
ESTIMATION OF EFFECTIVE DIFFUSION COEFFICIENTS WITH NERNST-PLANCK EQUATIONS IN THE DIRECT BOROHYDRIDE-PEROXIDE FUEL CELL

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ABSTRACT

This work develops a theoretical model for membranes for application in low-temperature liquid fuel cells, referring, particularly, to the direct borohydride-peroxide fuel cell (DBPFC), as a first step to create a numerical model. The DBPFC is based on the anodic oxidation of sodium borohydride (NaBH_4) in alkaline solution with the simultaneous cathodic reduction of hydrogen peroxide (H_2O_2) in acid media. The model is mainly based on the Nernst-Planck equations, where all components of the system are considered to explain the passage of the ions through the membrane used. The latter is split into one section where there is a constant electric field due to the potential difference between the electrodes, and another section without it, but where there is a local difference of electric potential between the two sides of the membrane, i.e., the membrane potential. The experiments performed allow investigating the mechanisms inside the membrane and finding the diffusivity of the components passing through it: a Python code was used to make an estimation of the effective diffusion coefficients of NaOH in Nafion N117, and obtaining a rough approximation of Na^+ to $9.82\text{E-}08 \text{ cm}^2\text{s}^{-1}$, and of OH^- to $1.04\text{E-}08 \text{ cm}^2\text{s}^{-1}$, at ambient temperature. The building of a more detailed diffusion function depending on temperature (for each ion involved) is the next step of the project purpose. This study aims to be a starting point to the creation of a numerical model where liquid solutions are involved, and thus suitable for modelling DBPFCs.

Keywords: liquid fuel cell, direct borohydride-peroxide fuel cell, diffusion coefficients, numerical model, Python

INTRODUCTION

This work develops a numerical model for application in low-temperature liquid fuel cells, namely in the direct borohydride-peroxide fuel cell (DBPFC). This device uses fuel and oxidant that are liquid at room temperature, making it ideal for power generation in space and underwater applications, where O_2 gas is not easily available. Besides the electrodes, the membrane separator is the main component to focus on in DBPFC, as it inhibits shorting between anode and cathode and the mixing of fuel and oxidant solutions. The promising high performance of DBPFCs is being hindered by the disparate pH requirements for the fuel oxidation (highly alkaline) and the oxidant reduction (highly acidic). Presently, cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs) are used, but understanding the mechanism behind their behavior will also lead to an improvement of the recently proposed pH-gradient-enabled microscale bipolar interface (PMBI).

In the laboratory development of DBPFC, the membrane has been used until now as a black box, where the initially selected inputs lead to obtaining the fuel cell polarization and power density curves as outputs. So far, numerical models (and CFD models) for fuel cells have been mainly used for gaseous flows involved, as in the well-studied proton-exchange membrane fuel cell (PEMFC), but a working numerical model for liquid fuel cells is not available in the literature. This study aims to be a starting point to the creation of a corresponding model where liquid solutions are involved, and thus suitable for modelling DBPFCs. A numerical model could give us some solutions/indications of the process occurring in the membrane, to better explain the passage of the ions through the membrane and to study some effects related to the crossover (for example, the crossover of borohydride from one compartment to the other decreases the efficiency of the system). This thesis could give that input to further enhance the performance of the membrane, also for what will be studied in the near future, which is the development of pH-gradient-enabled microscale bipolar interface

(PMBI). Ion-selective membranes used for fuel cells can be:

- Cation Exchange Membrane (CEM)
- Anion Exchange Membrane (AEM)
- pH-gradient-enabled microscale bipolar interface (PMBI).

The latter is more specific because PMBI is supposed to be able to sustain the high pH difference on each side of the membrane. The reason is that the borohydride side works in alkaline media, and the hydrogen-peroxide side works in acid media. A numerical model could be very useful to do the analysis: it allows us to make a direct comparison between the different types of membranes, see which one seems more suitable, and what will be the advantages. The numerical model is enriched with the data obtained from the lab experiments, which allowed us to work with real data. The numerical model for liquid fuel cells is the novelty of the present work. It will be a starting point to create an even more complex system taking care of all the variables involved, and it could lead in the future to the construction of a CFD model and an even optimized new 3D-printed direct borohydride fuel cell.

STATE-OF-THE-ART

The State-of-the-Art of membranes in direct borohydride fuel cells is well organized in the book *Direct Liquid Fuel Cells: Fundamentals, Advances and Future* [1], thanks to the study and research of B. Šljukić and D.M.F. Santos, while the different interaction of the different membrane with positive ions, negative ions and neutral molecules are highlighted in the work of the same authors titled "Anion- or cation-exchange membranes for $NaBH_4/H_2O_2$ fuel cells?" [2]. In addition, Wang et al. recently described efficient pH-gradient-enabled microscale bipolar interfaces in direct borohydride fuel cells [3], including a microscale visualization of these new PMBI.

From lab tests on solutions and electrodes [4,5] the suggested optimized solutions for DBPFC are proposed: the anolyte solution has 1 M $NaBH_4$ + 4 M NaOH and the catholyte has 3M H_2O_2 + 1M HCl.

Not only Nafion membranes have been tested in the laboratory, but other works [2, 6, 7] tested also

“homemade” membranes, intending to reduce the costs, seeing that commercial membranes are very expensive.

The membranes in the lab have been used mainly for fundamental research, where there is no catalytic ink painted or sprayed, but where the materials are very close to the membrane: this allows reusing the same membrane for different tests.

THEORETICAL MODEL

The DBPFC system is split into one section where there is a constant electric field due to the potential difference between the electrodes (where the current is different from zero), and another section without it (where the current is equal to zero), but where there is a local difference of electric potential between the two sides of the membrane, i.e., the membrane potential (Figure 1).

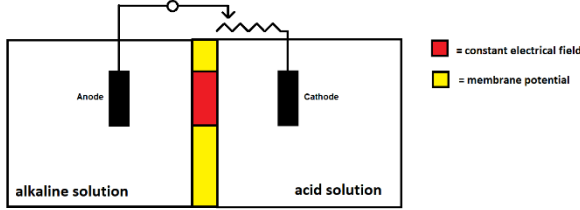


Figure 1 - Membrane sections.

The innovative part of the model is that the passage of the ions is considered individually for each species involved. The DBPFC system is successively divided into sub-systems for each component of the solutions involved. Each sub-system is considered to work independently based on the different concentrations on each side of the membrane and the specific membrane potential created.

The proposed model is mainly based on the Nernst-Planck equations (Eq. 1 and 2), where all components of the system are considered to explain the passage of the ions through the membrane used. In this dissertation, the example of the subsystem of 4 M of NaOH (in one compartment) and water (in the second compartment) is considered, in the case of only membrane potential (and not external electrical field).

$$N^+ = -D^+ \frac{dC_s(x)}{dx} - C_s D^+ \frac{F}{R^*T} \frac{d\Psi(x)}{dx} \quad (1)$$

$$N^- = -D^- \frac{dC_s(x)}{dx} + C_s D^- \frac{F}{R^*T} \frac{d\Psi(x)}{dx} \quad (2)$$

Resolving the differential equations, the equations of the membrane potential (Eq. 3) and of the concentrations (Eq. 4) can be obtained:

$$\Psi(x) = \Psi_0 + \frac{\beta}{A} * \left[\ln \left(\frac{C_{s0}}{C_{s0} - A * x} \right) \right] \quad (3)$$

$$C_s(x) = C_{s0} - A * x \quad (4)$$

With the parameter A defined as Eq. 5:

$$A = \frac{N * (D^- + D^+)}{2 * D^+ * D^-} \quad (5)$$

Considering the boundary conditions, an additional linearization of the Nernst-Planck equations (Eq. 6 and 7) can be proposed:

$$N = -D^+ \frac{\Delta C_s}{\Delta x} - C_{s1} D^+ \frac{F}{R^*T} \frac{\Delta \Psi}{\Delta x} \quad (6)$$

$$N = -D^- \frac{\Delta C_s}{\Delta x} + C_{s1} D^- \frac{F}{R^*T} \frac{\Delta \Psi}{\Delta x} \quad (7)$$

Three scenarios are possible:

- If $D^+ = D^-$, there is no electrical potential gradient
- If $D^+ > D^-$, the electrical potential will retard the cations and accelerate the anions
- If $D^+ < D^-$, the electrical potential will accelerate cations and retard the anions

The innovative part of the model is that the passage of the ions is considered individually for each species involved (Figure 2). Each sub-system is considered to work independently based on the different concentrations on each side of the membrane and the specific membrane potential created. The total membrane potential (of the whole DBPFC system) is, consequently, the overlaid effect of all sub-systems, according to the superposition principle and considering the flux direction of the solutions inside the compartments (Eq. 8).

$$\Delta \Psi_{i,membrane} = \Sigma \Delta \Psi_i = \Delta \Psi_{NaBH_4} + \Delta \Psi_{NaOH} - \Delta \Psi_{HCl} - \Delta \Psi_{H_2O_2} \quad (8)$$

This model is an upgrade to the generally accepted approach where specific kinds of ions are blocked/hindered by the ion-selective membrane

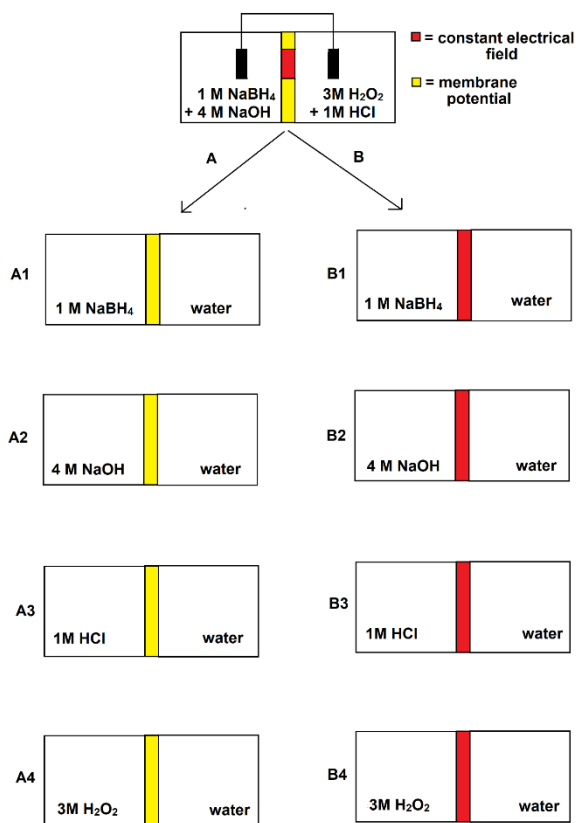


Figure 2 - DBPFC proposed model.

The whole system can be expressed with the overlaid effects of all the sub-systems A1, A2, A3, A4, B1, B2, B3, and B4.

Knowing this model, with a measured flux of ions inside the membrane, an iterative process could be created to obtain the two unknowns of each sub-systems, which are the diffusivities of the ions. Knowing the diffusivities of each ion in each membrane, the flux of ions in each type of membrane can be predicted.

EXPERIMENTAL

NAOH-NAFION EXPERIMENT

To validate the proposed model, an example of a sub-system of the DBPFC is taken, to show experimentally that the ions from a 4 M NaOH solution will pass through a Nafion membrane, increasing the pH of the second compartment containing only distilled water. Therefore, not only Na^+ will be transferred inside the Nafion CEM, but also OH^- will pass to maintain the electroneutrality

of the solutions. As the Na^+ ions will pass at the same velocity of OH^- , there will be a delayed Na^+ passage through the membrane due to the OH^- hindering.

11 tests (with the same concentration) were performed, with 3 different membranes.

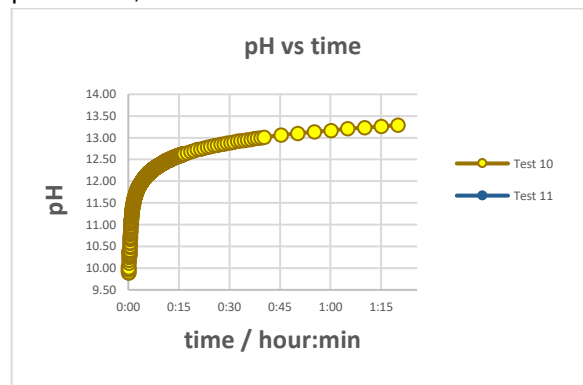


Figure 3 - Tests 10 and 11: pH measurement along time.

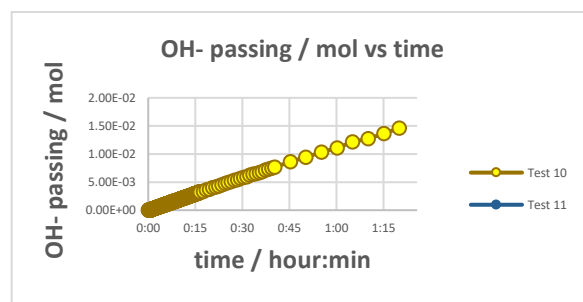


Figure 4 - OH- moles passing with time, in tests 10 and 11.

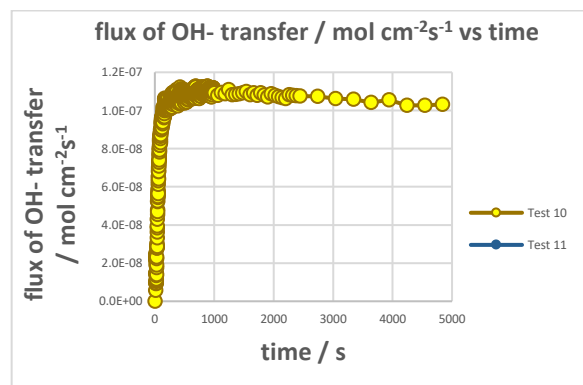


Figure 5 - OH- flux with time, in tests 10 and 11.

The measurement of pH (Figure 3), of OH^- moles passing (Figure 4) and OH^- flux (Figure 5) are recorded second by second for tests 10 and 11, where solutions are kept homogeneous thanks to nitrogen bubbling.

RESULTS AND DISCUSSION

DIFFUSIVITIES FINDER – PYTHON CODE

With a code created in Python, considering the electroneutrality of the solutions (Donnan's equilibrium), it is possible to iterate step by step, to compare the ions flux, and obtain the diffusivities of the ions in the membranes.

The values of temperature, flux, C_{s1} , and ΔC , were used to feed the code, and to get as results the two different diffusivities of Na^+ and OH^- (for each test).

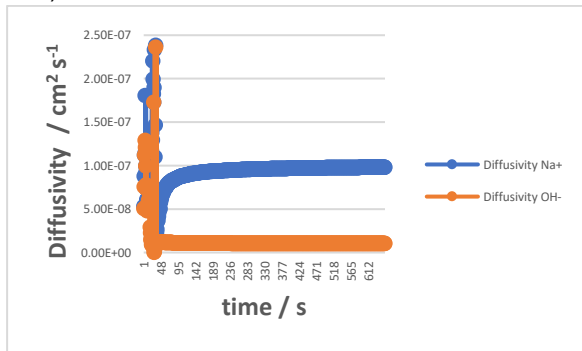


Figure 6 - Test 10, diffusivities values using a diffusivities finder in Python code.

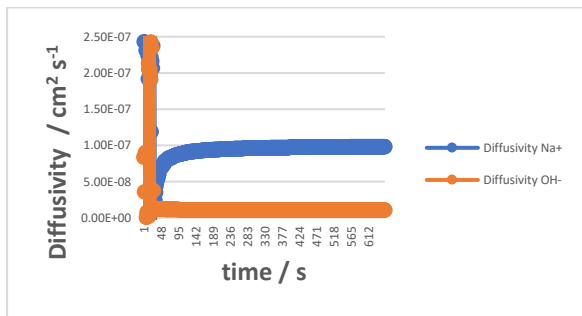


Figure 7 - Test 11, diffusivities values using a diffusivities finder in Python code.

In Figure 6 and 7, it is shown that the diffusivity of Na^+ in Nafion N117 is roughly stabilized with time in a value very near to $9.82\text{E-}08 \text{ cm}^2\text{s}^{-1}$, and diffusivity of OH^- is very near to $1.04\text{E-}08 \text{ cm}^2\text{s}^{-1}$, like in others experiment tests.

More consistent results were expected, also using different non-linear methods to resolve the Nernst-Planck equations, but the outputs are influenced by the initial guess. Better initial values will give us better outputs values. In the subsystem considered, it seems that OH^-

diffusivity is one order-of-magnitude lower than the one of Na^+ , which is against most experimental evidence in systems with aqueous solutions.

So, the results are not perfect, that is why the diffusivities found will be called “effective diffusion coefficients”: in any case the values are supported from real data taken from the experiments. The results are of course function of the temperature that has been recorded second by second in the experiments, and the idea is that this simple experiment will be replicated to get more trustable diffusivity values for the ions involved, to create an ion diffusivity function of temperature, and then pass to perform similar experiment also to the others ions involved (from the others subsystems). All the information gathered from more experiments will be fundamental to having a diffusivity function for each ion and for membrane involved.

CONCLUSIONS

In this dissertation, the concept that selective membrane blocking opposite charge ions was demystified, because each ion will pass inside. The whole molecule will pass through the membrane only when dissociated in ions, with the same velocity due to the membrane potential gradient (when an external electrical field is not applied in the region).

A theoretical model to understand the whole system of a DBPFC has been proposed, considering Nernst-Planck equations for each sub-system, with only one component per time, and having in mind the flux direction of the whole fuel cell.

Experimental tests were performed, to show the importance of the membrane potential, and to prove that negative ions will pass through a CEM membrane (in this case Nafion N117). These data have been used to feed a Python code, to make an estimation of the effective diffusion coefficients of NaOH in Nafion N117, and obtain a rough approximation of Na^+ to $9.82\text{E-}08 \text{ cm}^2\text{s}^{-1}$, and of OH^- to $1.04\text{E-}08 \text{ cm}^2\text{s}^{-1}$, at ambient temperature. With better initial guessing values a better accuracy could be reached, but nobody has ever tested something like this, so the values found will

be the first initial guess for the ones that will have more accurate values in the future. An outstanding accuracy cannot be reached for these results if the initial data are rough measurements in the lab. The critical parameter remains the diffusivity, and the key to resolve the system is to perform more similar experiments, to have a whole diffusivity function of temperature for each ion (and for each membrane, because of the diffusivity of the same ions could change between a CEM and a AEM).

So, this is the first step to define a general DBPFC model with diffusivity inside the membrane, applicable also to other liquid fuel cells. Thus, this must be seen as a starting point for a creation of a numerical model where liquid solutions are involved, and this work paved the basement to reach a deep knowledge of the membrane mechanisms inside the DBPFCs, pushing the borders of their actual State-of-the-Art.

For future development, the way to reach the creation of a CFD model was shown (once all the diffusivities involved have been found). With the creation of new information also a machine learning algorithm could be implemented, to get more insight from the mole of data created. In addition, numerical optimization of the cell will lead also to the creation of new high-performance DBPFC, thanks to 3D printing.

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