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Sotirios Karellas, Tryfon Roumpedakis, Konstantinos Braimakis

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PREFACE

This book of proceedings presents the inspiring work of conference ECOS2024, where experts from all over the world have gathered to share knowledge, experiences and innovative solutions in the field of efficiency, cost, optimization, simulation and environmental impact of energy systems.

Several parallel sessions, panel discussions and presentations, covering diverse research areas and ground-breaking ideas have been shared within the ECOS2024 conference. In total 336 full papers were accepted for oral presentations and 90 submissions were assigned to poster presentations.

On behalf of the conference organizing committee, I would like to thank all participants for their commitment and outstanding contributions. Special thanks to the reviewers, for their thorough contribution towards ensuring the high quality and relevance of the papers presented in this book.

We would like to thank our sponsors for their generous contributions and our co-workers for their indispensable technical and secretarial assistance.

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IMPROVEMENT OF A METHANOL ELECTROLYSIS CELL PERFORMANCE THROUGH RESPONSE SURFACE METHODOLOGY

Vladimir L. Meca[1,2,*], Oscar Santiago[3], Elena Posada[1,2], Rafael d'Amore-Domenech[1,2], Antonio Villalba-Herreros[1,2] and Teresa J. Leo[1,2]

[1]Universidad Politécnica de Madrid, ETSI Navales, Dept. Arquitectura, Construcción y Sistemas Oceánicos y Navales, Madrid, Spain

[2]Universidad Politécnica de Madrid, Grupo de Investigación UPM Pilas de Combustible, Tecnología del Hidrógeno y Motores Alternativos (PICOHIMA), Madrid, Spain

[3]University of Bremen, Center for Environmental Research and Sustainable Technology (UFT), Bremen, Germany

*Corresponding Author: vl.meca@upm.es

ABSTRACT

The global energy sector is increasingly reliant on renewable energies, but the distance of renewable energy sources from energy consumption centres requires effective energy transmission. The stochastic and intermittent nature of sources like wind and solar underscores the need for adaptable energy storage and transport solutions. Converting renewable electrical energy into green hydrogen addresses these challenges, offering an environmentally friendly approach. However, the low energy density of hydrogen requires specialized transportation methods, adding complexity and cost. In contrast, methanol is a green hydrogen-derived fuel that is liquid at ambient conditions and therefore easier to manage than compressed and liquid hydrogen. Hydrogen logistics under the form of methanol entails three different stages: packing (methanol synthesis from hydrogen), transport, and unpacking (hydrogen production from methanol). This study explores the use of methanol electrolysis cells (MECs) as devices for the unpacking stage, focusing on their working conditions. To optimize MEC performance, Response Surface Methodology is employed to systematically vary parameters (methanol flow rate, concentration, and MEC temperature) and to study the influence of their combination on the performance of the MEC. The research aims to identify optimal conditions yielding the lowest electricity consumption for hydrogen production from methanol, contributing valuable insights to enhance the efficiency of methanol electrolysis in advancing renewable energy integration strategies.

1 INTRODUCTION

In the growing hydrogen economy, a primary objective revolves around the generation of electricity through fuel cells, particularly proton exchange membrane fuel cells (PEMFC). In this context, a prerequisite is the utilization of high-purity hydrogen (Coutanceau & Baranton, 2016). Presently, hydrogen predominantly stems from fossil fuels (e.g. natural gas, oil, and coal) (Fu et al., 2022), using energy-intensive and environmentally adverse industrial processes entailing intricate steps for the extraction of carbon monoxide and carbon dioxide in order to obtain high purity hydrogen (Hao et al., 2022). One form of hydrogen production that avoids this drawback is water electrolysis. This process generates a high-purity hydrogen stream, and by incorporating renewable primary energy sources, such as wind or solar, is environmentally sustainable. However, as hydrogen has a low volumetric energy density (11.3 MJ/Nm^3) (Lemmon et al., 2010) it is required to increase its density, with processes such as liquefaction and subsequent storage, or storage and transport as compressed gas (d'Amore-Domenech et al., 2023). These processes involve a high cost and energy loss, so alternatives such as liquid organic hydrogen carriers (LOHC) can be explored and compared. Within this framework, methanol emerges as a prominent candidate as a hydrogen vector, which can play a pivotal role in this transition towards a more sustainable hydrogen economy. Methanol has the potential to achieve carbon

neutrality when produced through a synthesis process with green hydrogen and CO_2 obtained through industrial capture, from biomass or directly from the atmosphere (Roode-Gutzmer et al., 2019). Besides, this fuel is liquid at ambient temperature and pressure, which simplifies its handling and distribution.
The conversion of methanol into hydrogen can be accomplished through either thermal processes or electrochemical processes (Menia et al., 2018). Thermal processes have undergone significant advancements, but the hydrogen stream obtained from these processes requires treatment before utilization in PEMFC (Yazici et al., 2021). In contrast, electrochemical processes, exemplified by the electrolysis of methanol in aqueous solution, yield a purer hydrogen (Wei et al., 2018), but have not reached yet a commercial status. For this reason, research efforts are imperative to elevate the Technology Readiness Level (TRL) of this technology. However, methanol electrolysis involves electrical energy consumption. This consumption has direct implications for the use of methanol as a hydrogen carrier, since once the methanol reaches its destination and hydrogen is to be obtained from methanol electrolysis, electrical energy must be supplied. Taking this into account, for the use of methanol as hydrogen vector to be economically profitable, the price of electricity at the hydrogen production facility from water must be lower than that of electricity at the destination, and the energy consumption of methanol electrolysis compared to water electrolysis must be much lower. In this case, with the lower transport costs due to the use of methanol instead of hydrogen, and the lower electricity consumption at the destination, methanol has its place as an economically profitable hydrogen carrier (Meca et al., 2022).
Methanol electrolysis is an electrochemical process in which methanol (CH_3OH) is broken down into its basic components, hydrogen (H_2) and carbon dioxide (CO_2), using electricity. The reactions that occur in a methanol electrolyser are (Lamy, 2020; Xiao et al., 2017):

$$\text{Anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$\text{Cathode: } 6e^- + 6H^+ \rightarrow 3H_2 \quad (2)$$

$$\text{Overall: } CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (3)$$

The initial consideration of on-site hydrogen production through the electrolysis of aqueous methanol dates back to 1948, as documented in the NASA Brief Technical Report (Coutanceau & Baranton, 2016; Jeffries-Nakamura B et al., 1948). Later, a system for the electrolysis of aqueous organic solutions to produce hydrogen was patented (Narayanan, 1998). They built a methanol electrolysis cell (MEC) with Nafion 117 as electrolyte and Pt and Pt-Ru electrodes for cathode and anode, respectively. When working with methanol, for a given current density, the voltage of the MEC was approximately one third of that needed for water electrolysis, implying a great reduction in electrical energy consumption, fulfilling the premise that allows the economically viable use of methanol as a hydrogen vector using methanol electrolysis when the price of electricity at the hydrogen production facility from water electrolysis is lower than that of electricity at the methanol electrolysis facility.
The amount of hydrogen produced in a MEC has also been studied previously (Take et al., 2007). During that study, hydrogen production at the cathode exhibited an incremental trend corresponding to the current density, closely adhering to the Faraday's law. Ultimately, the electrical energy required for hydrogen production proved to be less than 60% of that needed for water electrolysis. Moreover, analysing the relation between voltage and current density, they observed a small voltage variation, from 0.95 to 1.34 V when the current density increased from 43 to 350 mA/cm^2. These results have also been reached by other researchers, who report an energy requirement for methanol electrolysis as a function of the volume of hydrogen produced of 1 kWh/(Nm^3) compared to the 5 kWh/(Nm^3) required for water electrolysis (Guenot et al., 2015).
The purity of hydrogen obtained with methanol electrolysers was also analysed. Values of up to 99.8% of purity have been reported, the remaining 0.20% being due to the presence of CO_2 in the cathode (Sasikumar et al., 2008). They also studied the effect of methanol concentration on hydrogen production and the behaviour of a MEC in the range of 1 to 10 M, with the best performance obtained between 4 and 6 M. The temperature effect on current density and hydrogen produced in the range of 30 to 80 ºC was also investigated, revealing an increase in both parameters at a fixed voltage when temperature is increased, attributed to enhanced catalytic activity and decrease in ohmic resistance. Another study

reported the influence of temperature and methanol concentration on the polarization curves of a MEC, observing a much smaller influence of concentration (Lamy et al., 2015).
The importance of methanol electrolysis and 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. This work focuses on the improvement of performance of a methanol electrolysis cell by incorporating the volumetric flow rate parameter into the study. In addition, the influence of the interaction of the effects of temperature, methanol concentration and volumetric flow rate on the behaviour of the MEC is also evaluated using the Response Surface Methodology (RSM).

2 METHODOLOGY

To explore and optimize operating parameters in a MEC, a single cell configuration was employed. The cell consists of two stainless steel 316L plates, a Membrane Electrode Assembly (MEA) and two gaskets. The plates, adopting a single-channel serpentine geometry with channels of 1.0 mm depth, facilitate reactant distribution and by-product evacuation and minimizes pressure drops between channel inlet and outlet (Kianimanesh et al., 2012). Each plate encompasses 25 channels, each with a width of 1.0 mm. Gaskets prevent electrical contact between plates and ensure fluid tightness. The MEA comprises two electrodes (anode and cathode) separated by a Nafion®-117 polymeric membrane serving as electrolyte. The anode features catalyst PtRu/C 20wt% 3 mg/cm^2, while the cathode incorporates Pt/C 40wt% 1 mg/cm^2. Both electrodes are homemade and use Toray carbon paper TGP-H-60 as gas diffusion layer. Methanol is supplied to the anode through plate channels for the oxidation reaction of this fuel to occur when an electric current is supplied to the device. No fluid was introduced to the cathode.
As highlighted in the introduction, this study aims to investigate the influence of three parameters (methanol volumetric flow rate, methanol concentration, and MEC temperature) on MEC performance using RSM. This methodology is a technique used in design of experiments that allows exploring the relationship between several variables of interest, called factors, and the response of an experimental system, being able to optimise the values of these factors to achieve the desired response of the analysed system. With this methodology, the minimum number of combinations of the factor values are selected, the experimental response of the system to these input parameters is obtained and a mathematical model is adjusted to predict the response of the system throughout the design space (Myers et al., 2016). This methodology has several advantages, including reducing the number of experiments required compared to traditional trial-and-error methods and analysing the relationship between factors and how this affects the system response (Özgür & Mert, 2022).

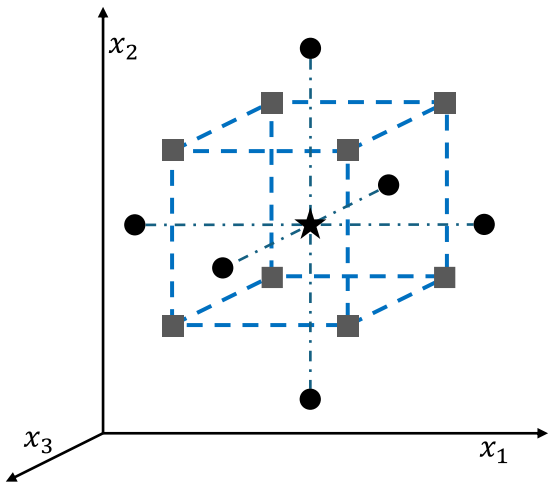

Figure 1: Schematic representation of the Central Composite Design (CCD) model for three factors. The stars represent the centre point, the circles the axial points and the squares the factorial points

Within the Response Surface Methodology, the Central Composite Design (CCD) represented in Figure 1 is used to study the effect of three factors (x_1, x_2, x_3) and is characterised by the inclusion of centre and axial points. Centre point is represented with a star in Figure 1, while the axial points are represented with a circle. These points are combinations of the values of the three factors, input variables in the experiment. When the system is tested by setting the values of the factors according to these combinations, each point is associated with a response. The centre point allows the combined effect of the factors to be assessed at the midpoint of the experimental range, while the axial points allow possible quadratic effects to be explored and the linearity of the model to be assessed.

The application of this methodology in this work starts with the choice of the parameters to be studied, which are methanol volumetric flow rate, methanol concentration and MEC temperature. These parameters were chosen because of their significant impact on the anodic reaction, as methanol flow rate and methanol concentration directly influence the availability of methanol for oxidation and temperature has an impact on catalytic activity.

In this study, the CCD is employed, allowing exploration of a wide parameter range with a limited number of experiments. The CCD model incorporates the three factors at five levels (-α, -1, 0, +1, and +α), 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. Here, α is set to √3, ensuring all investigated parameter combinations lie within a sphere. Experimental data, including the response of the system analysed, which is the power density consumed at a given current density for each parameter combination, is utilized to fit a second-order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum \sum_{i<j} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \varepsilon \quad (4)$$

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, β_{ii} are the quadratic coefficients and ε represents the statistical error. This equation characterizes the relationship between parameters and MEC performance, offering insights for optimization and design.

To obtain the value of the coefficients of Equation (4), the methanol electrolyser single cell tests are carried out for each of the points defined by applying the CCD model. During each of these tests, the MEC polarization curve is recorded, and from this curve the power density curve is obtained multiplying the current density by the measured voltage. From the power density curve, the power density of the MEC at a given current density is obtained, which is the parameter chosen as the response in this work.

3 RESULTS AND DISCUSSION

In this study, the analysis of the MEC power density at 300 mA/cm^2 is used to determine the effect of the combination of the parameters on the MEC performance. For each one of the combinations of methanol volumetric flow rate, methanol concentration and MEC temperature presented in Table 1, obtained by applying the CCD model, polarization and power density curves are plotted. From these power density curves the MEC power density value at 300 mA/cm^2 is determined. This current density value has been chosen as it is an operating condition within the ohmic zone of the polarization curve, which represents a high current density and which is prior to the zone most affected by the concentration overpotential.

Table 1: Combinations of the parameters used to perform the experimental tests and the power density values obtained

V (ml/min)	M (mol/l)	T (ºC)	Power density at 300 mA/cm^2 (mW/cm^2)
1.90	2.00	50.0	377.9
3.00	1.00	40.0	405.5
3.00	1.00	60.0	375.1
3.00	3.00	40.0	399.8
3.00	3.00	60.0	340.3
4.50	0.27	50.0	618.1
4.50	2.00	32.7	431.6
4.50	2.00	50.0	375.4
4.50	2.00	50.0	375.7
4.50	2.00	50.0	377.0
4.50	2.00	50.0	374.7
4.50	2.00	67.3	348.0
4.50	3.73	50.0	360.4
6.00	1.00	40.0	526.0
6.00	1.00	60.0	374.2
6.00	3.00	40.0	437.9
6.00	3.00	60.0	318.5
7.10	2.00	50.0	403.8

With the values presented in Table 1, RSM is applied, and Equation (5) is obtained, which mathematically represents the relationship between the three parameters studied and the predicted response to be obtained from the MEC:

$$y = 319.6 + 101.1V - 139.8\mathrm{M} + 3.4T - 8.6V\mathrm{M} - 1.5VT + 4 \cdot 10^{-2}\mathrm{M}T + 4 \cdot 10^{-2}V^2 + 32.9\mathrm{M}^2 - 3 \cdot 10^{-3}T^2 \quad (5)$$

In this equation y represents the predicted MEC power density at 300 mA/cm^2, V is the methanol volumetric flow rate in ml/min, M stands for the methanol concentration in mol/l and T is the MEC temperature in ºC.

Figure 2a) shows the polarization and power density curves obtained for the centre point of the model proposed in this work, a flow rate of 4.5 ml/min, a concentration of 2M and a temperature of 50 ºC. Figure 2b) represents the response surface obtained by setting the temperature to 50 ºC and modifying the methanol concentration and volumetric flow rate values using equation (5) to obtain the power density response. As can be seen in Figure 2b), by setting the temperature at 50 °C, a higher methanol flow rate implies an increase in the power required to obtain hydrogen from methanol when working at low concentrations. In this case, the limited presence of methanol due to low concentration (Sasikumar et al., 2008) and the poor fuel utilization due to high methanol flow rates (Casalegno et al., 2007; Farah Atiqah Abdullah et al., 2020) require an increase in power to support methanol electrolysis.

The combined influence of temperature and methanol concentration is reflected in the response surface in Figure 3a) when the volumetric flow rate is set to 4.5 ml/min. It can be observed that at low temperatures and low concentration the electrical energy required in the MEC increases. This may be attributed to a decrease in the reaction kinetics with decreasing temperature and a decrease of the amount of methanol available for the oxidation reaction when decreasing fuel concentration (Lamy et al., 2015). Increased MEC power density can also be observed when working at high methanol concentrations. This effect can be attributed to the hygroscopic property of methanol which can adsorb water molecules on the proton exchange membrane, leading to the decrease of the ionic conductivity (Uhm et al., 2012).

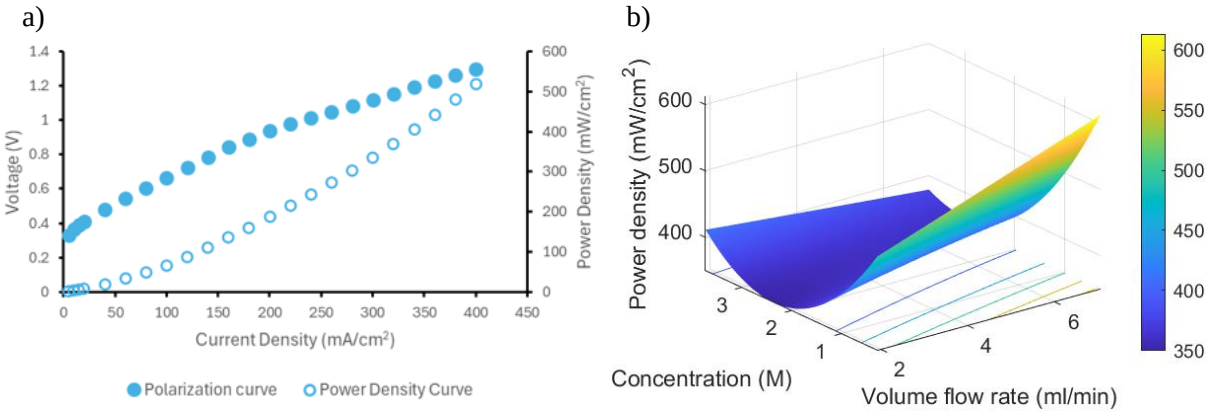

Figure 2: a) Polarization and power density curves of the MEC single cell of this study obtained at a temperature of 50 ºC, methanol concentration of 2 M and methanol volumetric flow rate 4.5 ml/min; b) MEC power density at 300 mA/cm^2 as a function of the concentration and methanol volumetric flow rate keeping the temperature at 50 ºC

Figure 3b) shows the influence of MEC temperature and methanol volumetric flow rate on the power density of the device under study. By setting the methanol concentration at 2M an a temperature lower than 55 ºC, an increase of the volumetric flow rate leads to an increase of the electrical power consumption. This can be caused by the decreased residence time of methanol in the diffusion layer, which makes it difficult for it to react properly reducing fuel utilization efficiency (Ramasamy et al., 2022). This could also be related to a decrease in the catalytic layer temperature due to the introduction of a liquid solution at room temperature to a system that is working at temperatures higher than 40 °C (Zhao et al., 2023).

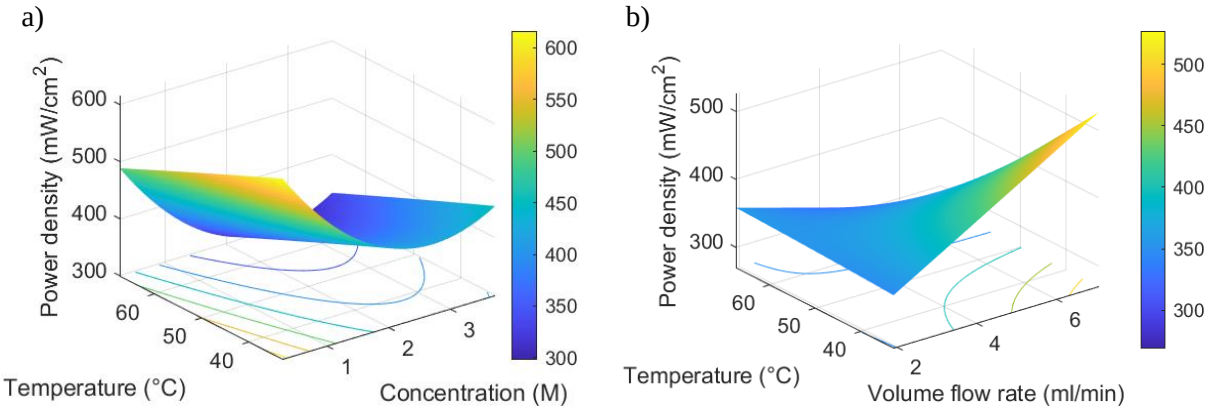

Figure 3: Power density at 300 mA/cm^2 as a function of the: a) Temperature and methanol concentration keeping the methanol volumetric flow rate at 4.5 ml/min; b) MEC temperature and methanol volumetric flow rate keeping the concentration at 2 M

To further study the influence of the studied parameters on the power density of the MEC, an analysis of variance (ANOVA) of the model obtained is performed, the results of which are presented in Table 2.

Table 2: Results of the analysis of variance test

Variable	Estimate	Standard Error	tStat	p-Value
Volumetric flow rate (A)	101.057	69.278	1.459	0.183
Concentration (B)	-139.834	96.848	-1.444	0.187
Temperature (C)	3.383	12.386	0.273	0.792
AB	-8.607	9.746	-0.883	0.403
AC	-1.512	0.975	-1.551	0.160
BC	0.041	1.462	0.028	0.978
A^2	0.037	4.957	0.007	0.994
B^2	32.867	11.153	2.947	0.019
C^2	-0.003	0.112	-0.025	0.981

In the results presented in Table 2 it cannot be observed a strong influence of the studied parameters on the MEC power density response, except for the quadratic term of methanol concentration, which shows a p-Value lower than 0.05. However, it has been observed from Table 1 and Figures 2b) and 3 that there is a relationship between the parameter values and the energy consumed in the electrolyser. This implies a need for refinement of the model obtained to be able to observe with this mathematical model the relationships between the parameters and MEC power density observed previously: a decrease in power density with increasing temperature at higher volumetric flow rate than 3 ml/min, and an increase in power density consumed with decreasing methanol concentration and volumetric flow rate. Thus, optimisation of the three factors studied would result in a reduction of the power consumed by the electrolyser for the same hydrogen production while maintaining the current density, improving the MEC performance.

Degradation of the catalysts used due to the presence of methanol can occur by poisoning of the catalytic surface through adsorption of species, such as CO, or dissolution of platinum and ruthenium during electrolysis in the presence of methanol (Becker et al., 2023). This means that, after several tests, the catalytic layer becomes less effective and more electrical energy is needed for methanol electrolysis to occur. This would alter the results obtained for certain test conditions, as the power density may increase for the same test conditions due to MEA degradation after several tests.

Despite not having observed a strong influence in the ANOVA test, it can be seen in Figure 4a) the linear trend of the power density obtained during the tests and that predicted by the model. This implies an explanation of more than 80% of the experimental response. Moreover, the residuals in Figure 4b) do not show a clear pattern and all of them present adequate values except one. This discordant point is related to the test in almost extreme working conditions for the MEA evaluated (4.5 ml/min, 0.27 M, 50 ºC; see Table 1) due to the large increase in power density required as there is not enough methanol for the methanol oxidation reaction and water electrolysis can occur (Lamy et al., 2015). This test, due to the high voltage and power density reached, could have a great influence in the catalytic layer degradation and in the alteration of the results detected.

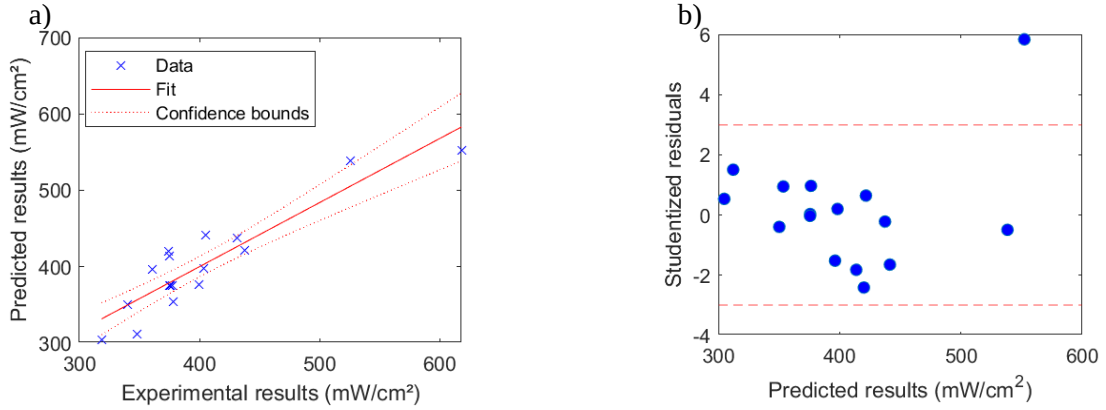

Figure 4: a) Comparison of power density obtained experimentally and predicted with the model; b) Comparison of studentized residuals values of power density and predicted values

4 CONCLUSIONS

In this work, the influence of the volumetric flow rate of methanol, its concentration, and the operating temperature of a Methanol Electrolysis Cell (MEC) on the electrical energy required to produce hydrogen has been studied for the first time, using the Response Surface Methodology. It has been possible to observe the high influence of the methanol concentration, as it is an inducer of the quantity of this fuel available for the oxidation reaction to take place at the anode. Furthermore, it has been seen that there is a joint influence of the combination of the parameters and not only each parameter separately has its effect. An increase in temperature improves the reaction kinetics and thus decreases the energy required for methanol electrolysis. The methanol concentration and the volumetric flow rate have an influence on the fuel availability and its transport through each gas diffusion layer, and both parameters must be controlled at the same time to decrease the energy needed by the MEC, improving MEC performance. To further study these effects, the model used could be refined and the effects of MEA degradation during testing should be analysed as it may influence the results presented especially at high voltages.

To optimise the operating conditions of a methanol electrolyser, it is possible to complement the results shown in this study analysing the power needed for the methanol electrolysis at different current densities. Besides, it would be interesting to relate these variables to the amount of hydrogen generated at a given current density, obtaining information on the overall process through further testing.

REFERENCES

Becker, H., Murawski, J., Shinde, D. V, Stephens, I. E. L., Hinds, G., & Smith, G. (2023). *Impact of impurities on water electrolysis: a review*. https://doi.org/10.1039/d2se01517j

Casalegno, A., Grassini, P., & Marchesi, R. (2007). Experimental analysis of methanol cross-over in a direct methanol fuel cell. *Applied Thermal Engineering*, *27*(4), 748–754. https://doi.org/10.1016/J.APPLTHERMALENG.2006.10.007

Coutanceau, C., & Baranton, S. (2016). Electrochemical conversion of alcohols for hydrogen production: a short overview. *Wiley Interdisciplinary Reviews: Energy and Environment*, *5*(4), 388–400. https://doi.org/10.1002/WENE.193

d'Amore-Domenech, R., Meca, V. L., Pollet, B. G., & Leo, T. J. (2023). On the bulk transport of green hydrogen at sea: Comparison between submarine pipeline and compressed and liquefied transport by ship. *Energy*, *267*, 126621. https://doi.org/10.1016/J.ENERGY.2023.126621

Farah Atiqah Abdullah, Siti Kartom Kamarudin, Azran Mohd Zainoodin, & Mohd Shahbudin Masdar. (2020). Parametric studies of direct methanol fuel cell under different modes of operation. *Jurnal Kejuruteraan*. http://www.ukm.my/jkukm/volume-321-2020/

Fu, X., Shi, R., Jiao, S., Li, M., & Li, Q. (2022). Structural design for electrocatalytic water splitting to realize industrial-scale deployment: Strategies, advances, and perspectives. *Journal of Energy Chemistry*, *70*, 129–153. https://doi.org/10.1016/J.JECHEM.2022.02.010

Guenot, B., Cretin, M., & Lamy, C. (2015). Clean hydrogen generation from the electrocatalytic oxidation of methanol inside a proton exchange membrane electrolysis cell (PEMEC): effect of methanol concentration and working temperature. *Journal of Applied Electrochemistry*, *45*(9), 973–981. https://doi.org/10.1007/S10800-015-0867-3/TABLES/4

Hao, A., Wan, X., Liu, X., Yu, R., & Shui, J. (2022). Inorganic microporous membranes for hydrogen separation: Challenges and solutions. *Nano Research Energy*, *1*(2). https://doi.org/10.26599/NRE.2022.9120013

Jeffries-Nakamura B, Narayanan SR, Valdez TI, & Chun W. (1948). *Making hydrogen by electrolysis of methanol*.

Kianimanesh, A., Yu, B., Yang, Q., Freiheit, T., Xue, D., & Park, S. S. (2012). Investigation of bipolar plate geometry on direct methanol fuel cell performance. *International Journal of Hydrogen Energy*, *37*(23), 18403–18411. https://doi.org/10.1016/J.IJHYDENE.2012.08.128

Lamy, C. (2020). Electrocatalytic oxidation of low weight oxygenated organic compounds: A review on their use as a chemical source to produce either electricity in a Direct Oxidation Fuel Cell or

clean hydrogen in an electrolysis cell. *Journal of Electroanalytical Chemistry*, *875*, 114426. https://doi.org/10.1016/j.jelechem.2020.114426

Lamy, C., Guenot, B., Cretin, M., & Pourcelly, G. (2015). Kinetics Analysis of the Electrocatalytic Oxidation of Methanol inside a DMFC working as a PEM Electrolysis Cell (PEMEC) to generate Clean Hydrogen. *Electrochimica Acta*, *177*, 352–358. https://doi.org/10.1016/j.electacta.2015.02.069

Lemmon, E. W., Huber, M. L., & McLinden, M. O. (2010). NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties (REFPROP), Version 9.0. In *Physical and Chemical Properties*. https://doi.org/citeulike-article-id:11896451

Meca, V. L., d'Amore-Domenech, R., Crucelaegui, A., & Leo, T. J. (2022). Large-Scale Maritime Transport of Hydrogen: Economic Comparison of Liquid Hydrogen and Methanol. *ACS Sustainable Chemistry & Engineering*, *10*(13), 4300–4311. https://doi.org/10.1021/acssuschemeng.2c00694

Menia, S., Lassouane, F., Tebibel, H., & Khellaf, A. (2018). *Hydrogen Production from Methanol Electrolysis BT - Exergy for A Better Environment and Improved Sustainability 2: Applications* (F. Aloui & I. Dincer, Eds.; pp. 455–460). Springer International Publishing. https://doi.org/10.1007/978-3-319-62575-1_32

Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. C. (2016). Response Surface Methodology: Process and Product Optimization Using ... -. In *Wiley Series in Probability And Statistics, 4th ed., John Wiley & Sons Inc., New Jersey* (4th ed.). Wiley. https://www.wiley.com/en-us/Response+Surface+Methodology%3A+Process+and+Product+Optimization+Using+Designed+Experiments%2C+4th+Edition-p-9781118916018

Narayanan, S. R. C. W. J.-N. B. V. T. I. (1998). *Hydrogen generation by electrolysis of aqueous organic solutions* (Patent US6299744B1).

Özgür, C., & Mert, M. E. (2022). Prediction and optimization of the process of generating green hydrogen by electrocatalysis: A study using response surface methodology. *Fuel*, *330*, 125610. https://doi.org/10.1016/J.FUEL.2022.125610

Ramasamy, J., Palaniswamy, K., Kumaresan, T., Chandran, M., & Chen, R. (2022). Study of novel flow channels influence on the performance of direct methanol fuel cell. *International Journal of Hydrogen Energy*, *47*(1), 595–609. https://doi.org/10.1016/J.IJHYDENE.2021.10.033

Roode-Gutzmer, Q. I., Kaiser, D., & Bertau, M. (2019). Renewable Methanol Synthesis. *ChemBioEng Reviews*, *6*(6), 209–236. https://doi.org/10.1002/CBEN.201900012

Sasikumar, G., Muthumeenal, A., Pethaiah, S. S., Nachiappan, N., & Balaji, R. (2008). Aqueous methanol eletrolysis using proton conducting membrane for hydrogen production. *International Journal of Hydrogen Energy*, *33*(21), 5905–5910. https://doi.org/10.1016/j.ijhydene.2008.07.013

Take, T., Tsurutani, K., & Umeda, M. (2007). Hydrogen production by methanol-water solution electrolysis. *Journal of Power Sources*, *164*(1), 9–16. https://doi.org/10.1016/j.jpowsour.2006.10.011

Uhm, S., Jeon, H., Kim, T. J., & Lee, J. (2012). Clean hydrogen production from methanol–water solutions via power-saved electrolytic reforming process. *Journal of Power Sources*, *198*, 218–222. https://doi.org/10.1016/j.jpowsour.2011.09.083

Wei, X., Wang, S., Hua, Z., Chen, L., & Shi, J. (2018). Metal–Organic Framework Nanosheet Electrocatalysts for Efficient H2 Production from Methanol Solution: Methanol-Assisted Water Splitting or Methanol Reforming? *ACS Applied Materials & Interfaces*, *10*(30), 25422–25428. https://doi.org/10.1021/acsami.8b06948

Xiao, J., Zhang, X., Gao, T., Zhou, C., & Xiao, D. (2017). Electrochemical formation of multilayered NiO film/Ni foam as a high-efficient anode for methanol electrolysis. *Journal of Solid State Electrochemistry*, *21*(8), 2301–2311. https://doi.org/10.1007/S10008-017-3570-Y/FIGURES/7

Yazici, M. S., Dursun, S., Borbáth, I., & Tompos, A. (2021). Reformate gas composition and pressure effect on CO tolerant Pt/Ti0.8Mo0.2O2–C electrocatalyst for PEM fuel cells. *International Journal of Hydrogen Energy*, *46*(25), 13524–13533. https://doi.org/10.1016/J.IJHYDENE.2020.08.226

Zhao, Z., Li, D., Xu, X., & Zhang, D. (2023). An Adaptive Joint Operating Parameters Optimization Approach for Active Direct Methanol Fuel Cells. *Energies 2023, Vol. 16, Page 2167*, *16*(5), 2167. https://doi.org/10.3390/EN16052167

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