

Model for fuel cell membrane resistance to proton flow

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Abstract

A theoretical procedure of measuring the resistance offered by a proton exchange membrane to proton flow through it has been outlined. The process has been modeled using simple mass transfer laws and electrical analogies. The final result showed that a second order differential equation, incorporating the membrane resistance, described the process completely. A major assumption that has been made use of is that steady state prevails throughout. The predictions of the model can be validated by an experiment that makes use of a specially designed cell, a strong inorganic acid and a pH meter.

Keywords: Membrane resistance; Proton exchange membrane; Steady state; Inorganic acid; pH meter; Fuel cells

Nomenclature

n' = Molar flux of protons

ka = Mass transfer coefficient in acid phase

kw = Mass transfer coefficient in water phase

R = Membrane resistance

$Cm1, Cm2$ = Interfacial concentrations of protons on either side of the membrane

r = Effective resistance

Ca = Proton concentration in bulk of acid phase

Cw = Proton concentration in bulk of water phase

t = Instant of time

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1. Introduction

Fuel cells have received a lot of attention in recent times. They hold the promise of “clean energy” which is absolutely essential these days. A fuel cell consists of an anode, a cathode and an electrolyte sandwiched in between them [1]. Hydrogen is fed at the anode, while oxygen is fed at the cathode. Hydrogen splits into two protons and two electrons. The electrons are directed into an external electric circuit. After performing some useful electric work, they reach the cathode. The protons travel through the electrolyte, to the cathode, where they combine with the incoming electrons and oxygen to give water, which is theoretically the only by-product of a fuel cell.

When a membrane is used as the electrolyte, the fuel cell is called a Proton Exchange Membrane Fuel Cell (PEMFC). The membrane is mainly composed of an ionic polymer, otherwise known as an “Ionomer”. This kind of fuel cell is quite compact, and is slated to replace the Internal Combustion Engine (ICE) in automobiles. Allis Chalmers brought out the first fuel cell powered tractor in the 1960s [2]. Ballard Power Systems has already tested a fuel cell bus in Mexico City [3]. Pollution from fuel cell driven vehicles will be minimal.

Nafion, developed by DuPont in the early 1960, is the membrane that is currently used in almost all PEMFCs. Out of the two grades of Nafion (Nafion-115 & Nafion-117), mostly Nafion-117 has been used for both theoretical and experimental studies. Factors such as the pore conductance and the proton diffusion coefficient were predicted using Molecular Dynamics Simulation by Din and Michaelides [4]. Gates and Newman [5] measured methanol permeability of Nafion 117 and the results were fitted by a thermodynamically consistent equation. Other polymeric materials in consideration for use as proton exchange membranes are sulfonated polyetherketone, polybenzimidazole and sulfonated polysulfone [6]. The extent of hydration of the membrane determines how effectively it will conduct protons. Hydration of the membrane is enhanced by adding the sulfonic acid (SO_3H) group to the component polymer backbone [7]. This group has a great affinity for water. As a result, all the sulfonated regions in the polymeric membrane absorb water and thus become hydrated. Proton conduction through the membrane is as follows: the protons from the anode enter the membrane, get solvated by water molecules -giving rise to H_3O^+ ions - and travel through the hydrated regions to the cathode. The phenomenon of these protons ‘hitching’ a ride on the water molecules is called ‘Electro-osmosis’. Buchi and Srinivasan [8] have roughly estimated that one proton per water molecule makes its way through the membrane.

The resistance offered to proton flow in a fuel cell is mainly due to the membrane [8]. The electrode-membrane interface also contributes to the overall resistance. This resistance causes an ‘Ohmic Potential Drop’ in the fuel cell. In the present study, a simple model is proposed to estimate the resistance of a proton exchange membrane to proton flow. The apparatus that is used to validate the model is the same as that used by Pivovar et al [9] to measure the permeability of membranes such as polyvinyl alcohol and polybenzimidazole to methanol.

2. Theoretical model

Fig. 1 shows the proton exchange membrane in the conductivity cell, along with the concentration profiles of protons in the acid and water phases.

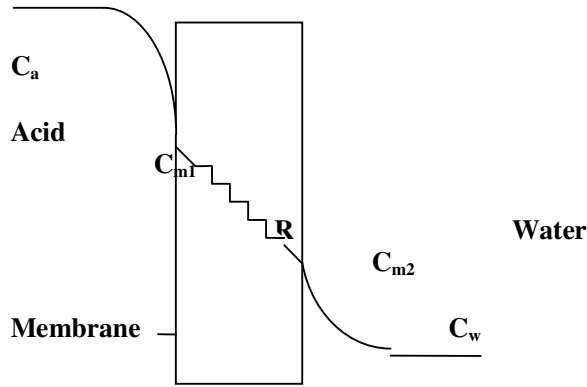


Fig. 1. Concentration profiles of protons in the acid and water cells

The molar flux of protons in the acid cell towards the membrane is expressed as the mass transfer coefficient in the acid multiplied by the concentration gradient [10].

$$n' = k_a (C_a - C_{m1}) \quad (1)$$

The resistance offered by the proton exchange membrane has been modeled as a resistor with a potential difference of $(C_{m1} - C_{m2})$ across it.

The resistor has a value R , which represents the resistance of membrane to proton flow. Assuming steady state, the number of protons leaving the acid cell per unit time equals the molar flux of protons through the membrane. Corresponding to Ohm's law, $V = IR$, we have:

$$n' R = C_{m1} - C_{m2} \quad (2)$$

Here, the molar flux, n' , is analogous to current flow.

For the water cell, once again assuming steady state (i.e. no accumulation of protons occurs in the membrane), we have:

$$n' = k_w (C_{m2} - C_w) \quad (3)$$

From equations (1) and (3), we get:

$$C_{m1} - C_{m2} = C_a - C_w - n' \left(\frac{1}{k_a} + \frac{1}{k_w} \right) \quad (4)$$

C_a and C_w vary with time.

Equating (2) and (4),

$$n'R = C_a - C_w - n' \left(\frac{1}{k_a} + \frac{1}{k_w} \right) \quad (5)$$

$$n' \left(R + \frac{1}{k_a} + \frac{1}{k_w} \right) = C_a - C_w \quad (6)$$

We also know that:

$$n' = -\frac{dC_a}{dt} \quad (7)$$

As steady state is maintained, the rate of loss of protons from the acid cell equals the rate of gain of protons in the water cell.

$$-\frac{dC_a}{dt} = \frac{dC_w}{dt} \quad (8)$$

$$r = \left(R + \frac{1}{k_a} + \frac{1}{k_w} \right) \quad (9)$$

r represents the total resistance offered by the membrane and the acid-membrane and water-membrane interfaces.

From equation (6), using equations (7), (8) and (9), we observe:

$$r \frac{dC_a}{dt} = C_w - C_a \quad (10)$$

$$\Rightarrow r \left(-\frac{dC_w}{dt} \right) = C_w - C_a \quad (11)$$

Differentiating equation (11) once with respect to t :

$$-r \frac{d^2C_w}{dt^2} = \frac{dC_w}{dt} - \frac{dC_a}{dt} \quad (12)$$

$$-r \frac{d^2C_w}{dt^2} = 2 \frac{dC_w}{dt} \quad (13)$$

$$\frac{d^2C_w}{dt^2} + \left(\frac{2}{r} \right) \frac{dC_w}{dt} = 0 \quad (14)$$

Equation (14) can be solved using a procedure suggested by Simmons [11], which is briefly described below for clarity:

$$C_w = e^{-pt} \tag{15}$$

Substituting (15) in (14):

$$p^2 + \left(\frac{2}{r}\right)p = 0 \tag{16}$$

$$\Rightarrow p\left(p + \frac{2}{r}\right) = 0 \tag{17}$$

∴ The roots of equation (17) are 0 and $-2/r$.

$$\Rightarrow C_w(t) = ae^0 + be^{-\left(\frac{2}{r}\right)t} \tag{18}$$

At $t = 0$ and $t = \infty$, the values of $C_w(t)$ are C_0 and C_f which can be determined from the experiment, the method of which is described in the next section.

Applying these values of $C_w(0)$ and $C_w(\infty)$ in equation (18), we can solve it for a and b .

$$\therefore C_w(t) = C_f + (C_0 - C_f)e^{-\left(\frac{2}{r}\right)t} \tag{19}$$

$$C_f > C_0 \Rightarrow C - C_f < 0 \tag{20}$$

$$\Rightarrow C_w(t) = C_f - (C_f - C_0)e^{-\left(\frac{2}{r}\right)t} \tag{21}$$

$$\Rightarrow C_w(t) = C_f \left(1 - \left[\frac{C_f - C_0}{C_f} \right] e^{-t/(r/2)} \right) \tag{22}$$

Equation (22) shows that the concentration of protons in the water cell increases with time and reaches the final value of C_f . From Equation (22), it can be seen that the relation between $C_w(t)$ and t is of the form $y = I - e^{-t/\tau}$, where τ is the time constant. In Equation (22), the term $r/2$ serves as the time constant.

At $t = (r/2)$:

$$\Rightarrow C_w(t) = C_f \left(1.3679 - 0.3679 \left[\frac{C_f - C_0}{C_f} \right] \right) \tag{23}$$

While conducting the experiment associated with this model, the values of C_0 and C_f

can be found. In Equation (23), the right hand side is completely known. Thus, the value of $C_w(t)$ at $t=r/2$ can be found. Using the graph plotted between $C_w(t)$ and t , the value of t corresponding to the calculated value of $C_w(t)$ can be determined. Let this value of t be T . We have:

$$\frac{r}{2} = R + \frac{1}{k_a} + \frac{1}{k_w} = T \tag{24}$$

r has the units of time. This can be explained in the following way. To attain a particular value of $C_w(t)$, i.e., a certain concentration of protons in the water cell, the time required will be r . The greater the value of r , the longer it takes the membrane to allow that number of protons to pass into the water cell. Therefore, r provides an indirect measure of the resistance of the membrane.

3. Proposed experiment

Fig. 2 shows the cell that can be used to obtain the data to validate the above model. Using this experiment, the values of C_f and C_0 can be found, which then leads to the determination of r .

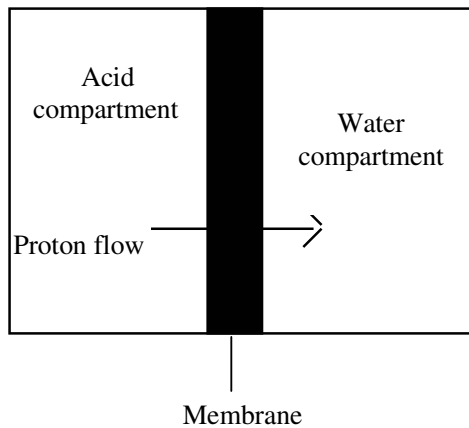


Fig. 2. Side view of proposed cell

The apparatus shown in Fig. 2 is consists of two cells - an acid cell containing concentrated HCl and a water cell. They are separated by the proton exchange membrane. There is a negative gradient in the concentration of protons as one move from the acid cell to the water cell. Theoretically, the protons should try to make their way across the membrane to the water side.

At the beginning of the experiment, the pH values of both the acid and the water are measured. Once the experiment commences, this is done at regular intervals of time.

The pH of the acid should increase due to the loss of protons, while the pH of water should decrease. The experiment is terminated once sufficient readings have been recorded. The final value of the pH in each cell is noted. The concentration of protons is obtained using the relation: $[H^+] = 10^{-pH}$.

4. Discussion

The assumption that steady state is maintained throughout the experiment is essential for the derivation of the final equation (22). Constant monitoring of the pH is required. The pH meter must be quite accurate to detect small changes in the pH of the two cells.

Several membranes can be experimented with, using the same initial concentration of protons in the acid and water cells. Using equation (24), the value of r can be found. Since the same conditions are maintained in all the trials, the value of $[(1/k_a) + (1/k_w)]$ remains constant throughout. Therefore, the value of r depends only on R , i.e. the membrane resistance. In this way, we can measure the resistance of each membrane to proton flow.

Normal conductivity estimations are carried out by the four-probe technique. AC Impedance measurements are carried out a frequency response analyzer along with Zplot software [12].

5. Conclusions

- A simple model for measuring the resistance offered by the proton exchange membrane to proton flow through it has been derived.
- An experiment to validate the model has also been described.
- The condition of steady state is assumed to hold throughout the duration of the experiment.
- The resistance of the membrane is obtained in terms of the time required by the membrane to allow a certain number of protons to permeate to the water cell.
- Keeping the value of $C_w(t)$ constant, the value of r can be found for various membranes, while maintaining the same experimental conditions. Comparison of the values of r thus obtained can give us an idea of the membrane that functions most efficiently.

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