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Oxygen Diffusion Coefficient and Solubility in a New Proton Exchange Membrane

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The electrochemical monitoring technique is used to measure the solubility and the diffusion coefficient of oxygen in a new proton exchange membrane that is being developed by Cape Cod Research, Inc. Using the method of least squares, the data were fit to an analytical solution of Fick's second law to determine D and c_0 . Values of $0.40 \times 10^{-6} \text{ cm}^2/\text{s}$ and $4.98 \times 10^{-6} \text{ mol/cm}^3$ were obtained for the diffusion coefficient and solubility, respectively, of the Cape Cod membrane. These values are significantly less than those of Nafion 117 tested under identical conditions.

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The electrochemical monitoring technique¹⁻³ has been used to determine diffusion coefficients and solubilities for gases in membranes. Fick's law and the appropriate boundary conditions presented in Eq. 1-4 are used to define the system

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \quad [1]$$

$$c(x, t) = 0 \quad \text{for } 0 \leq x \leq L \quad \text{for } t < 0 \quad [2]$$

$$c(x, t) = c_0 \quad \text{for } x = 0 \quad \text{for } t \geq 0 \quad [3]$$

$$c(x, t) = 0 \quad \text{for } x = L \quad \text{for } t \geq 0 \quad [4]$$

where D is the diffusion coefficient, c_0 is the solubility of the diffusing gas, and L is the thickness of the membrane. The steady-state limiting and reaction currents are described by Eq. 5 and 6, respectively

$$i_{\infty} = \frac{n_e}{s_{\text{O}_2}} \frac{FADc_0}{L} \quad [5]$$

$$i(t) = \frac{n_e}{s_{\text{O}_2}} FAD \left. \frac{\partial c(x, t)}{\partial x} \right|_{x=L} \quad [6]$$

where n_e is the number of electrons in the electrochemical reaction of interest, s_{O_2} is the stoichiometric coefficient of oxygen and is taken to be one-half, A is the cross-sectional area of the working electrode, and F is Faraday's constant. Fan⁴ solved the above system of equations using the LaPlace transform techniques resulting in Eq. 7

$$i(t) = \frac{n_e FADc_0}{s_{\text{O}_2} L} \left(\frac{2}{\sqrt{\pi\tau}} \sum_{j=0}^{\infty} \exp \left[-\frac{(2j+1)^2}{4\tau} \right] \right) \quad [7]$$

where

$$\tau = \frac{tD}{L^2} \quad [8]$$

Equation 7 can be used with data for $i(t)$ to obtain D and c_0 as discussed further below.

The method of least squares⁵ was used to fit the data from each trial to Eq. 7 and solve for the diffusion coefficient and solubility simultaneously. To determine the accuracy of values obtained for D and c_0 , confidence intervals were obtained by using the method described by Kimble and White⁶ shown in Eq. 9

$$P_k = \hat{P}_k \pm t_{\gamma} s_{\hat{P}_k} \sqrt{C_{kk}} \quad [9]$$

where \hat{P}_k is the estimate of parameter P_k found through the least-squares method, $s_{\hat{P}_k}$ is the standard deviation for the data set, and t is

the value of the t distribution (also known as the student distribution)^{5,7,8} with a confidence, γ . Equation 10 is solved for t_{γ} to obtain the t distribution

$$\int_{t_{\gamma}}^{\infty} \frac{\Gamma[(f+1)/2]}{\sqrt{\pi f} \Gamma(f/2)} \left(1 + \frac{x^2}{f} \right)^{-\frac{f+1}{2}} dx = \alpha \quad [10]$$

$$\alpha = (1 - \gamma)/2 \quad [11]$$

where f is the degrees of freedom and is equal to $n-m$, where n is the number of data points and m is the number of parameters (two in this case, D and c_0).

A value for C_{kk} in Eq. 9 can be obtained from the approximate Hessian matrix⁶

$$N = \begin{bmatrix} 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_D} \frac{\partial i(j)}{\partial P_D} & 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_D} \frac{\partial i(j)}{\partial c_0} \\ 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial c_0} \frac{\partial i(j)}{\partial P_D} & 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial c_0} \frac{\partial i(j)}{\partial c_0} \end{bmatrix} \quad [12]$$

where $i(j)$ is the current, i , recorded at each data point, j . Equation 12 is then inverted and the diagonal elements of that matrix, $\mathbf{N}[1,1]$ and $\mathbf{N}[2,2]$, are taken as C_{kk} (C_{DD} for diffusivity and $C_{c_0c_0}$ for solubility).

Experimental

The chemical plating technique⁹ was used to deposit platinum on Nafion 117 and Cape Cod membranes. In this technique, the membrane separates two compartments: one containing chloroplatinic acid and the other containing dimethylaminoborane, the reductant. Platinum is deposited onto the membrane once the reductant diffuses through the membrane to the chloroplatinic side of the membrane.⁹

The electrochemical monitoring technique¹⁻³ was used to generate current vs. time data for platinized Nafion 117 membranes and ion exchange membranes developed by Cape Cod Research, Inc. The test apparatus provided by Cape Cod was set up as shown in Fig. 1. Before the experiment was started, nitrogen gas was fed into the left chamber to remove any air present, and deaerated sulfuric acid electrolyte was poured into the right test chamber. Oxygen was eliminated from the electrolyte prior to experimentation by bubbling nitrogen through the electrolyte for approximately 5 min. A silver/silver chloride electrode was used as a reference electrode and a 1 cm² piece of platinum foil served as the counter electrode. A platinum wire in contact with the platinized side of the membrane acted as the current collector. The platinized side of the membrane faced the electrolyte filled chamber. Both sides of the chamber were sealed

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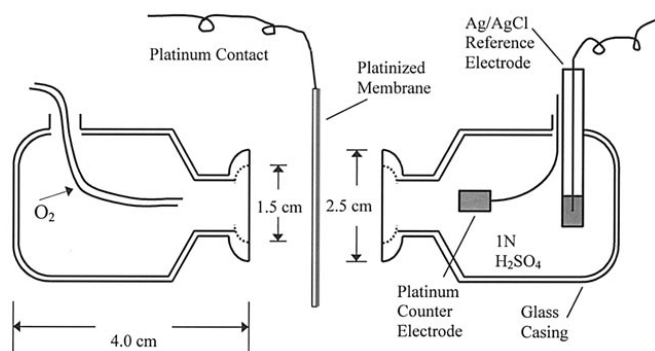


Figure 1. Apparatus used to generate current vs. time data.

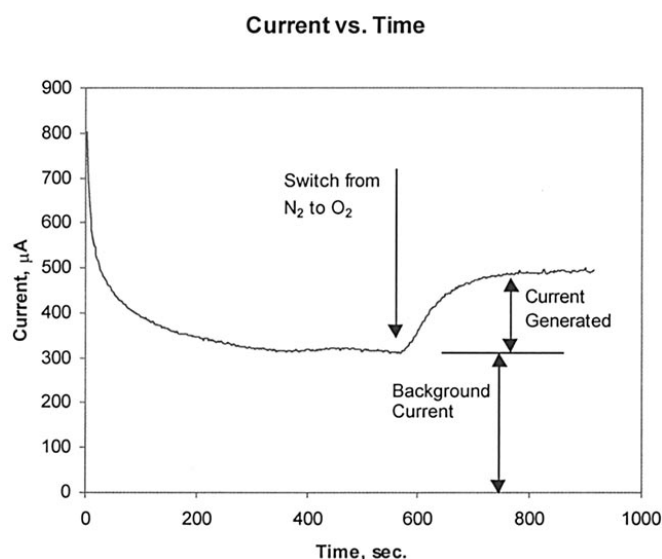


Figure 2. Data generated using the electrochemical monitoring technique for the Nafion 117 membrane.

to the membrane using high vacuum grease (Baxter) to prevent leakage of the electrolyte during the experiment.

Nitrogen was then fed to the left chamber to remove any oxygen present. For the size vessel described in Fig. 1, a nitrogen purge of 5 min was sufficient. Prior to applying a potential of +0.1 V, the open-circuit potential between the platinumized membrane and Ag/AgCl reference electrode was recorded. Once the operating potential of +0.1 V was applied between the platinumized membrane and the Ag/AgCl electrode, the potentiostat recorded current vs. time data until a steady state was reached (approximately 300 μA for the Nafion 117 membrane as shown in Fig. 2). Oxygen then replaced nitrogen as the gas being fed to the left side of the apparatus. This was considered the beginning of the experiment and the time, t , was set to zero. The potentiostat recorded current vs. time data until a new steady state (the limiting current, i_∞) was reached. For the Nafion 117 membrane, the experiment required 6-10 min to reach i_∞

Table I. Membrane parameters and parameters used in data analysis for Nafion 117 and Cape Cod membranes.

Membrane	Nafion 117	Cape Cod
L , cm	0.01778	0.026
A , cm^2	1.767	1.767
number of electrons transferred, n_e	2	2
γ , confidence	0.95	0.95

and for the Cape Cod membrane, this required 15 to 30 min. Because a maximum of 4000 data points could be recorded per trial, readings were taken every 0.375 s for trials using Nafion and 1.0 s for the Cape Cod membrane. This ensured that data would be recorded over a long enough time period that i_∞ was reached.

All membranes were tested at 25°C. All current and potential measurements were recorded using an EG&G Princeton Applied Resources potentiostat/galvanostat model 273A. The open-circuit potentials were measured at between +0.70 and +0.80 V vs. an Ag/AgCl electrode under deaerated conditions. With standard oxygen and platinum oxide activities, the open-circuit potential should be approximately 0.90 to 1.05 V.^{10,11} Due to the deaerated conditions in the electrolyte, the activities of oxidized platinum and oxygen were far from standard. This resulted in a shift of the open-circuit potential in the negative direction to approximately 0.7-0.8 V. After the background current is subtracted from the total measured current, the magnitude of the limiting currents were found to vary from 150 to 350 μA for the Nafion 117 and from 15 to 25 μA for the Cape Cod membrane.

Results and Discussion

Maple 5.0 was used to generate the code for the determination of the diffusion coefficients and solubilities as well as their confidence intervals. Table I shows the membrane parameters and parameters used in data analysis. A 95% confidence ($\gamma = 0.95$) was used in the calculation of all confidence intervals. Two different confidence intervals were calculated in this experiment. Current vs. time data were obtained in each trial for the two membranes. The data for each trial were fitted to Eq. 7 using the method of least squares in order to determine D and c_0 for each trial. Because the determination of the confidence interval for these two parameters requires comparing current vs. time data to results from applying the fitted values of D and c_0 to Eq. 7, it was necessary to use the method described in Eq. 9-12. Examples of fitted values and confidence intervals for individual trials are shown in Table II. The values obtained for the diffusion coefficient and solubility by Parthasarathy *et al.*¹² provided good first estimates of these values. Figure 3 compares data for an individual test of oxygen diffusion across Nafion 117 membrane and the numerical fit using D and c_0 extracted using the method of least squares and Eq. 7. Limiting currents between 15 and 25 μA were observed using the Cape Cod membrane, significantly less than the Nafion membranes (150-350 μA). This is shown in Fig. 4. For membranes with the same thickness, this means that the oxygen flow rate through the Nafion membrane was approximately six times higher than the membrane developed by Cape Cod Research.

Table II. Experimentally determined diffusion coefficients and solubilities for selected individual trials of Nafion 117 and the Cape Cod membrane.

Experiment	D ($\times 10^6 \text{ cm}^2/\text{s}$)	Confidence interval ($\times 10^6 \text{ cm}^2/\text{s}$)	c_0 ($\times 10^6 \text{ mol}/\text{cm}^3$)	Confidence interval ($\times 10^6 \text{ mol}/\text{cm}^3$)	Number of data points (n)
Nafion membrane 1	0.58692	0.002484	16.440	0.09169	870
Nafion membrane 2	0.64306	0.001184	14.661	0.03369	970
Cape Cod membrane 1	0.42231	0.0015862	3.93711	0.017528	2996
Cape Cod membrane 2	0.39445	0.0011658	4.97139	0.019598	1580

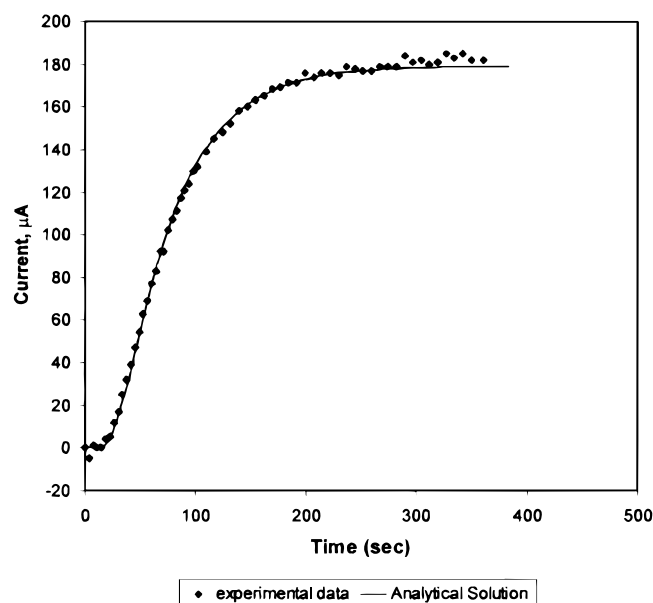


Figure 3. Comparison of the experimental data to the equation fitted with the diffusion coefficient and solubility determined from the method of least squares (Nafion 117).

The second confidence interval involves averaging the D and c_0 values determined from fitting data for the various trials of each membrane. A simpler equation may be used to determine this confidence interval associated with determining the average the diffusion coefficient and solubility as shown in Eq. 13

$$P_k = \bar{P}_k \pm t_\gamma \frac{s_{\hat{P}_k}}{\sqrt{f}} \quad [13]$$

where \bar{P}_k is the mean value of the parameter k (D or c_0), $f = n - m$ is the number of degrees of freedom, and t_γ is the t distribution. Note that $m = 1$ in the calculations of the confidence intervals surrounding the mean of each parameter. The average values for the diffusion coefficient and solubility of oxygen in Nafion 117 and Cape Cod membranes are shown in Table III. Table IV shows that the values for D and c_0 of the Nafion 117 membranes compare well with those found by Lehtinen *et al.*¹³ and Parthasarathy¹² at 25°C using the same method. The values obtained by Ogumi *et al.*³ were with fully humidified inlet gas (oxygen and nitrogen) in contact with the membrane resulting in a difference between their values for D and c_0 and those presented in this paper. In addition to the electrochemical monitoring technique, Lehtinen also uses a potential step technique¹³ with a platinum disk microelectrode to measure D and c_0 for fully humidified oxygen. Although the results using the potential step technique differ, they do agree qualitatively.

In fitting the data, it was also observed that the background current recorded while testing the Cape Cod membrane was much less than that for the Nafion 117 membrane. This can be seen by comparing Fig. 5 to Fig. 2. For all trials using the Cape Cod membrane, the background current was less than 25 μA , which is much less than the 150-350 μA observed when testing Nafion 117 membrane.

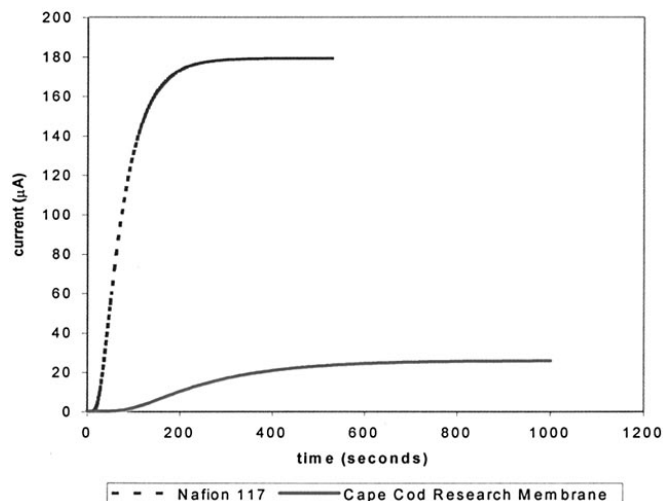


Figure 4. Current vs. time for Nafion 117 and Cape Cod membranes.

This background current may have been different because active area of the platinum on the Nafion 117 membrane is greater than that on the Cape Cod membrane. This can be the result of several factors.^{9,14,15} To ensure that both membranes were diffusion limited during experimentation, further measurements were performed at different potentials. By increasing the potential, the background current for each experiment increased for both membranes, but the current produced from oxygen reduction remained the same. This is because the hydrogen evolution reaction on the platinum working electrode attached to the membrane is kinetically limited, thus the current produced should vary with varying potential. The differences in background current between the Nafion and Cape Cod membranes is due to the different amount of active platinum area available for hydrogen evolution. The cause of this difference in area may be the result of several factors: a greater mass of platinum deposited on the Nafion membrane, a smaller platinum particle size on the Nafion membrane, or effects of using different membranes on the plating process. However, this difference in background current has no effect on the current produced due to oxygen diffusion as this is a diffusion-limited process dependant on the characteristics of the membrane under constant temperature, pressure, and bulk concentration of the electrolyte.

Conclusions

The electrochemical monitoring technique has been used to determine the diffusion coefficient and solubility of a Nafion 117 membrane and a novel membrane developed by Cape Cod Research, Inc. Results for the Nafion membrane compare well with data provided by Lehtinen¹³ and Parthasarathy.¹² At 25°C, the new membrane showed a significant reduction in oxygen solubility and diffusion across the membrane compared to the Nafion membrane.

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Table III. Comparison of diffusion coefficient and solubility values of the Cape Cod and Nafion 117 membranes.

Membrane	D ($\times 10^6$ cm ² /s)	Confidence interval ($\times 10^6$ cm ² /s)	c_0 ($\times 10^6$ mol/cm ³)	Confidence interval ($\times 10^6$ mol/cm ³)
Nafion 117	0.62	0.048	18.7	3.09
Cape Cod	0.40	0.076	4.98	0.606

Table IV. Comparison of diffusion coefficient and solubility values of oxygen to those found in literature. Nafion 117 was used in all cases.

Source	D ($\times 10^6$ cm ² /s)	c_0 ($\times 10^6$ mol/cm ³)
This report ^a	0.62	18.7
Lehtinen <i>et al.</i> ^{13,b}	0.70	13.0
Parthasarathy <i>et al.</i> ^{12,a}	0.74	26.0
Ogumi <i>et al.</i> ^{3,c}	0.24	7.2
Lehtinen <i>et al.</i> ^{13,b}	1.9	9.3

^a $T = 25^\circ\text{C}$.

^b $T = 20^\circ\text{C}$.

^c $T = 30^\circ\text{C}$.

List of Symbols

A	cross-sectional area of the membrane, cm ²
$c(x, t)$	oxygen concentration at a distance, x , from the membrane and a given time, t
c_0	solubility, mol cm ⁻³
C_{kk}	values of the inverted approximate Hessian matrix for element k where k represents D or c_0
D	diffusion coefficient, cm ² s ⁻¹
F	Faraday's constant, 96487 C equiv ⁻¹
$i(t)$	current, A
i_∞	limiting current, A
L	thickness of membrane, cm
m	number of variables
N	approximate Hessian matrix
n	number of data points taken in each trial
n_e	number of electrons transferred
P_k	k th parameter
\hat{P}_k	estimate of the k th parameter
$s_{\hat{P}_k}$	standard deviation
x	distance from the platinum coating, cm
t_γ	value of the t distribution
t	time, s
γ	confidence

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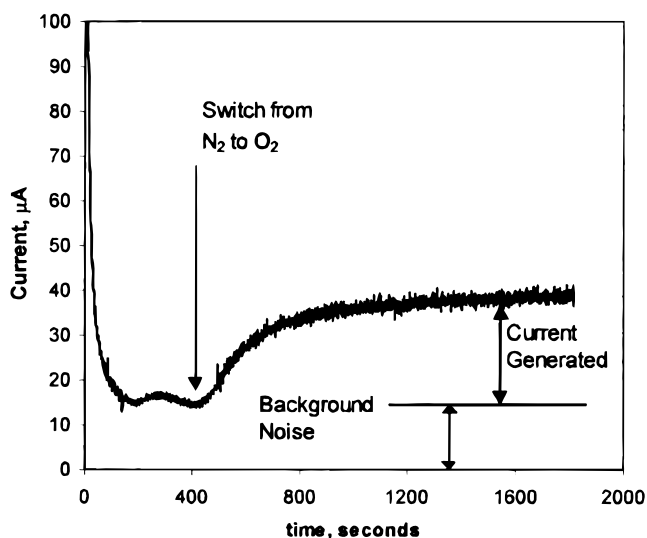


Figure 5. Data generated for the Cape Cod membrane using the electrochemical monitoring technique.

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