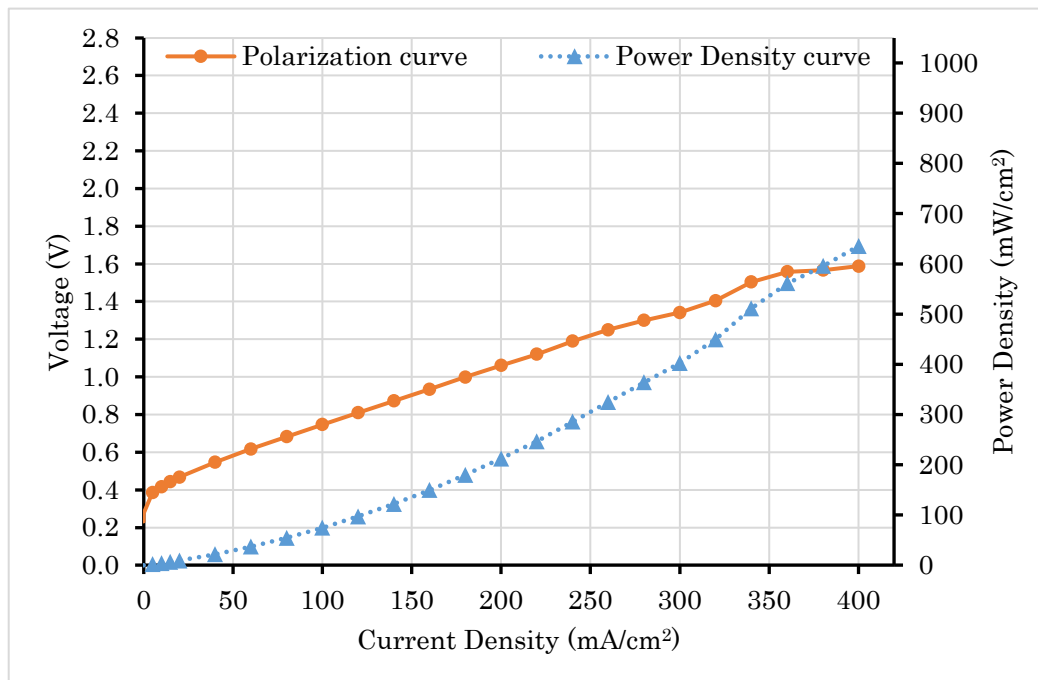


Figure C.48: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

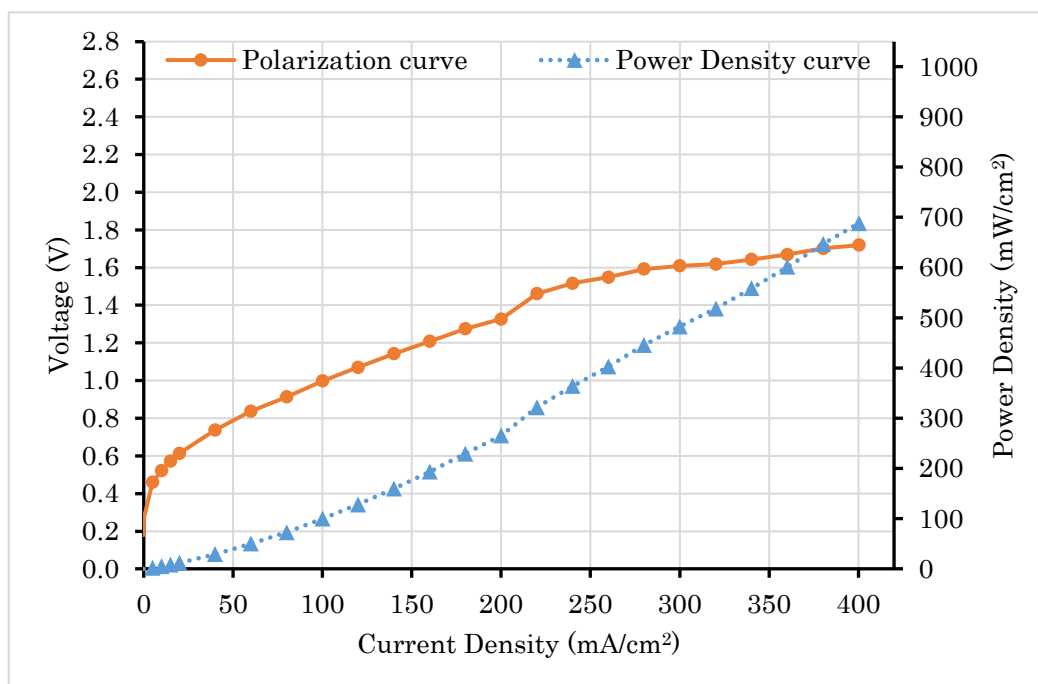


Figure C.49: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

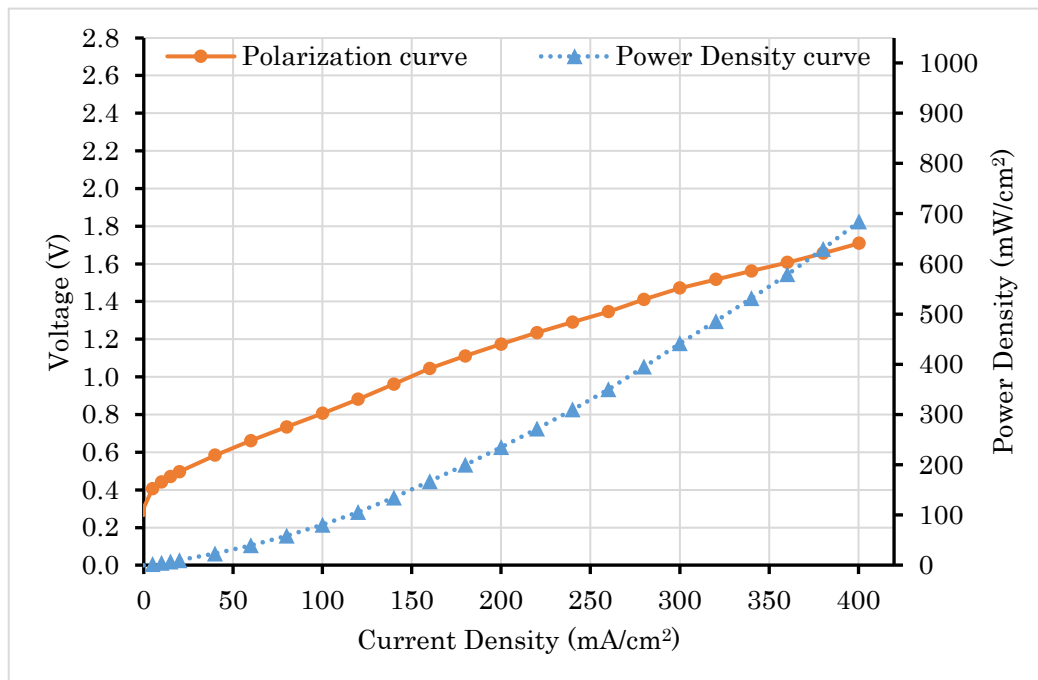


Figure C.50: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

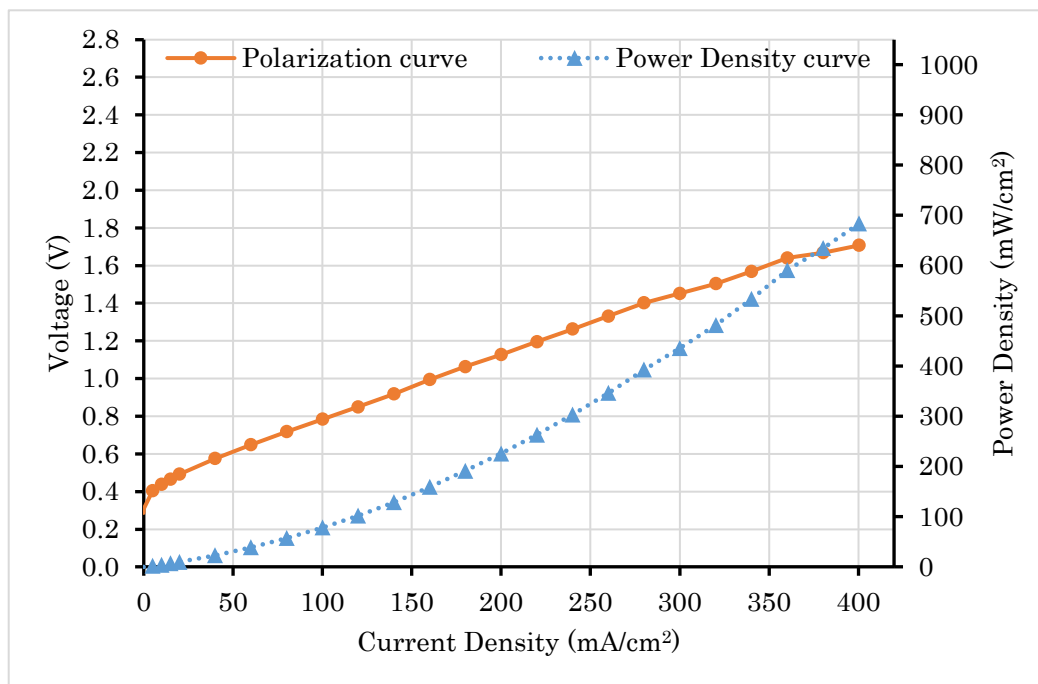


Figure C.51: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

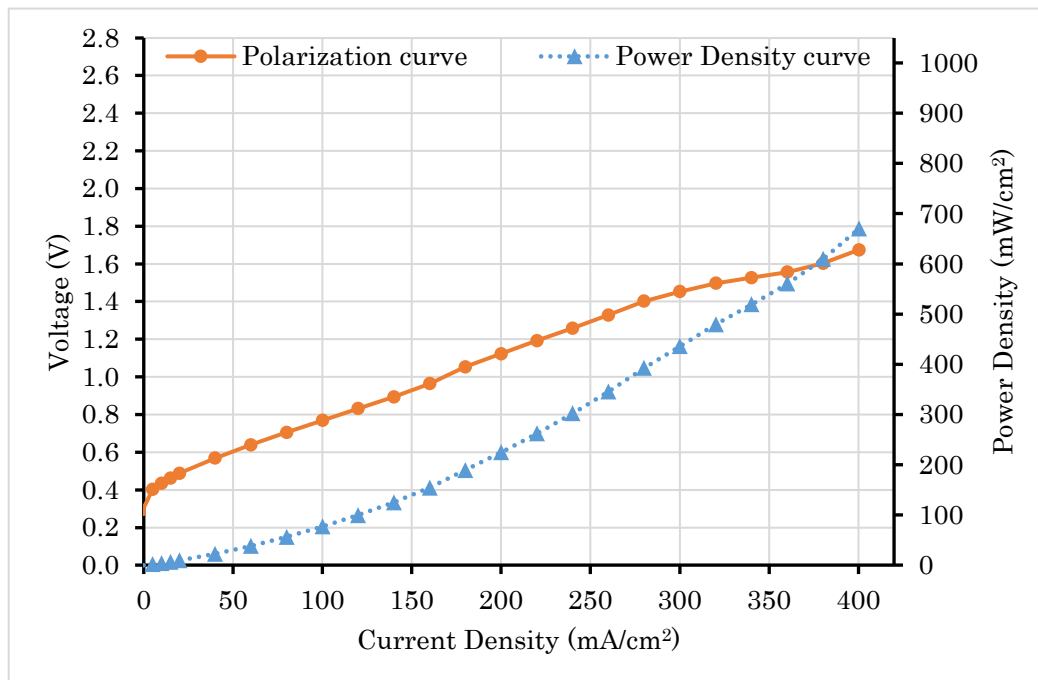


Figure C.52: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

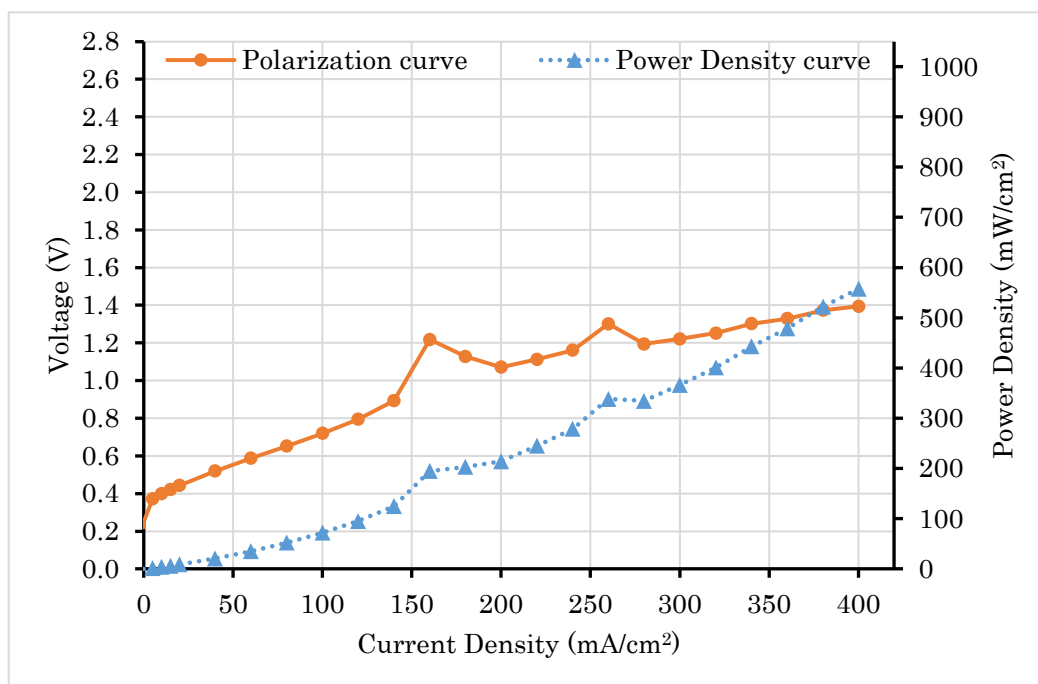


Figure C.53: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

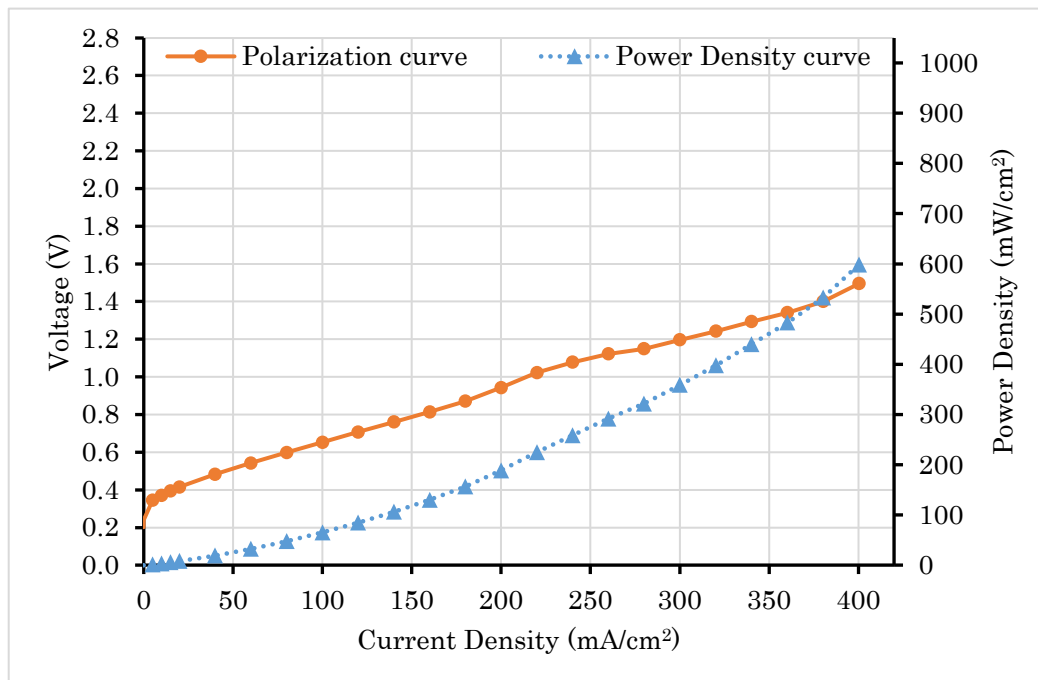


Figure C.54: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

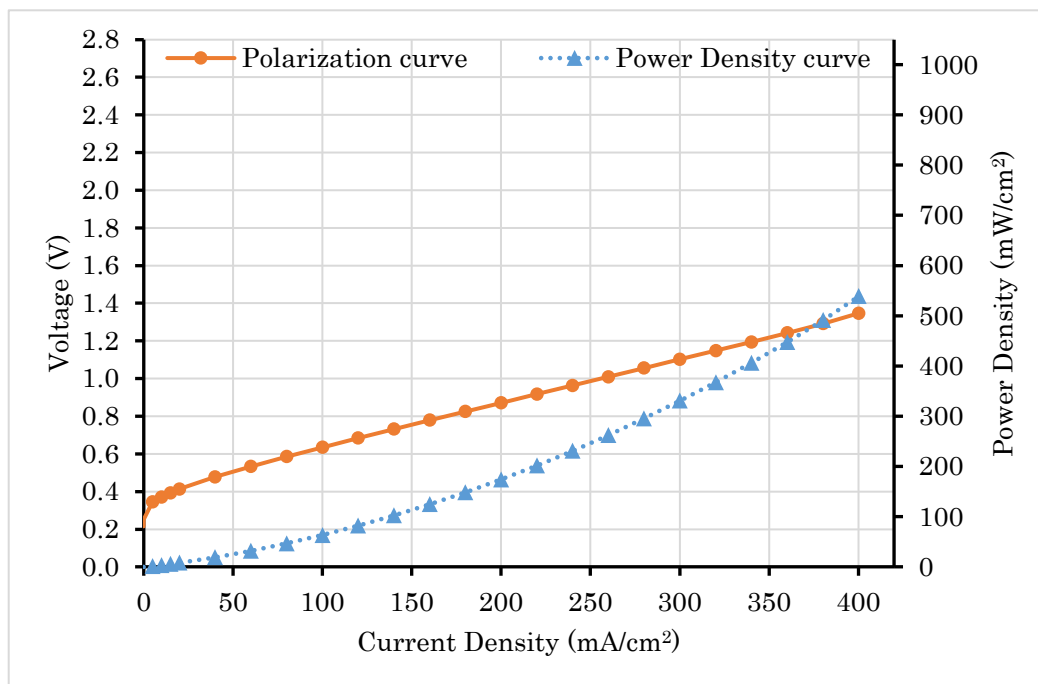


Figure C.55: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

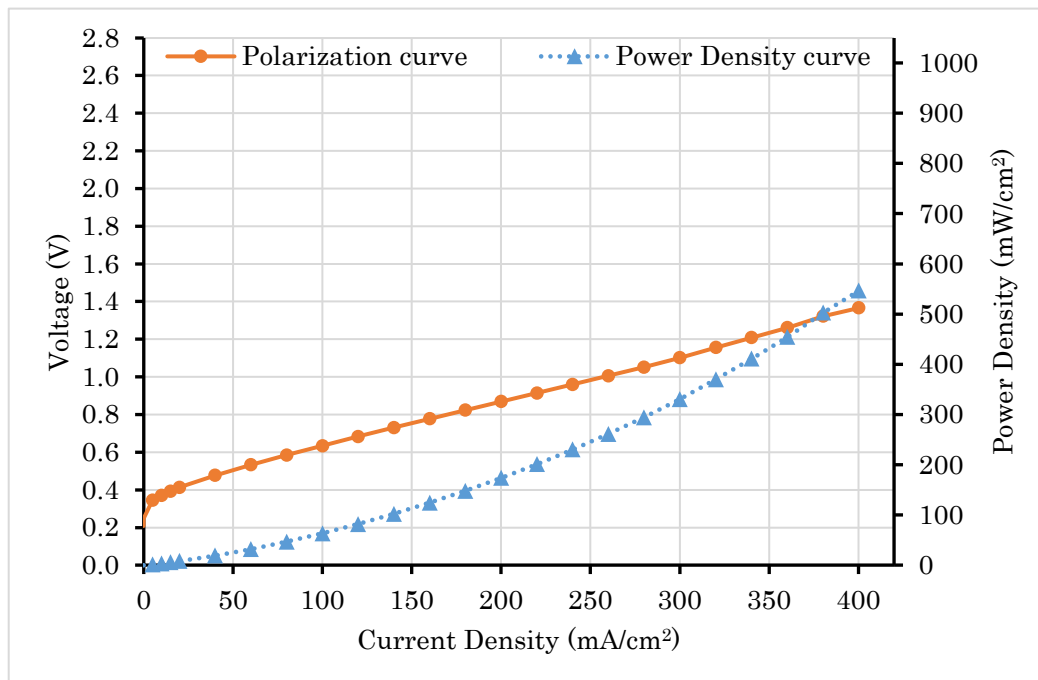


Figure C.56: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 3.00 ml/min.

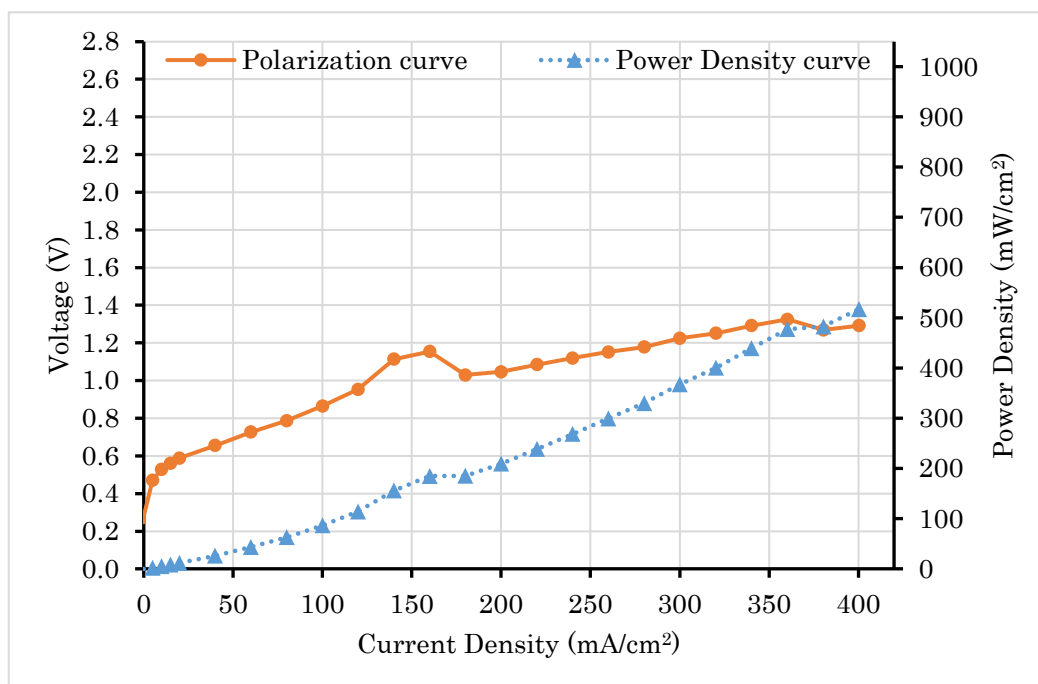


Figure C.57: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

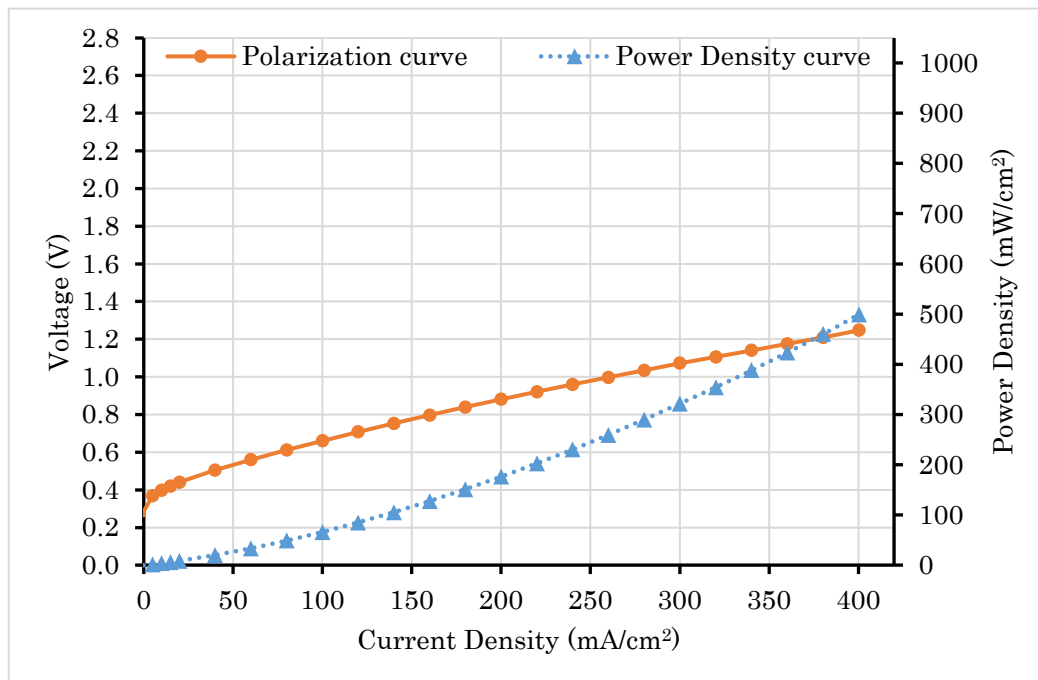


Figure C.58: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

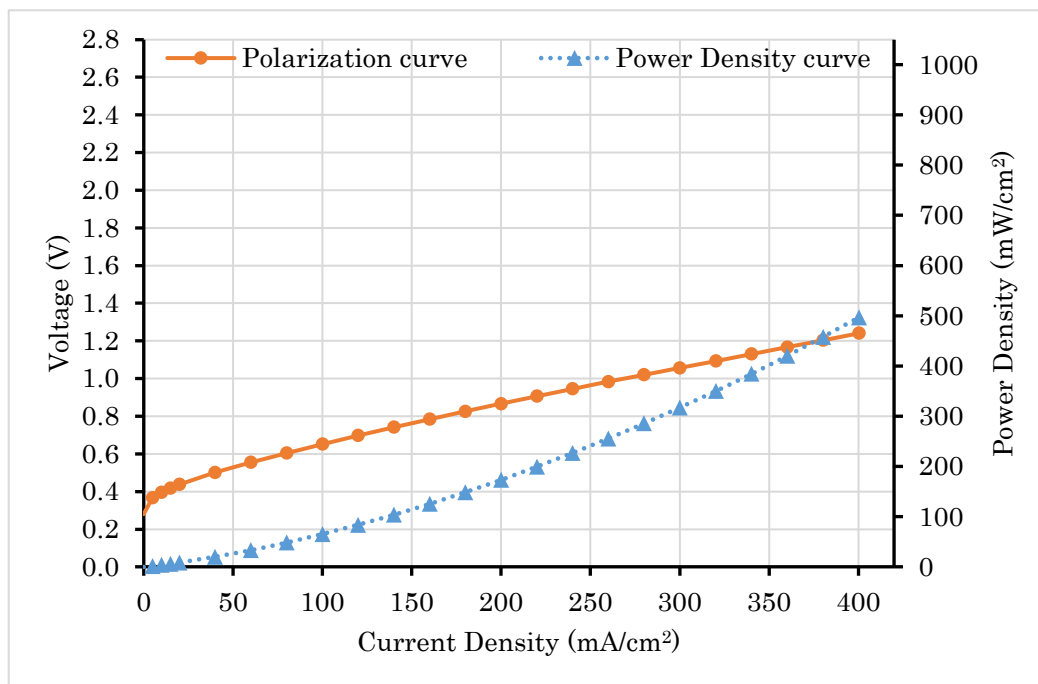


Figure C.59: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

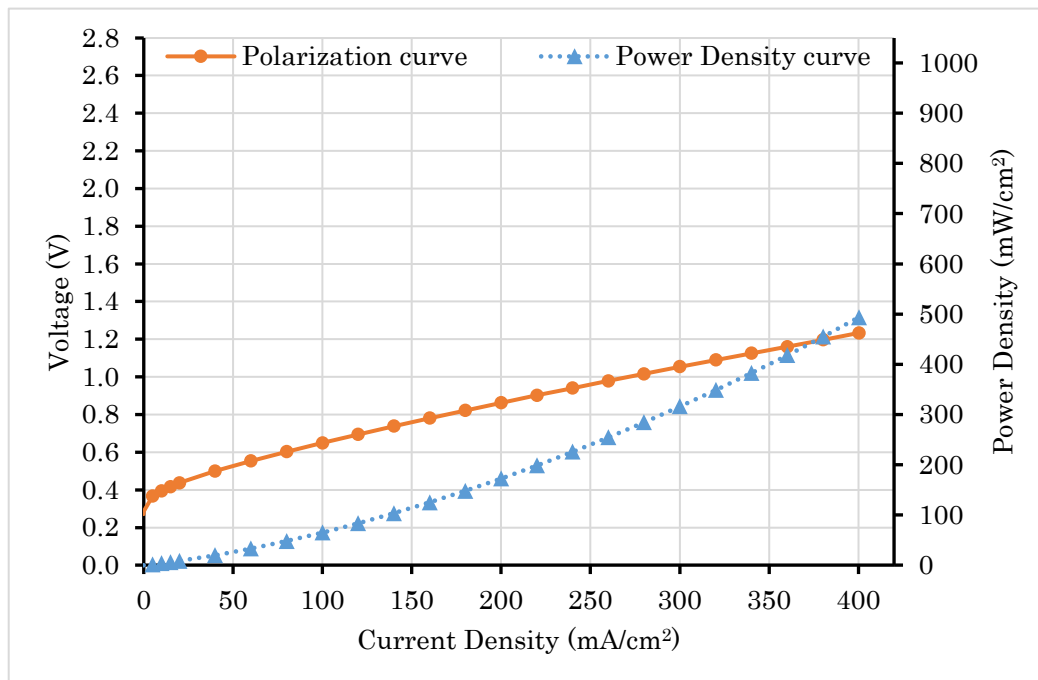


Figure C.60: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 60.0 °C, methanol concentration of 3.00 M and methanol volumetric flow rate 6.00 ml/min.

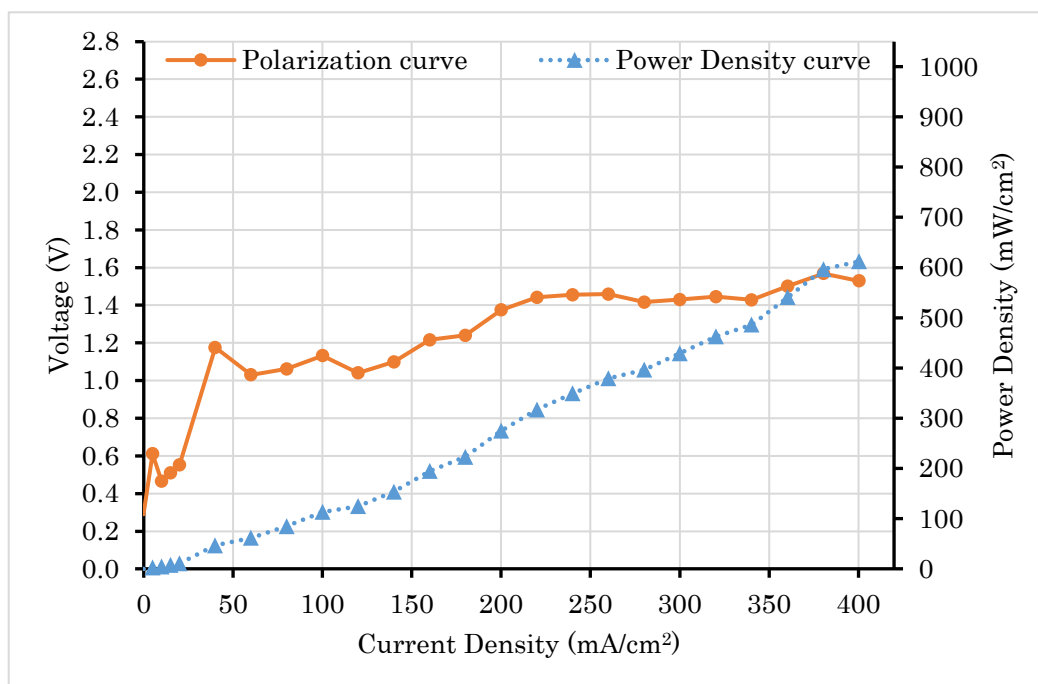


Figure C.61: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

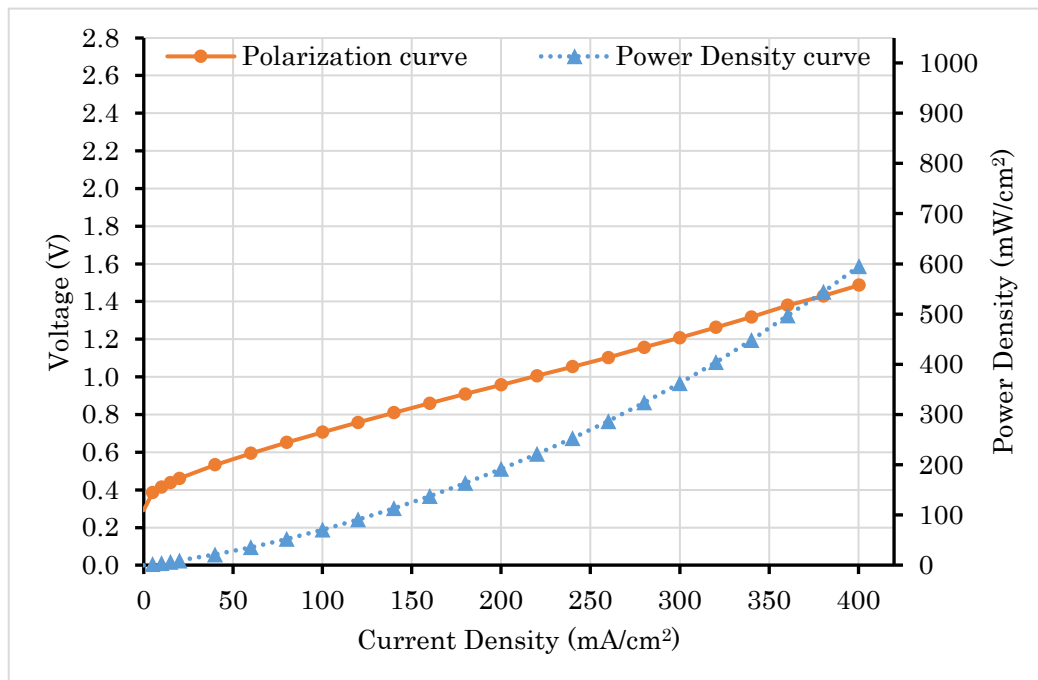


Figure C.62: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

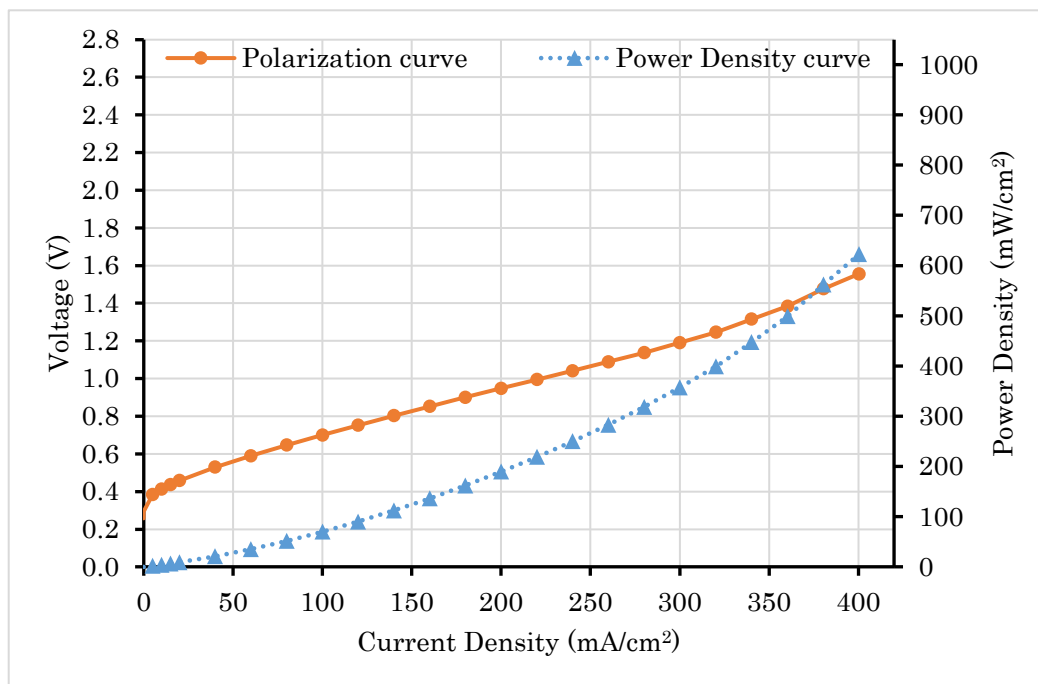


Figure C.63: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

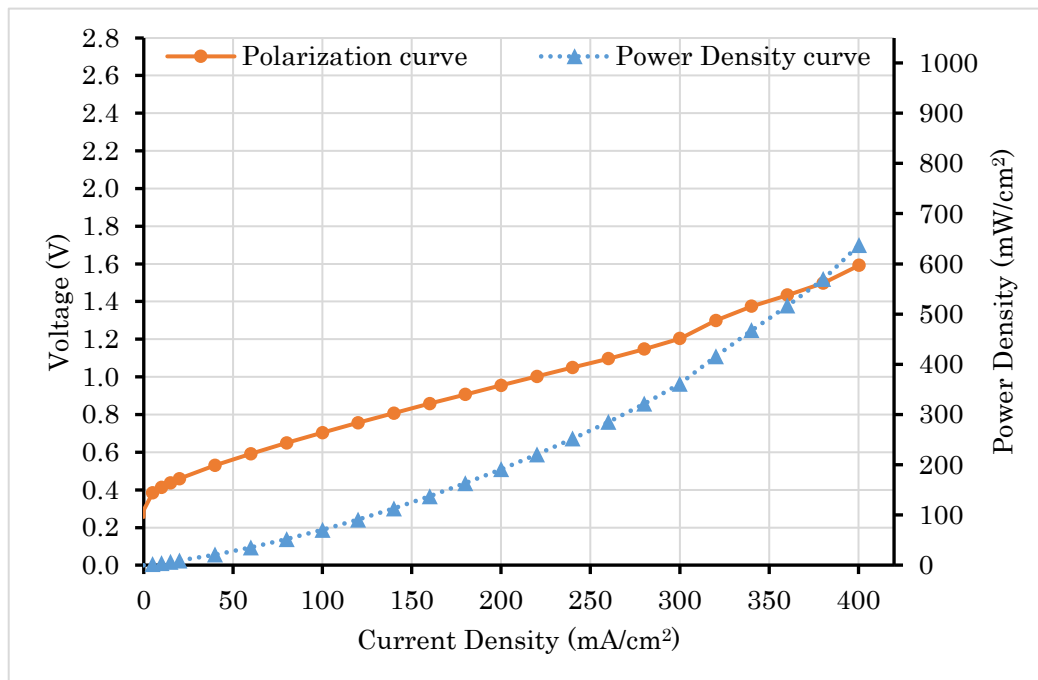


Figure C.64: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 3.73 M and methanol volumetric flow rate 4.50 ml/min.

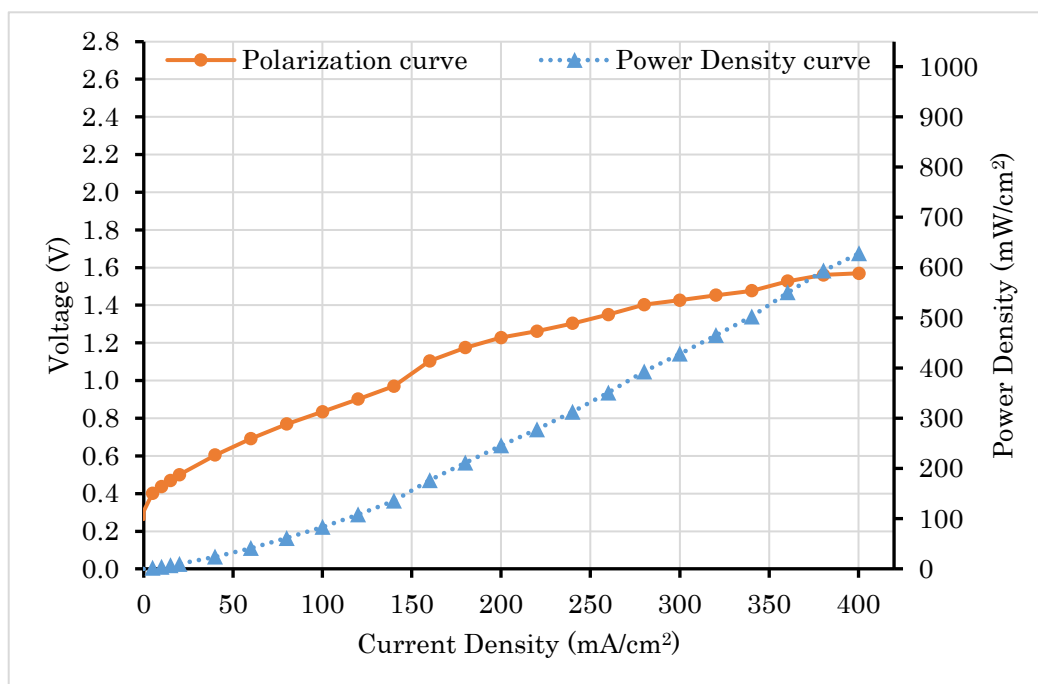


Figure C.65: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

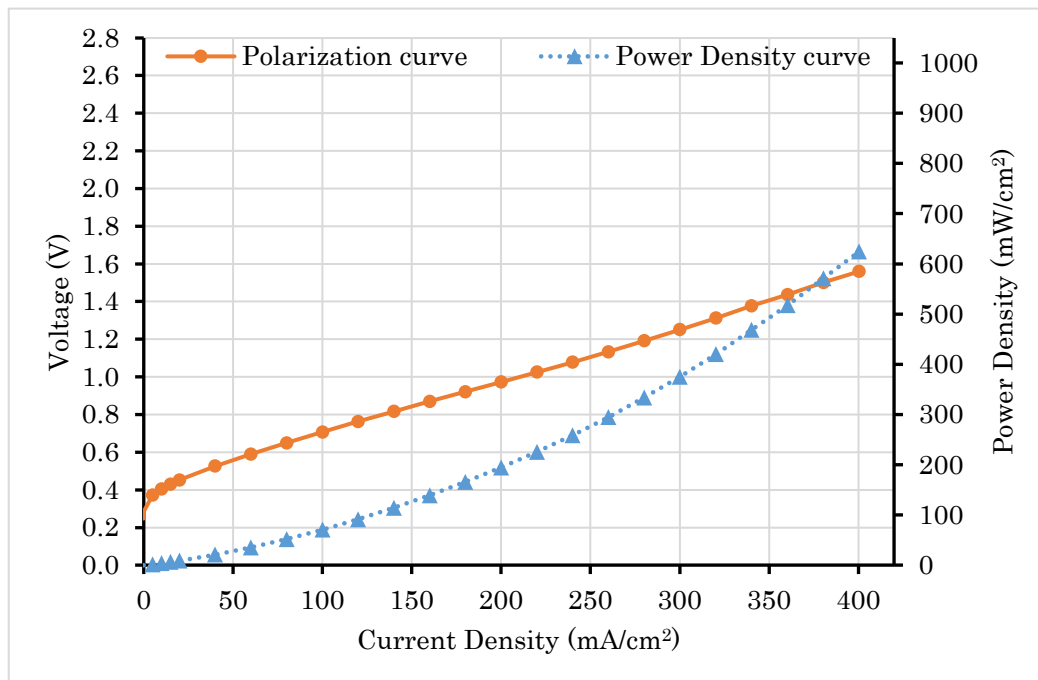


Figure C.66: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

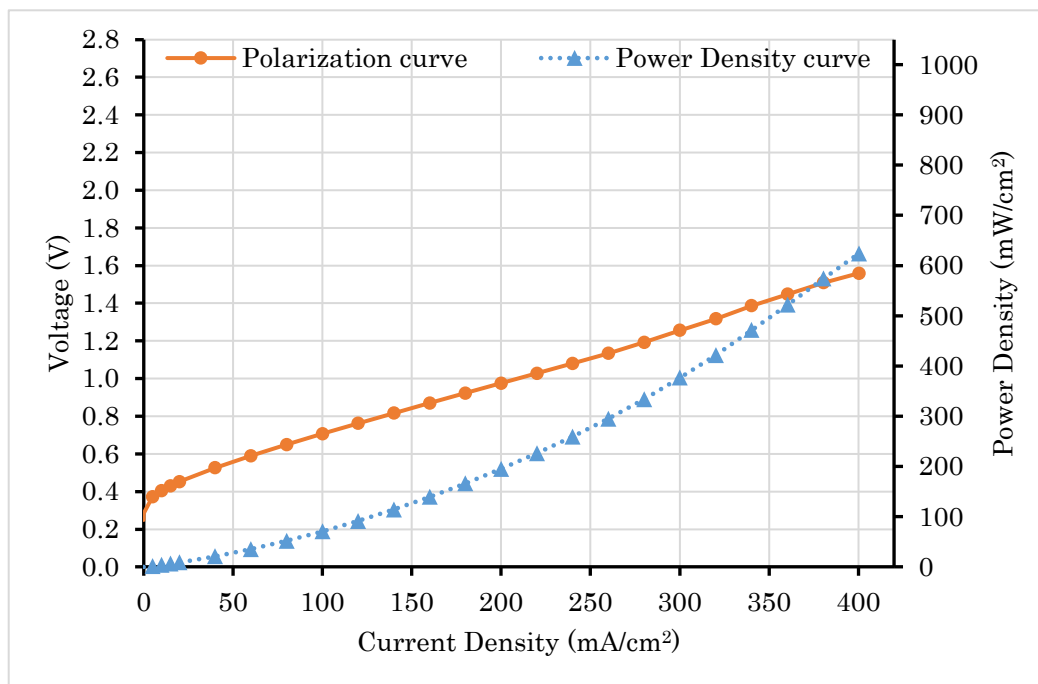


Figure C.67: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

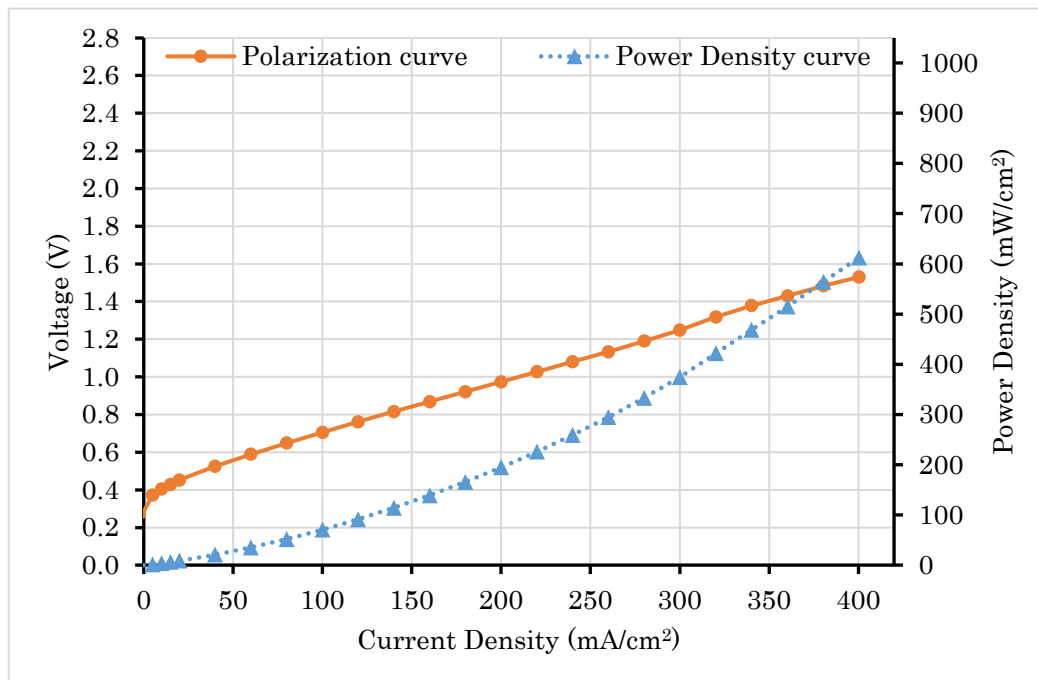


Figure C.68: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

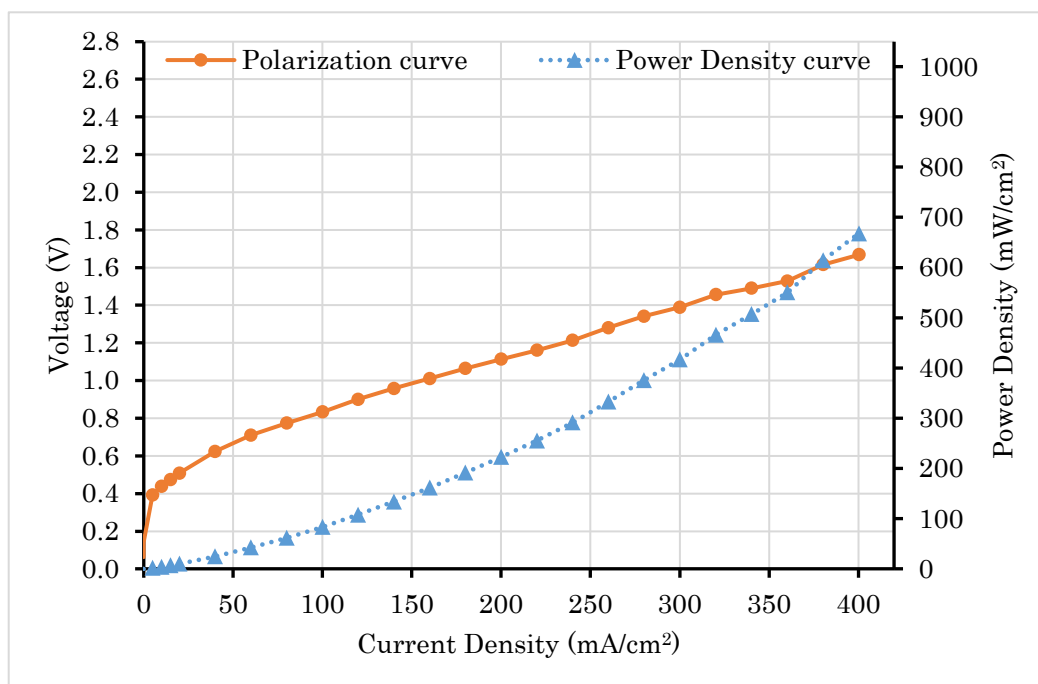


Figure C.69: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

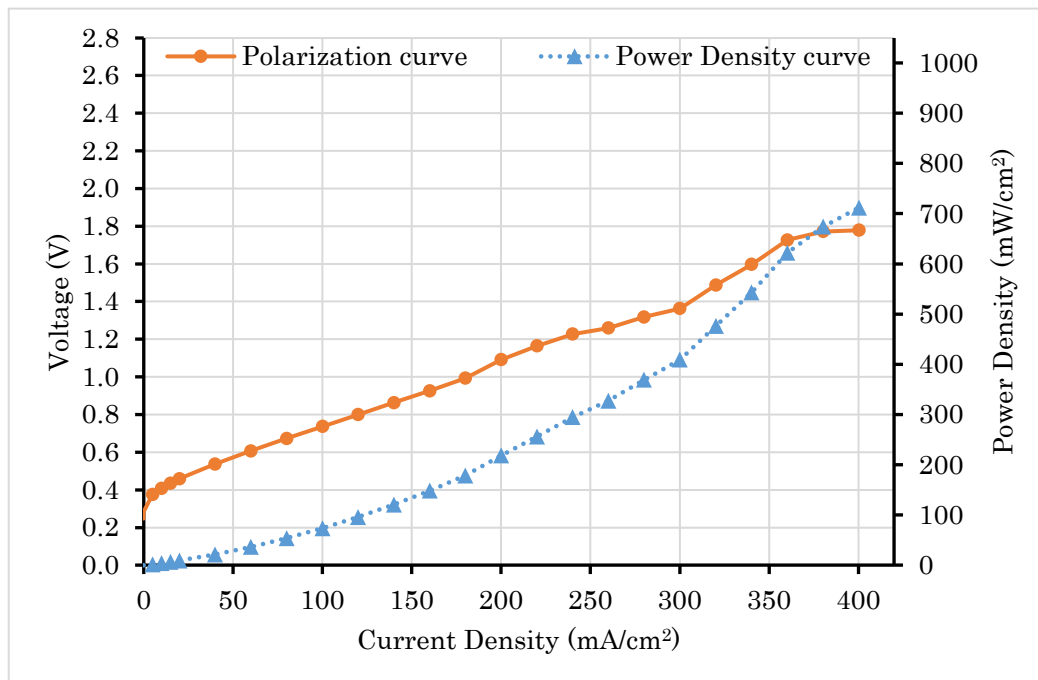


Figure C.70: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

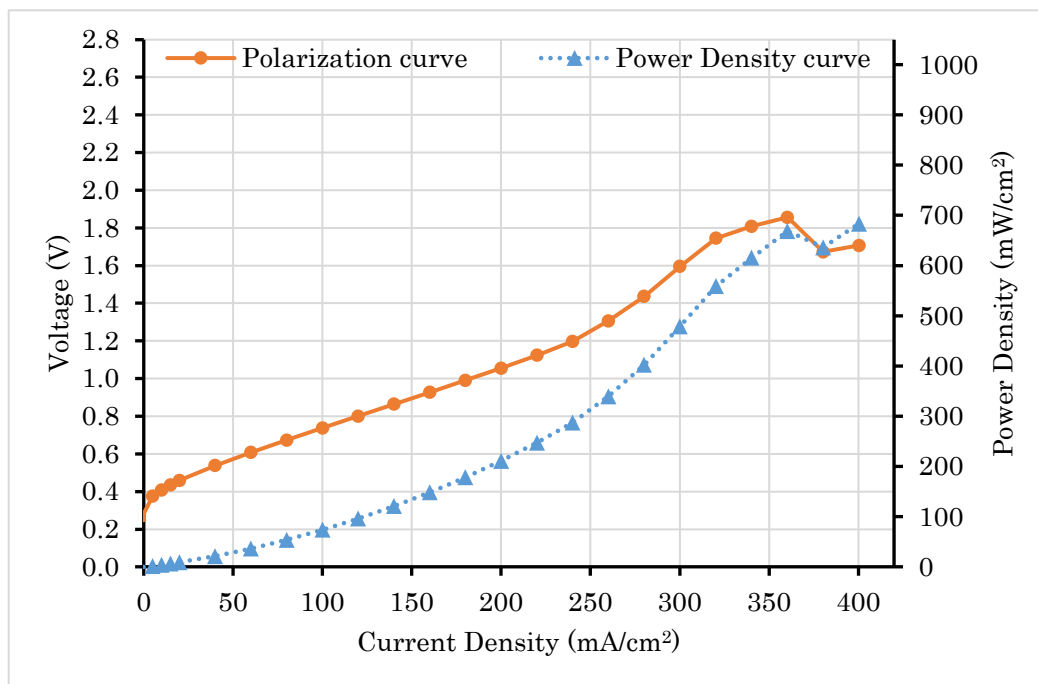


Figure C.71: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

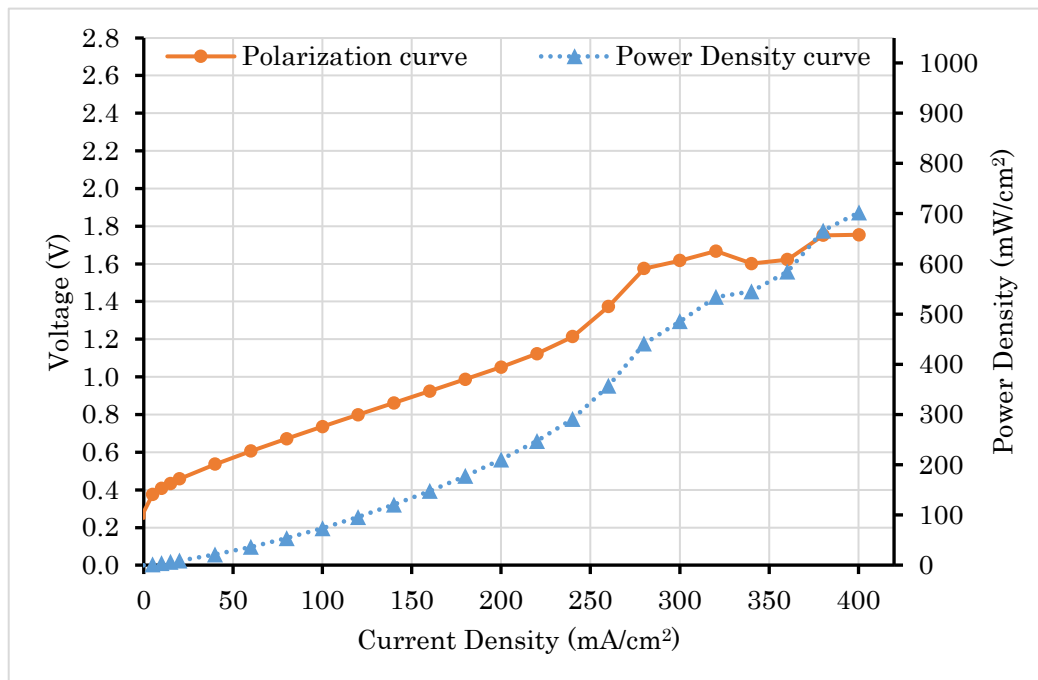


Figure C.72: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 50.0 °C, methanol concentration of 2.00 M and methanol volumetric flow rate 4.50 ml/min.

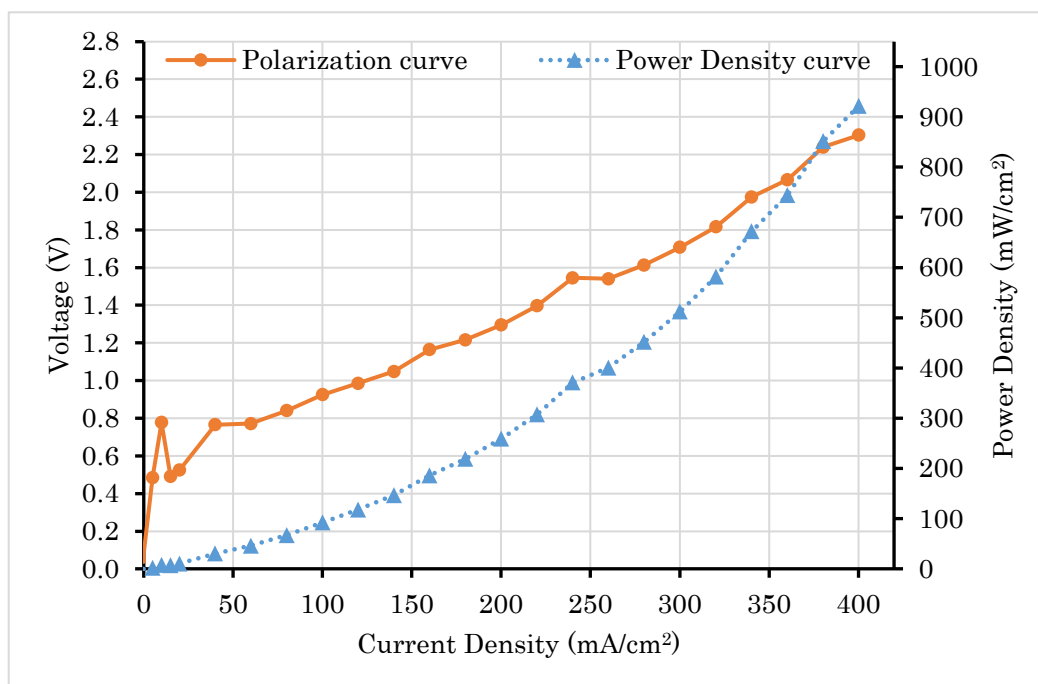


Figure C.73: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

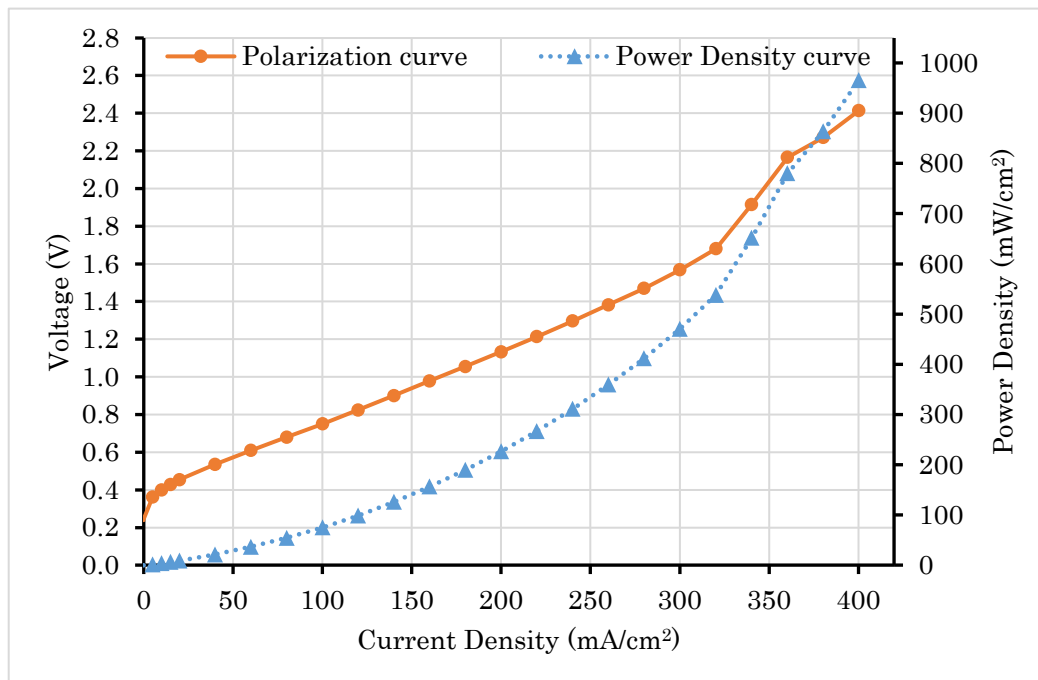


Figure C.74: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

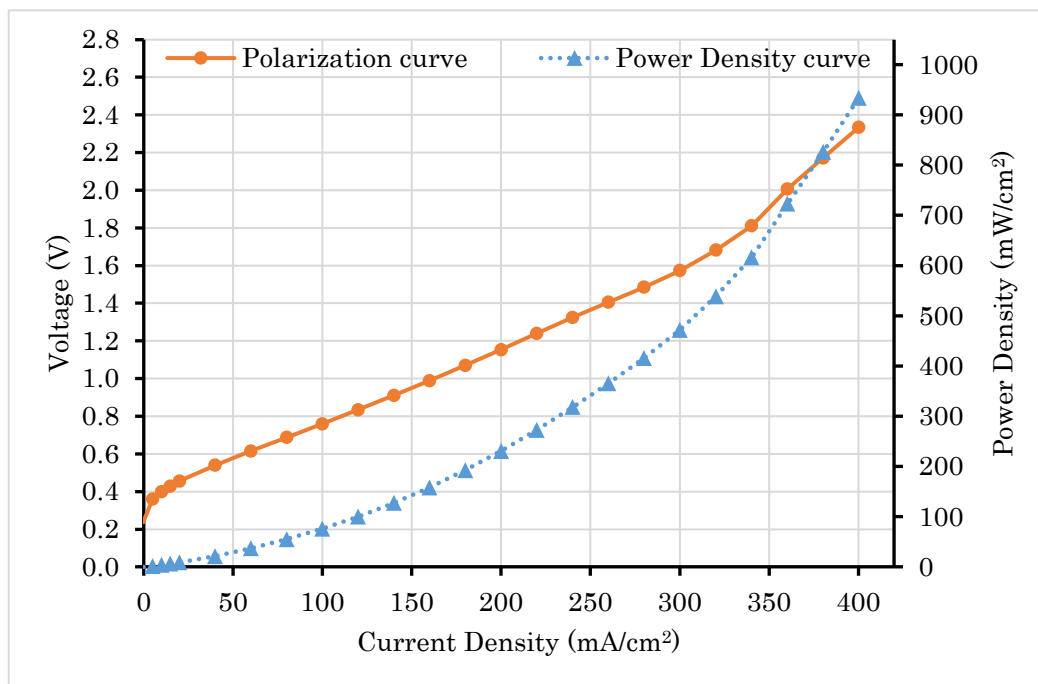


Figure C.75: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

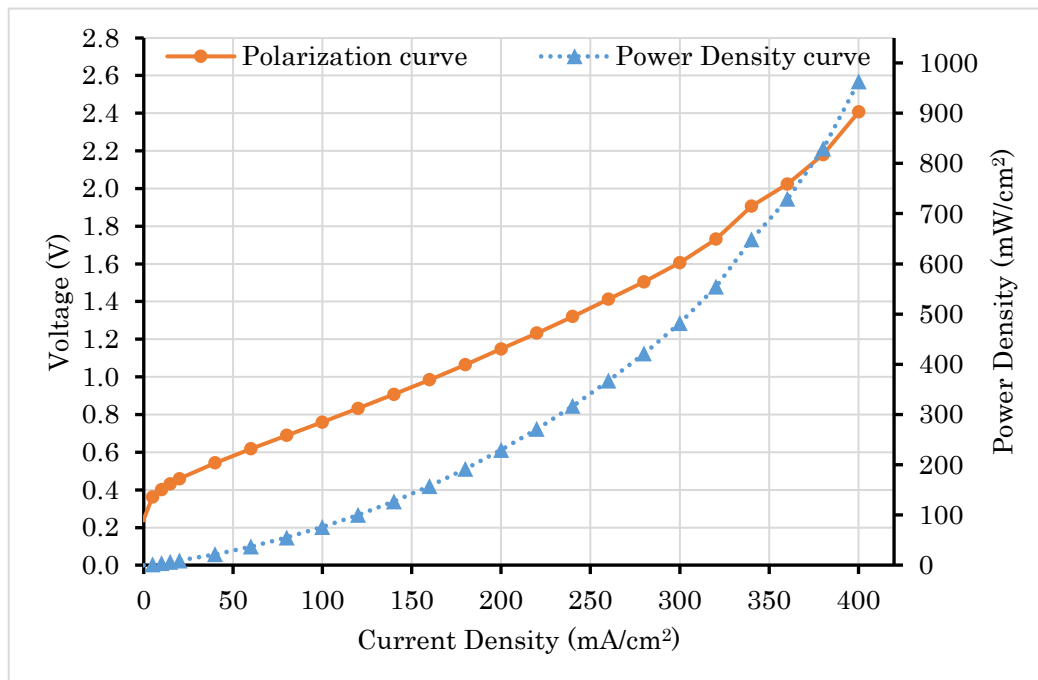


Figure C.76: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained at a temperature of 40.0 °C, methanol concentration of 1.00 M and methanol volumetric flow rate 3.00 ml/min.

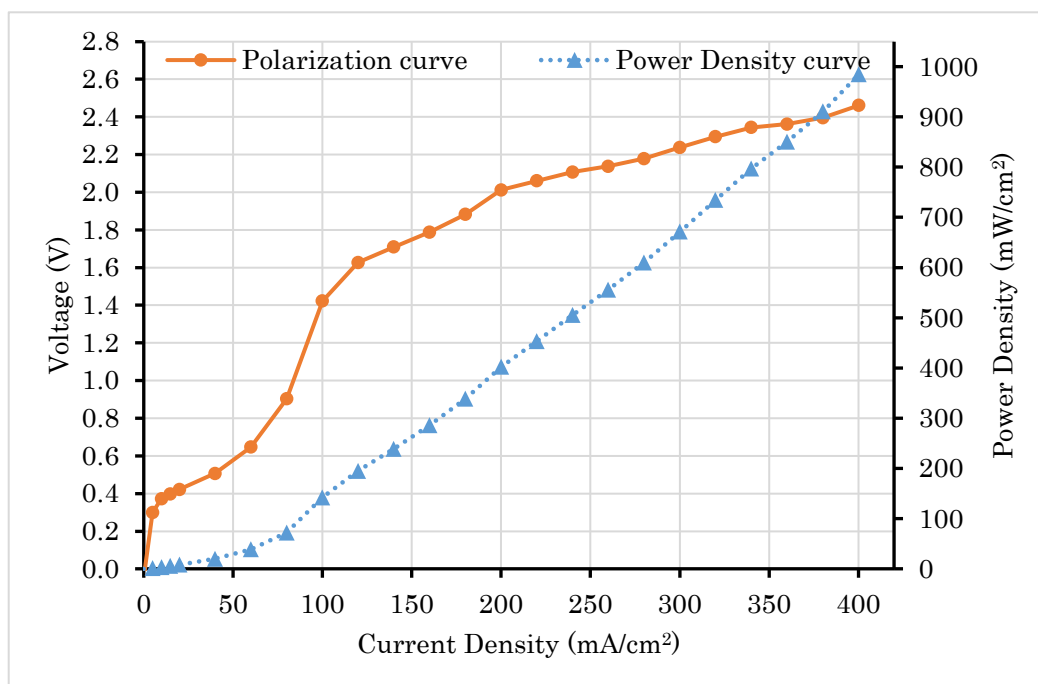


Figure C.77: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

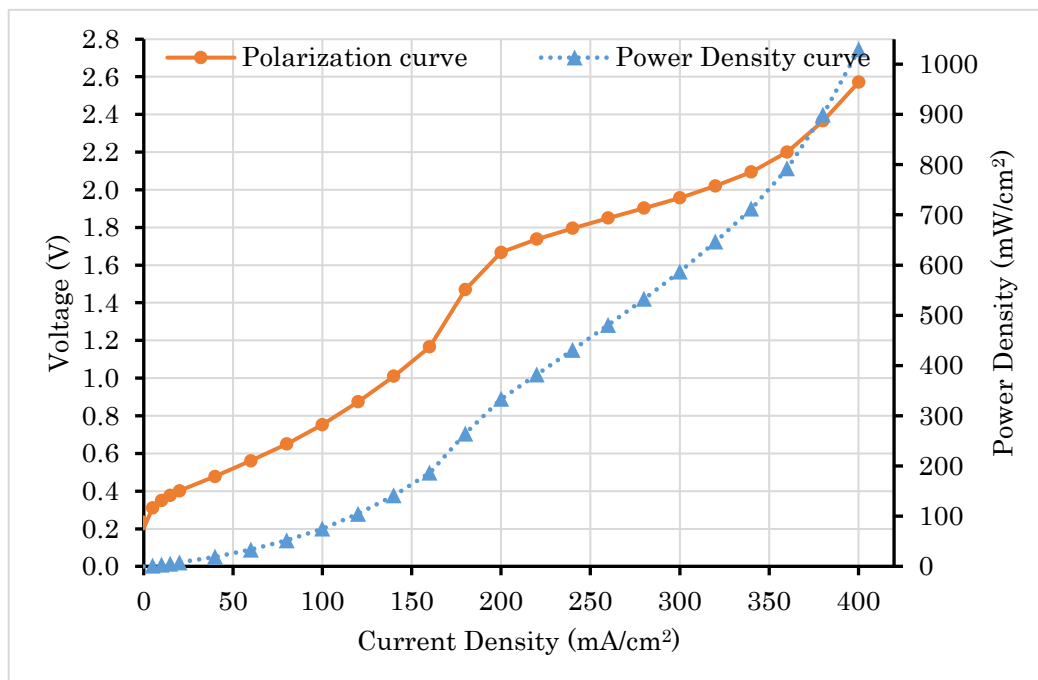


Figure C.78: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

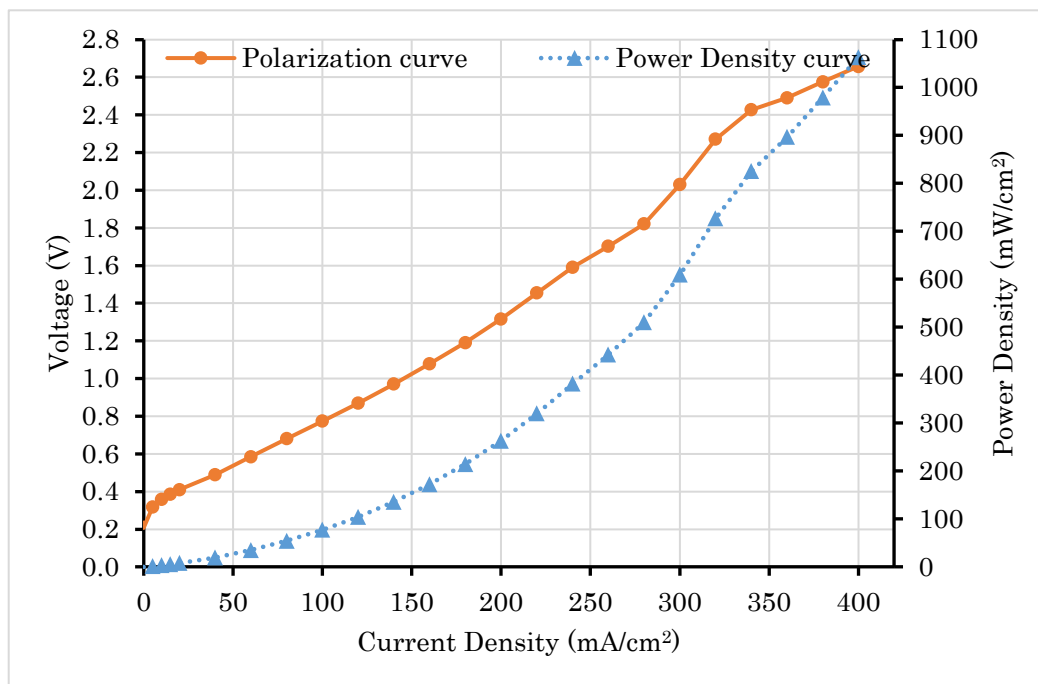


Figure C.79: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

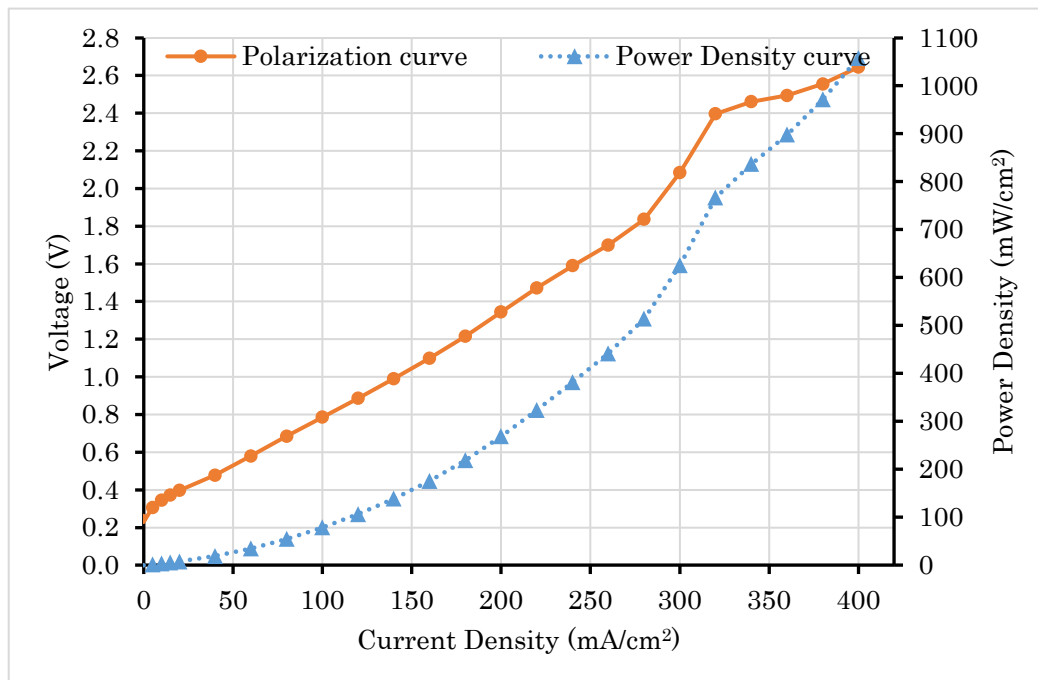


Figure C.80: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

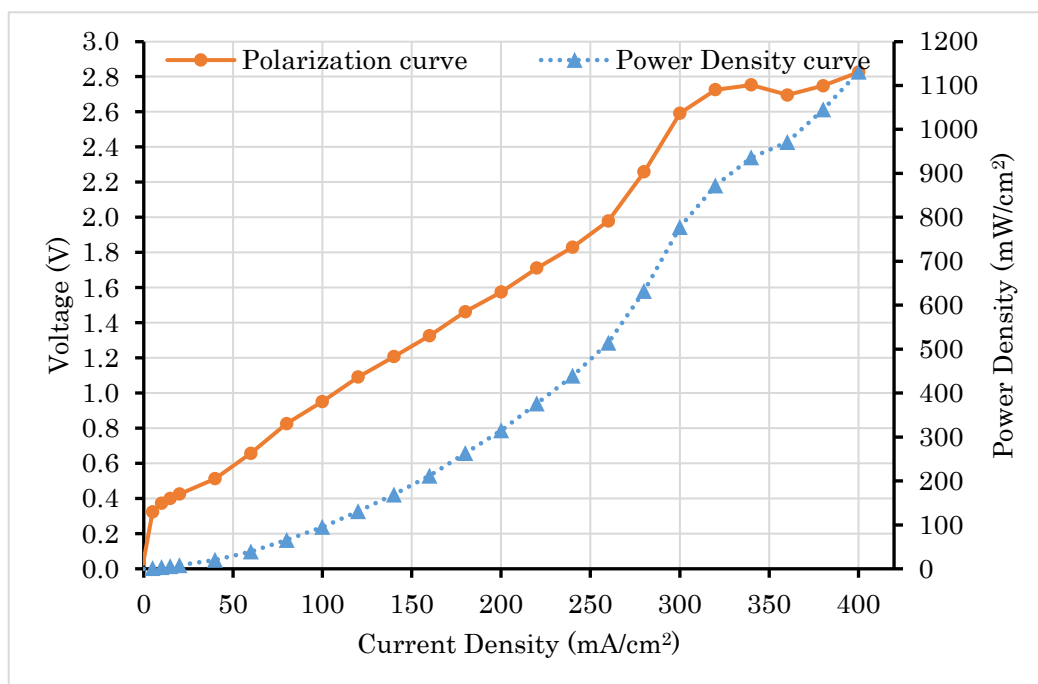


Figure C.81: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

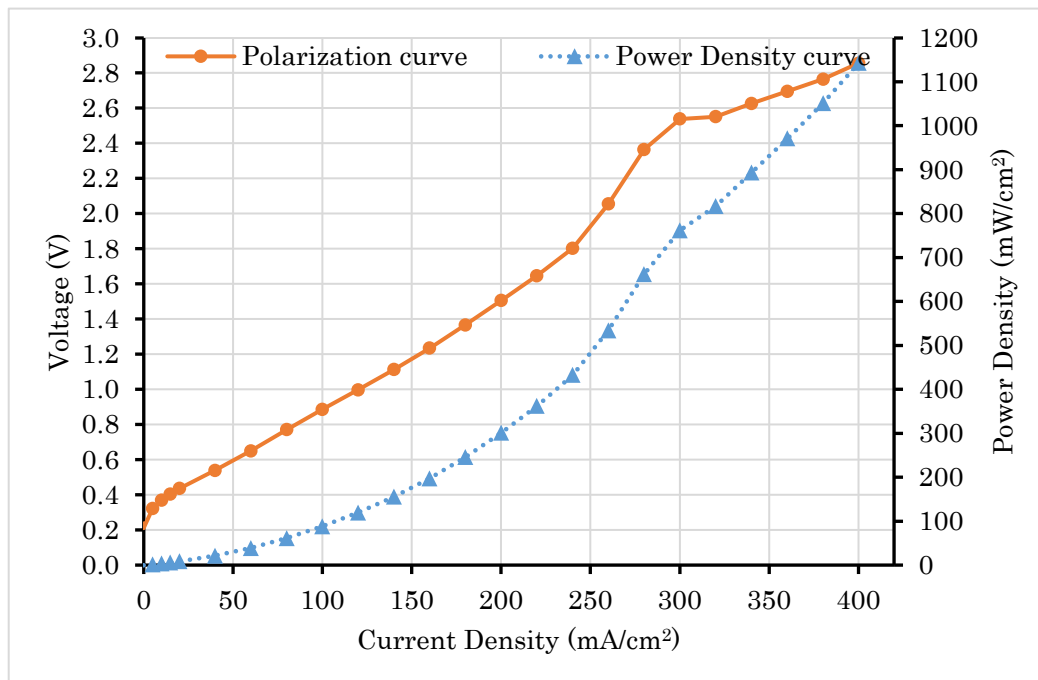


Figure C.82: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

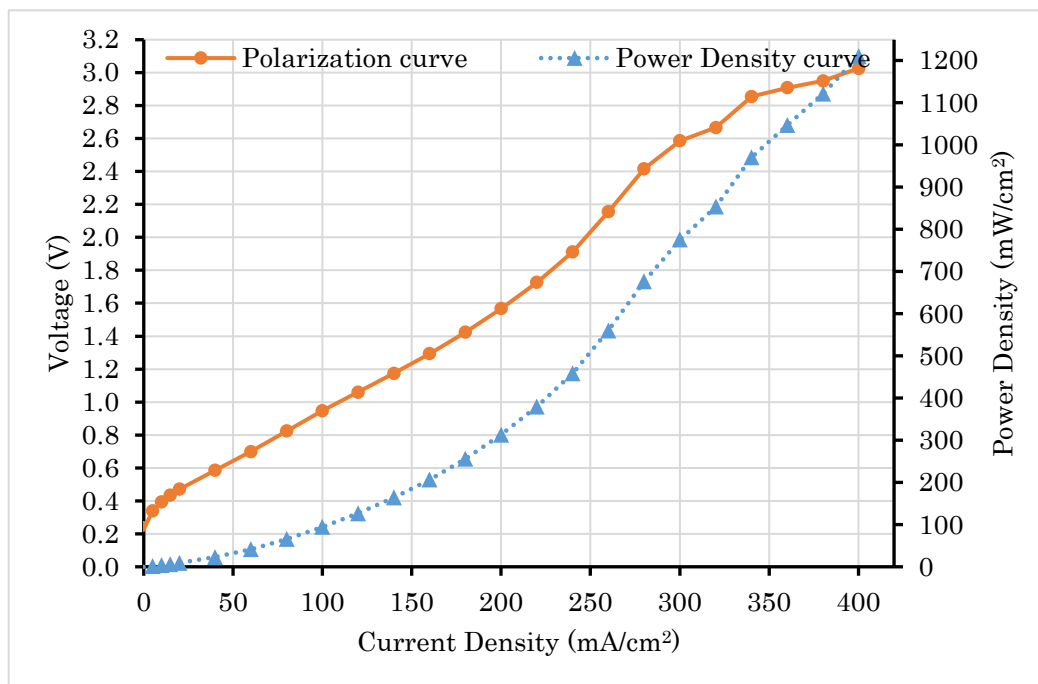


Figure C.83: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

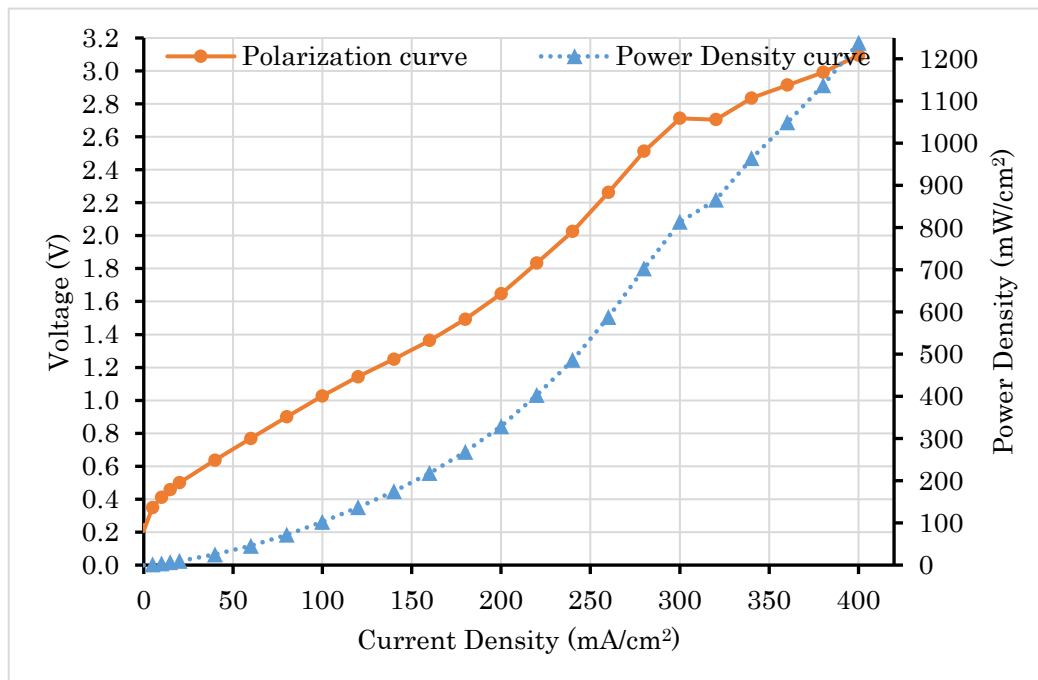


Figure C.84: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 19.2 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

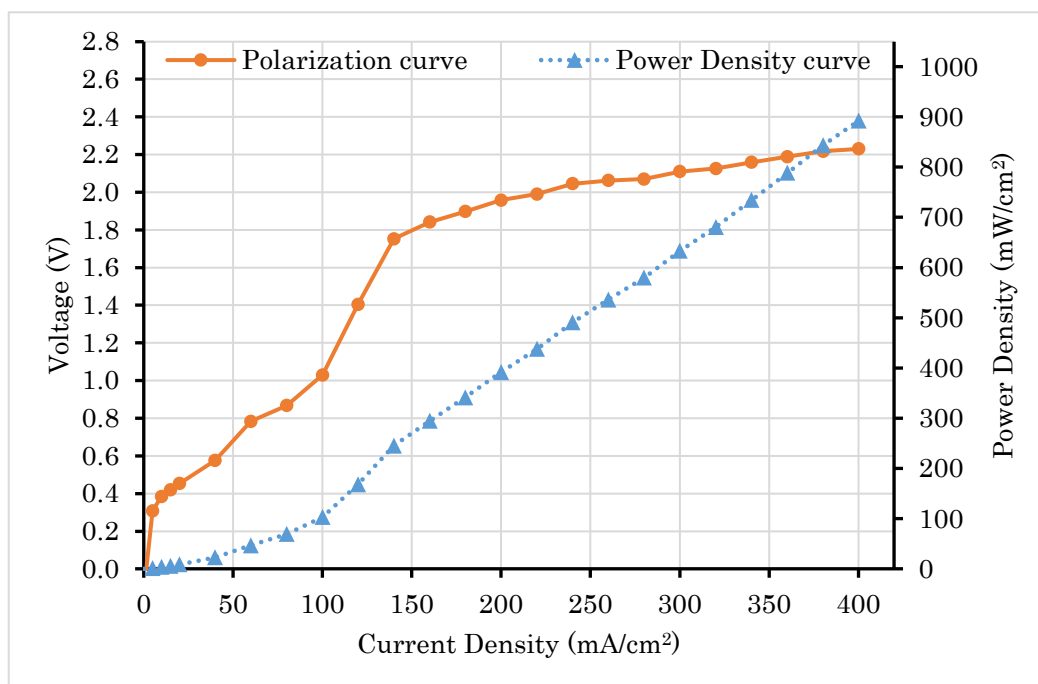


Figure C.85: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

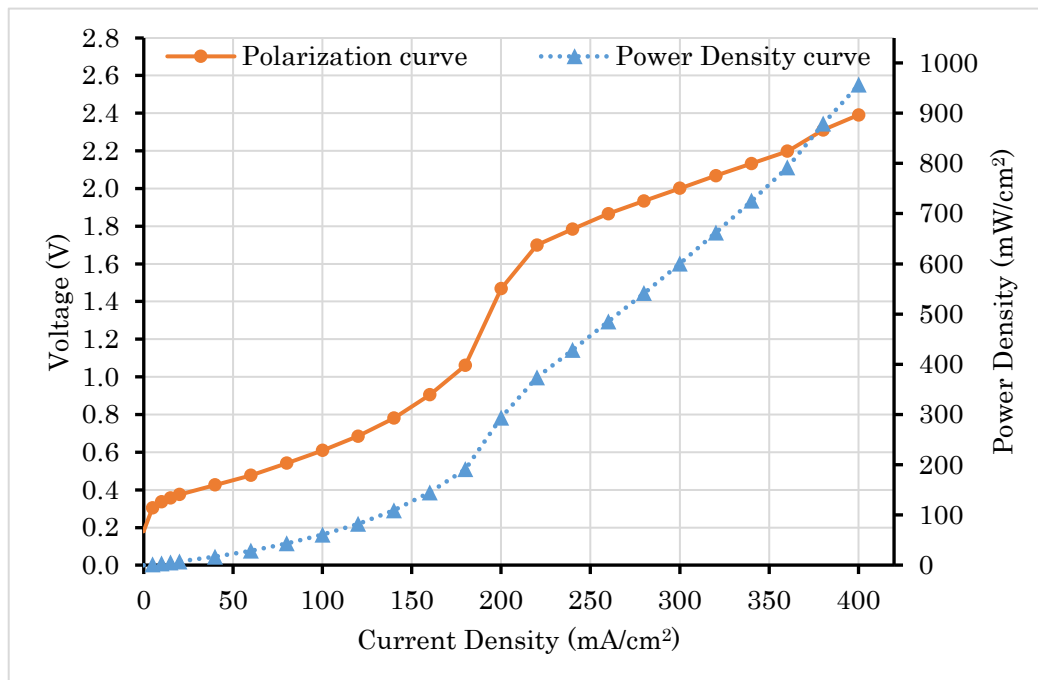


Figure C.86: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

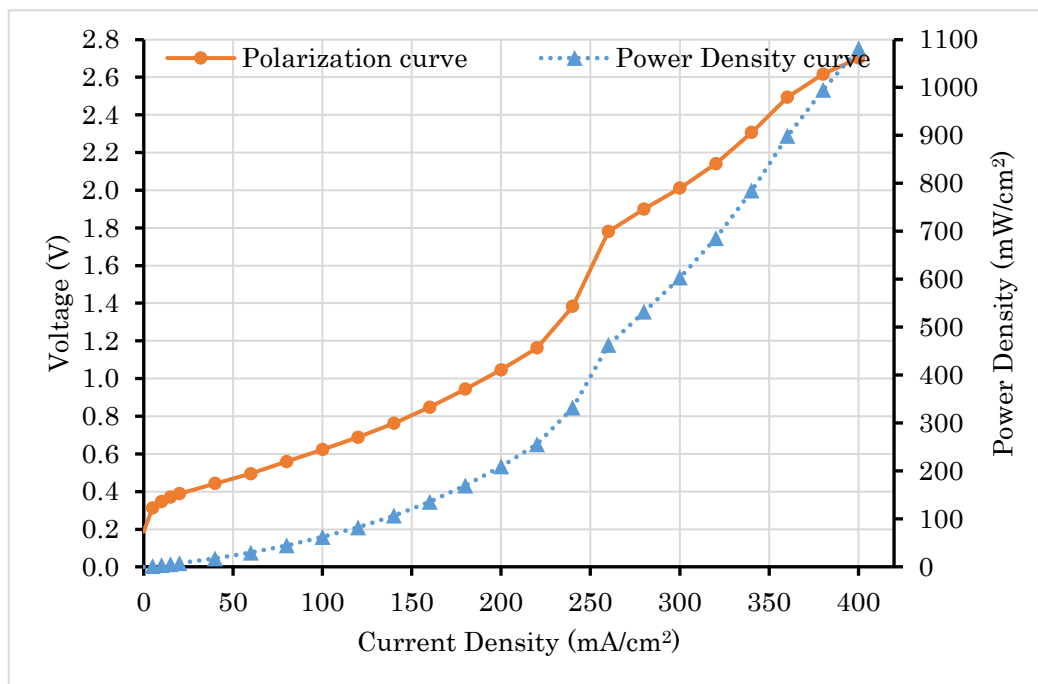


Figure C.87: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

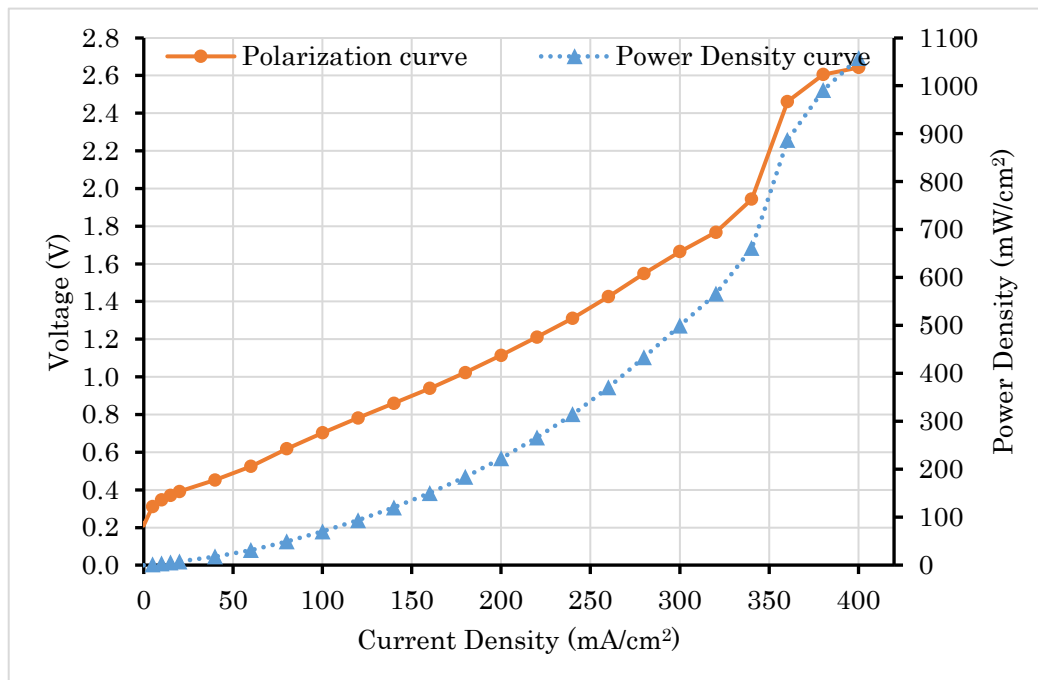


Figure C.88: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

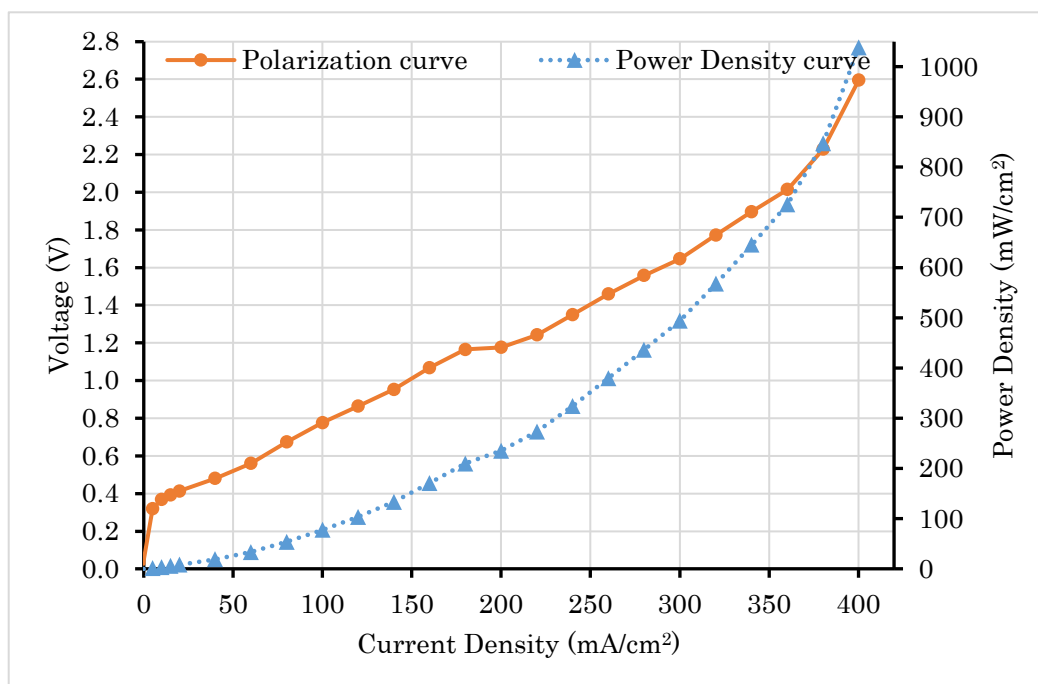


Figure C.89: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

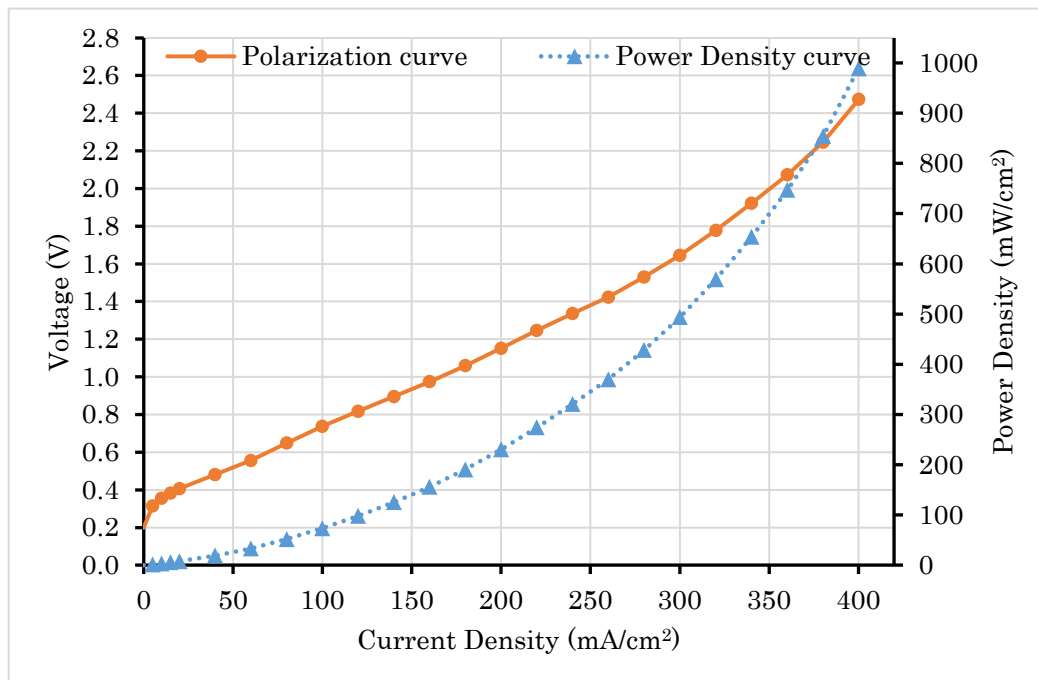


Figure C.90: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

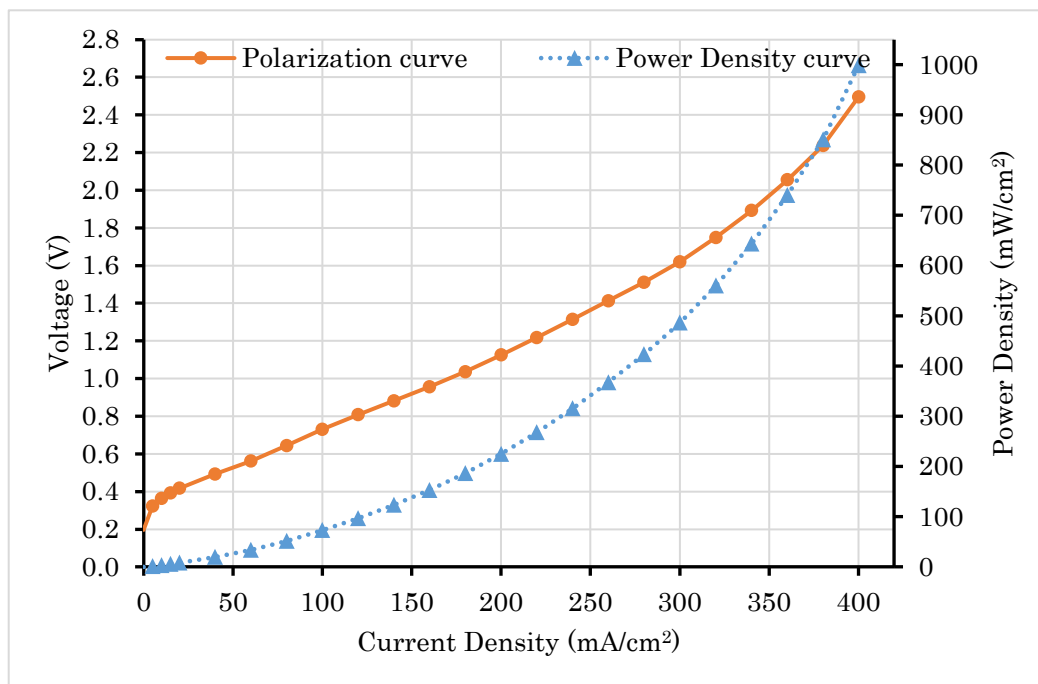


Figure C.91: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

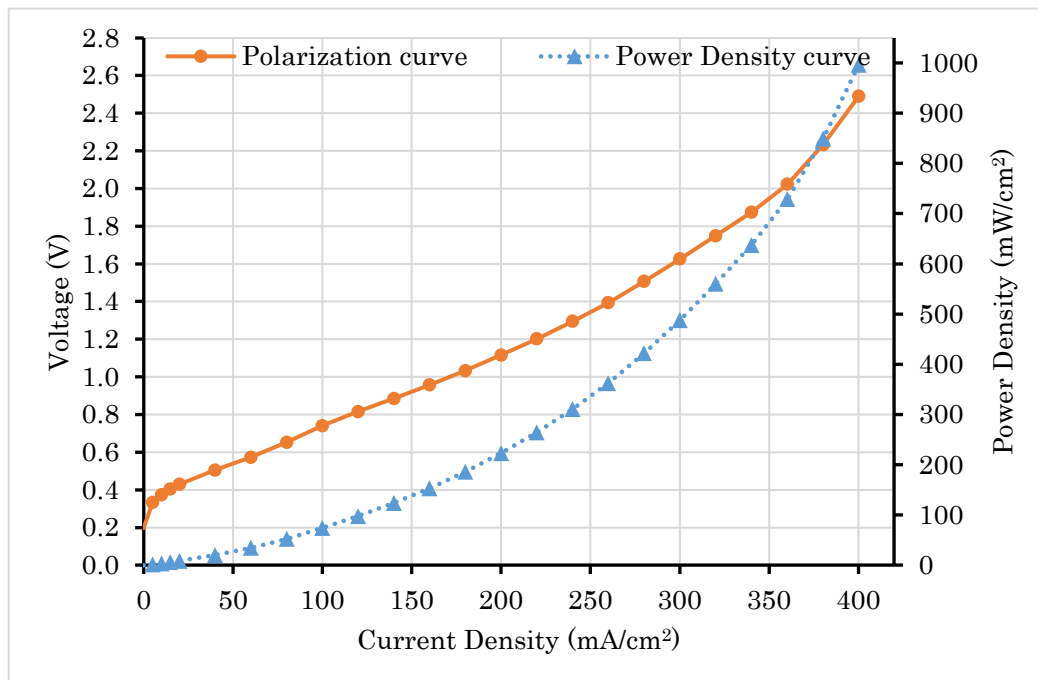


Figure C.92: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

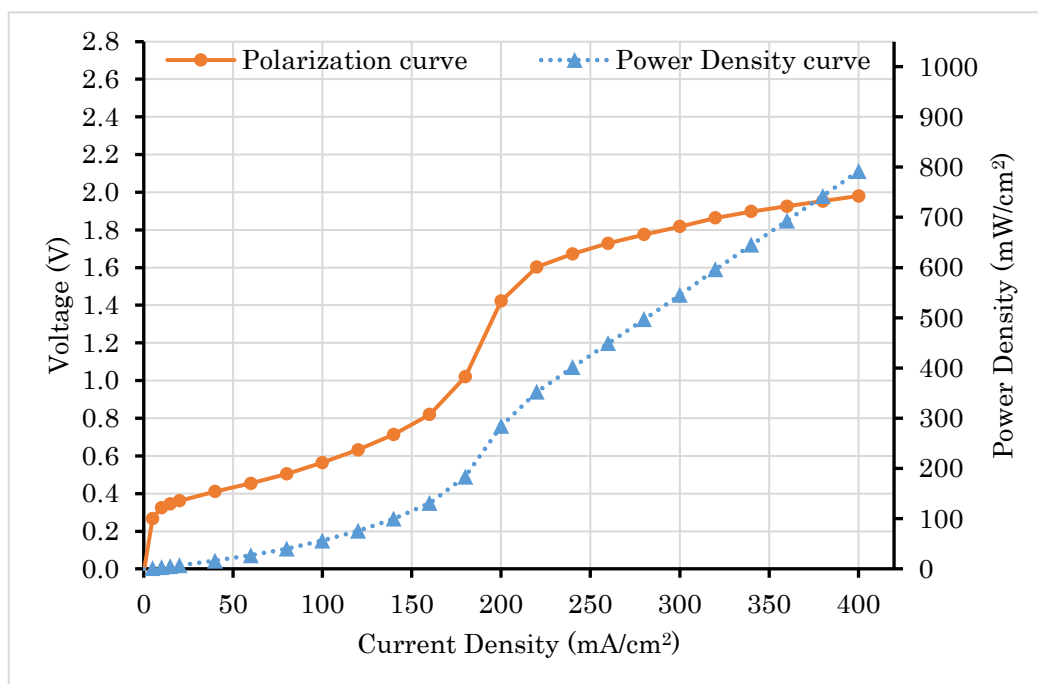


Figure C.93: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

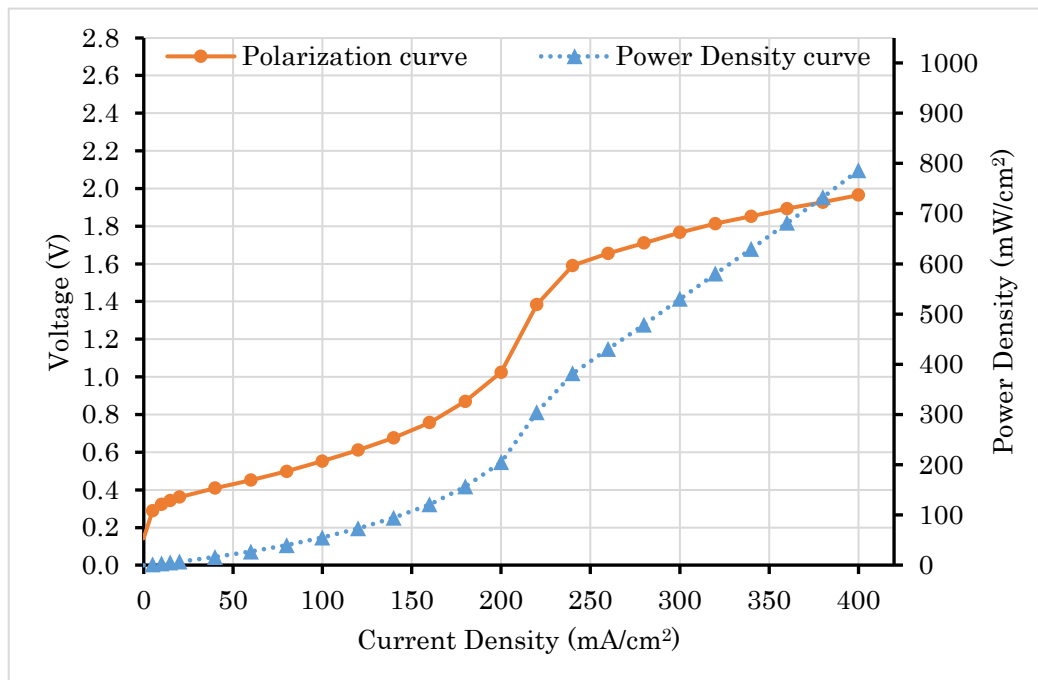


Figure C.94: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

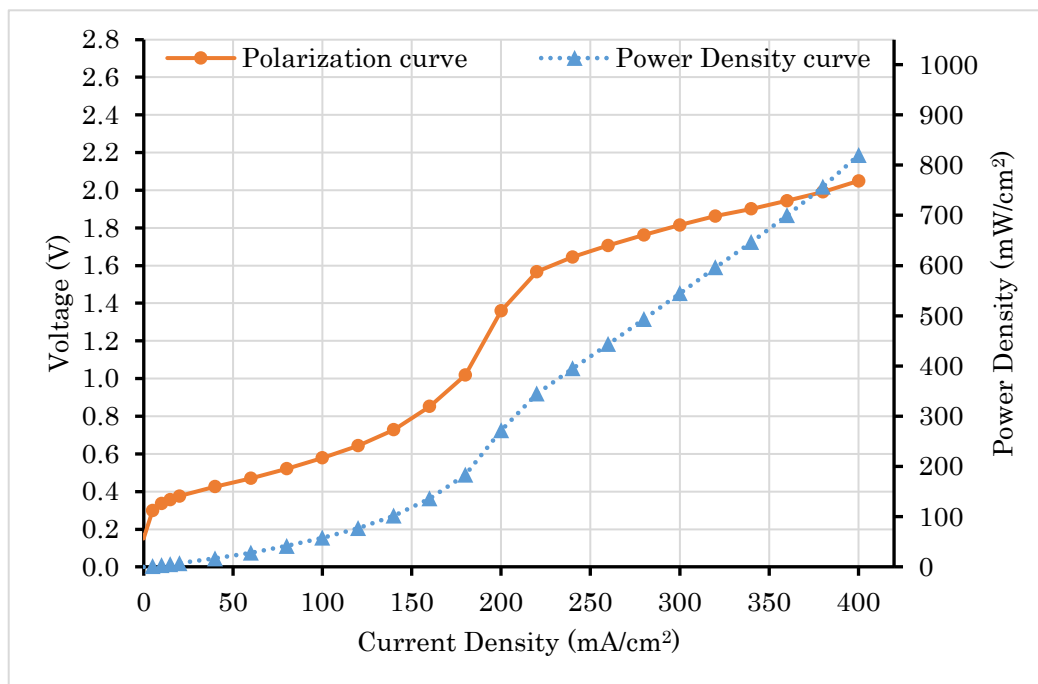


Figure C.95: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

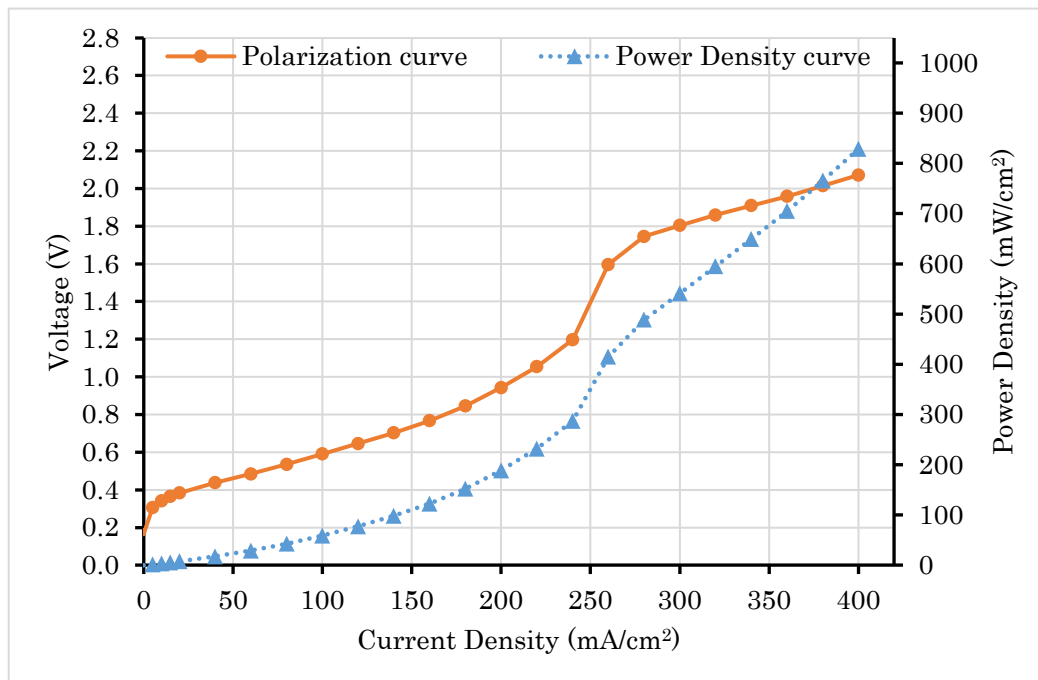


Figure C.96: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

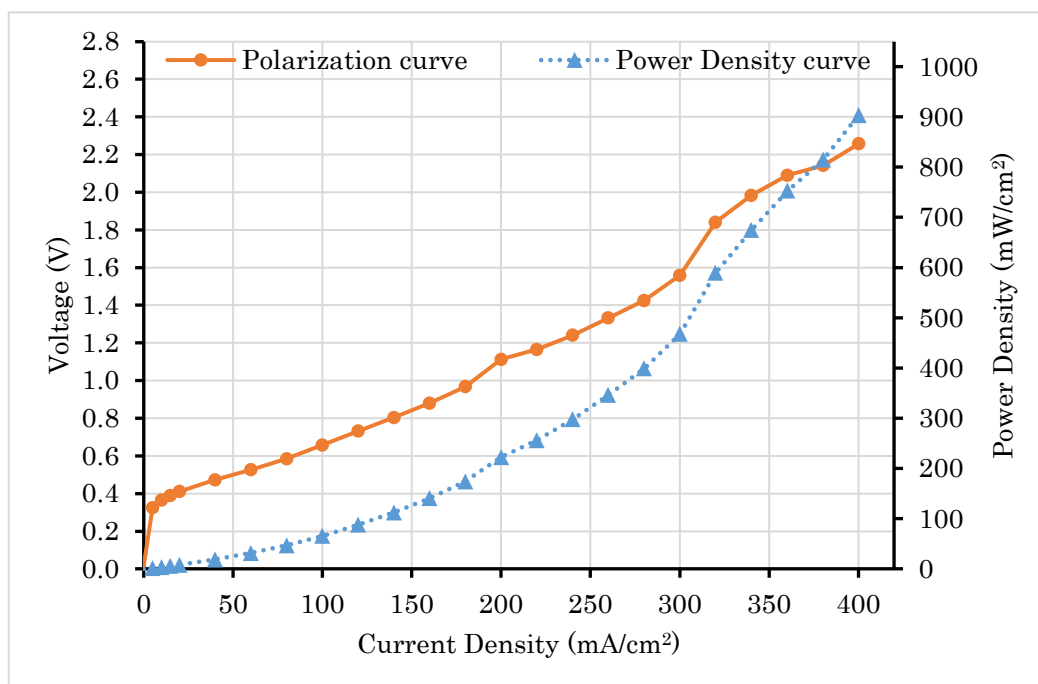


Figure C.97: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

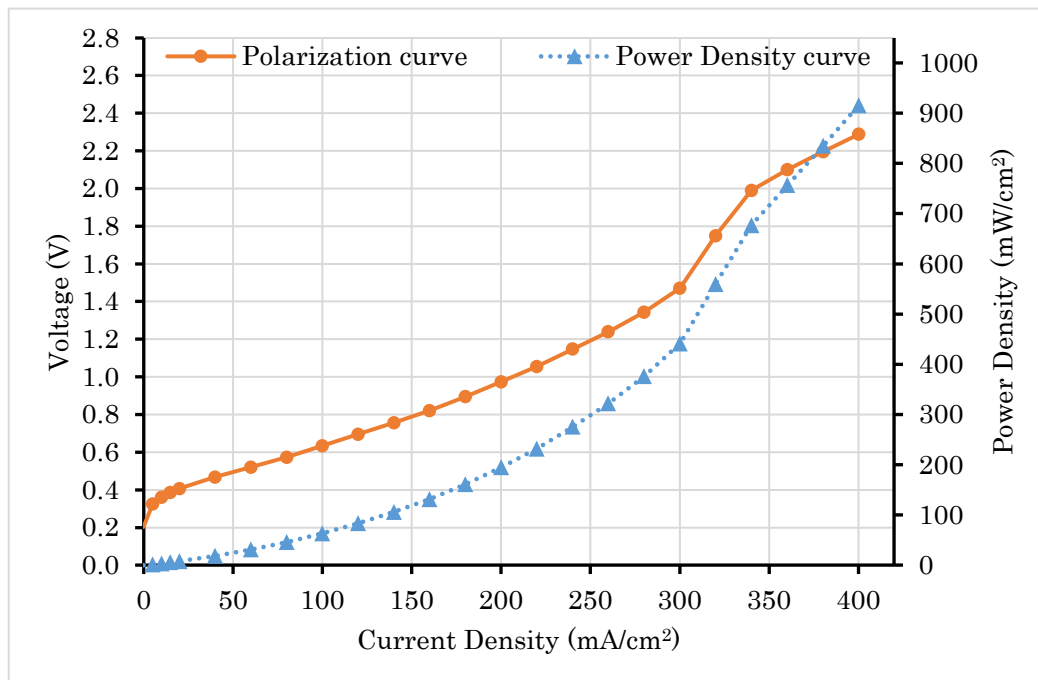


Figure C.98: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

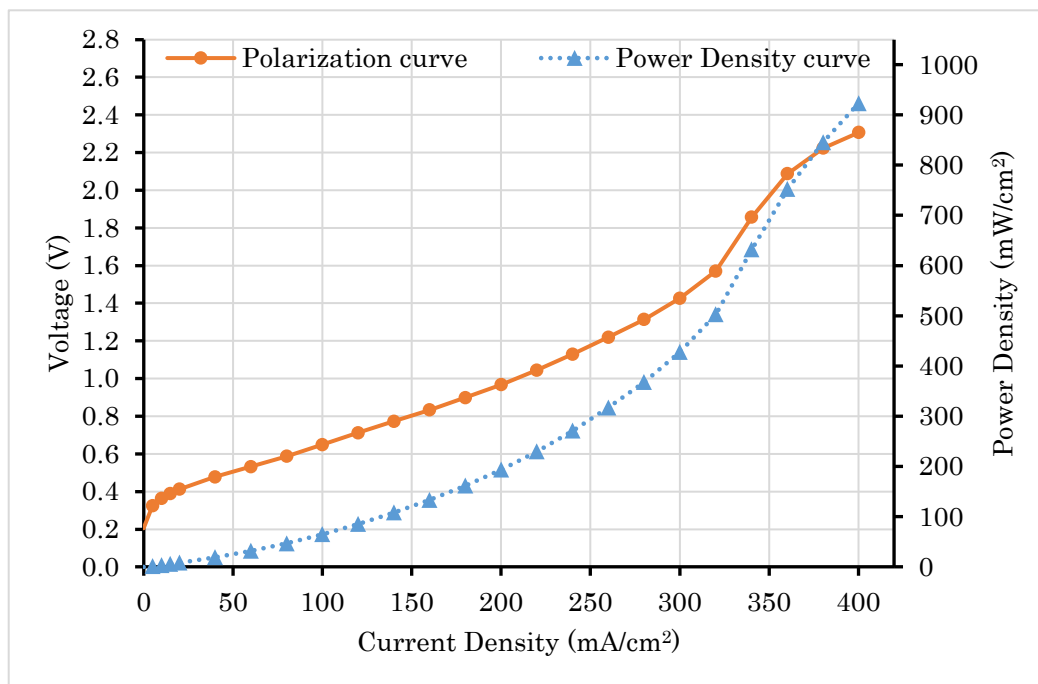


Figure C.99: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

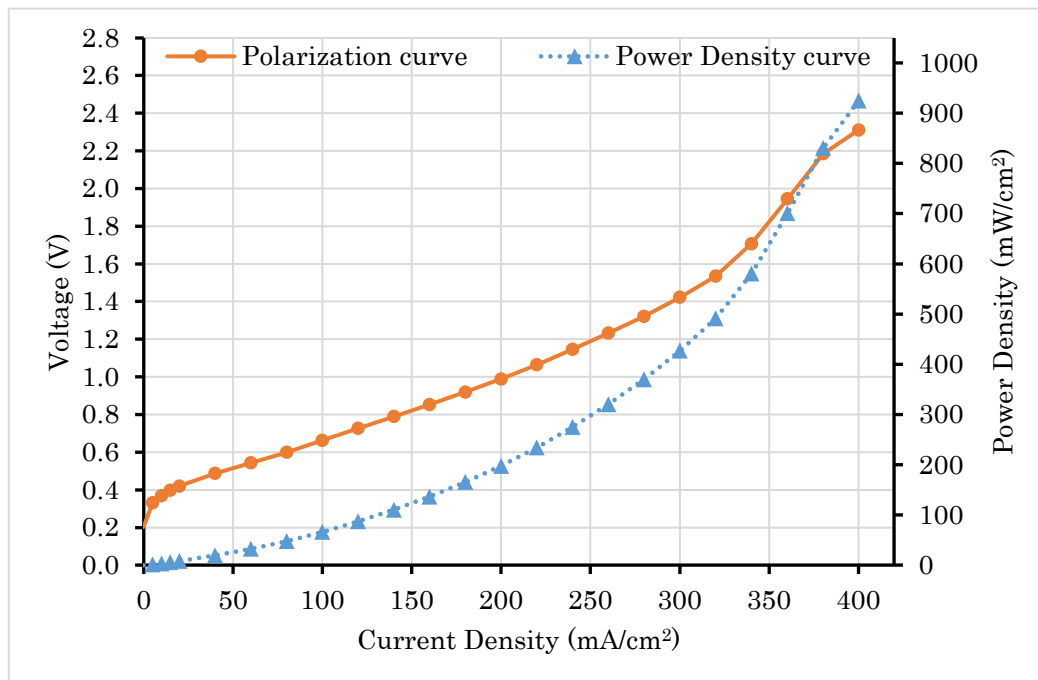


Figure C.100: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

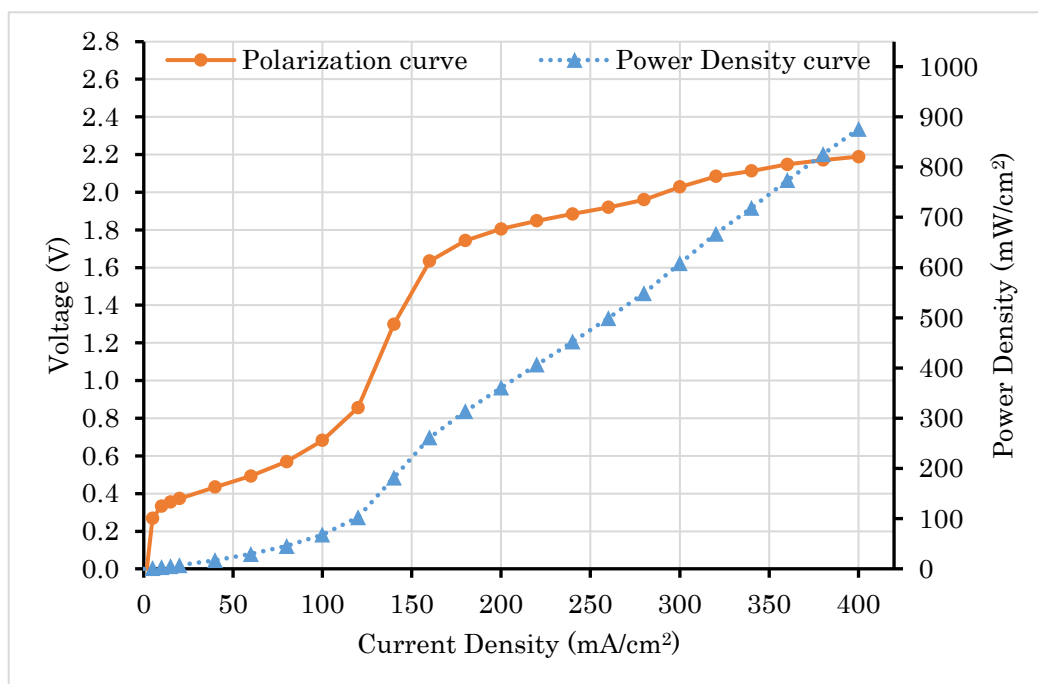


Figure C.101: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

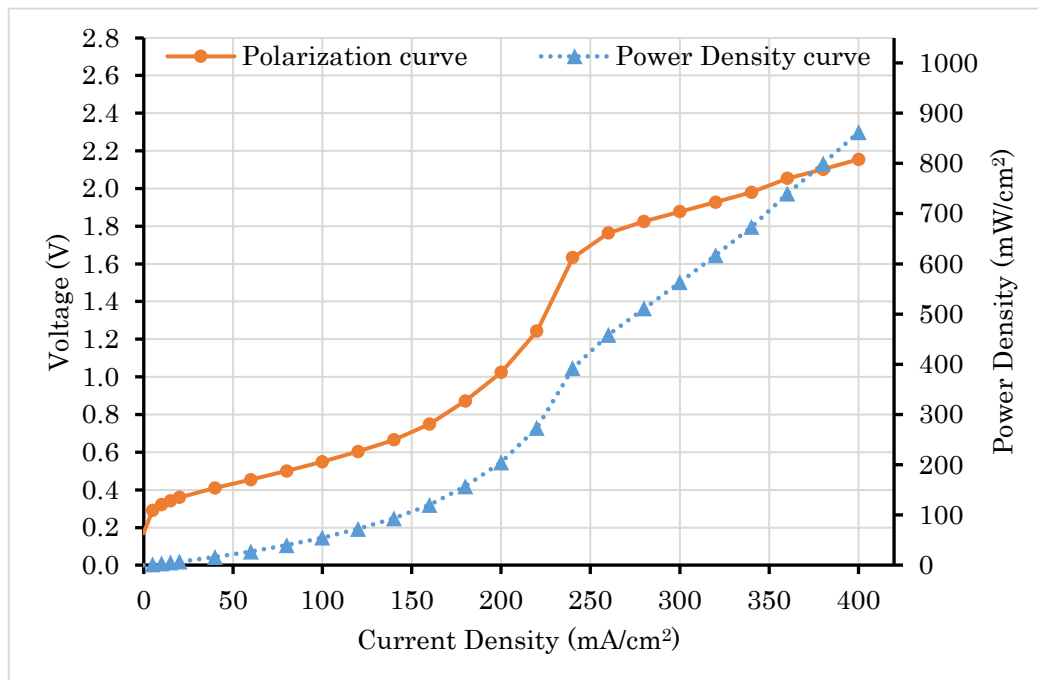


Figure C.102: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

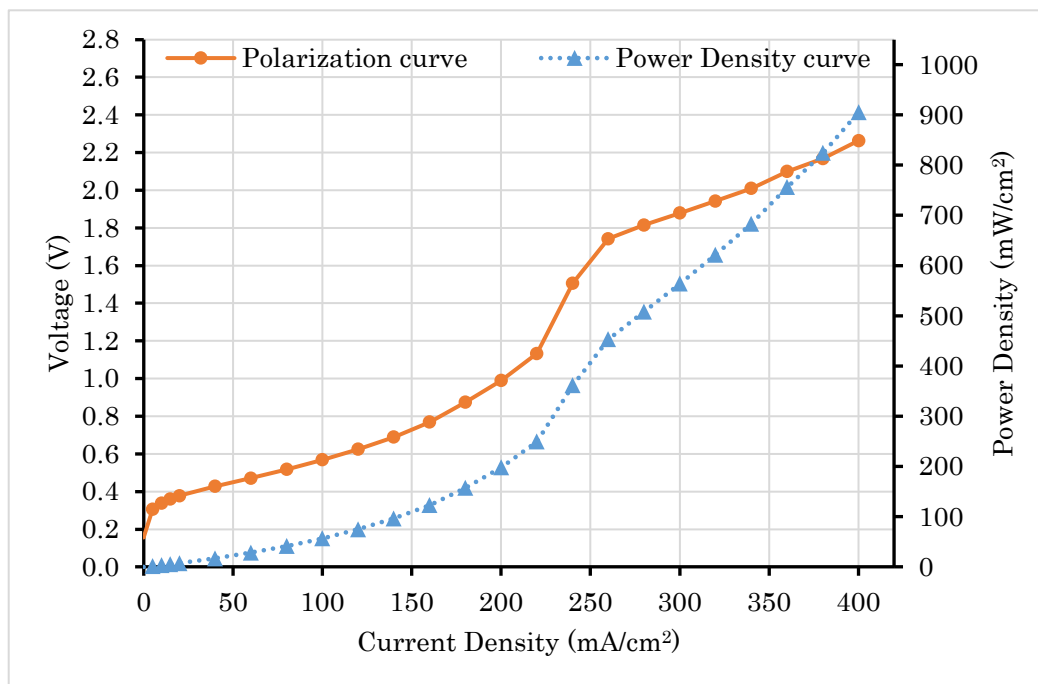


Figure C.103: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

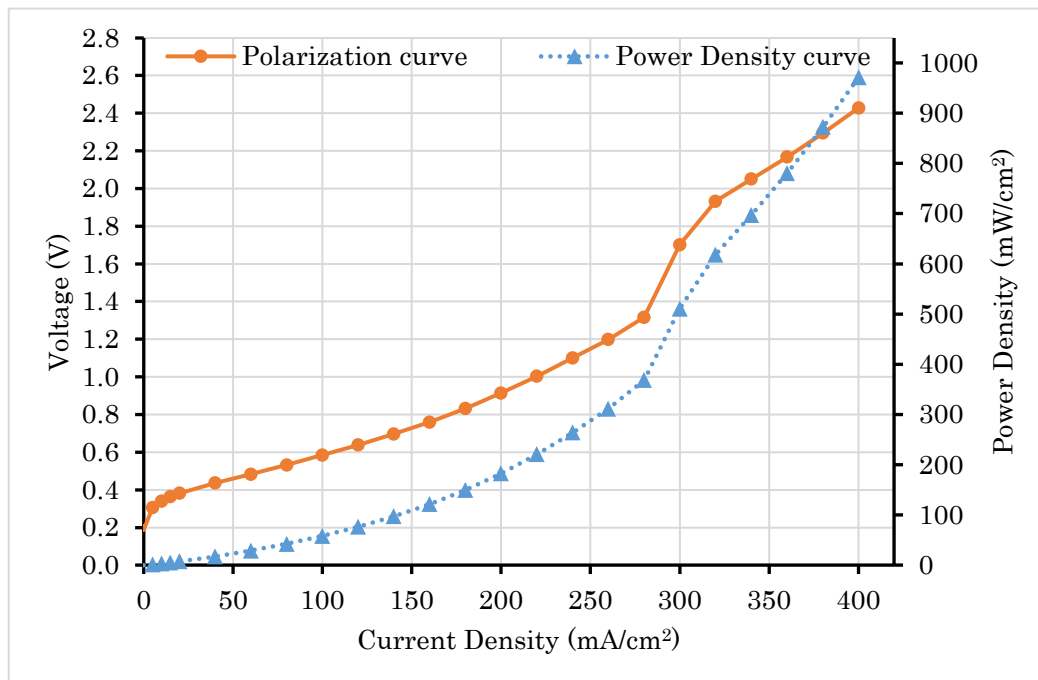


Figure C.104: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

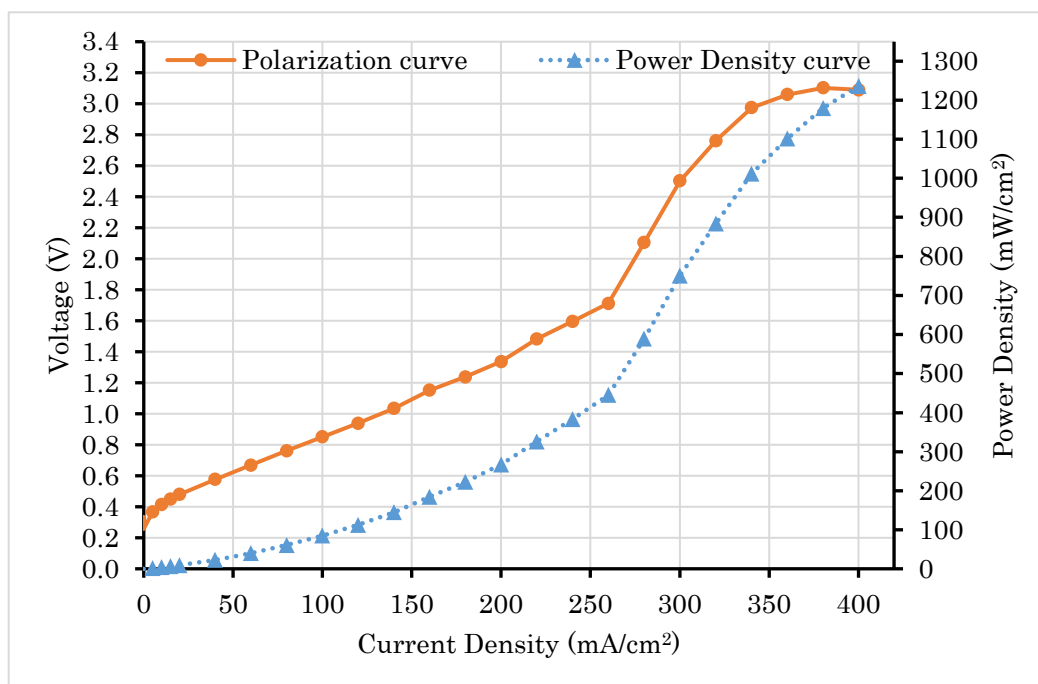


Figure C.105: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

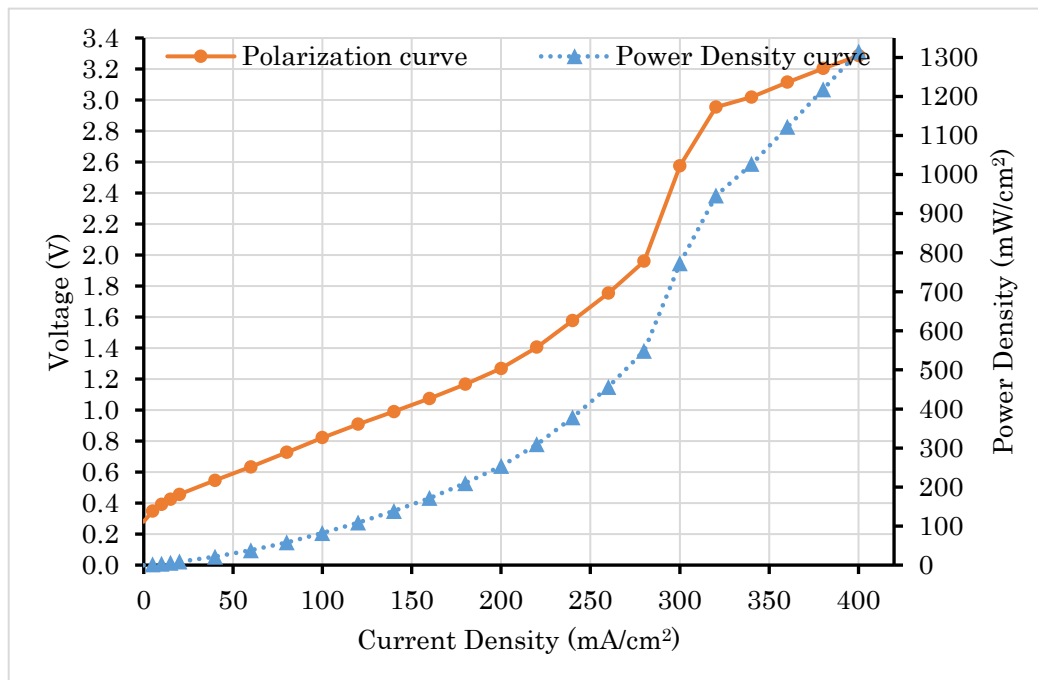


Figure C.106: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

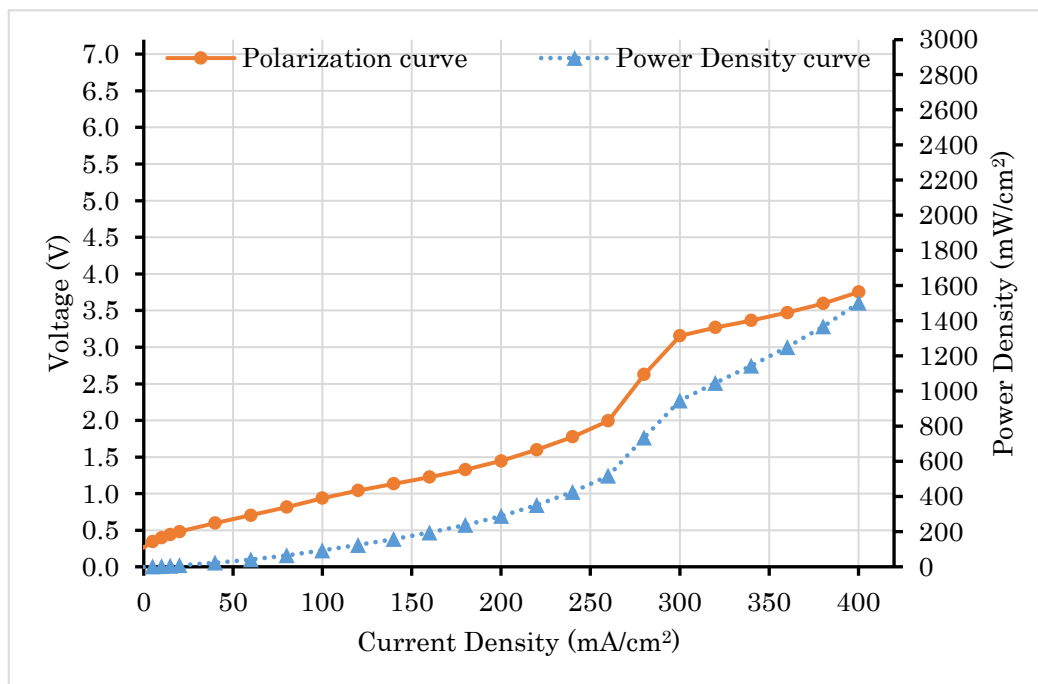


Figure C.107: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

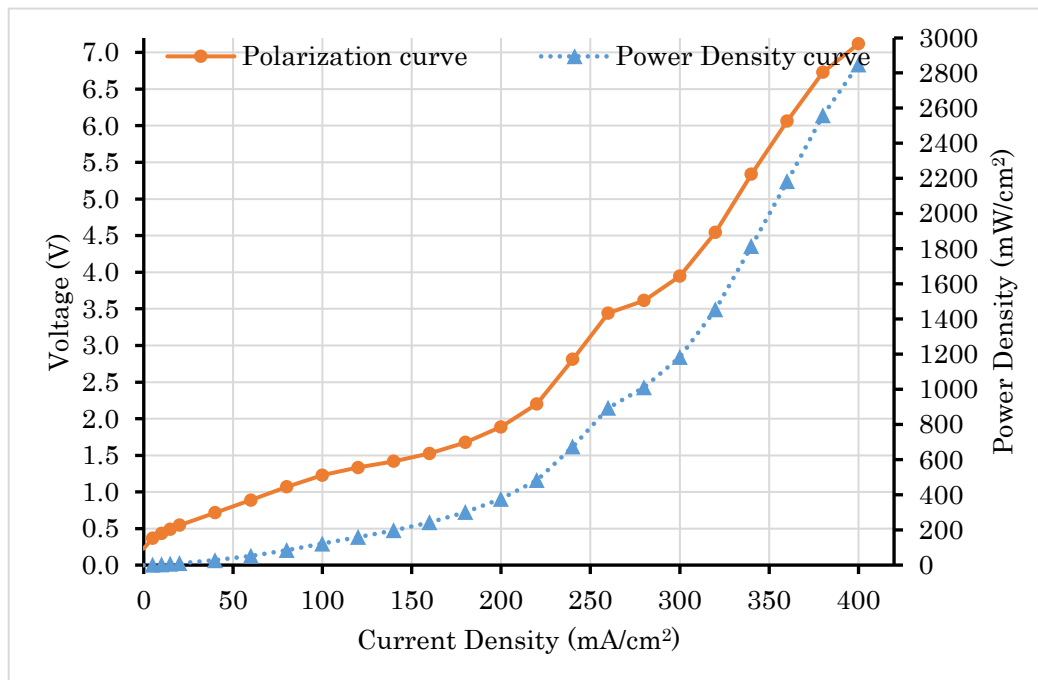


Figure C.108: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

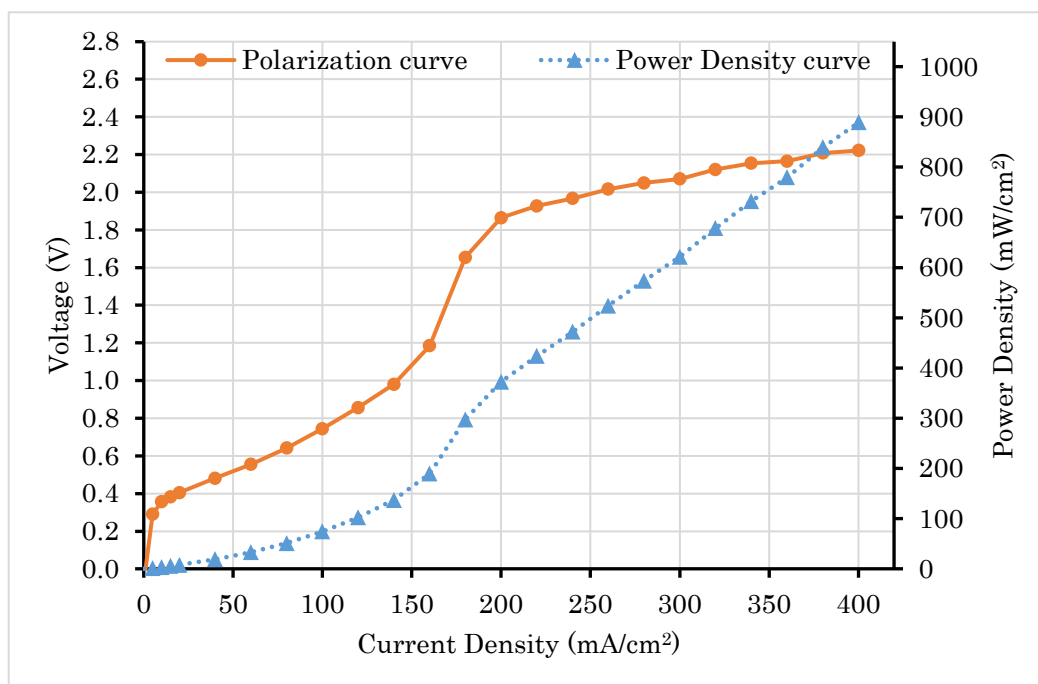


Figure C.109: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

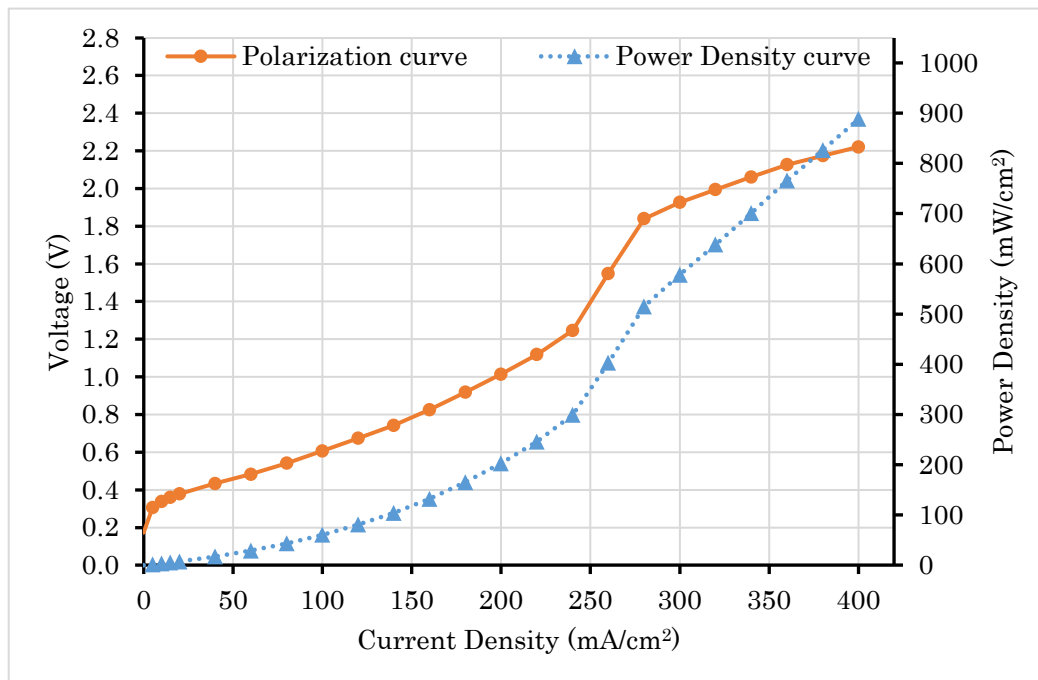


Figure C.110: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

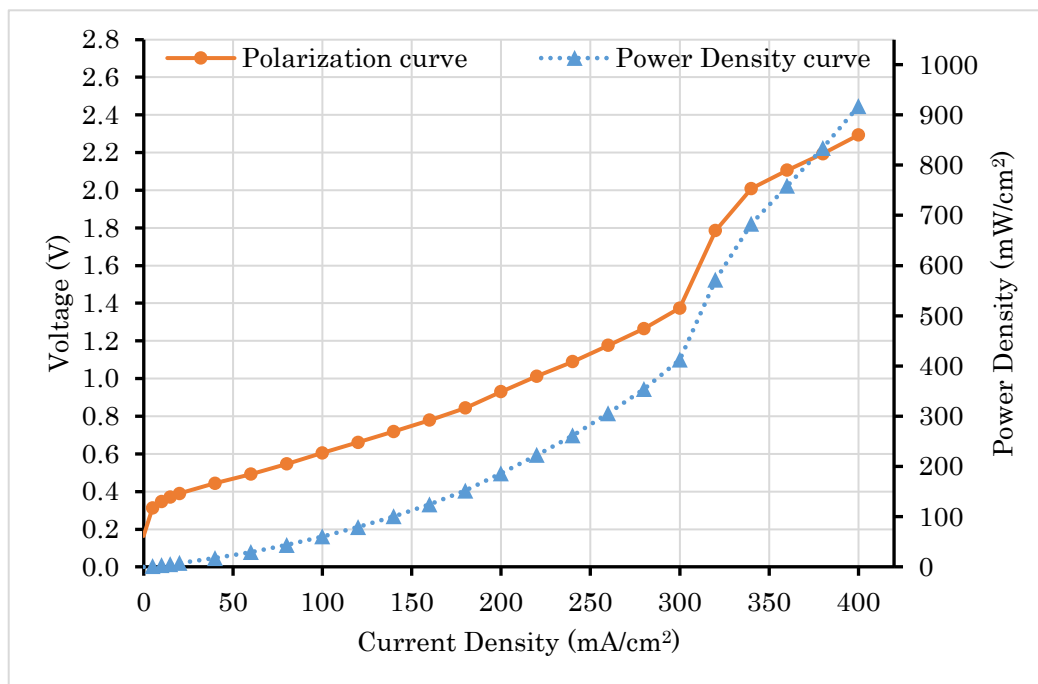


Figure C.111: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

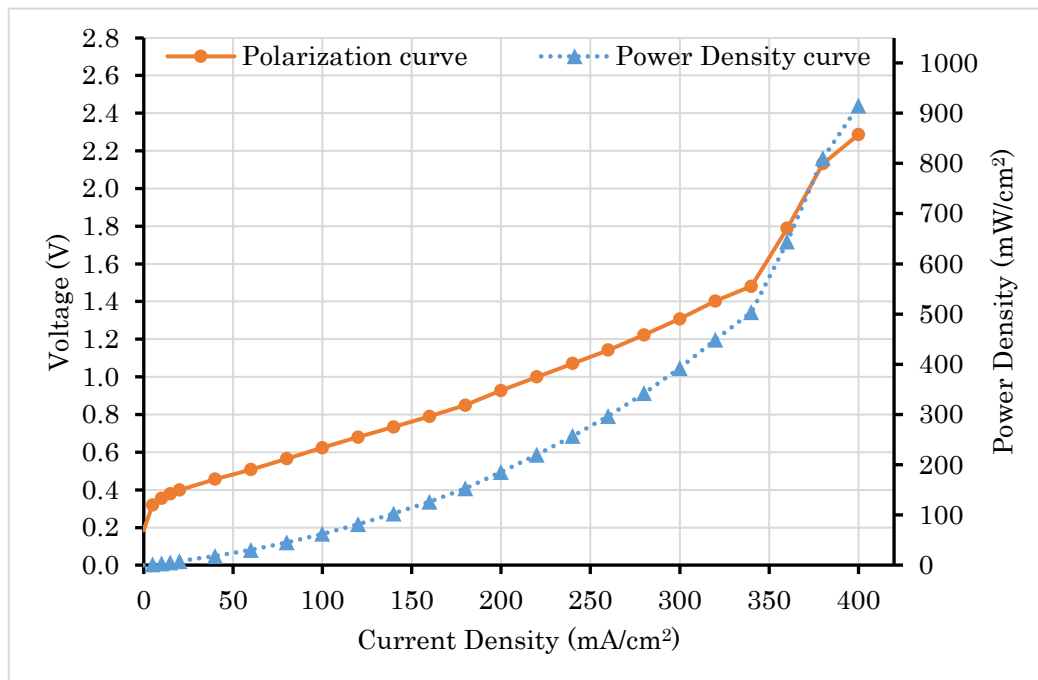


Figure C.112: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

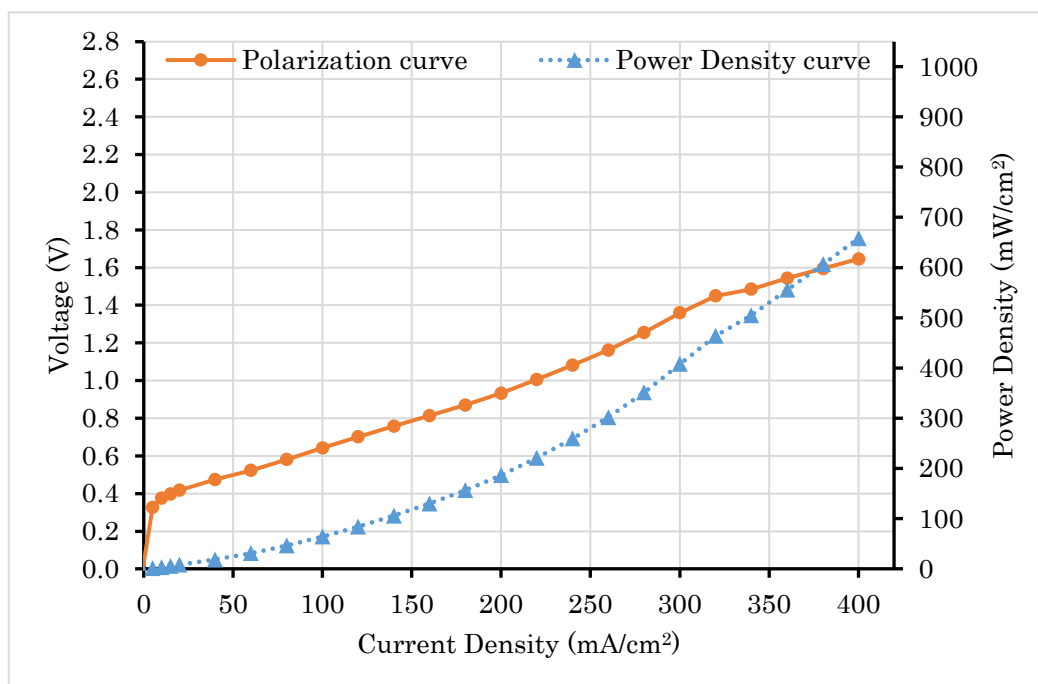


Figure C.113: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

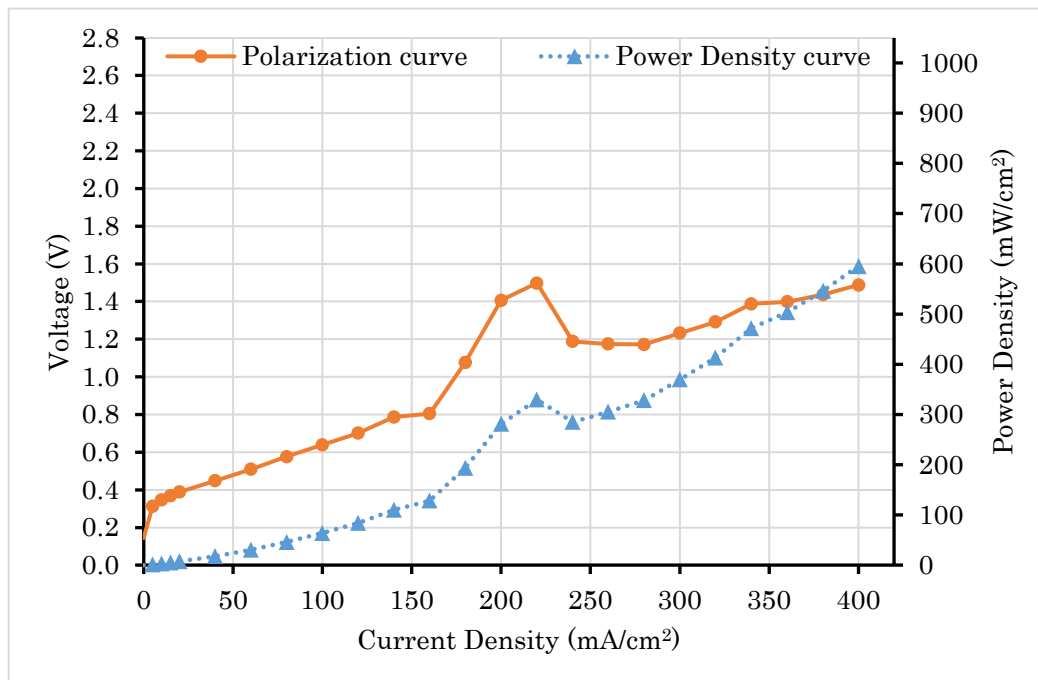


Figure C.114: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

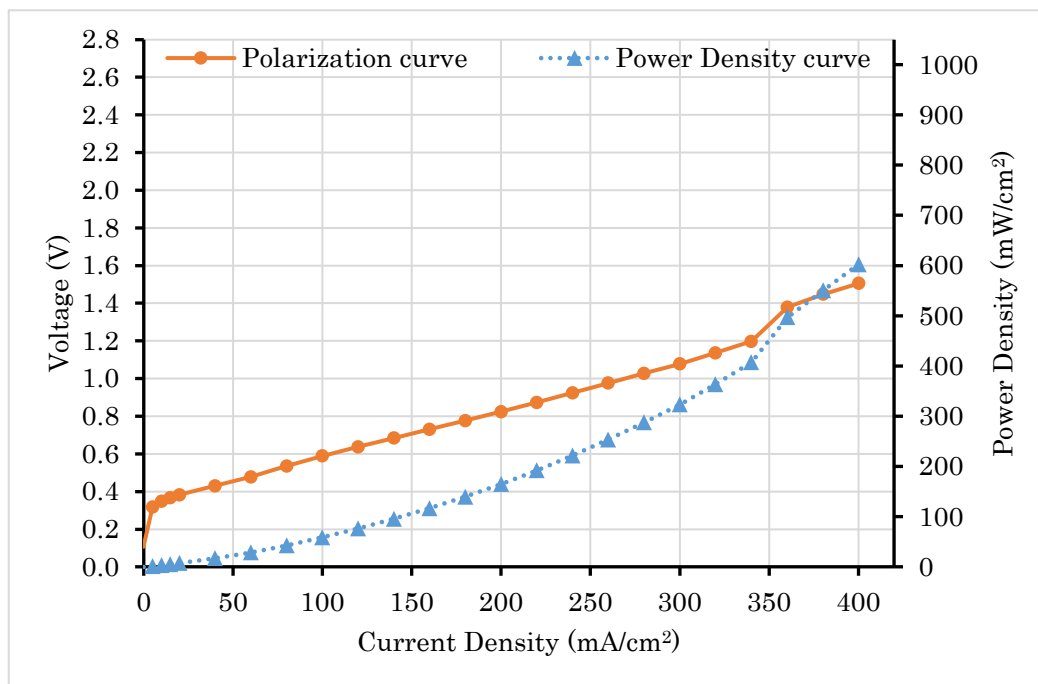


Figure C.115: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

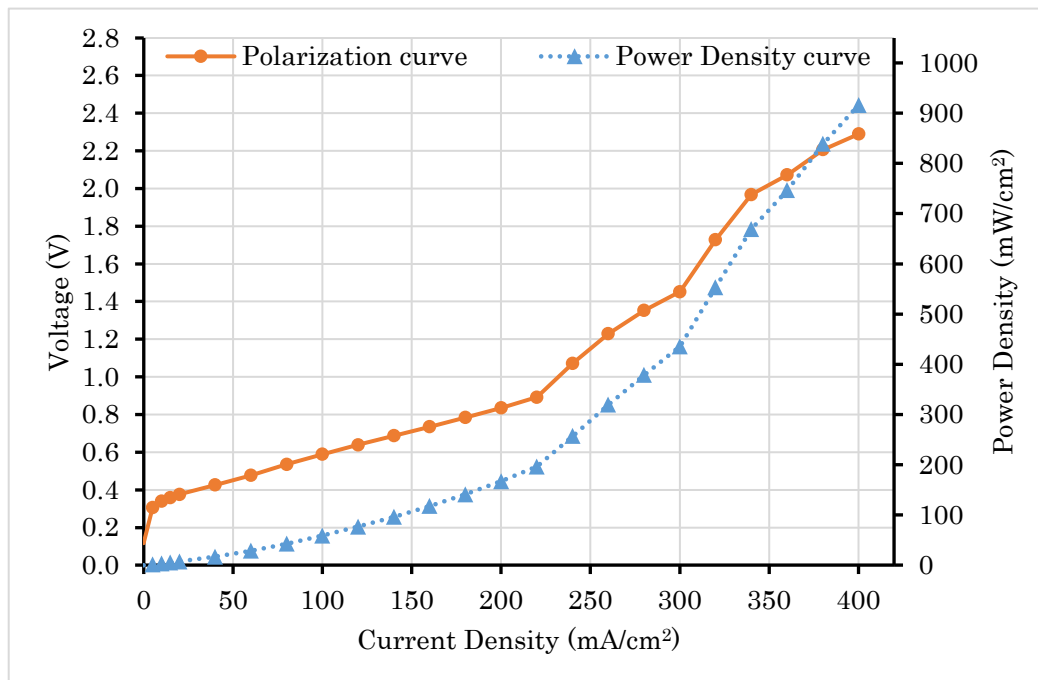


Figure C.116: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 30.3 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

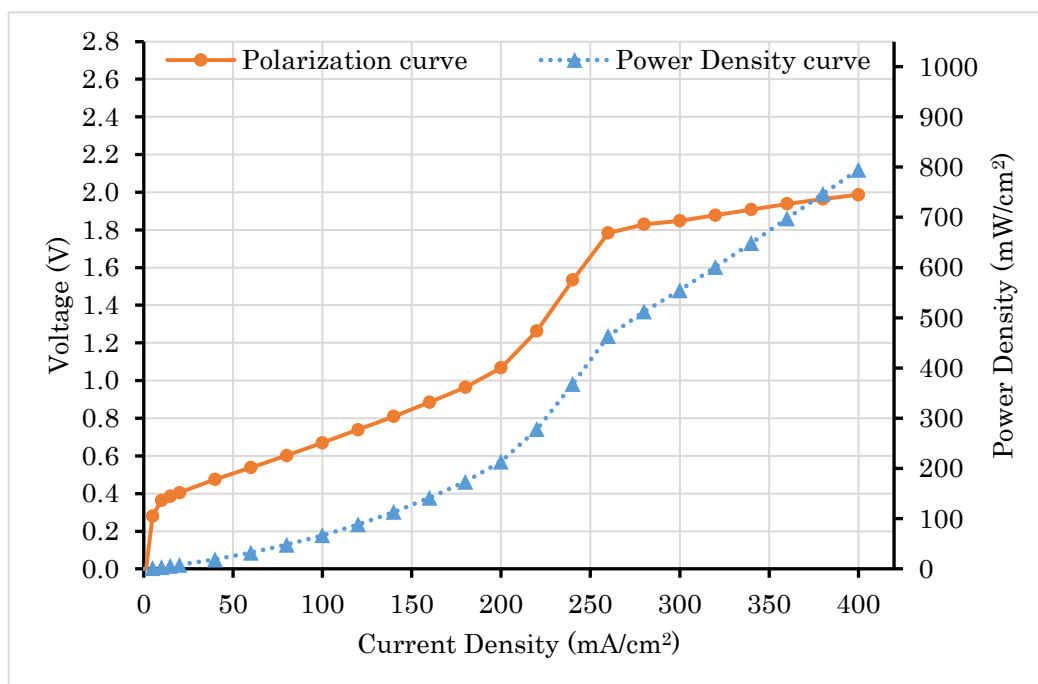


Figure C.117: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

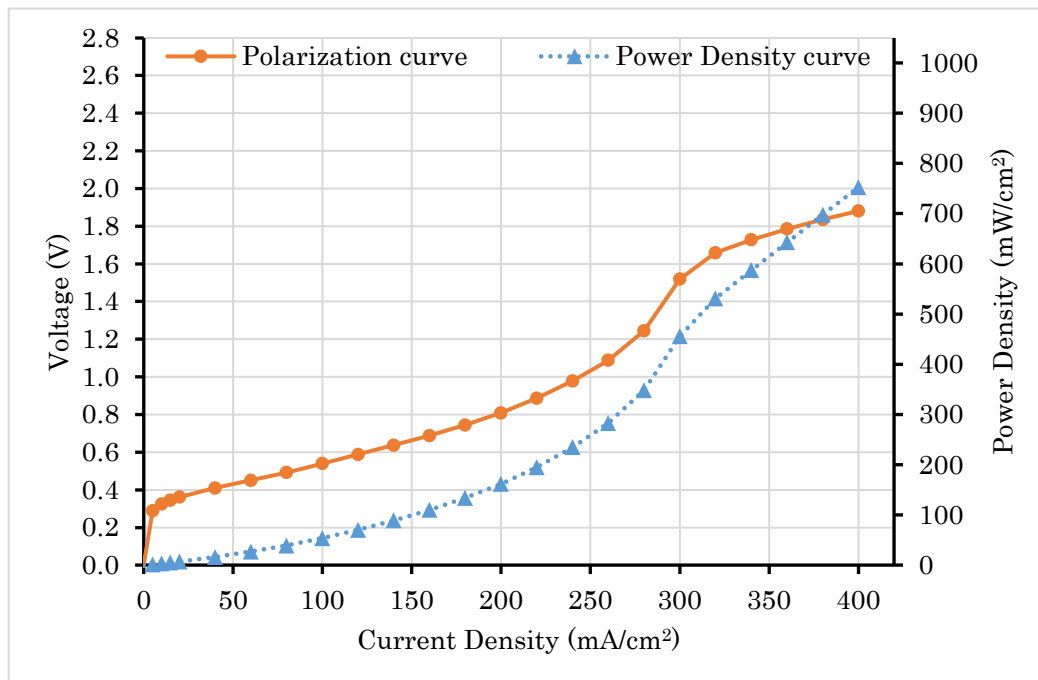


Figure C.118: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

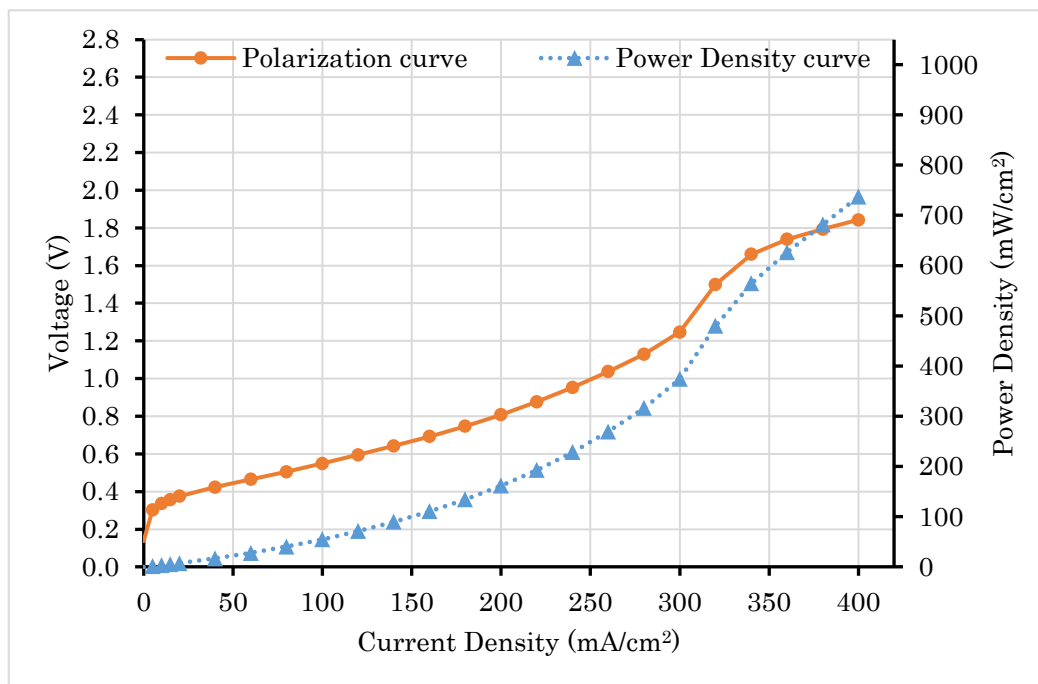


Figure C.119: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

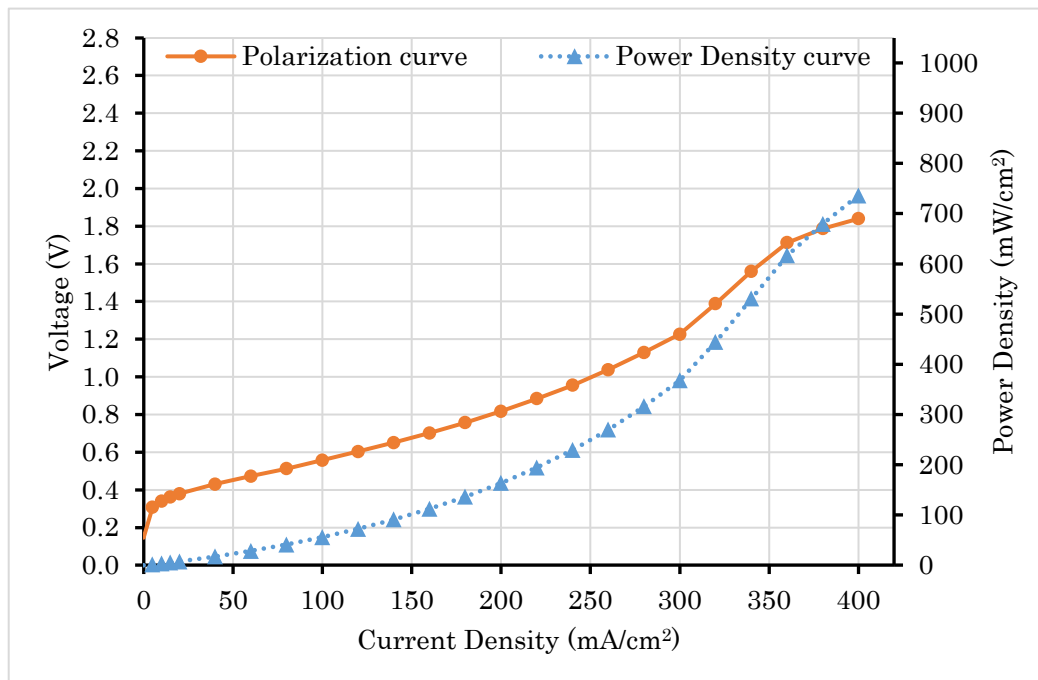


Figure C.120: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

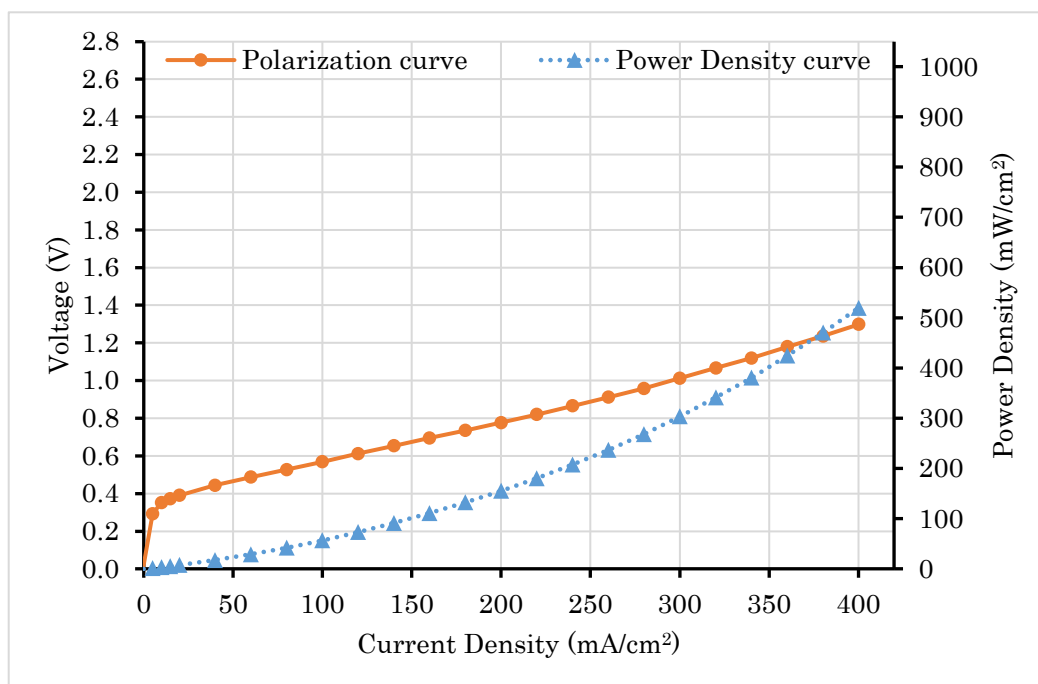


Figure C.121: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

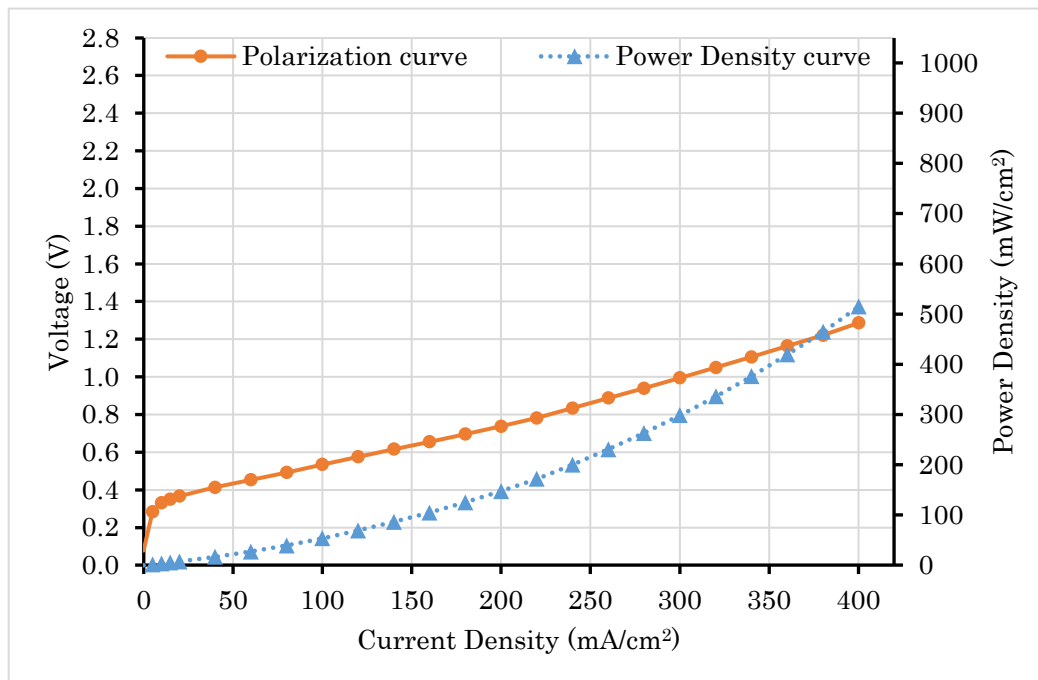


Figure C.122: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

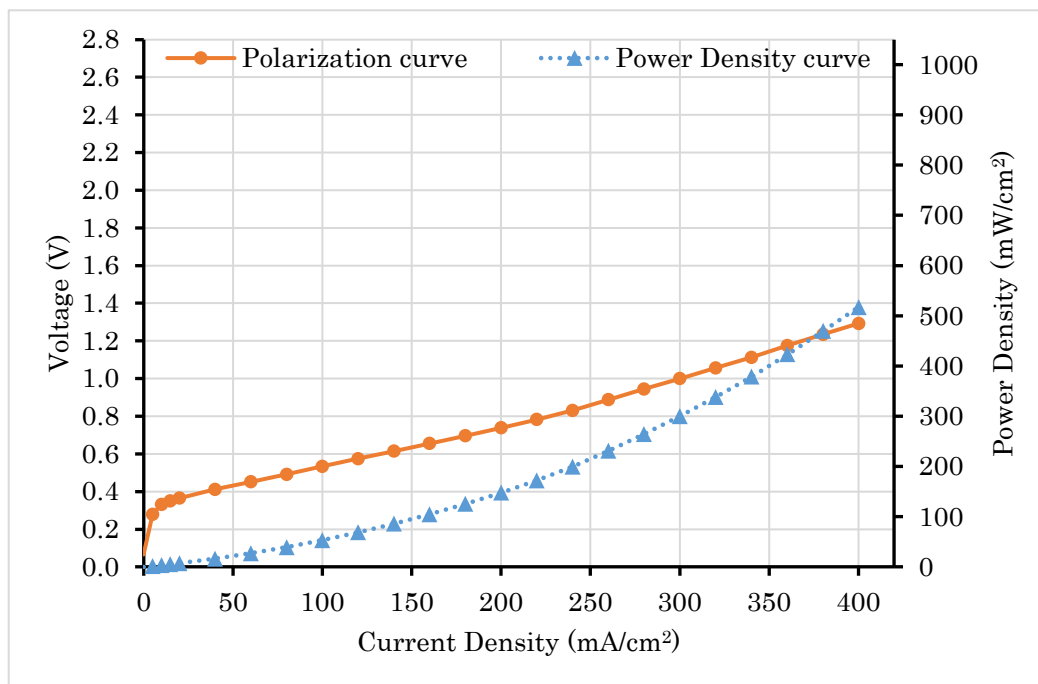


Figure C.123: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

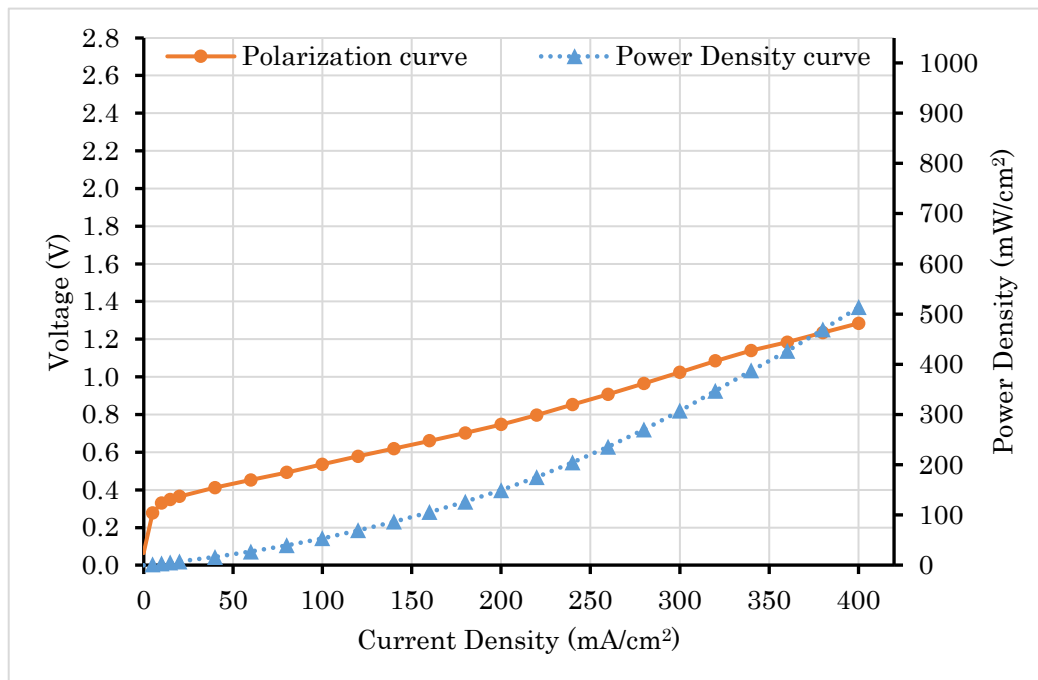


Figure C.124: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 1.25 mm and a channel depth of 1.30 mm.

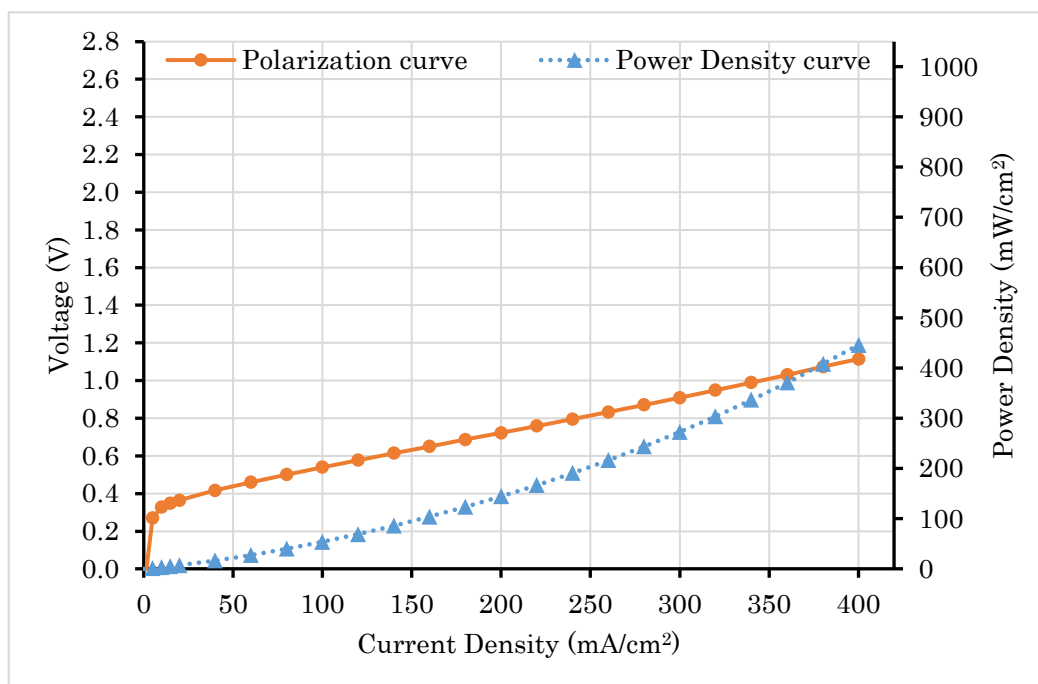


Figure C.125: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

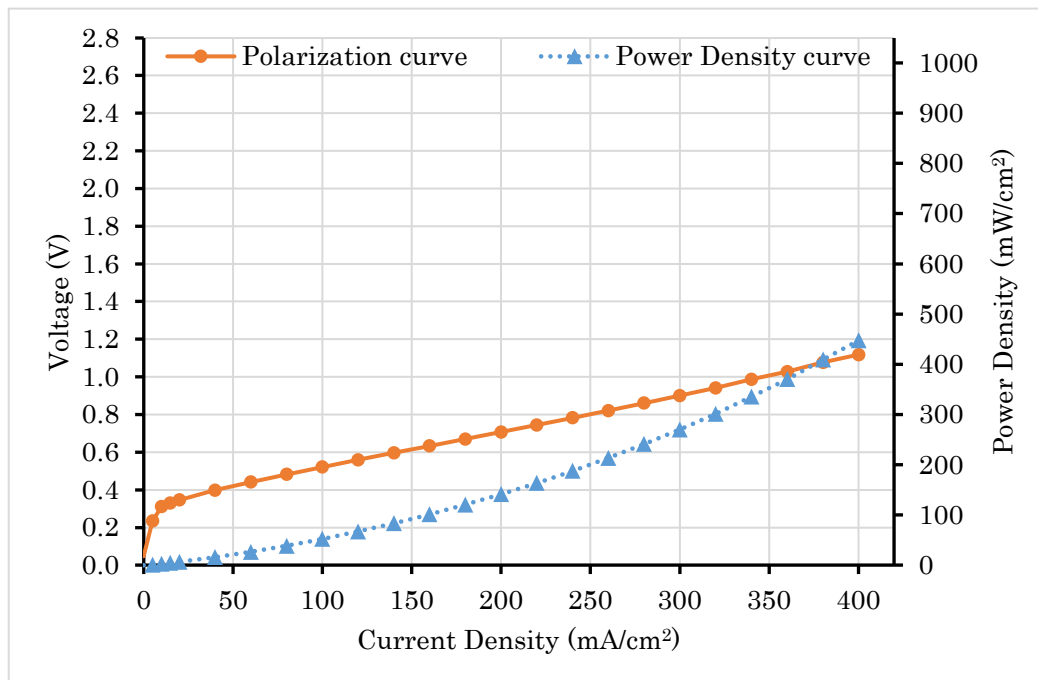


Figure C.126: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

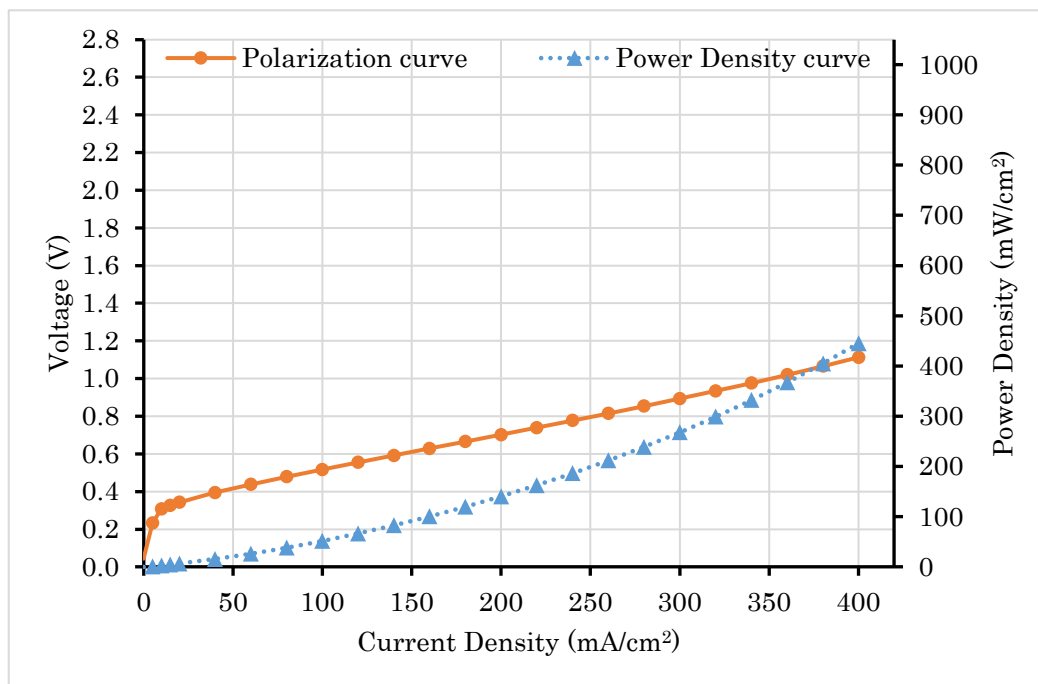


Figure C.127: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

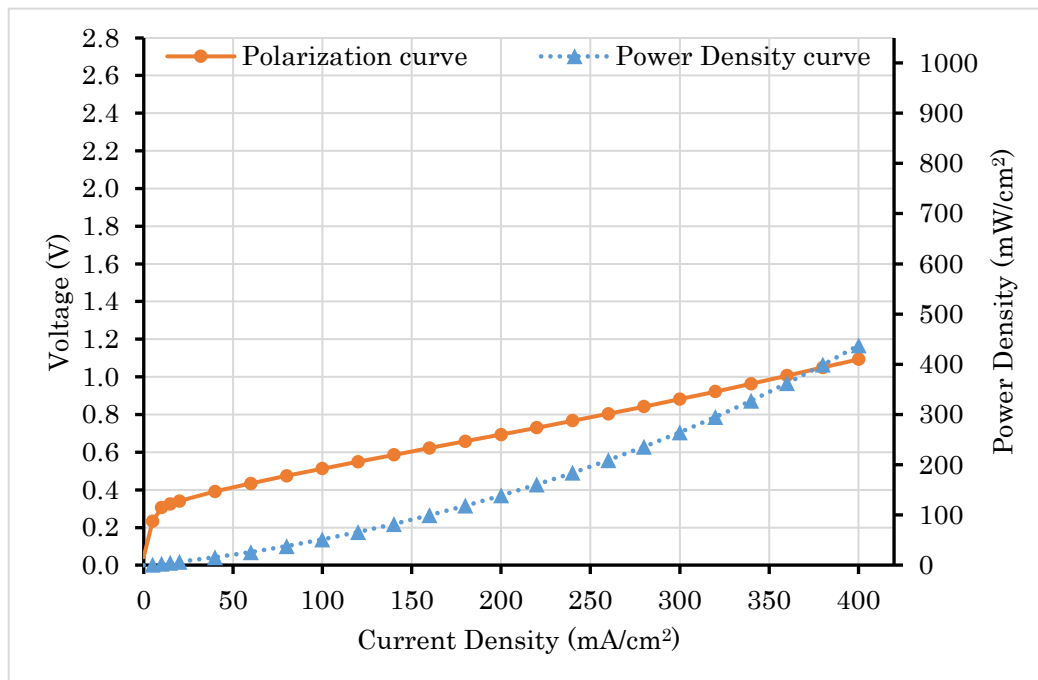


Figure C.128: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

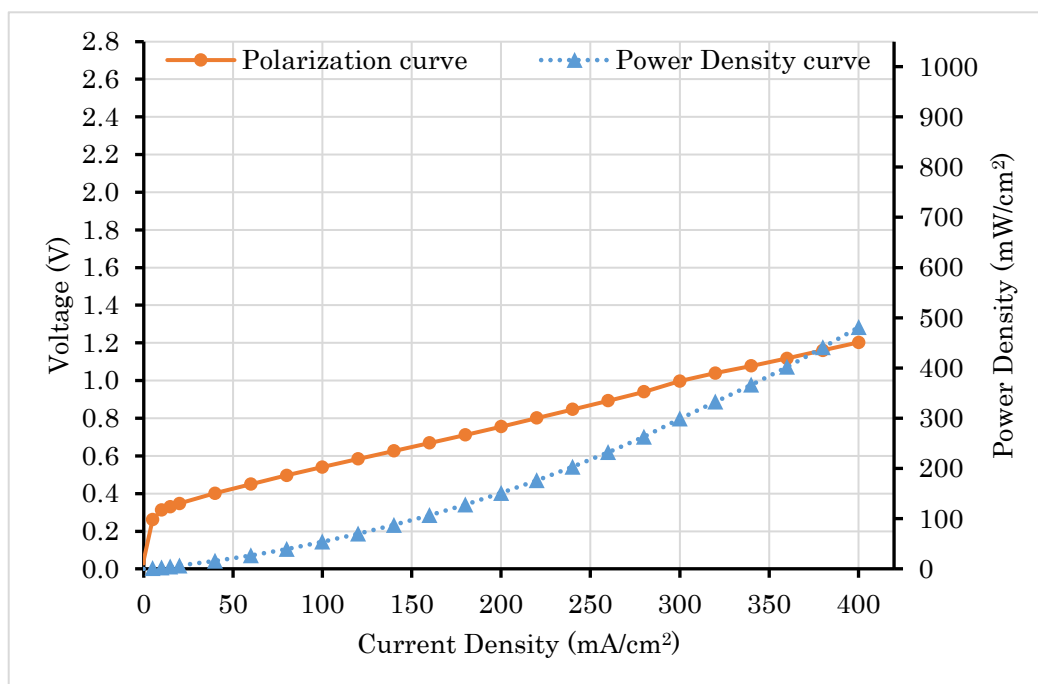


Figure C.129: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

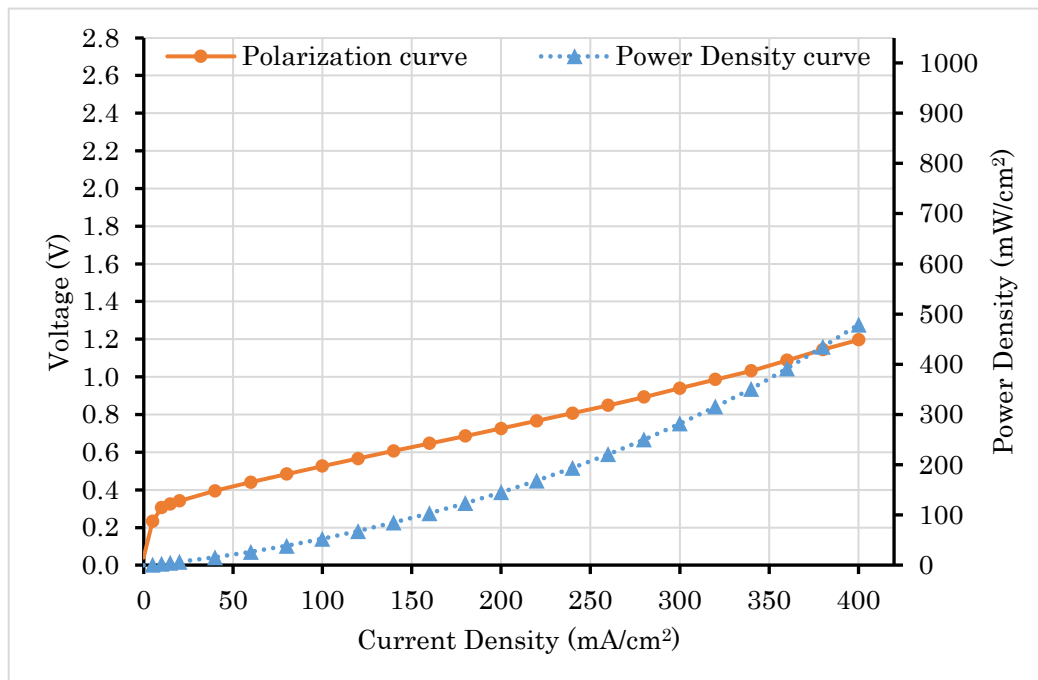


Figure C.130: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

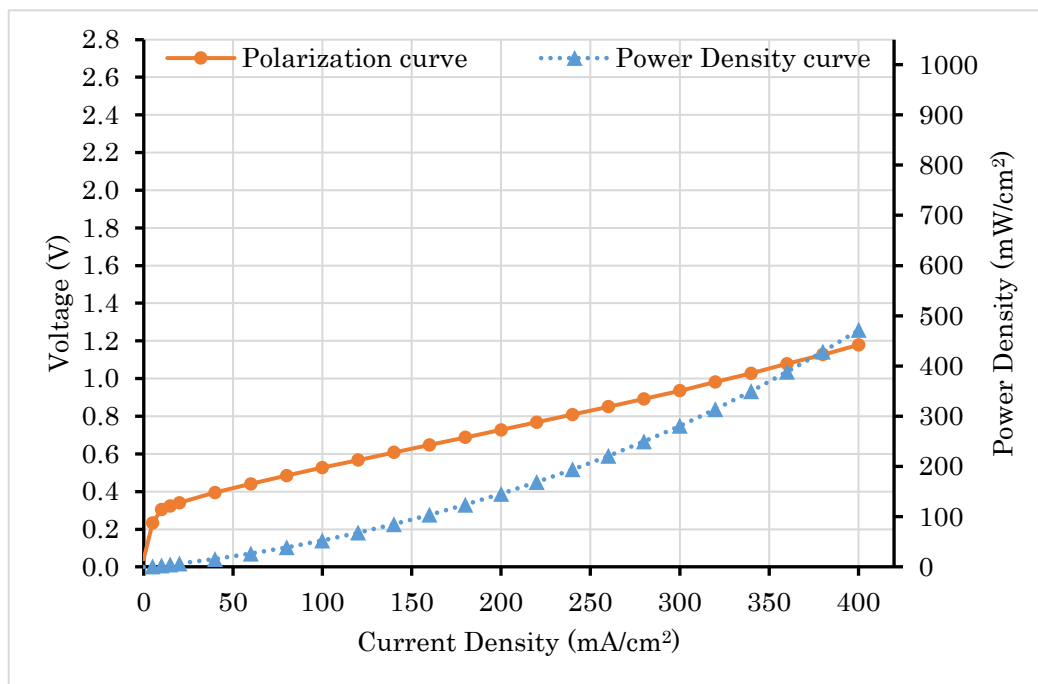


Figure C.131: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

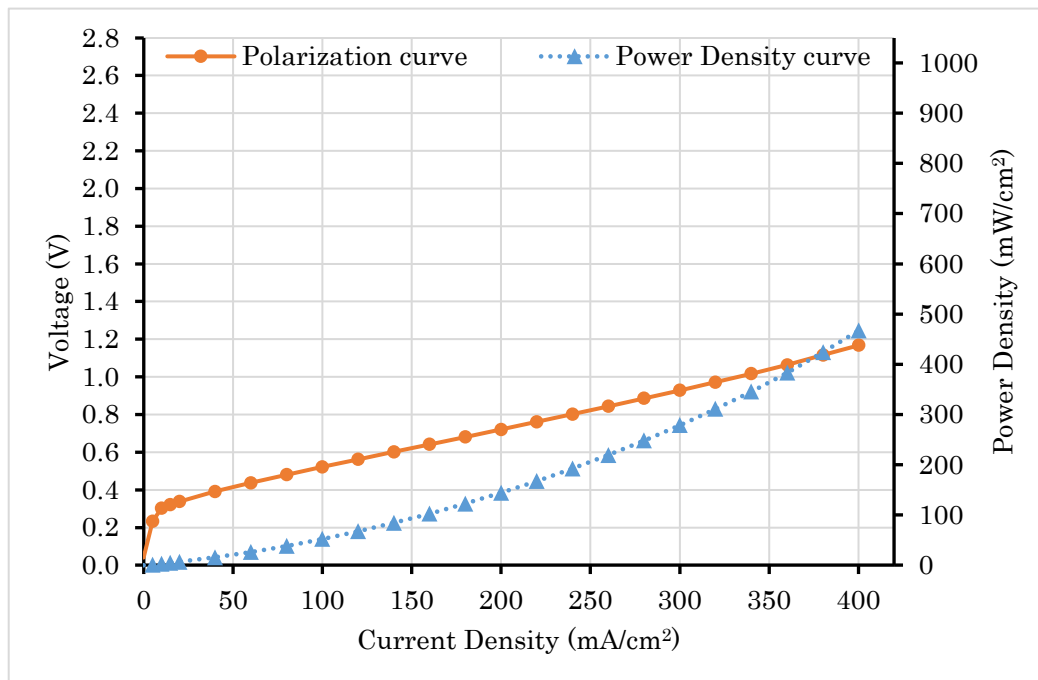


Figure C.132: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 0.61 mm.

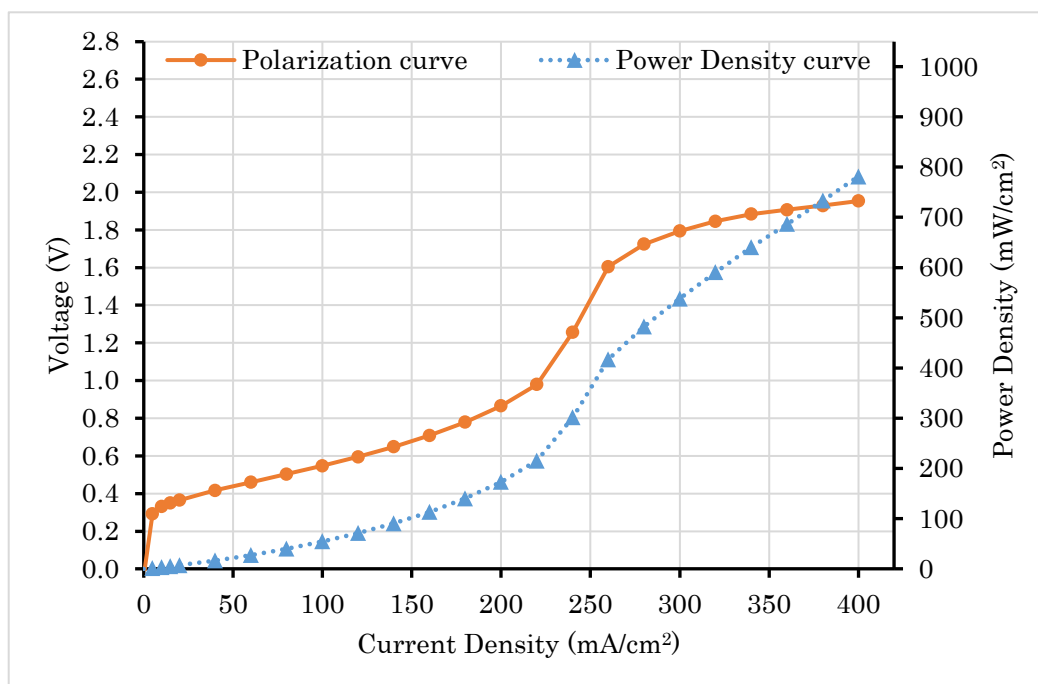


Figure C.133: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

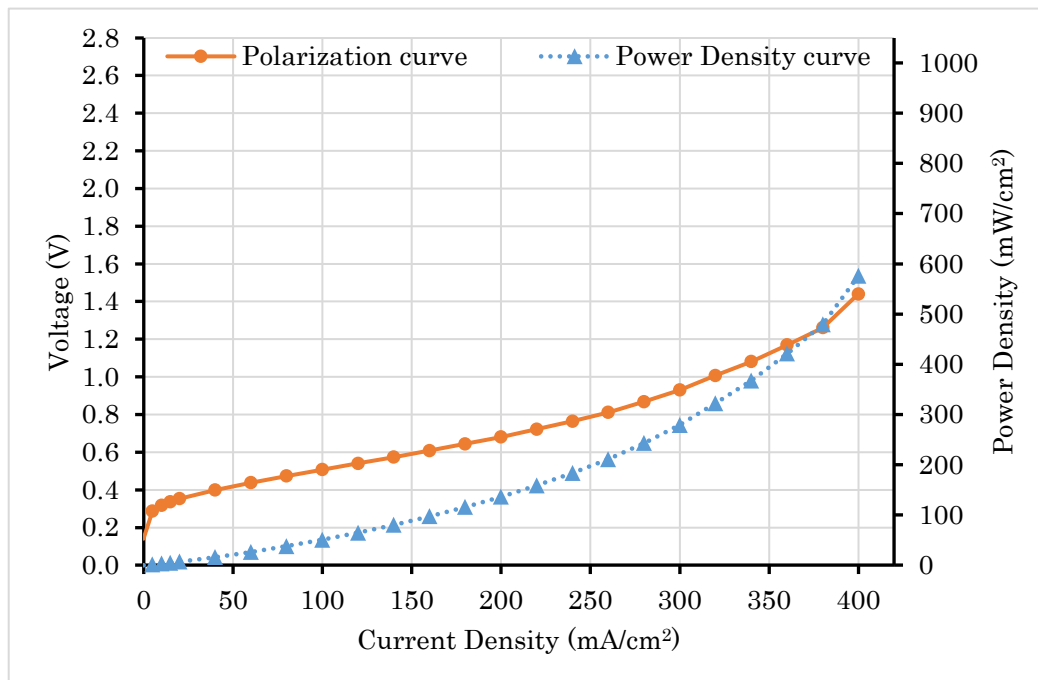


Figure C.134: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

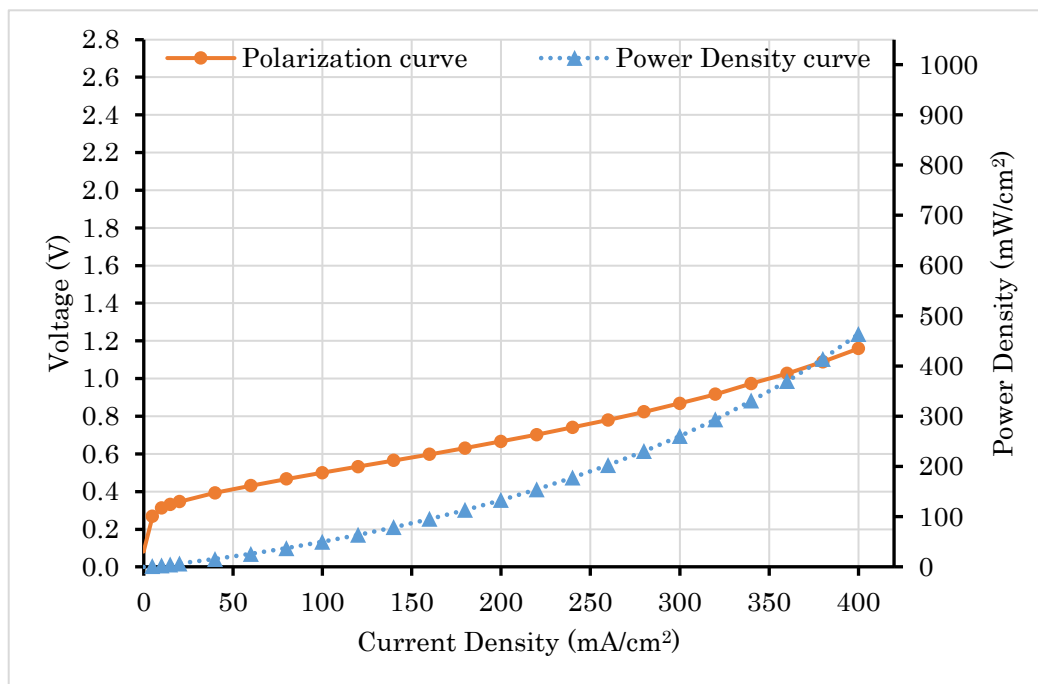


Figure C.135: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

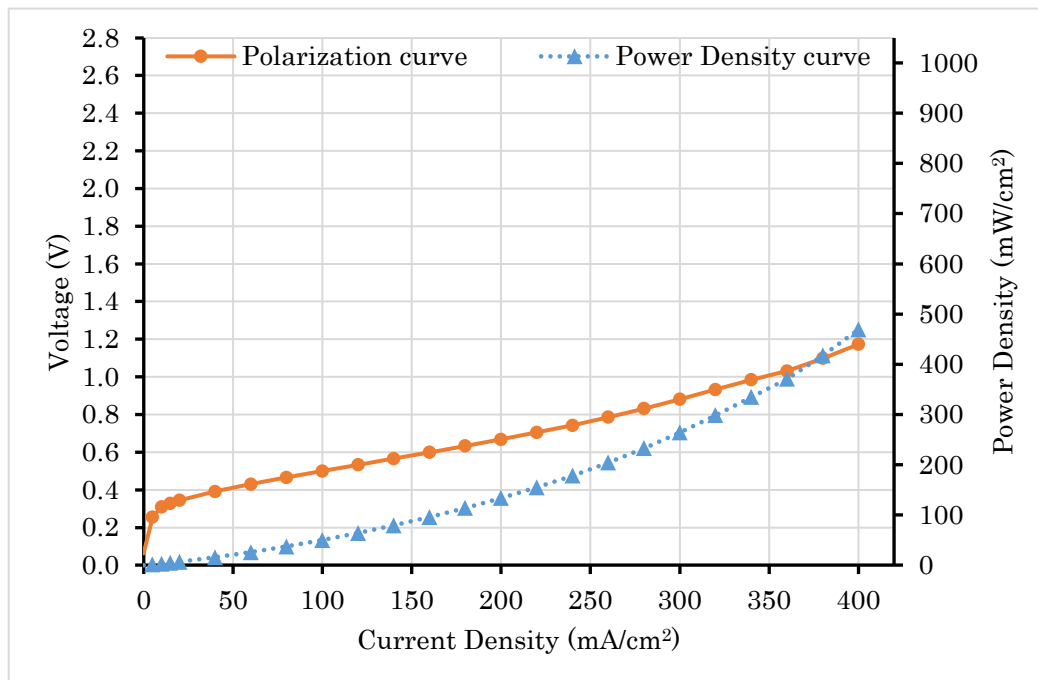


Figure C.136: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

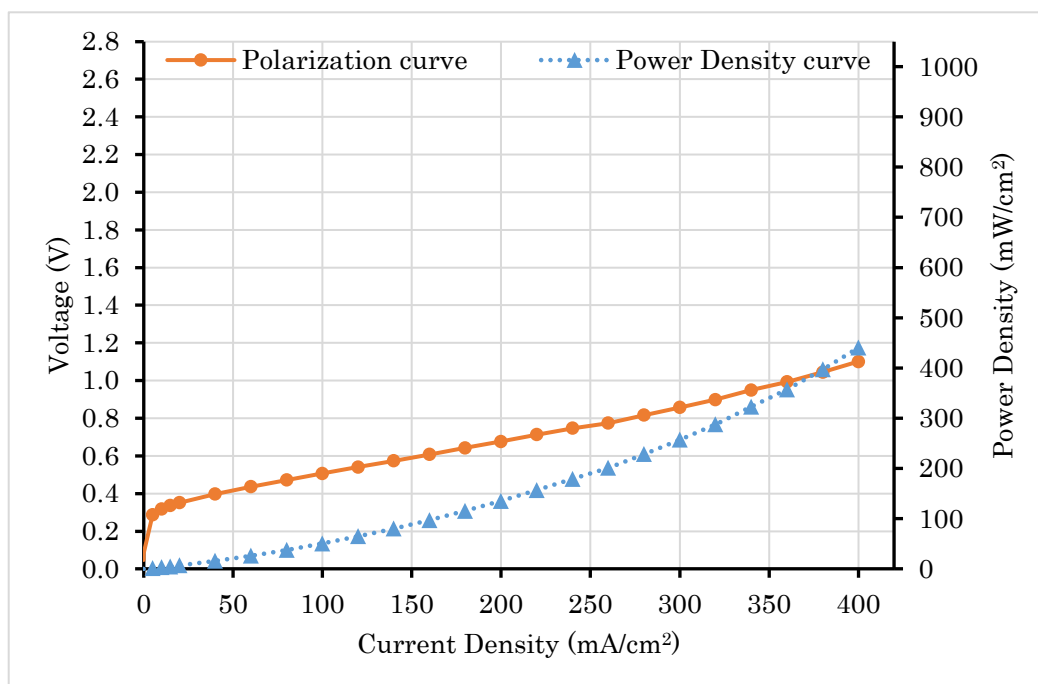


Figure C.137: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

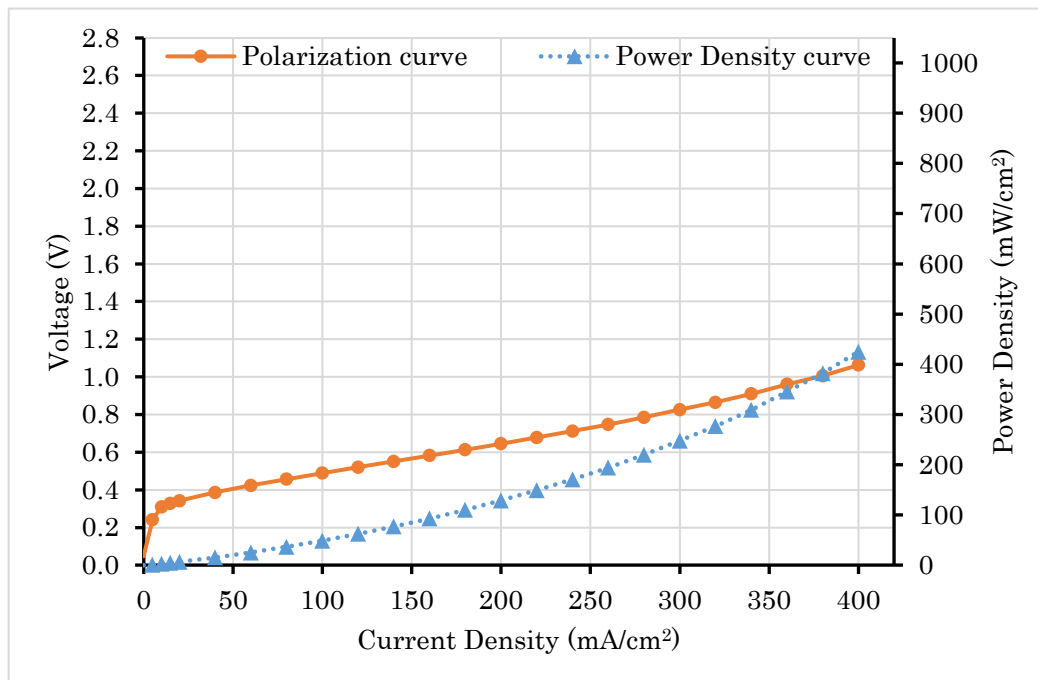


Figure C.138: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

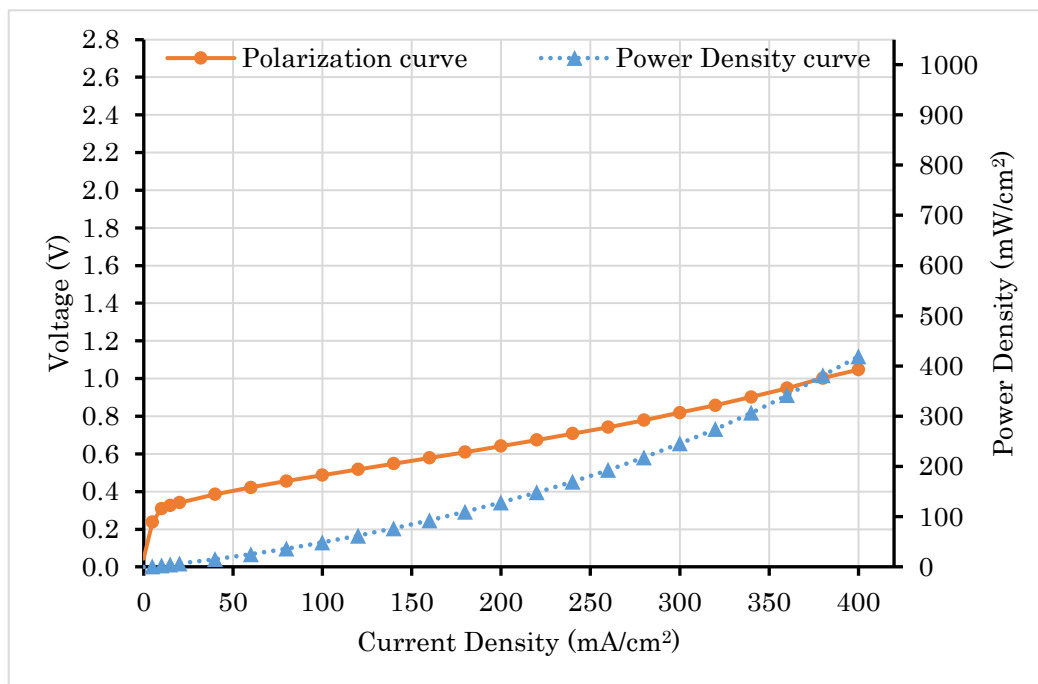


Figure C.139: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

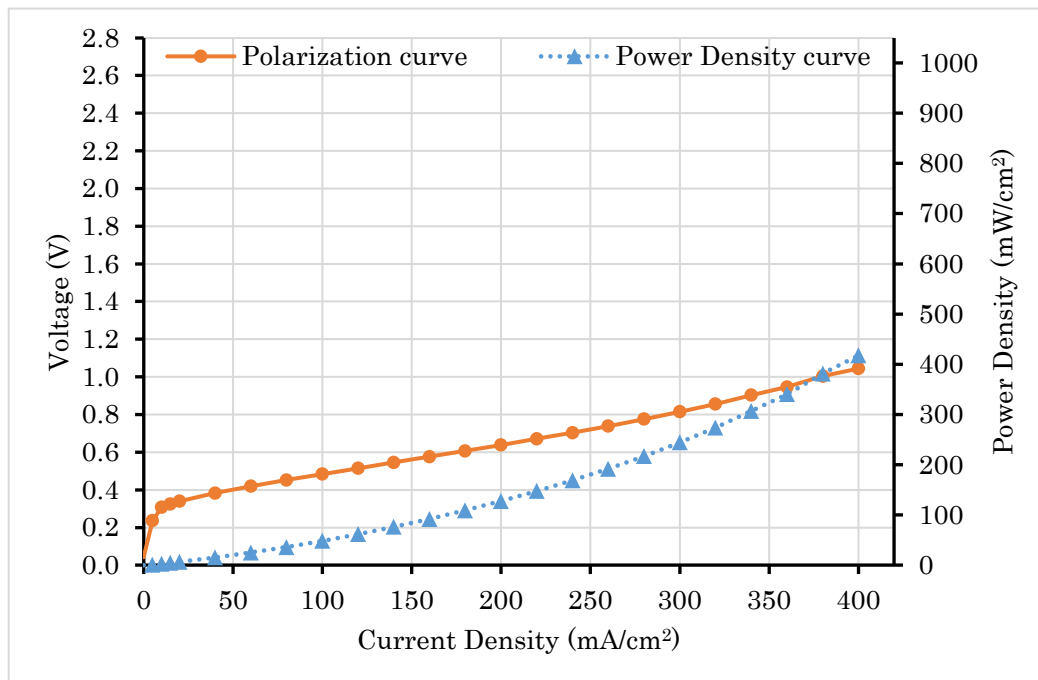


Figure C.140: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

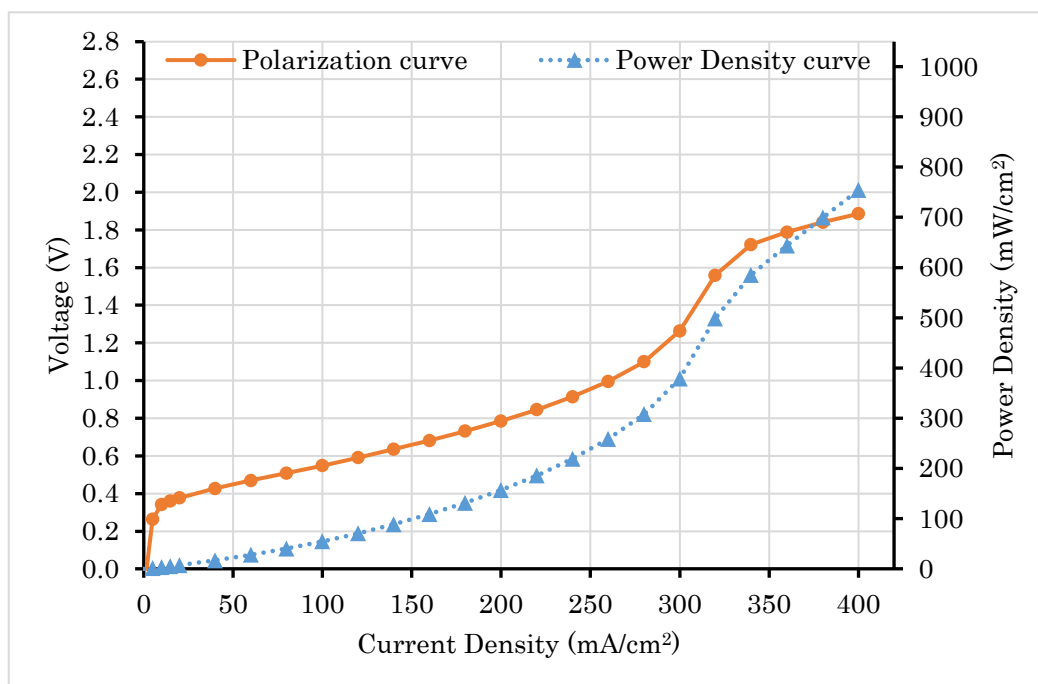


Figure C.141: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

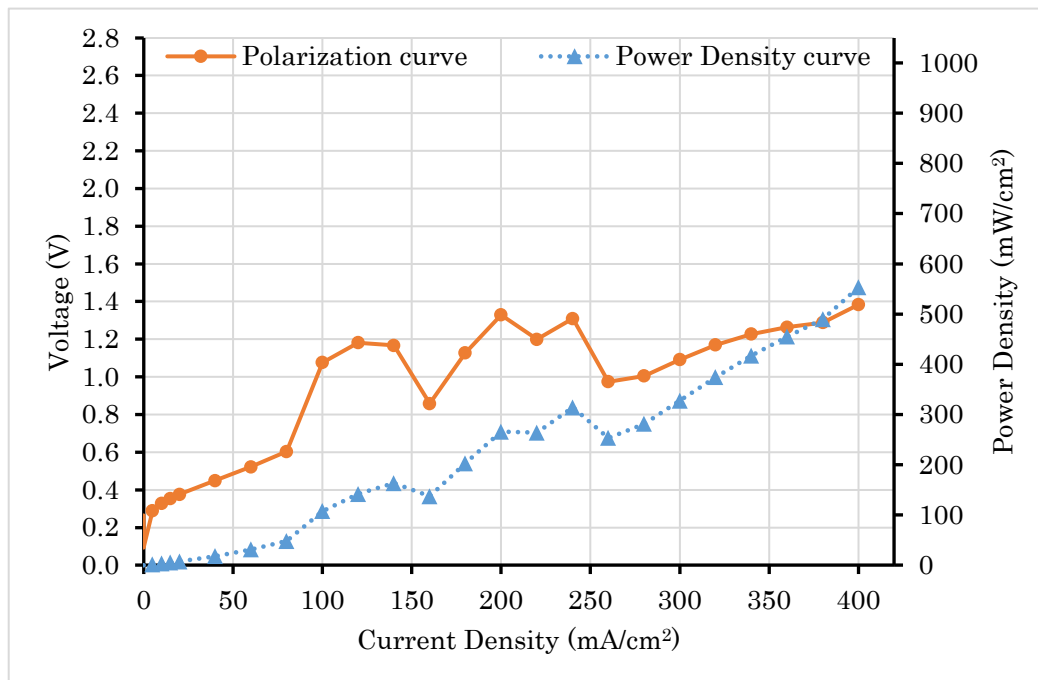


Figure C.142: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

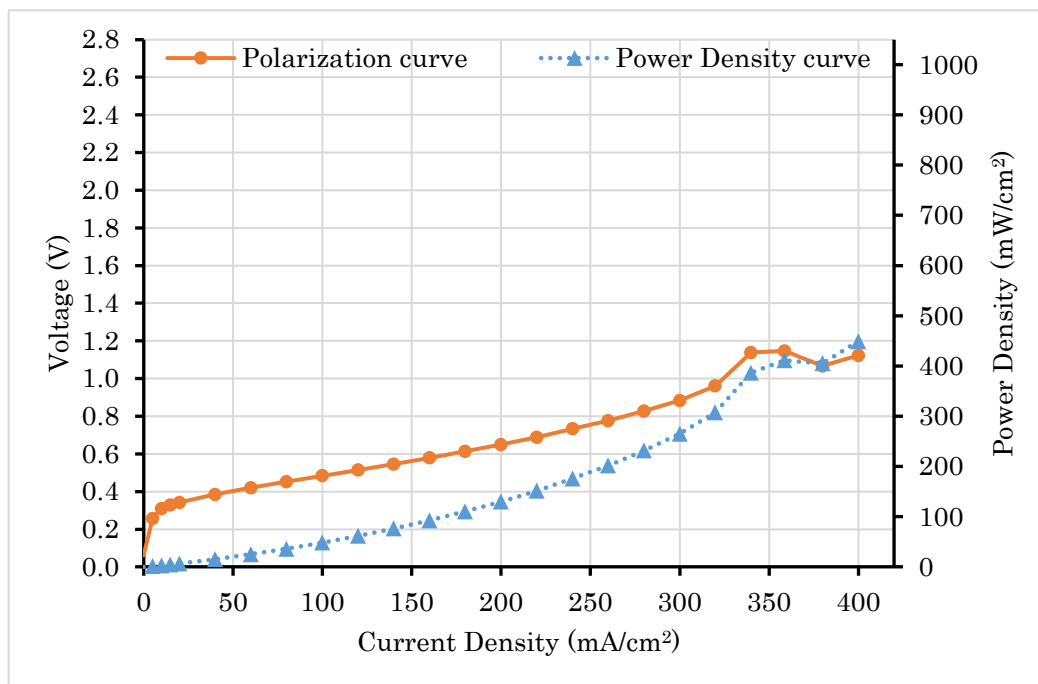


Figure C.143: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

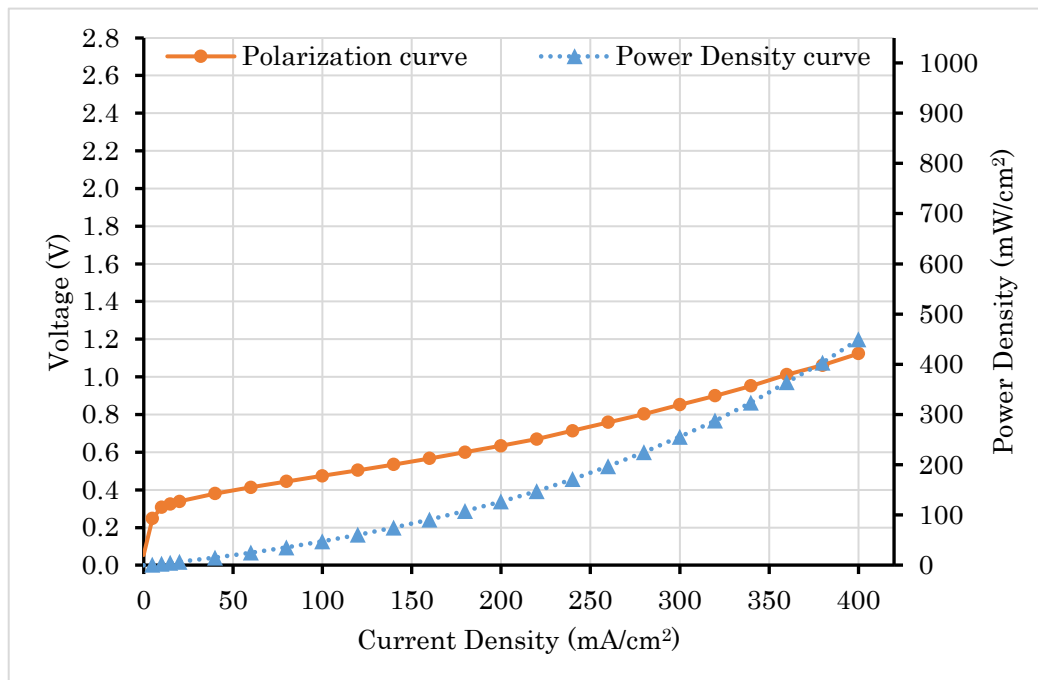


Figure C.144: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

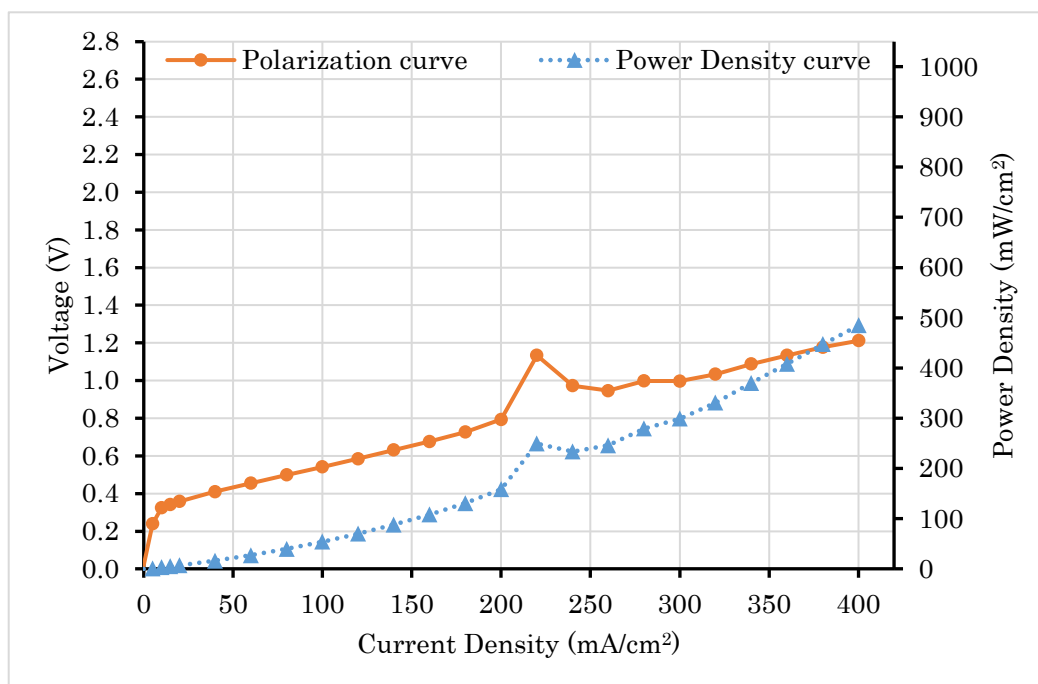


Figure C.145: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

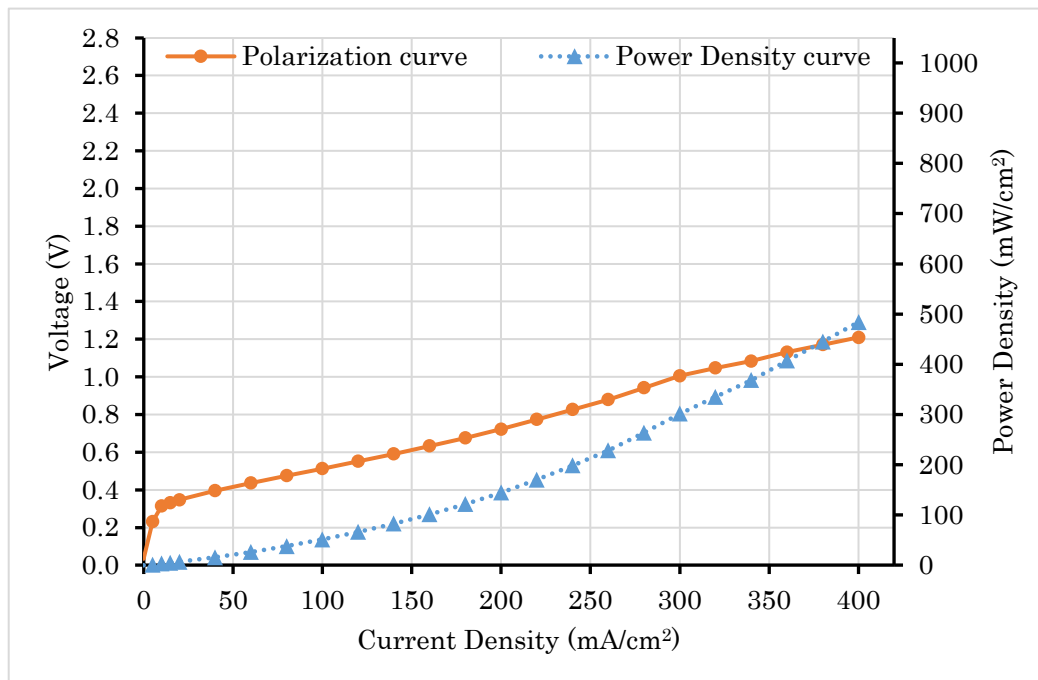


Figure C.146: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

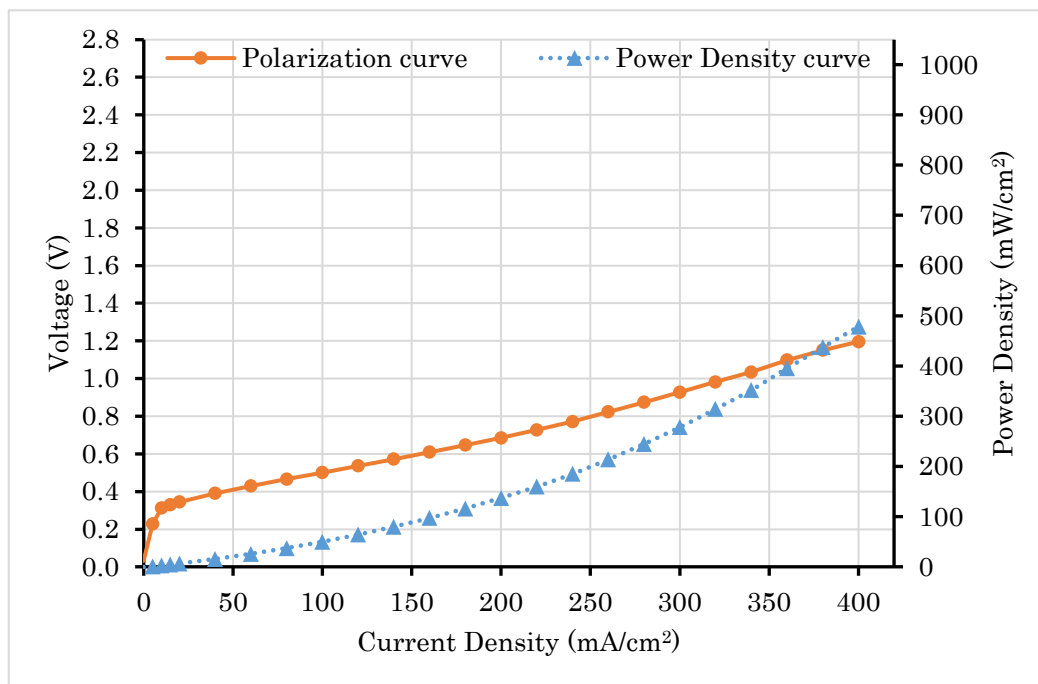


Figure C.147: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

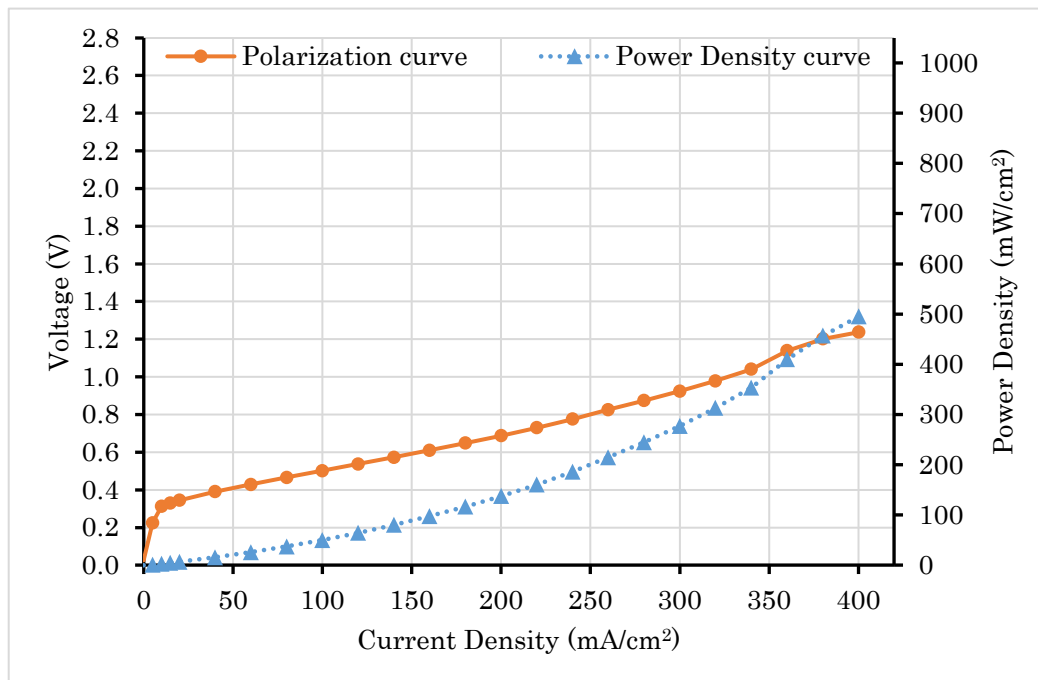


Figure C.148: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.98 mm and a channel depth of 1.99 mm.

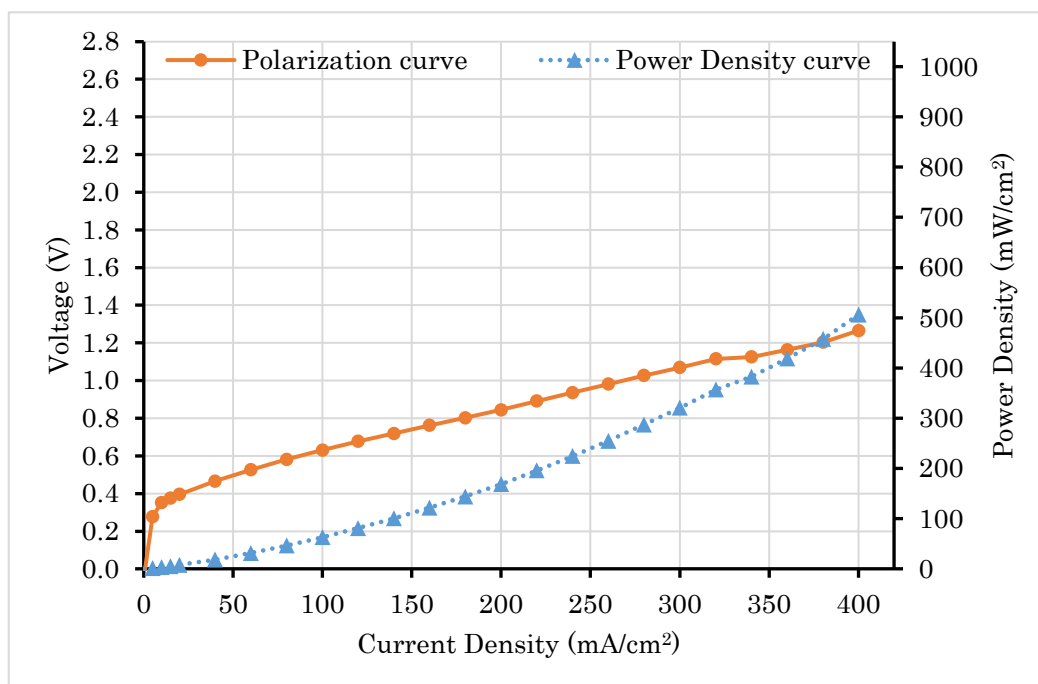


Figure C.149: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

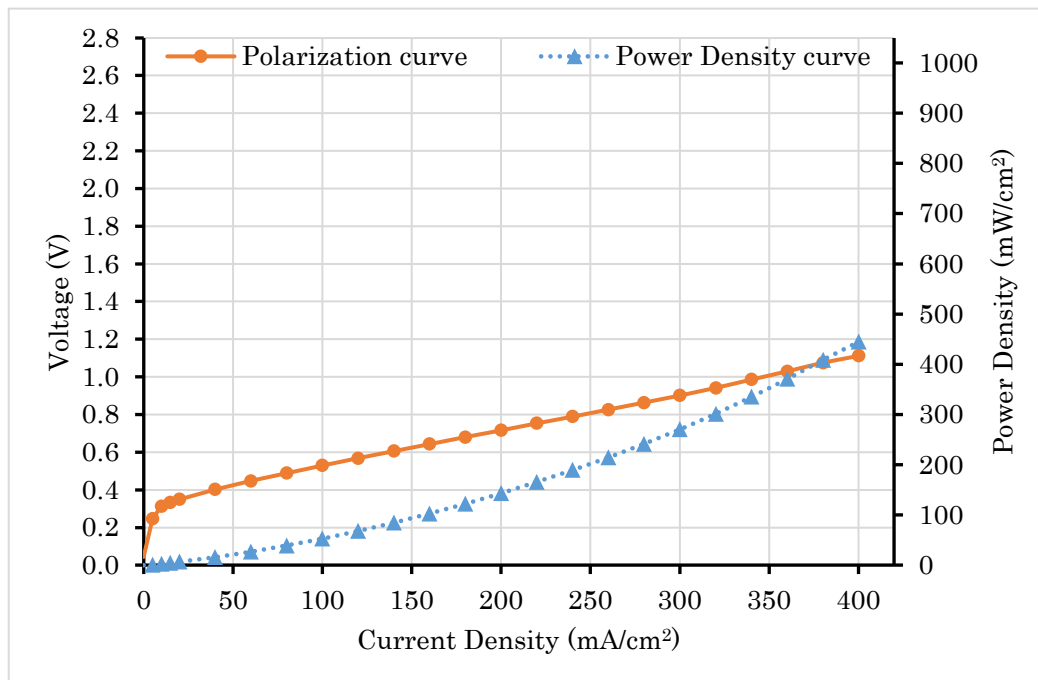


Figure C.150: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

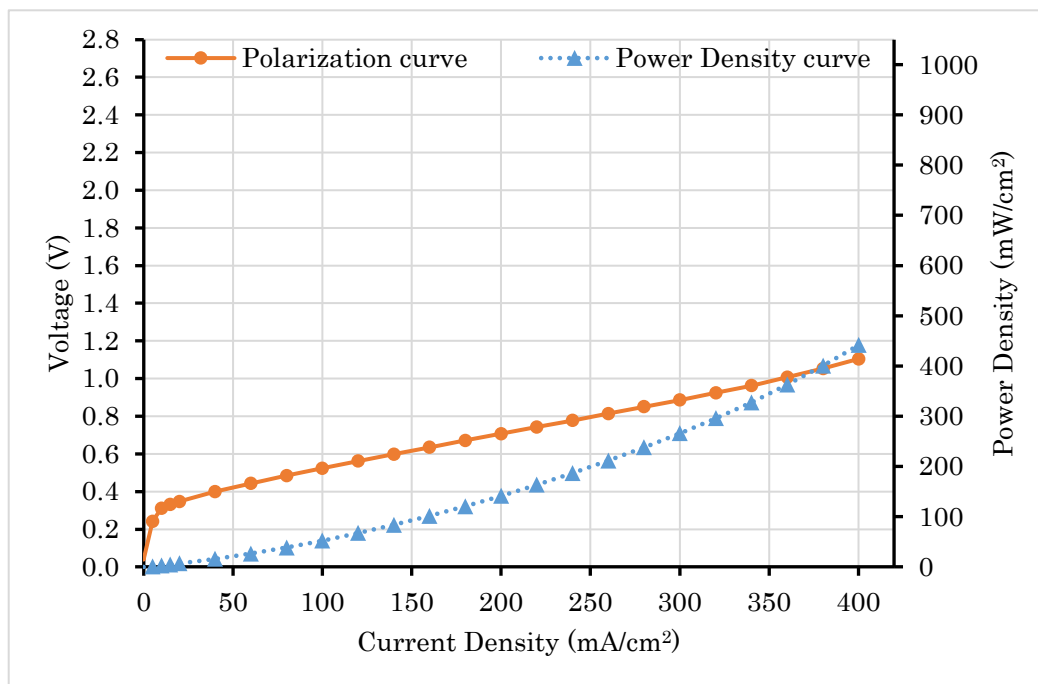


Figure C.151: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

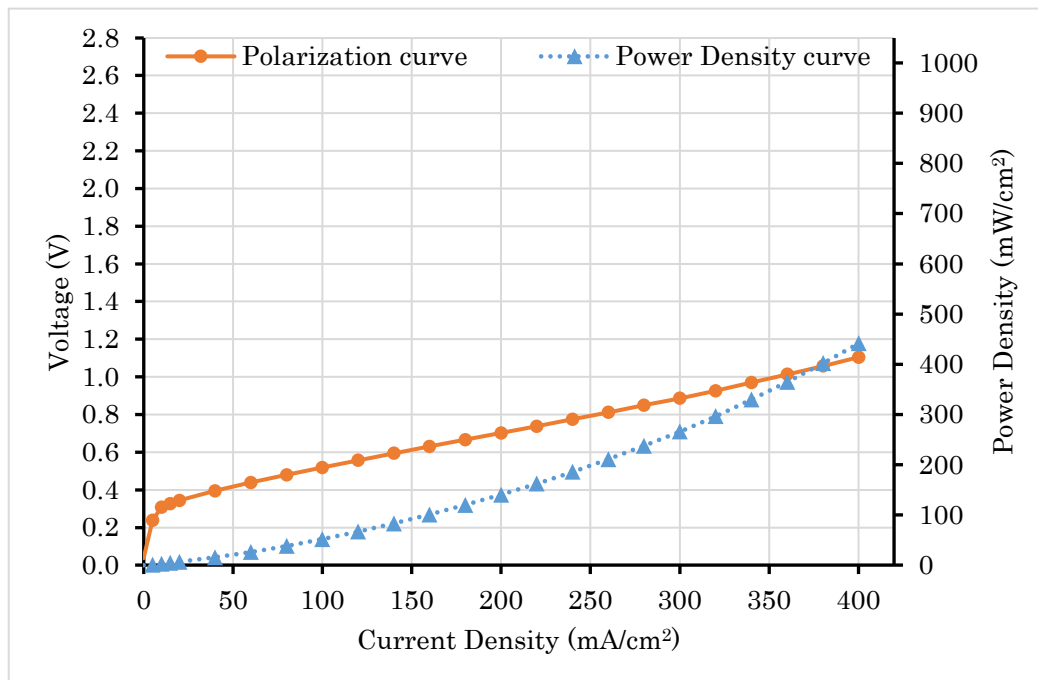


Figure C.152: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

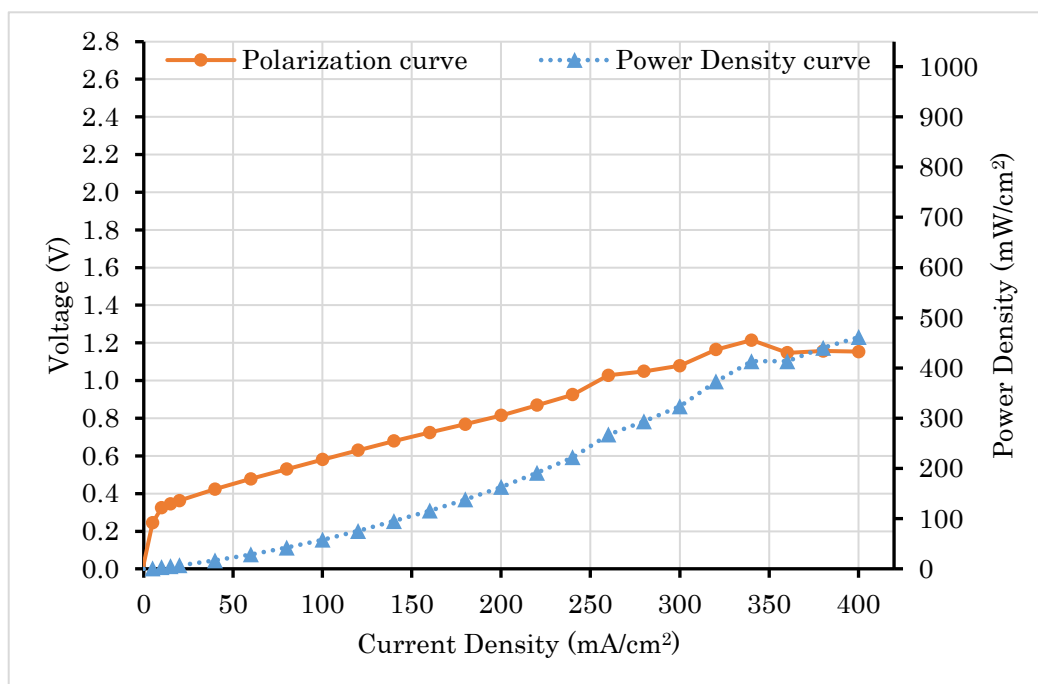


Figure C.153: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

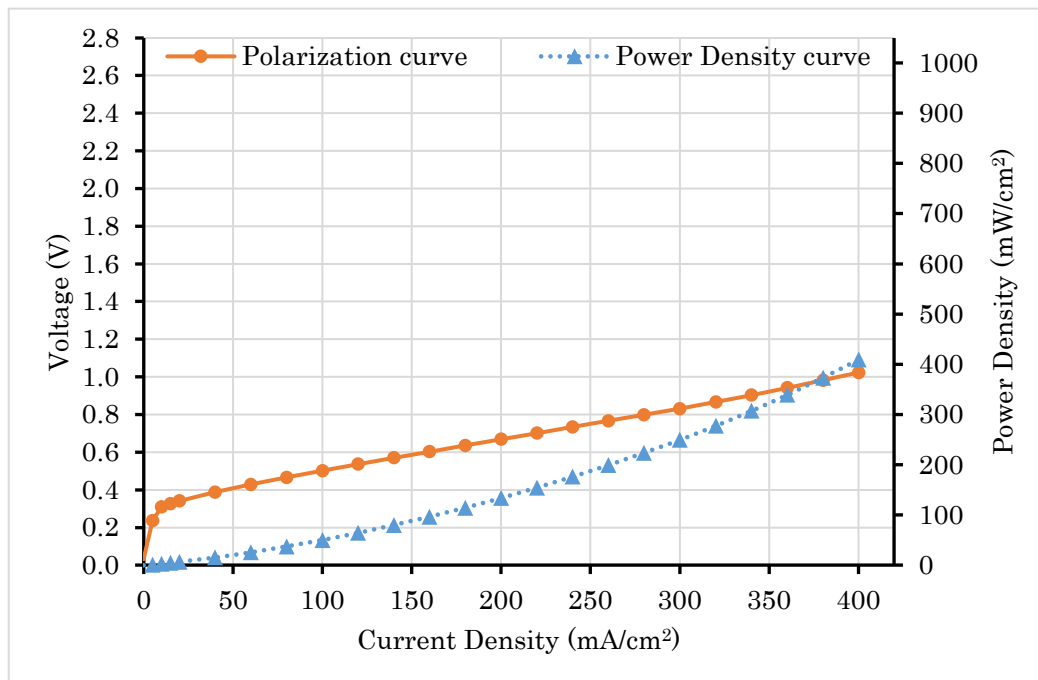


Figure C.154: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

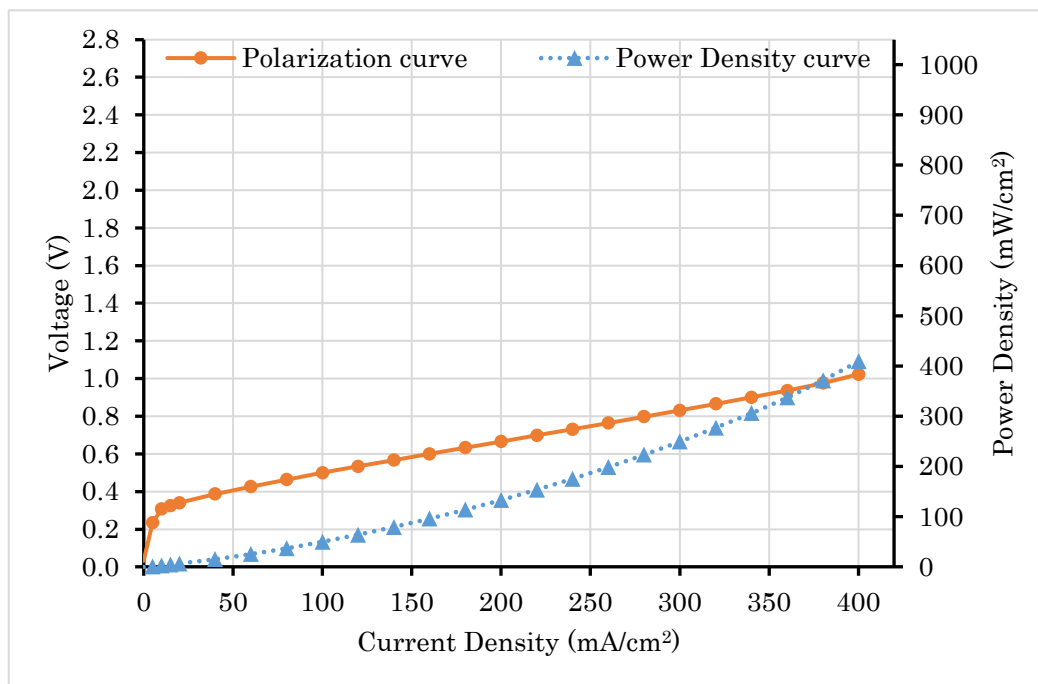


Figure C.155: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

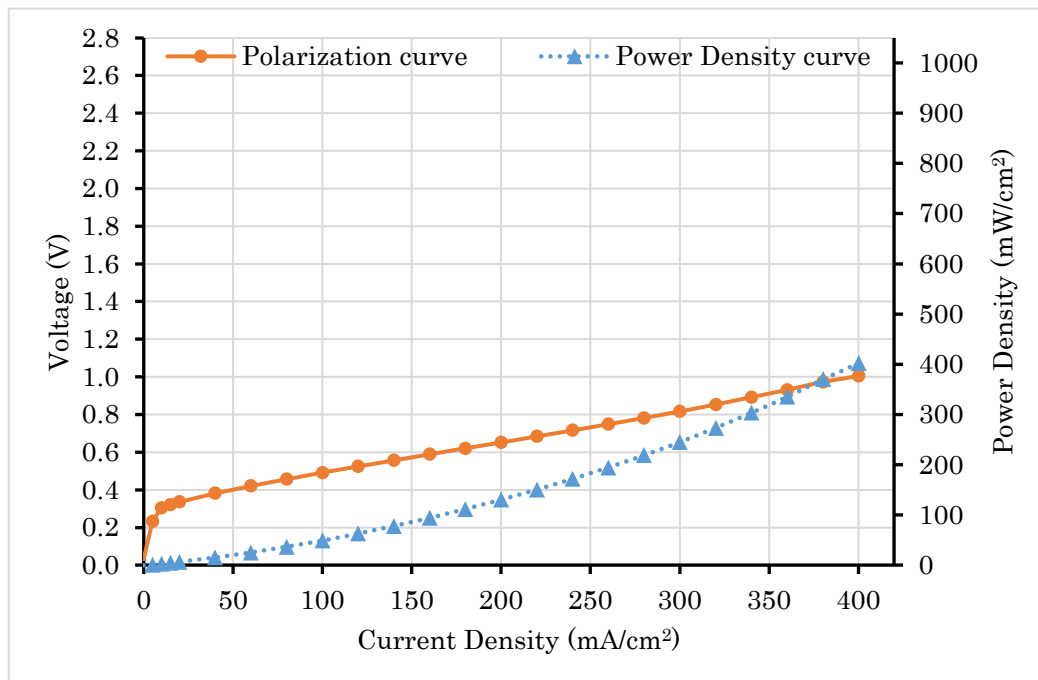


Figure C.156: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 0.90 mm.

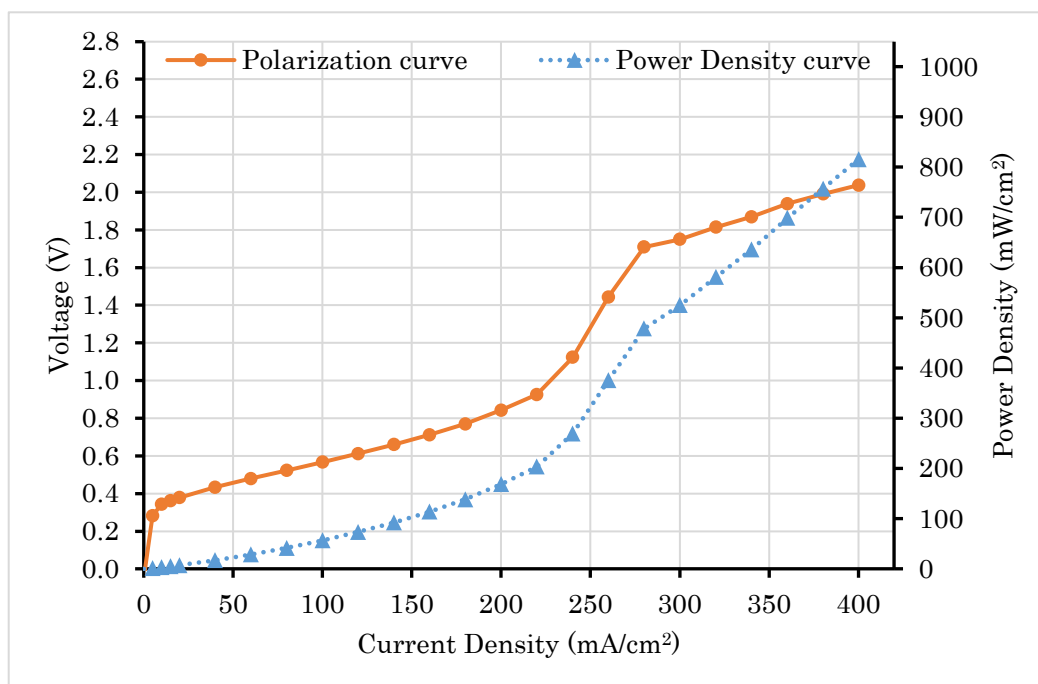


Figure C.157: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

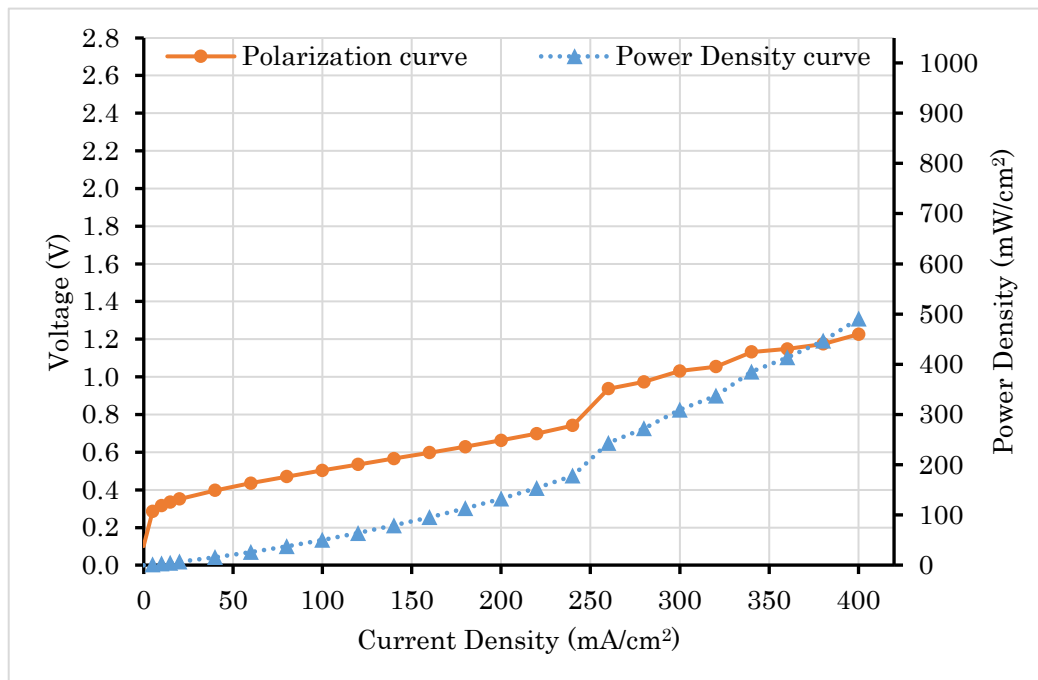


Figure C.158: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

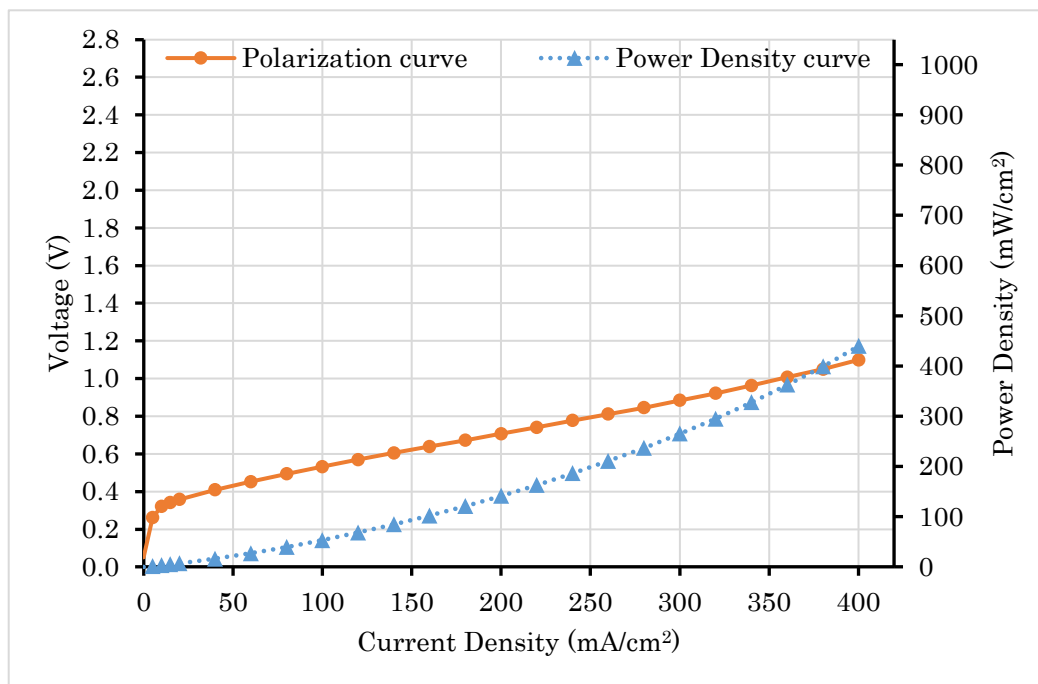


Figure C.159: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

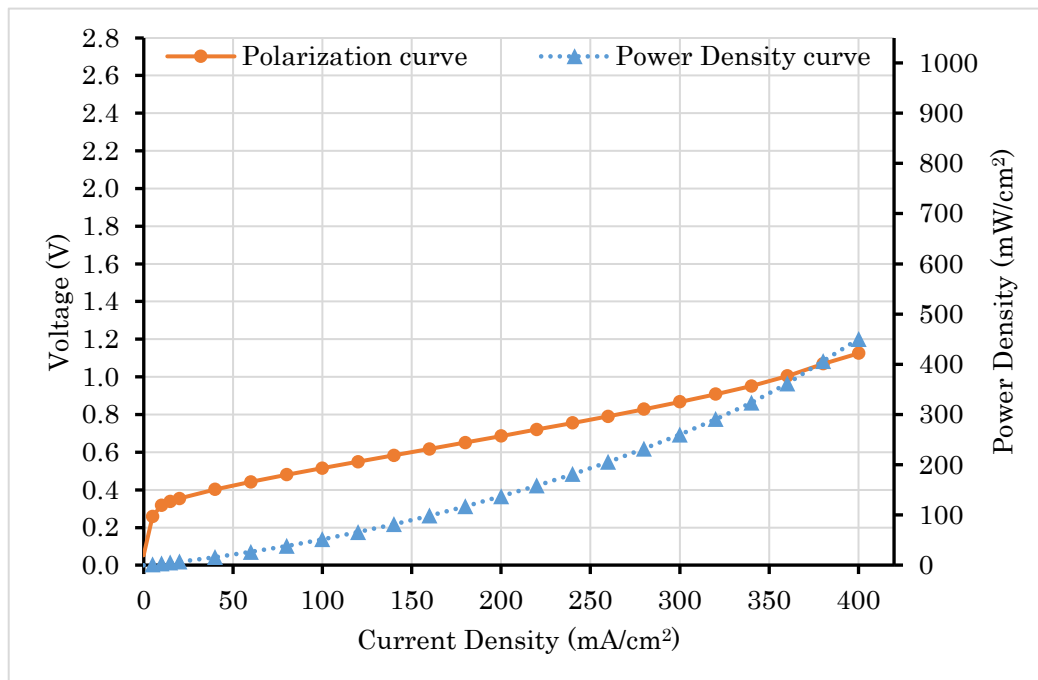


Figure C.160: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

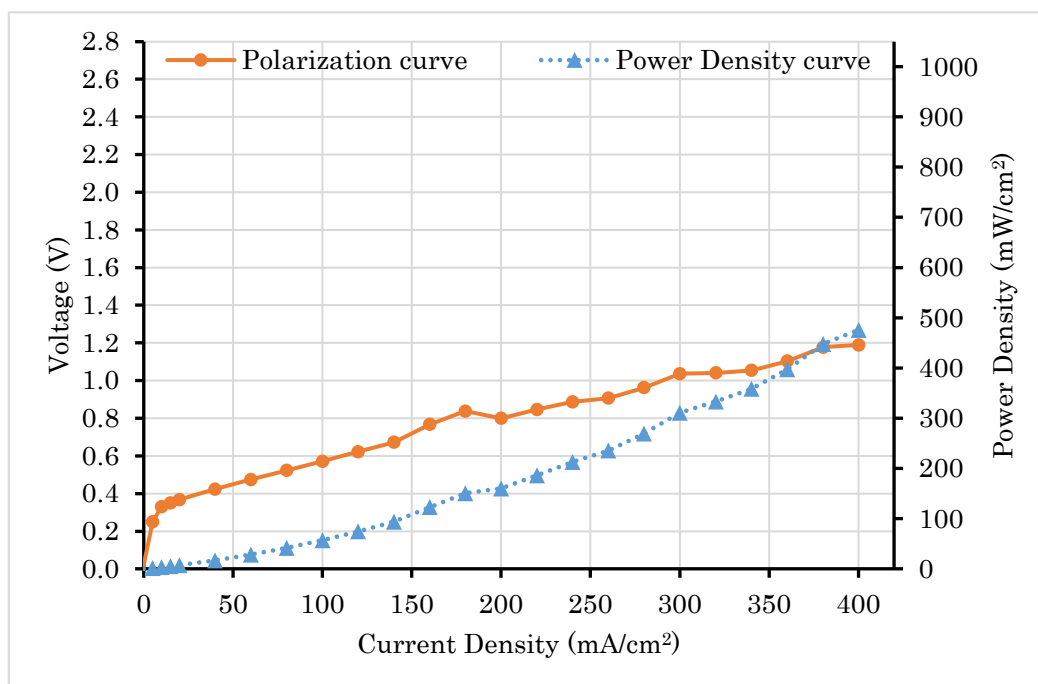


Figure C.161: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

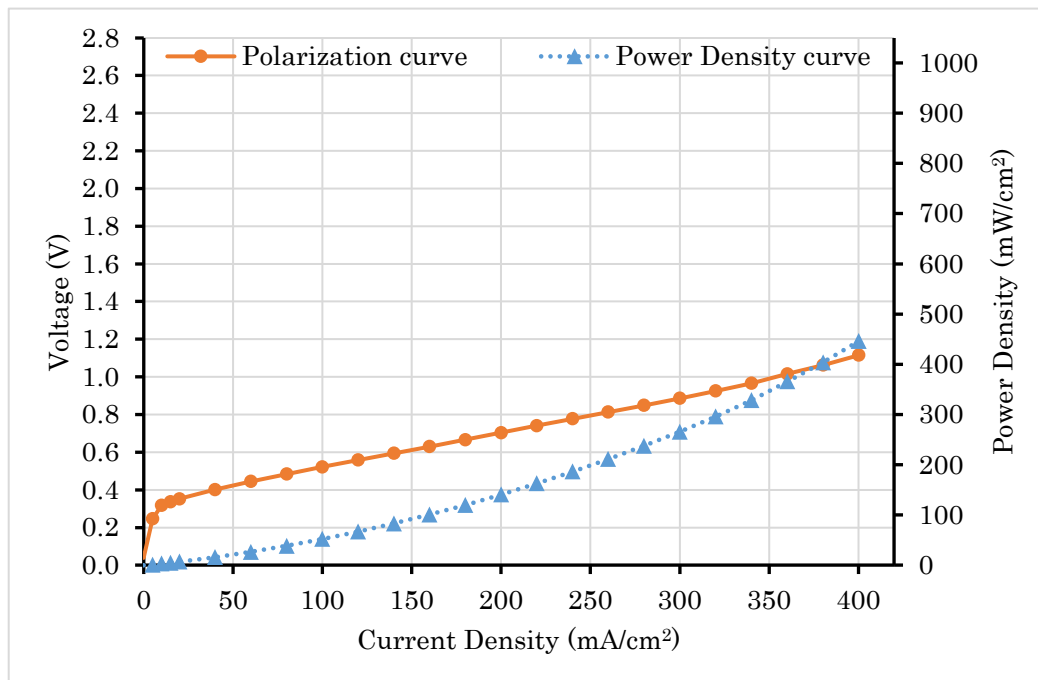


Figure C.162: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

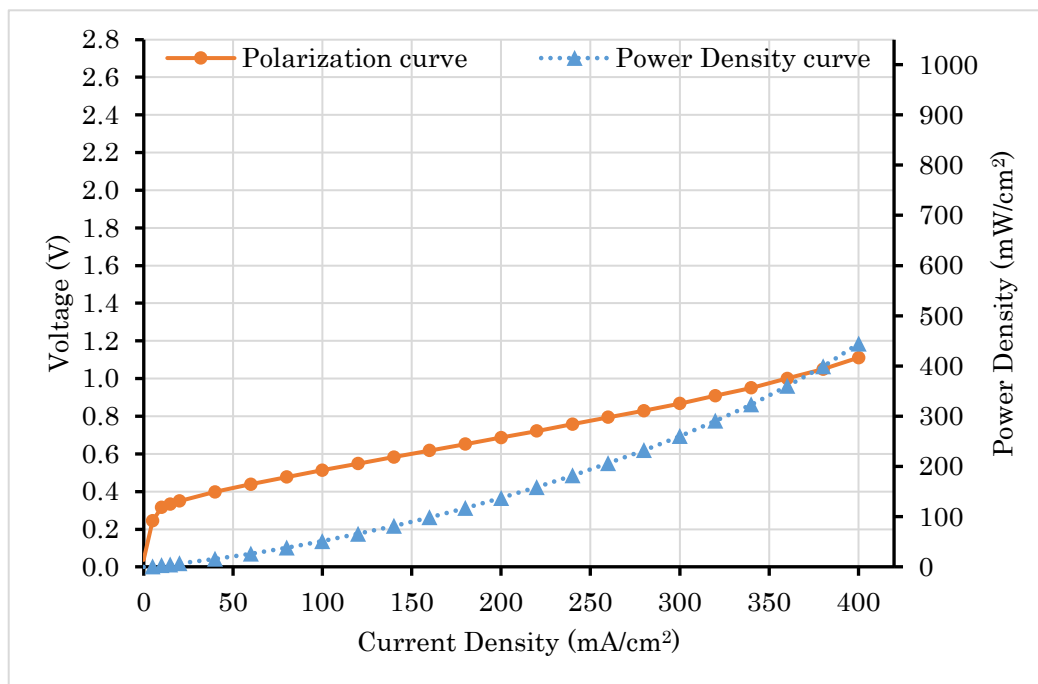


Figure C.163: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

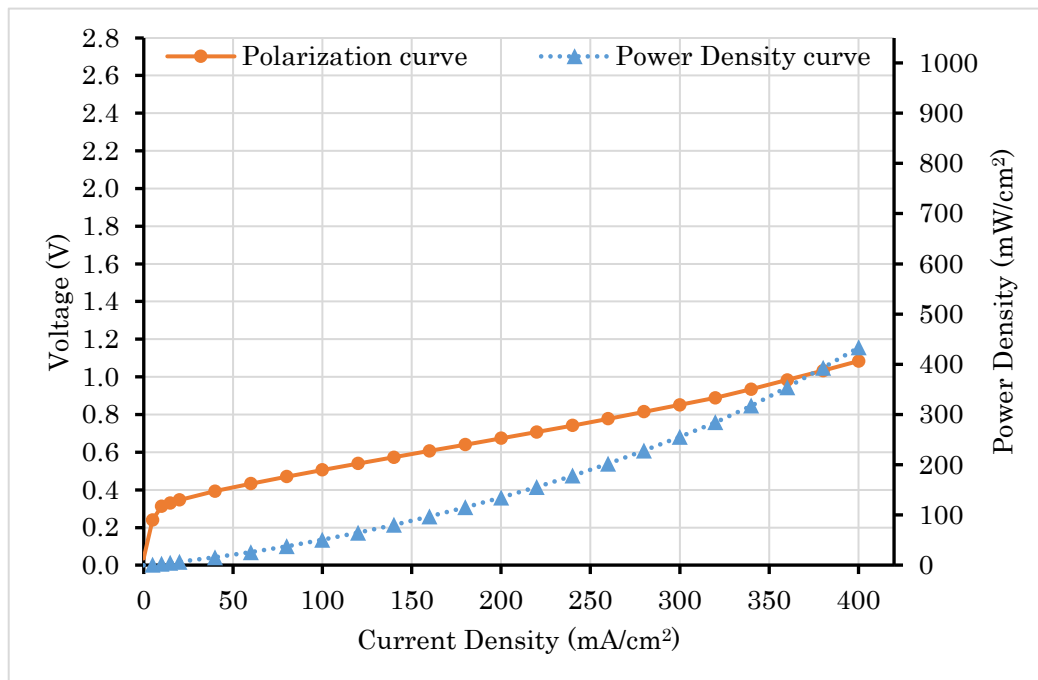


Figure C.164: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 1.13 mm and a channel depth of 1.70 mm.

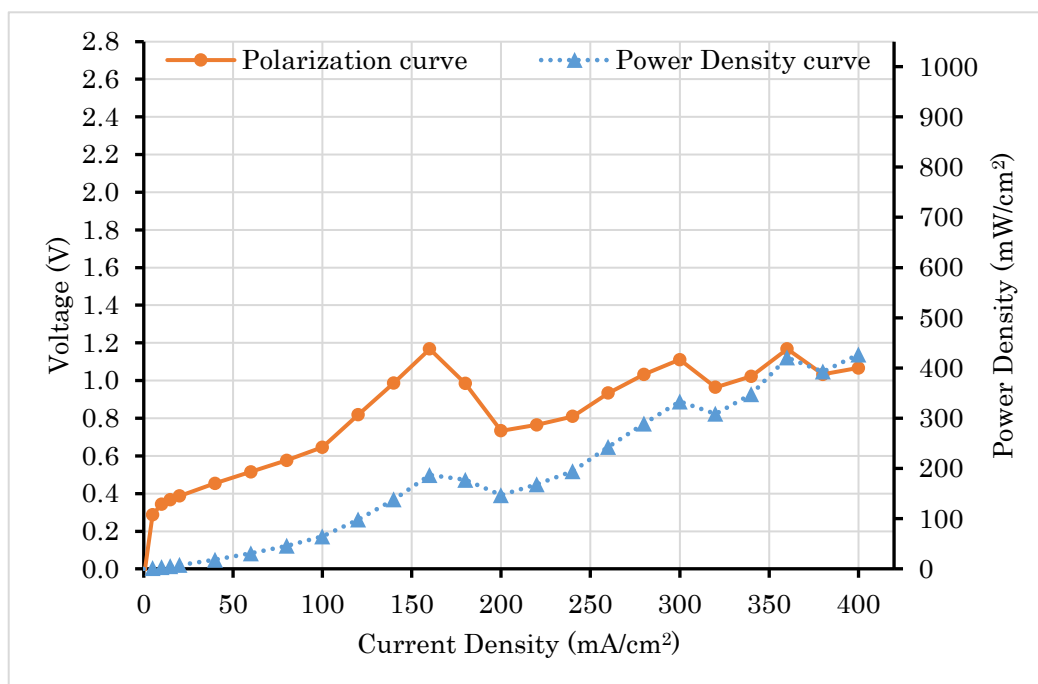


Figure C.165: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

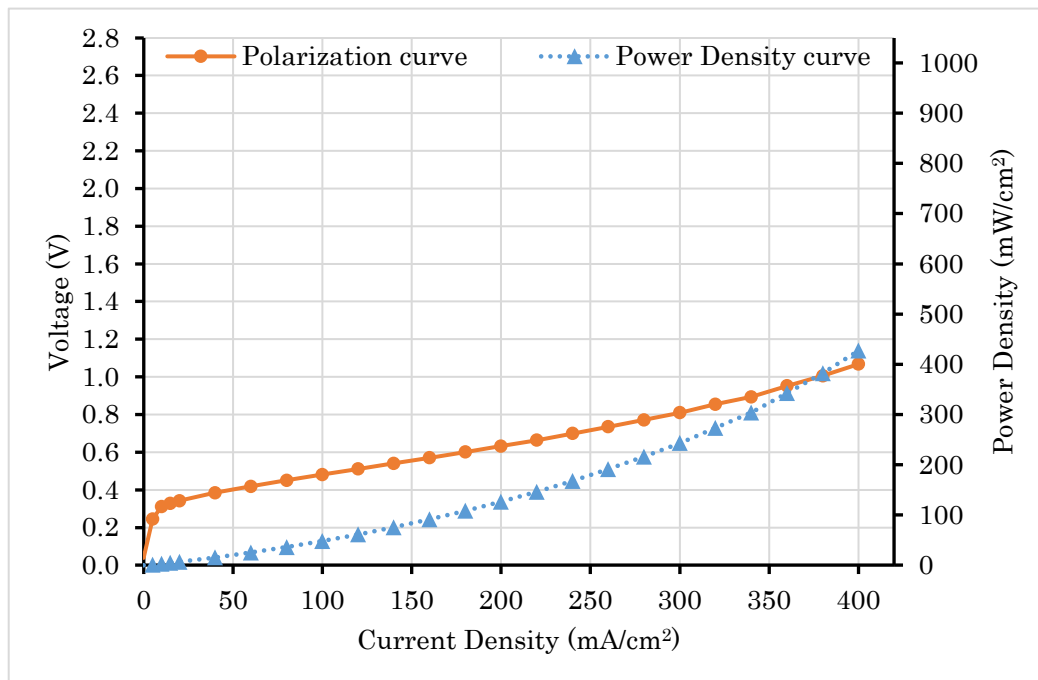


Figure C.166: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

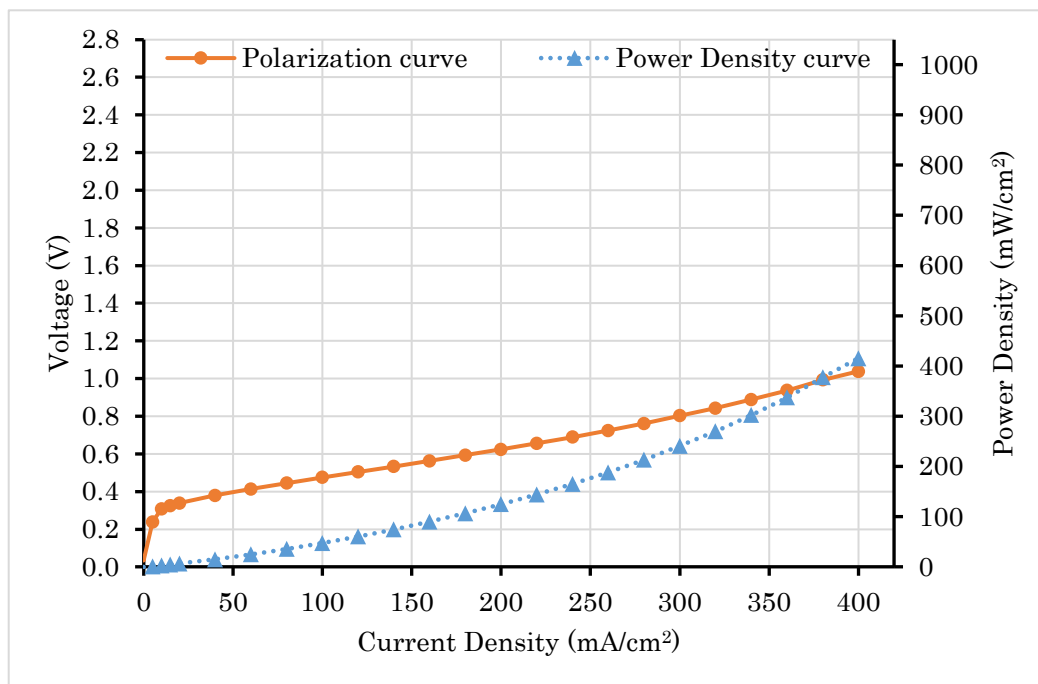


Figure C.167: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

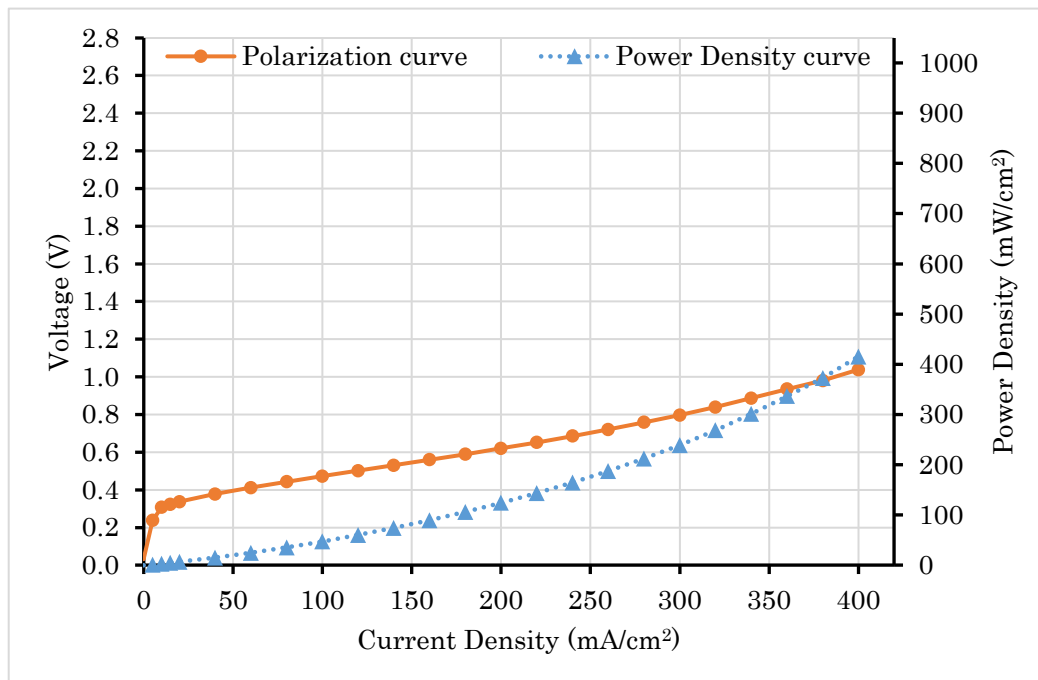


Figure C.168: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

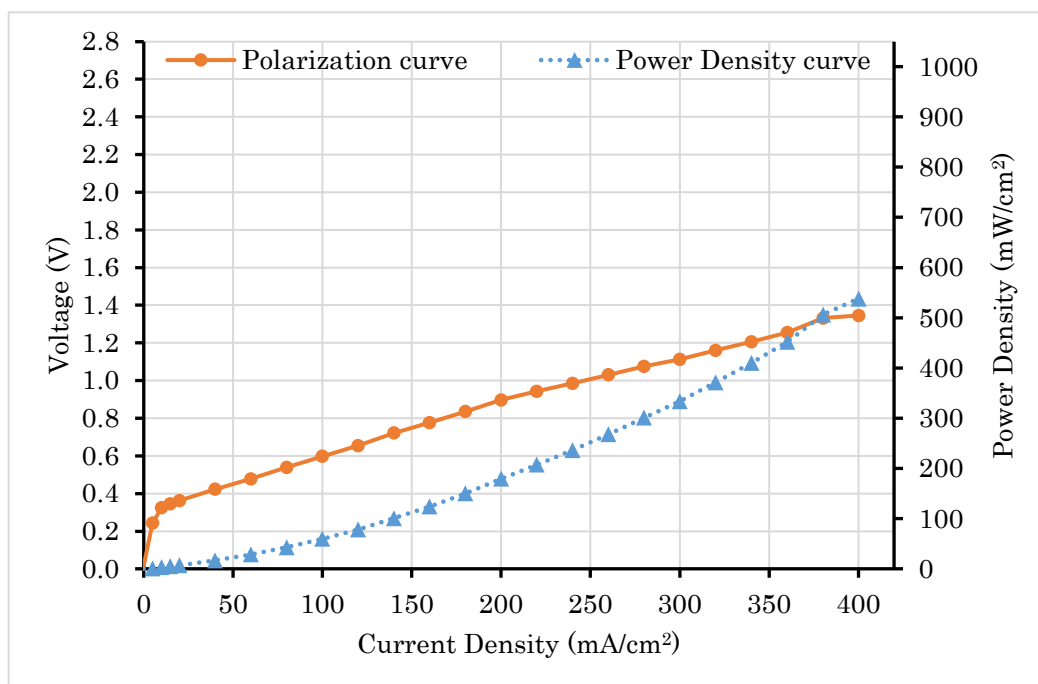


Figure C.169: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

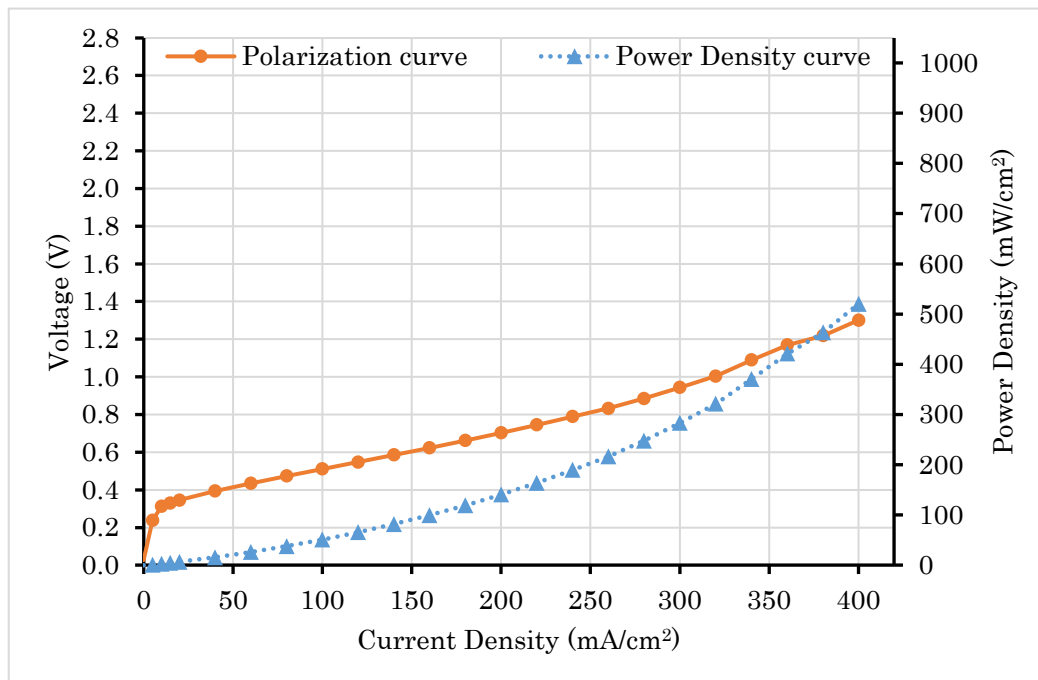


Figure C.170: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

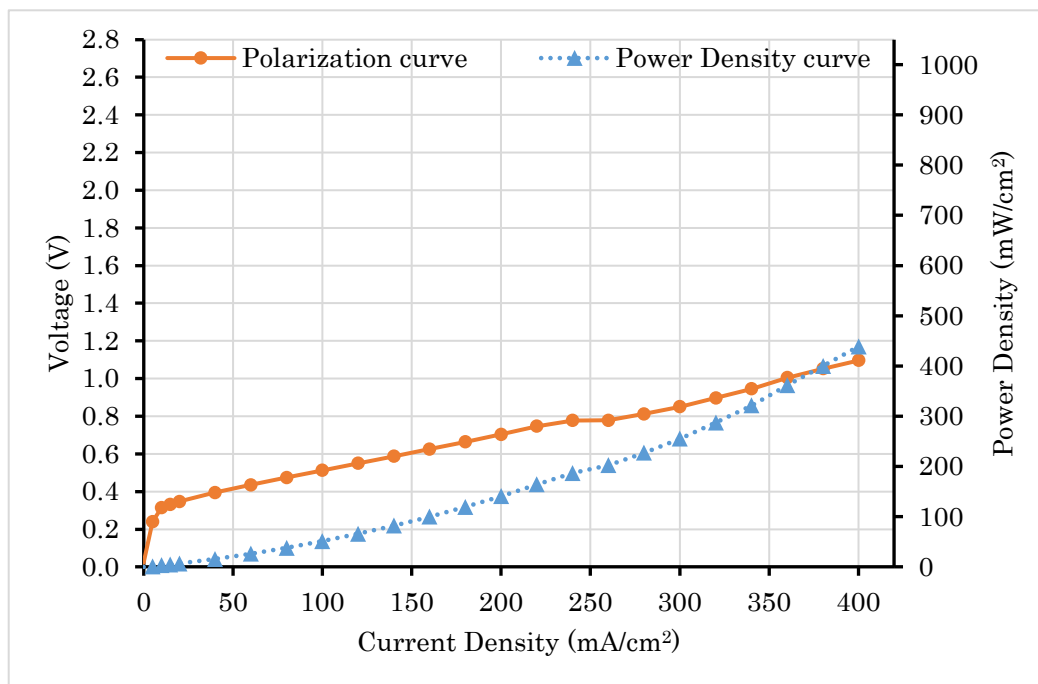


Figure C.171: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

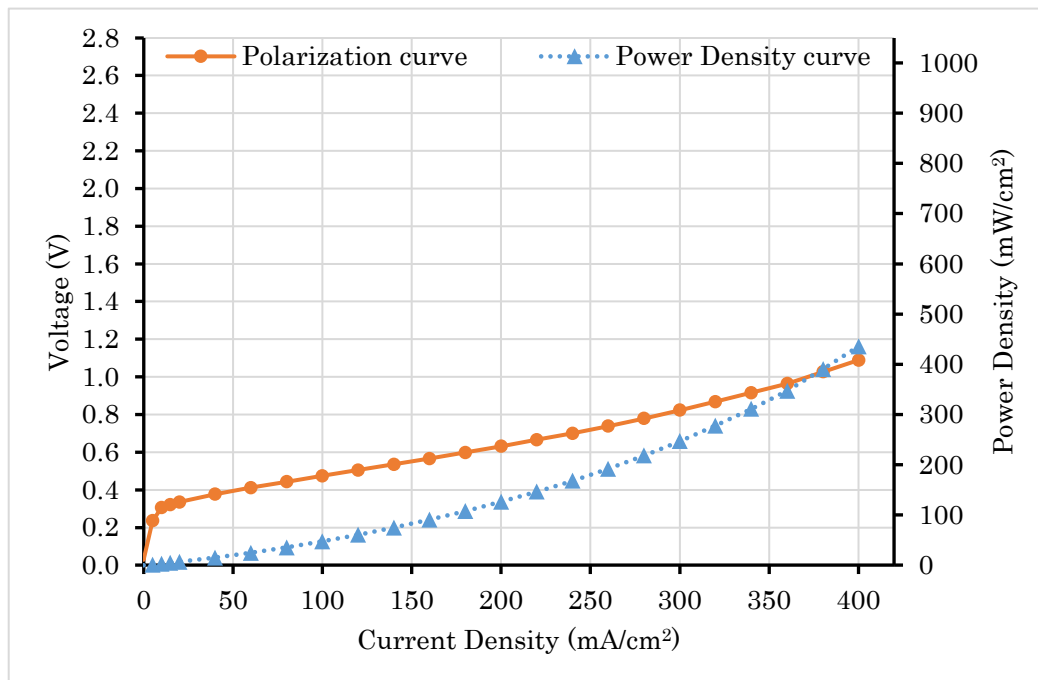


Figure C.172: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 45.4 %, a channel width of 0.71 mm and a channel depth of 1.30 mm.

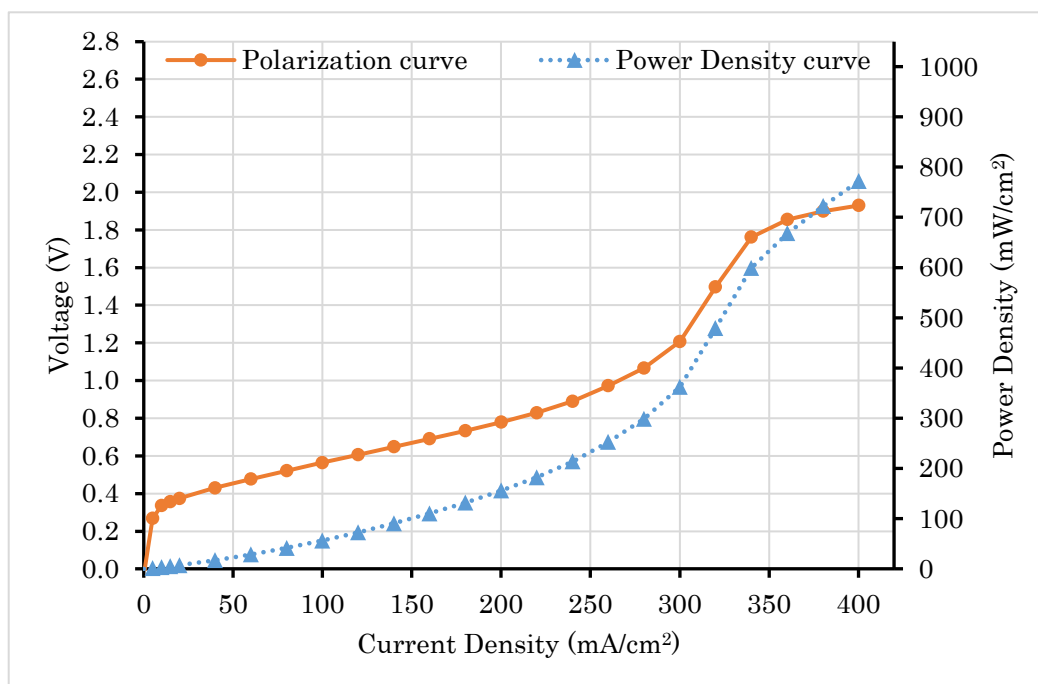


Figure C.173: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

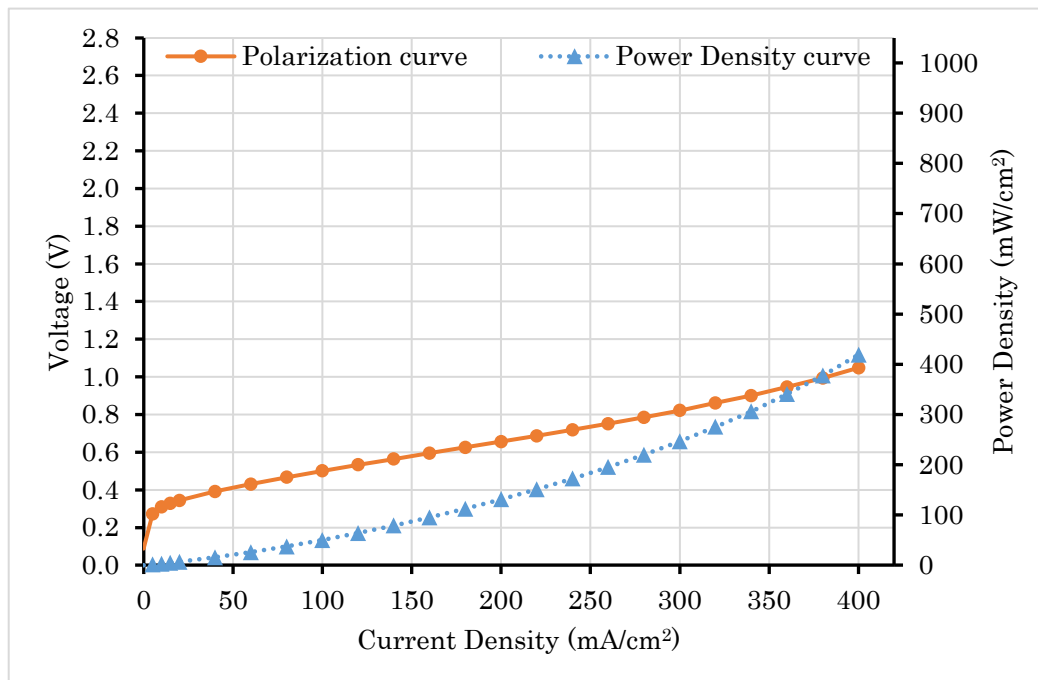


Figure C.174: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

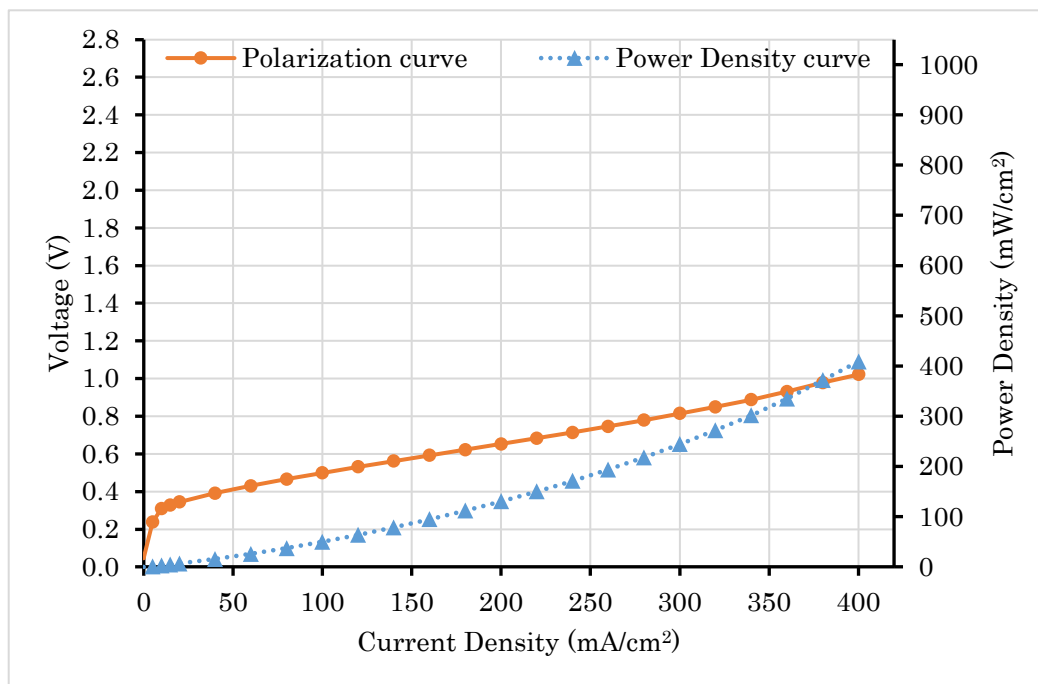


Figure C.175: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

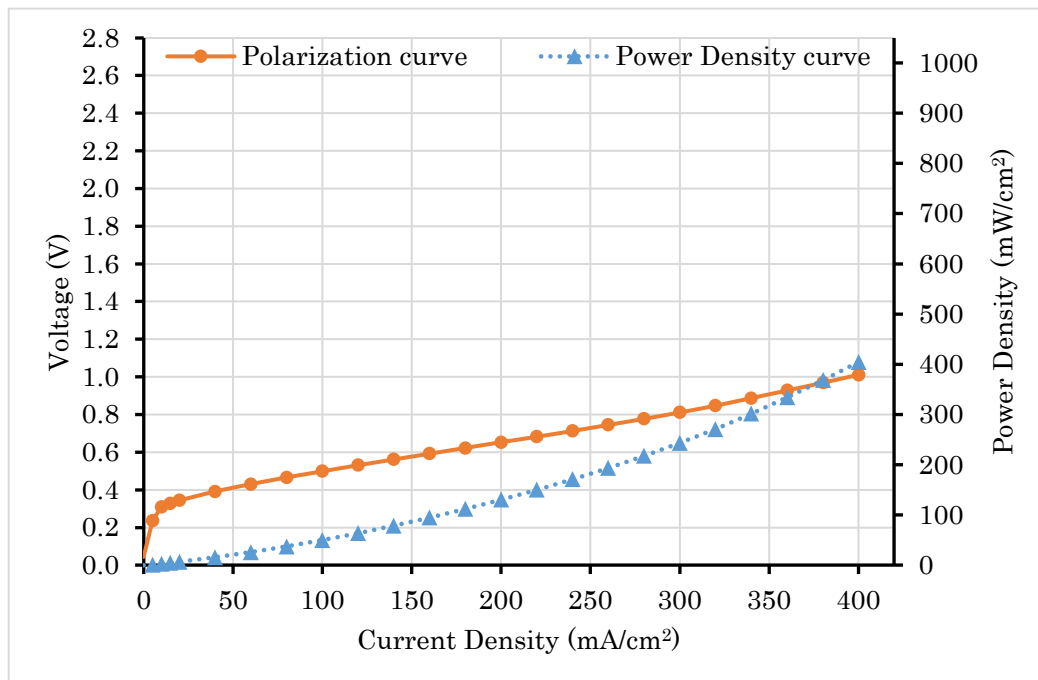


Figure C.176: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

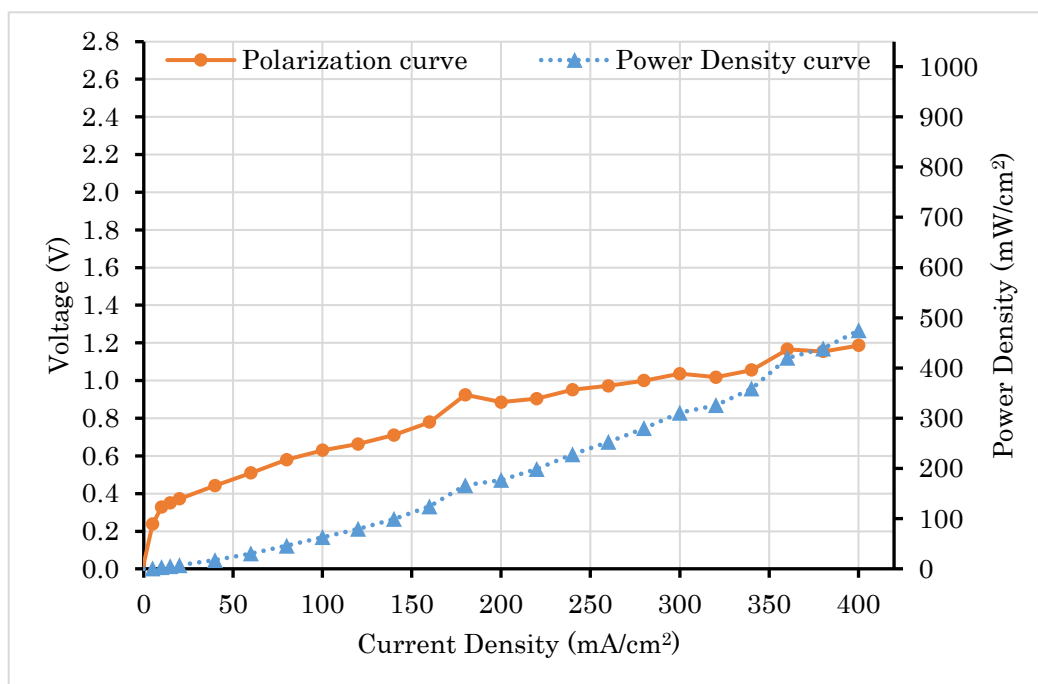


Figure C.177: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

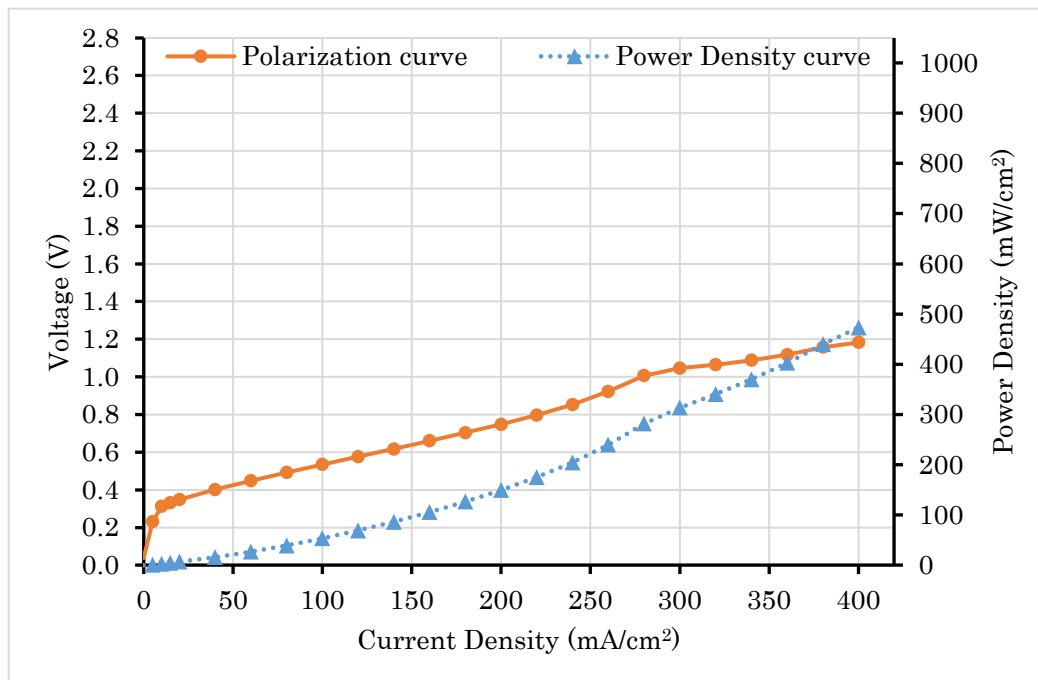


Figure C.178: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

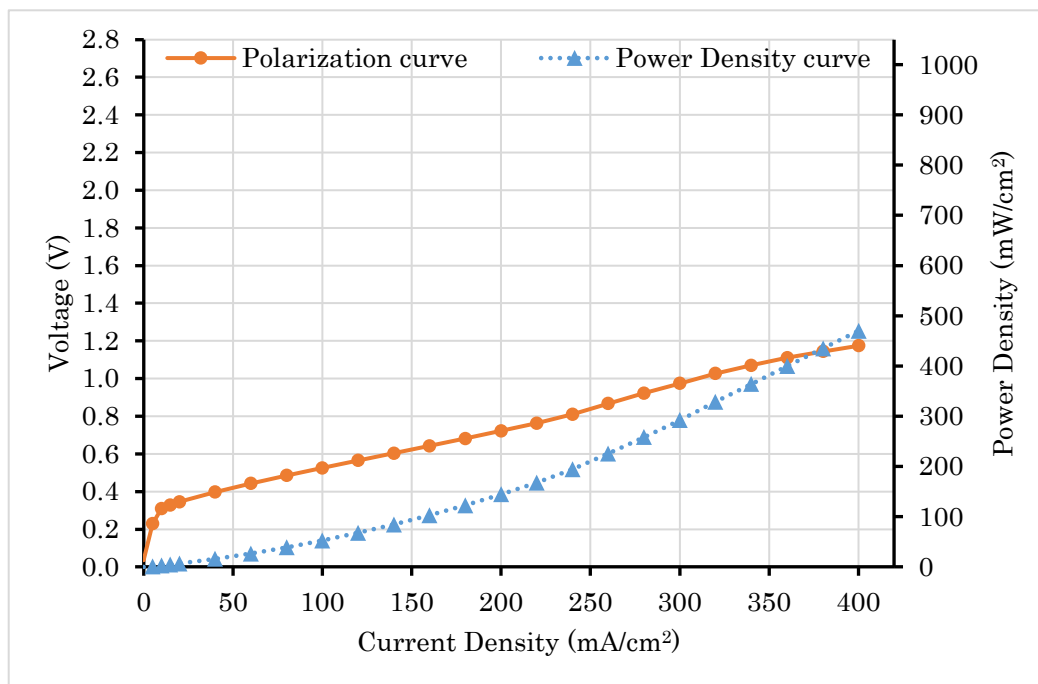


Figure C.179: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

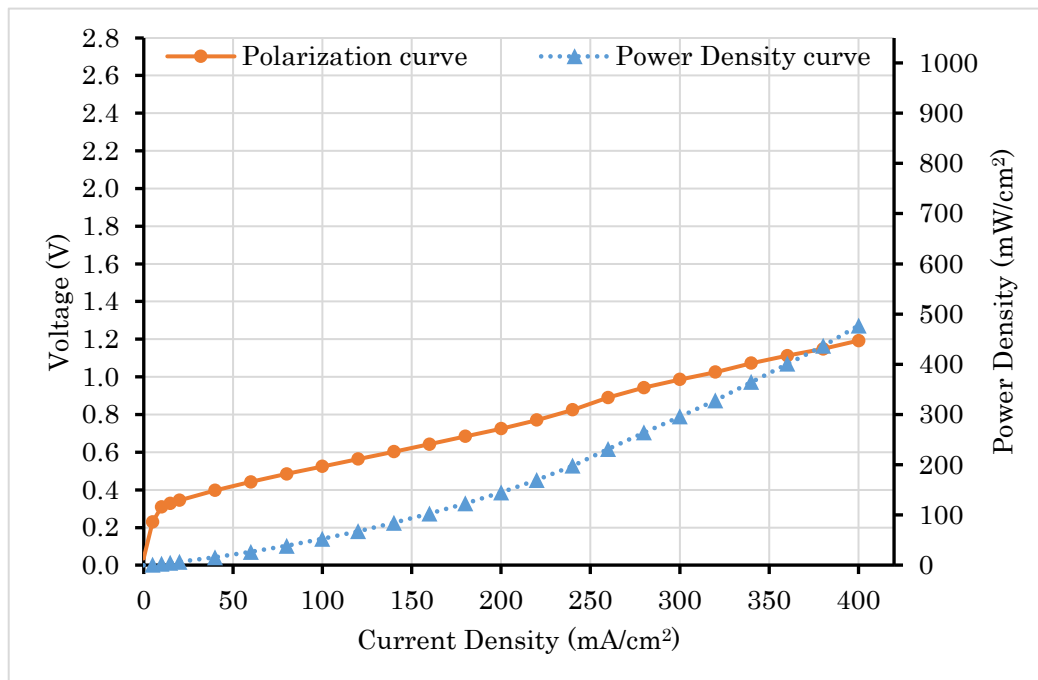


Figure C.180: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 0.90 mm.

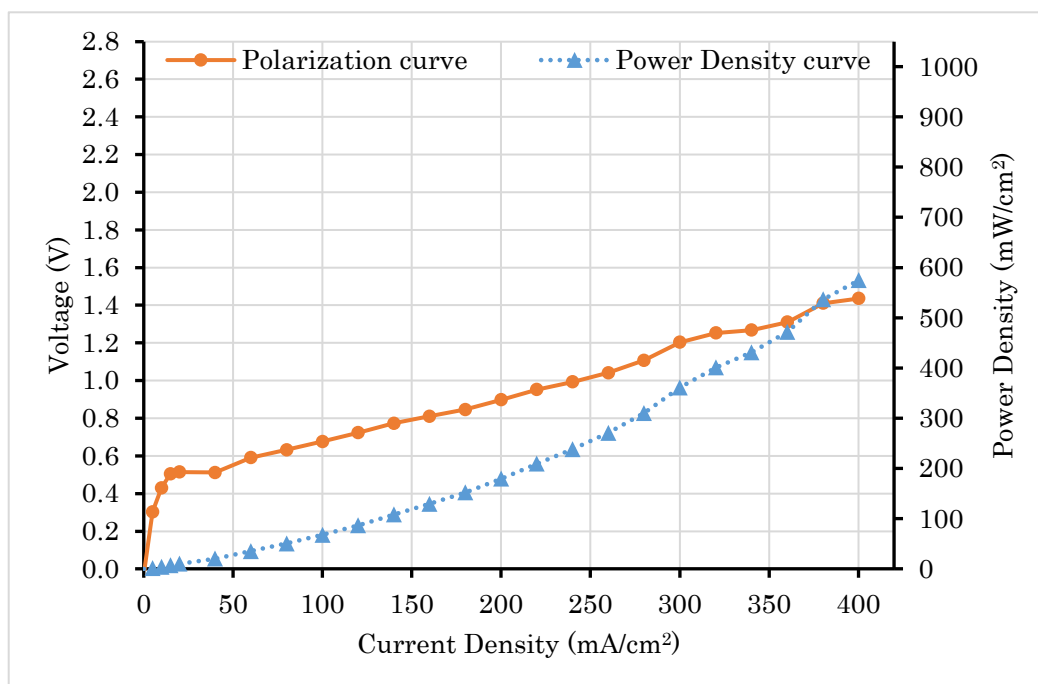


Figure C.181: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

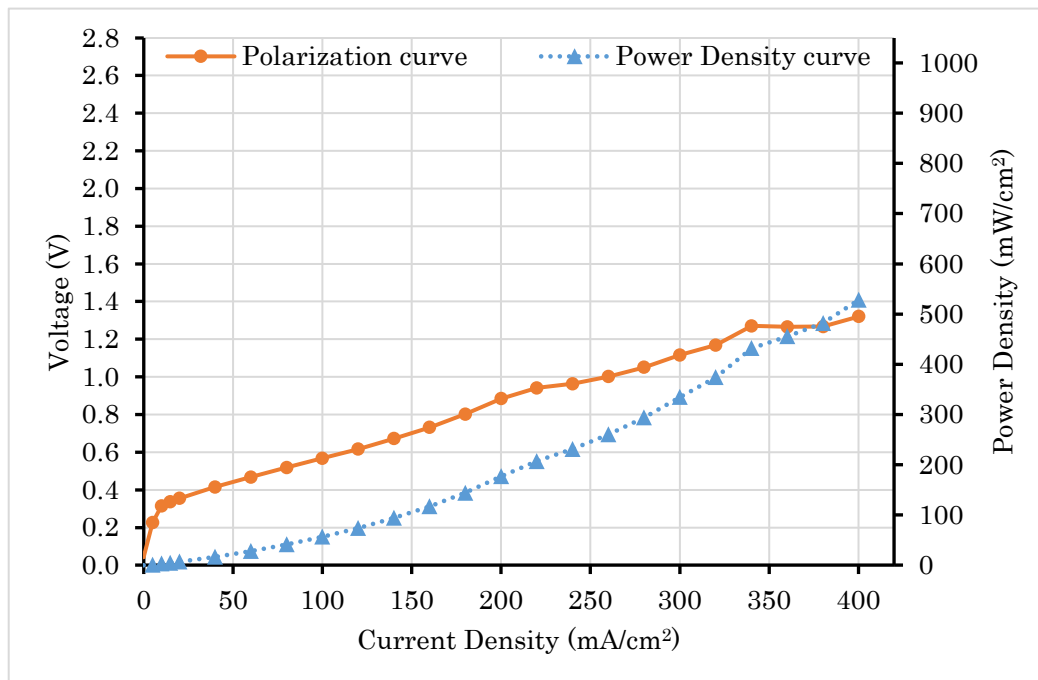


Figure C.182: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

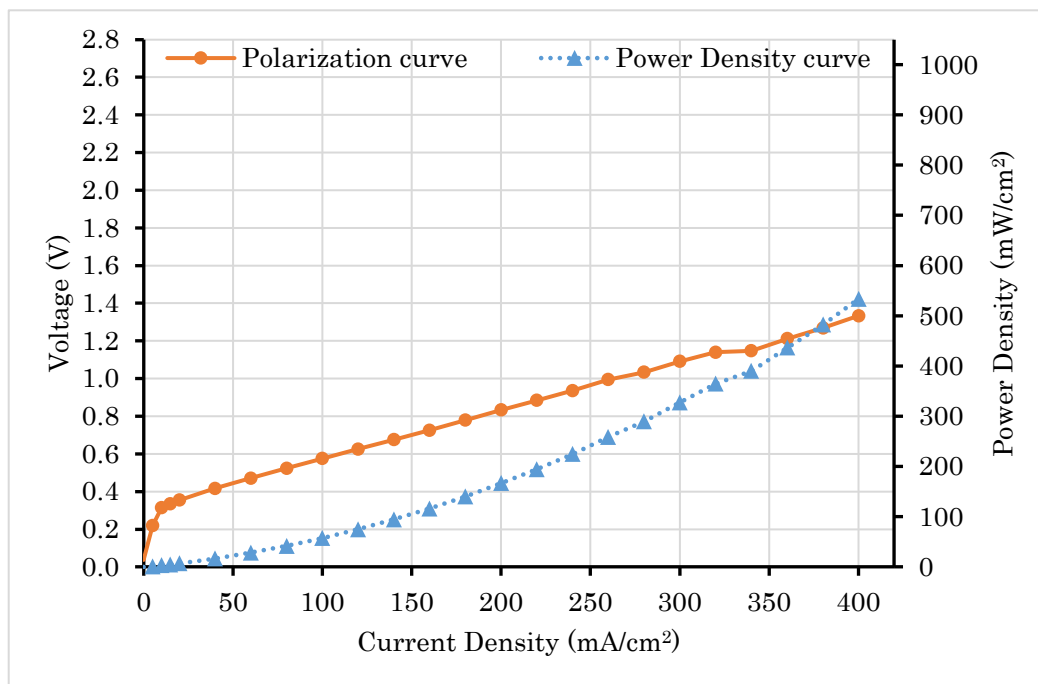


Figure C.183: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

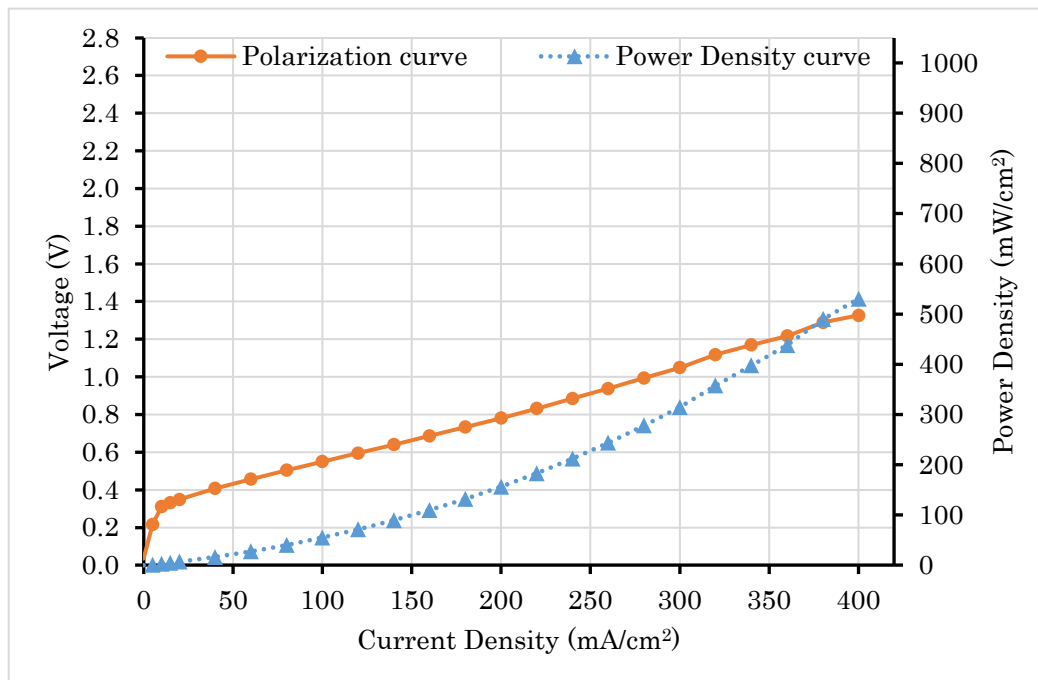


Figure C.184: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

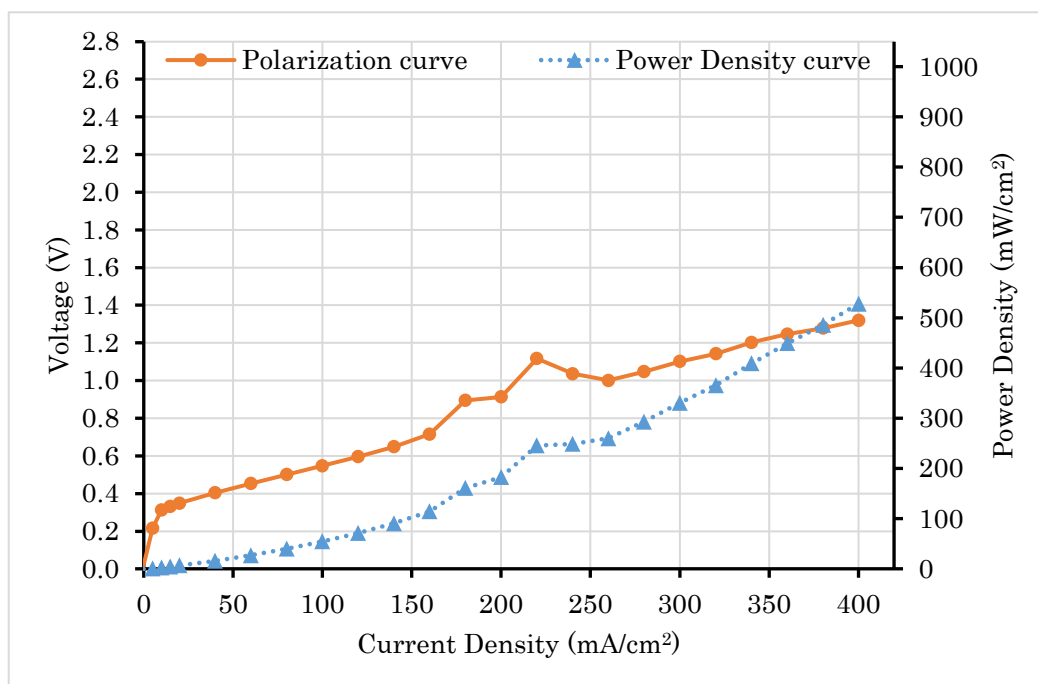


Figure C.185: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

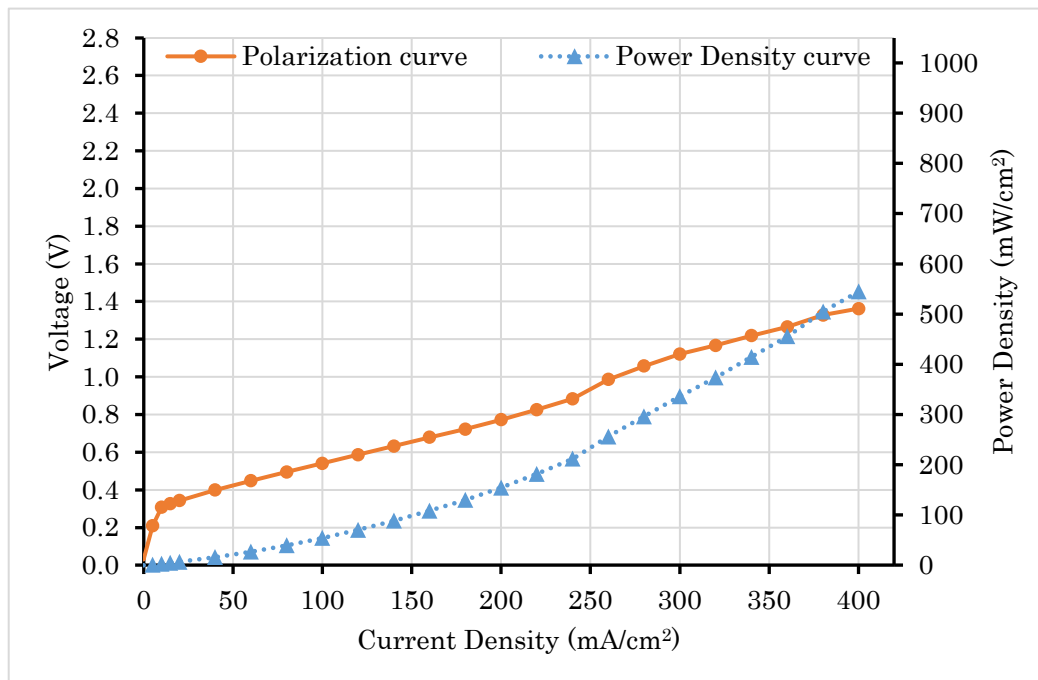


Figure C.186: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

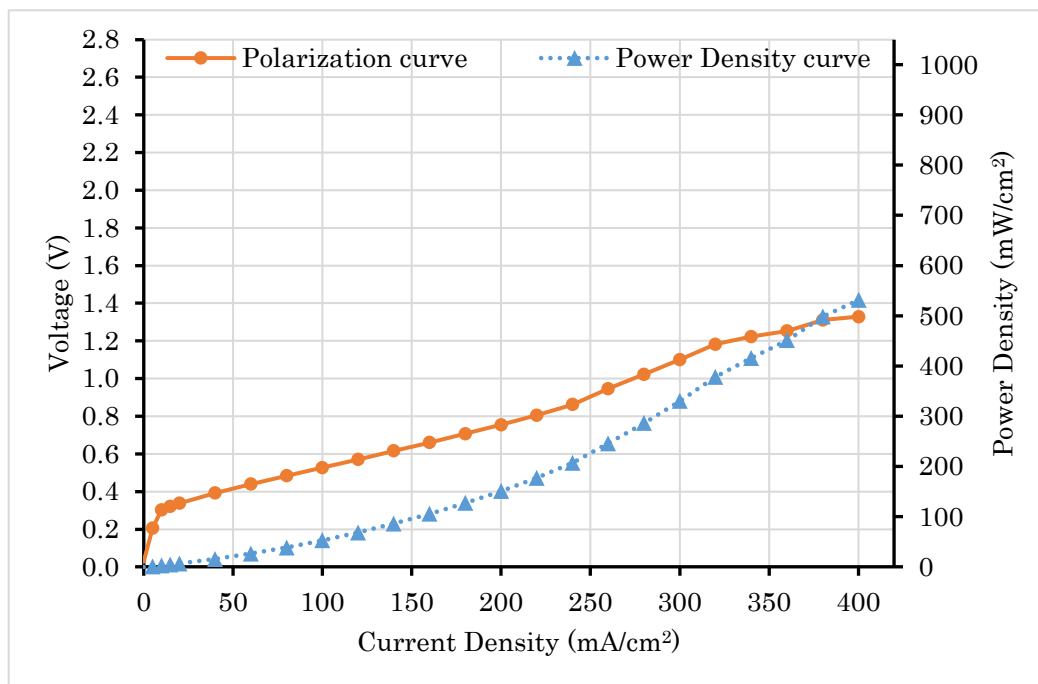


Figure C.187: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

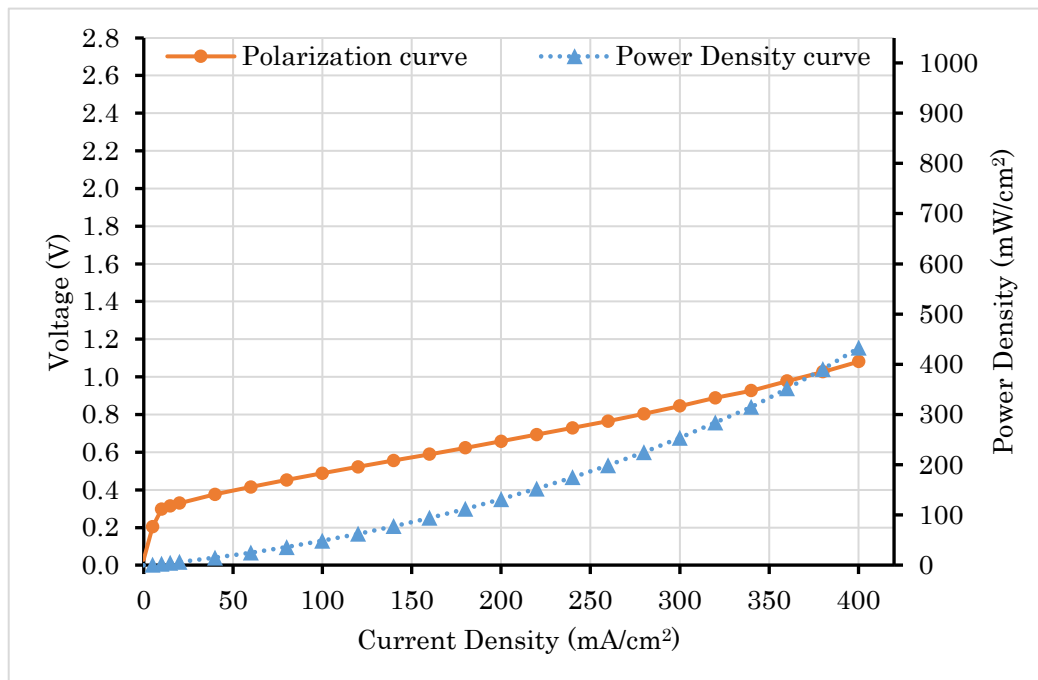


Figure C.188: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 60.6 %, a channel width of 0.83 mm and a channel depth of 1.70 mm.

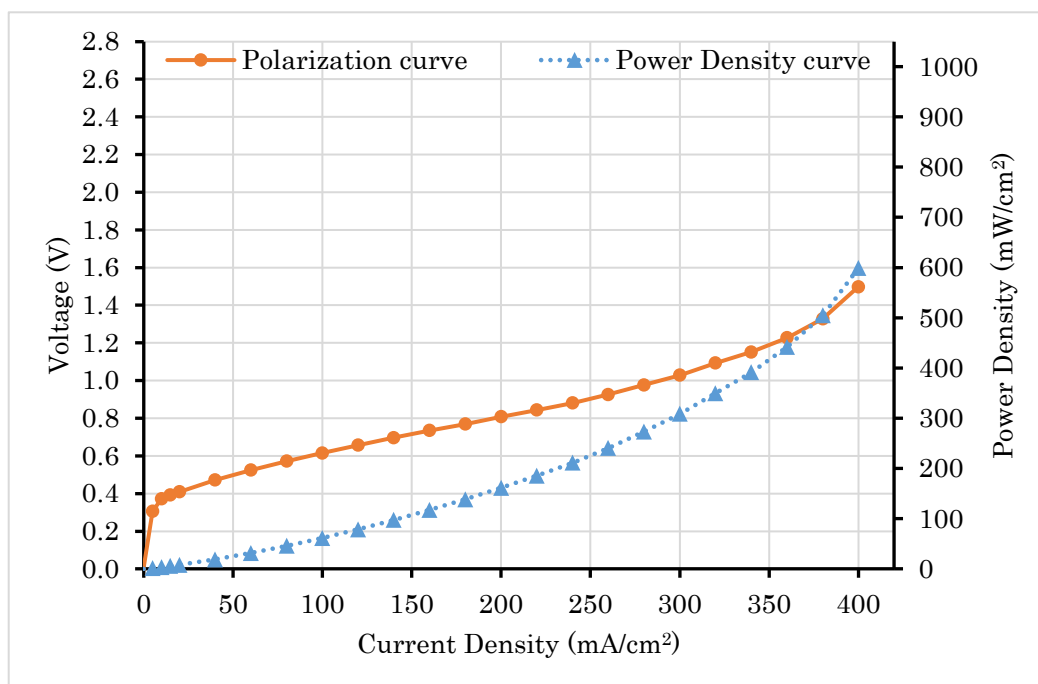


Figure C.189: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

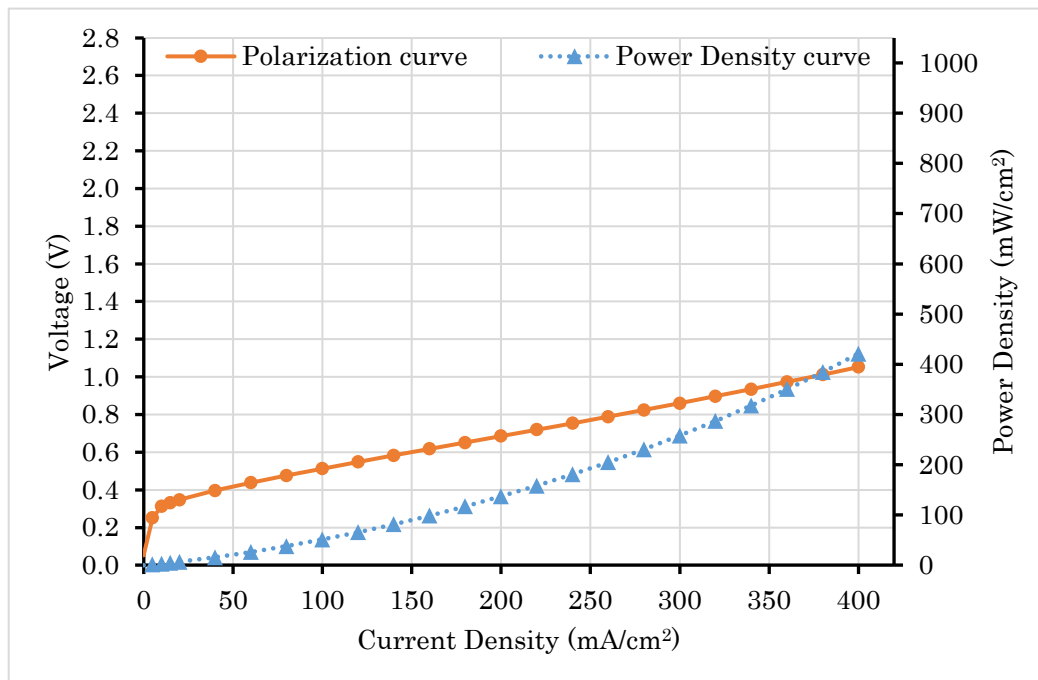


Figure C.190: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

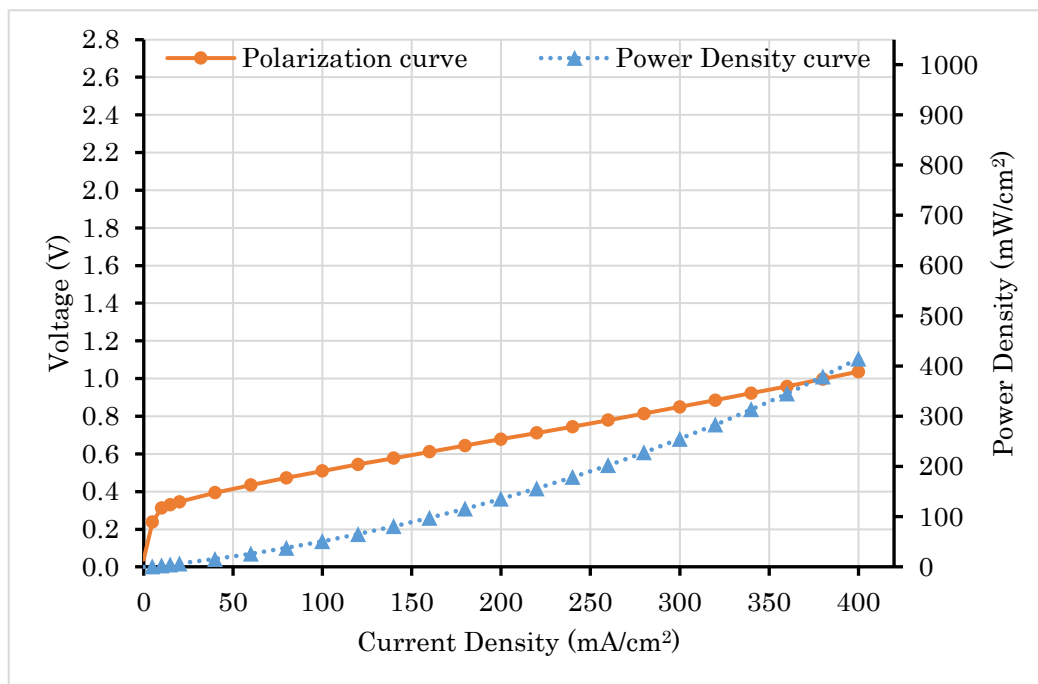


Figure C.191: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

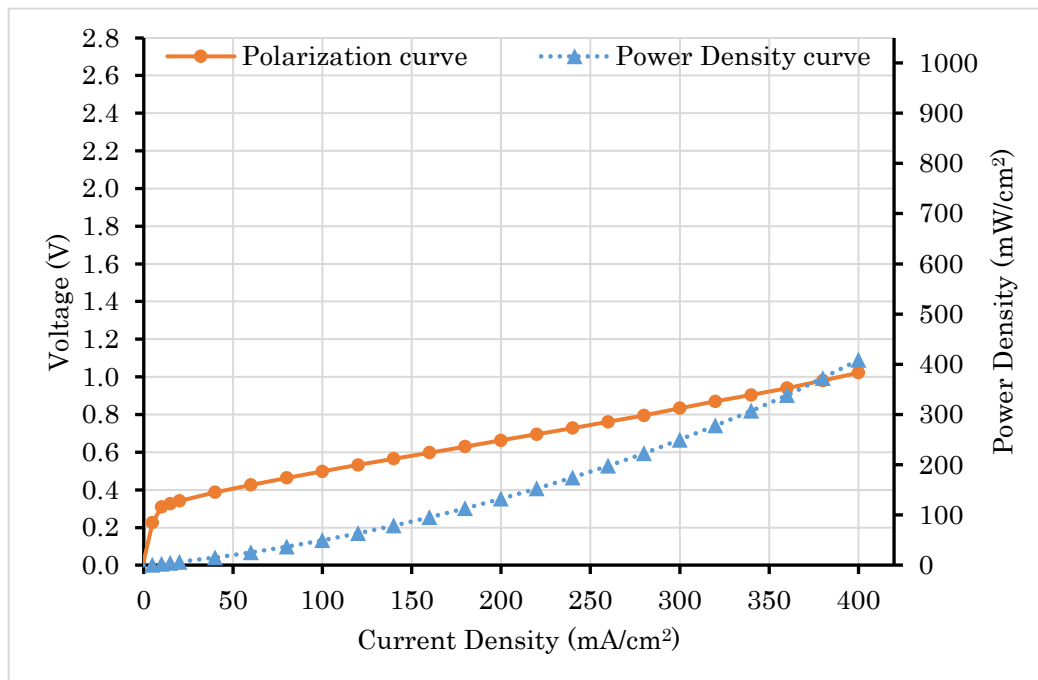


Figure C.192: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

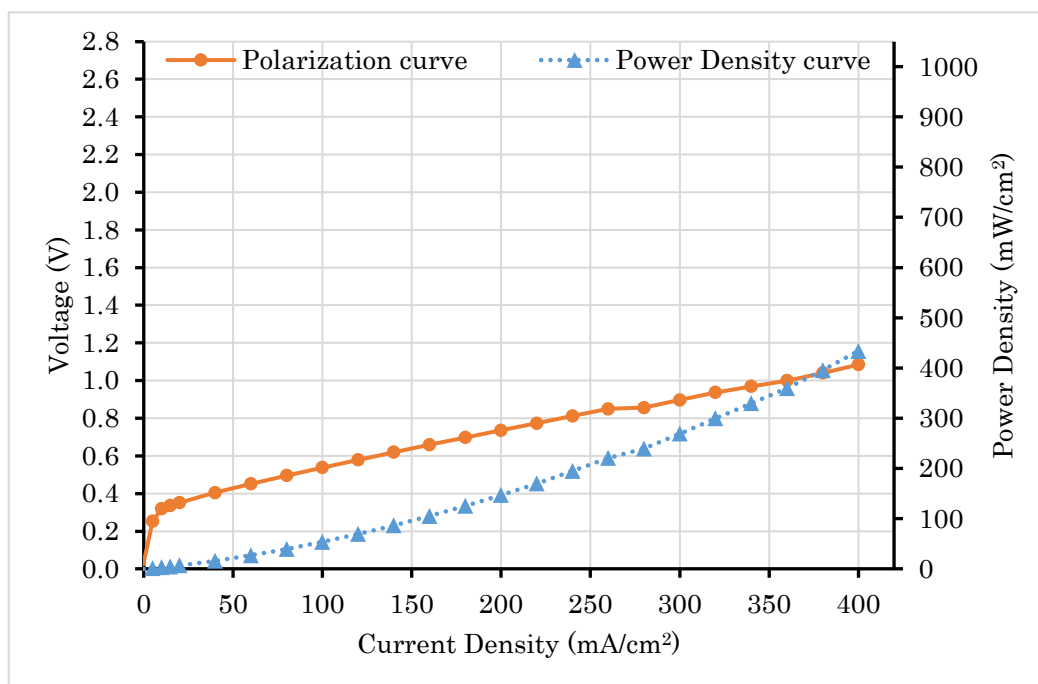


Figure C.193: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

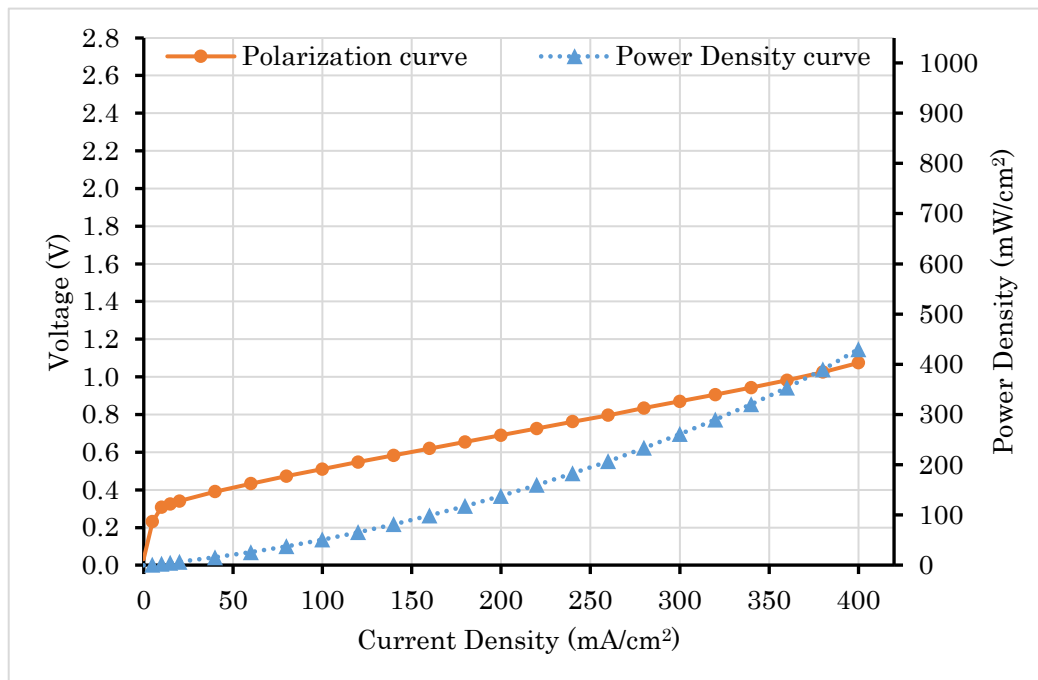


Figure C.194: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

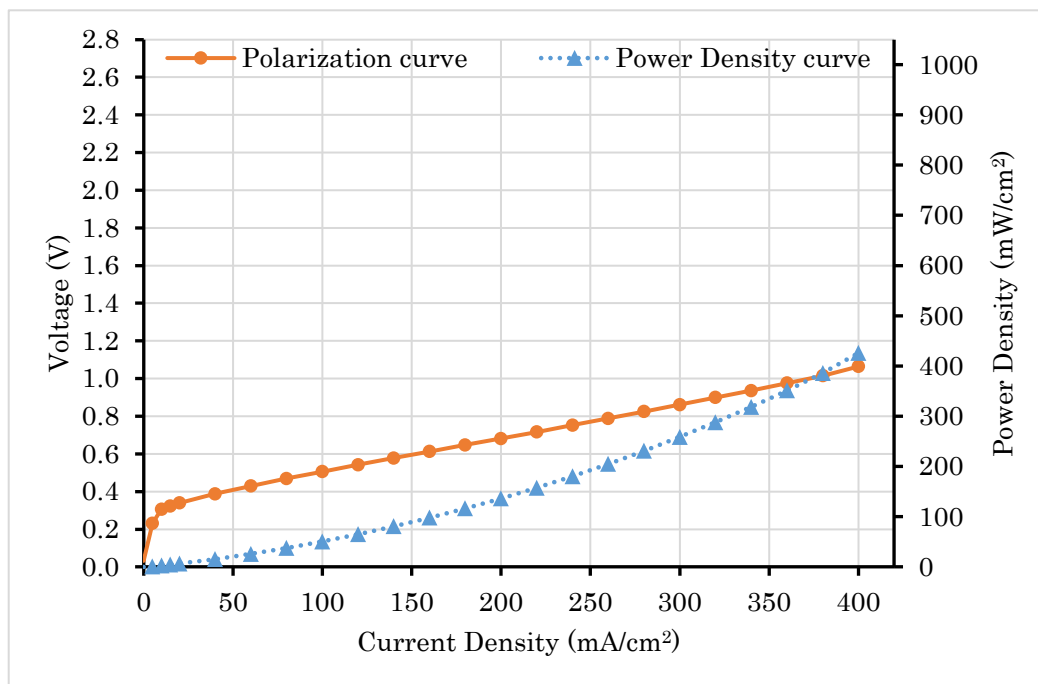


Figure C.195: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.

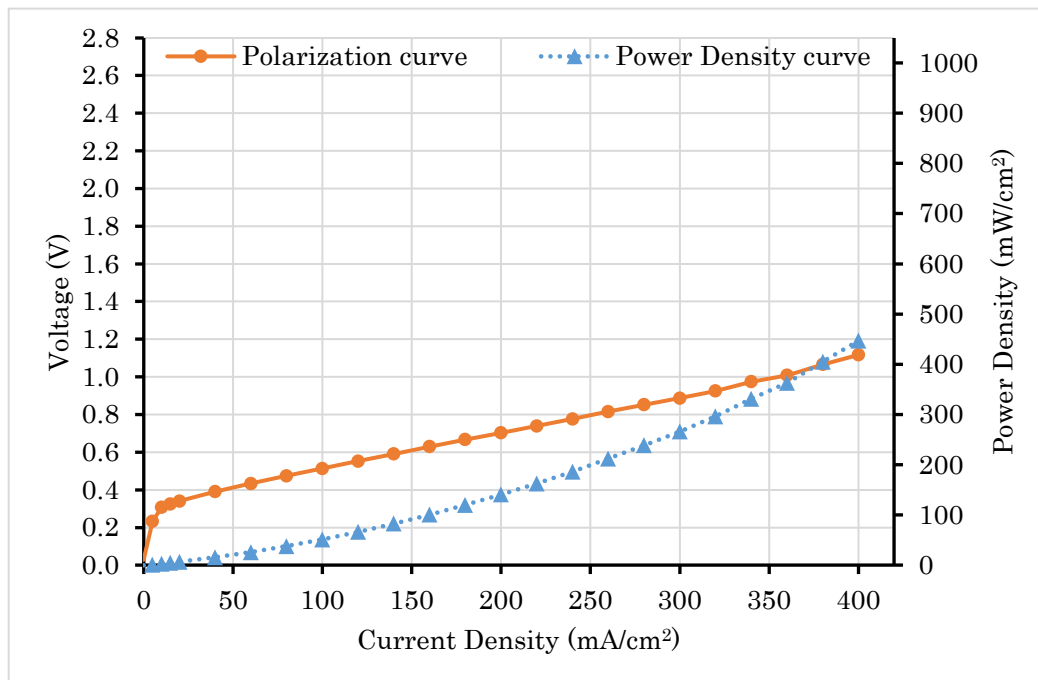


Figure C.196: Polarization curve and Power Density curve of the Methanol Electrolysis Cell (MEC) single cell obtained with an open ratio of 71.7 %, a channel width of 0.98 mm and a channel depth of 1.30 mm.