Concentration and polarization curve models for implantable glucose fuel cells

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1. Introduction

Lithium iodine batteries are actually the main power source for most implantable medical devices (IMDs). However, batteries lifespan is lower than expected. Moreover, IMDs with a higher power demand are being developed, which can increase the problem of batteries. Therefore, there is a great interest in developing an alternative power supply system capable of operating for long periods of time without maintenance. A potential option is the use of implantable glucose fuel cells, which make use of glucose and O_2 present in body fluids to generate a current through isolated electrochemical reactions. However, in body fluids glucose and oxygen are in the same solution, hindering the independent supply of reactants to each electrode. Moreover, no abiotical selective catalyst is known to oxidize glucose in presence of oxygen.

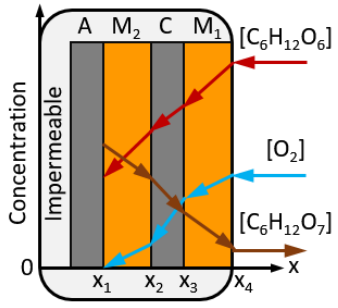

Fig. 1. Depletion design of implantable glucose fuel cell.

To overcome the problem, some options have been proposed [1], such as the use of variable porosity Pt electrodes as anode and cathode, or depletion layout, Fig. 1. Platinum is a catalyst that reacts with both glucose and oxygen. Nevertheless, under physiological conditions low roughness factor (RF) Pt electrodes show cathodic potentials while high RF Pt electrodes present anodic potentials. "Depletion design" has only one opening, membrane M_1, through which both reactants come into the fuel cell. The cathode (C) is placed at the entrance and the anode (A) is located inside the fuel cell, between an impermeable surface and the membrane M_2. Thus, the solution that reaches the anode is partially free of O_2. However, at low current densities a certain amount of O_2 reaches the anode because not all the O_2 present in the inlet solution reacts at the cathode.

Until now, tests with abiotically catalysed implantable glucose fuel cells have been carried out. However, no mathematical model has been developed in order to improve the knowledge of the phenomena occurring in this kind of fuel cells, as well as to optimize their design. The aim of this work is to develop a polarization curve model for these fuel cells and to check that the behaviour predicted by the model is consistent with the available experimental data.

2. Mathematical model

2.1 Assumptions

Some assumptions must be made in order to present an accurate description of the system: *i*) the anode is a high RF Pt electrode while the cathode is a low RF Pt electrode; *ii*) the electro-osmotic drag is not considered; *iii*) the inlet reactants and outlet products concentrations are known and constant; *iv*) the O_2 reacts homogeneously along the porous cathode, *v*) the O_2 and glucose that reach the anode react directly on its surface; *vi*) the amount of O_2 reaching the anode depends on the fuel cell current density, *j*. The higher the current density, the greater the amount of O_2 that reacts at the cathode and the lower the molar flux of O_2 that reaches the anode. Nonetheless, the O_2 concentration at the anode is zero because all oxygen reaching this electrode directly reacts with glucose; *vii*) membrane M_2 is not an electrolyte, its function is to electrically isolate the electrodes; *viii*) membrane M_1 simulates the diffusion resistance expected due to tissue capsule formation around the implant.

2.2 Concentration model

Development of polarization curve models previously needs a concentration model that allows to know each reactant concentration at the electrodes as a function of *j*. The main mass transport mechanism in these fuel cells is the diffusion. Therefore, Fick's laws are used to describe the concentration model. Here, the differential equations have been solved for each component of the fuel cell and reactant [2]. The assumption *vi*) allows to calculate the O_2 molar flux (N^O_{cross}) through the membrane M_2 and complete the equations system. There may be two cases depending on whether N^O_{cross} is greater than zero or zero. If N^O_{cross} is greater than zero, the O_2 reacts homogeneously along the entire cathode thickness. However, when N^O_{cross} is zero, the O_2 is totally consumed inside the cathode. Therefore, the homogeneous reduction of the O_2 only takes place along a

thin section of the cathode. The thickness of this section is always less than the cathode thickness and decreases when current density increases. The limiting case is that all O_2 reacts directly at the fuel cell section x_3, the cathode inlet.

2.3 Polarization curve model

The developed polarization curve model consists of five terms: the Nernst potential ($E_{T,P}$), anode activation overpotential, anode and cathode concentration losses and ohmic overpotential. Activation overpotential term is a modification of Butler-Volmer equation in which the diffusion is included [3]. The developed model has two free parameters, the anodic transfer coefficient (α) and the exchange current density of the glucose oxidation reaction ($j_{0,a}$), obtained by fitting experimental data to the model:

$$V = E_{T,P} - \frac{RT}{\alpha F} ln\left(\frac{j + j_{cross}}{j_{0,a}\frac{cg_{x1}(j)}{cg_{x1}{}^*}}\right) - \frac{RT}{z_c F} ln\left(\frac{cox_{x3}{}^*}{cox_{x3}(j)}\right) - \frac{RT}{z_a F} ln\left(\frac{cg_{x3}{}^*}{cg_{x3}(j)}\right) - j \cdot R$$

where j_{cross} represents the crossover equivalent current density, cg_{x1} depicts the glucose concentration at the anode while cox_{x3} is the O_2 concentration at the cathode. Finally, *V* stands for the voltage, *T* the temperature, F is the Faraday constant and z_c and z_a are the electron moles per O_2 and glucose moles, respectively. The electric resistance, R, is estimated based on the conductivity of the solution used during tests. Terms with (*) stand for *j*=0 conditions.

3. Results and Discussion

Two experimental polarization curves of an in vitro implantable glucose fuel cell have been fitted by the model proposed [4], as can be seen in Table 1 and Fig. 2. Case 1 depicts the complete model, Case 2 the model without ohmic losses, Case 3 is the simplest model because the ohmic and anode transport losses are considered negligible, and Case 4 corresponds to Case 1 without the anode transport overpotential. All cases show the same behaviour. This suggest that to use the simplest model (Case 3) to fit the performance of this type of fuel cells is possible. Therefore, the main phenomena that govern the behaviour of implantable glucose fuel cells with depletion design are the slow kinetics of GOR and the O_2 transport to the cathode, which is consistent with the experimental tests.

The α values fitted for the different cases are in accordance with those obtained experimentally for porous Pt electrodes, from 0.052 to 0.256. Moreover, the small values of $j_{0,a}$ also indicate a slow reaction rate of glucose oxidation. Thus, it is possible to assume that in Pt electrodes with low RF, glucose does not react due to the higher reaction rate of O_2.

The curve with low O_2 concentration shows a worse coefficient of determination than those of higher concentration. This is due to the curve only presents one point after the slope change as well as the limited number of experimental data for low O_2 concentration.

Table 1. Fitting coefficients of two polarization curves with different O_2 concentrations (7% and 21% O_2 saturation)

Case	1	2	3	4
α (7%)	0.0781	0.0760	0.0753	0.0774
$j_{0,a}$ (7%) (μA·cm^{-2})	1.283	1.339	1.359	1.303
R^2 (7%)	0.824	0.825	0.824	0.823
α (21%)	0.1279	0.1213	0.1163	0.1224
$j_{0,a}$ (21%) (μA·cm^{-2})	1.219	1.388	1.555	1.381
R^2 (21%)	0.990	0.990	0.989	0.989

Moreover, the concentration model allows to estimate the limiting current density and the current density at which the slope change takes place. According to the model proposed, the change in the slope occurs when N^O_{cross} is zero, i.e., when O_2 transport problems start.

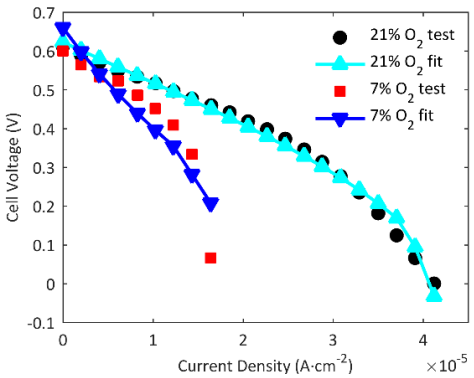

Fig. 2. Polarization curve fits

4. Conclusions

The concentration model proposed is a reliable method to estimate the concentration of the species in an implantable glucose fuel cell at any current density. Moreover, this model allows to calculate the limiting and the slope change current densities. The polarization curve models presented are able to replicate the behaviour of the available experimental data. The dominant overpotentials are the anode activation and the cathode concentration. Therefore, a simplified model including these terms can be used in order to fit the polarization curves.

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