ELECTRO-Osmotic DRAG COEFFICIENT OF WATER IN POLYMER ELECTROLYTES AT ELEVATED TEMPERATURES

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ABSTRACT

The electro-osmotic drag coefficient of water in two polymer electrolytes was experimentally determined as a function of water vapor activity and current density for temperatures up to 200 °C. The results show that the electro-osmotic drag coefficient varies from 0.2 to 0.6 in Nafion®/H₃PO₄ membrane electrolyte, but is essentially zero in a phosphoric acid doped PBI (polybenzimidazole) membrane electrolyte over the range of water vapor activity considered. The near zero electro-osmotic drag coefficient found in PBI indicates that this electrolyte should lessen the problems associated with water redistribution in PEM fuel cells.

INSTRUCTION

In order to assure long term stable cell performance, it is important to maintain an optimal chemical species distribution in solid electrolyte fuel cells. We are currently investigating the use of polymer electrolytes for direct methanol fuel cells operating at temperature exceeding 100 °C. It is believed that operation at these temperature can minimize the effects of catalyst poisoning associated with strongly adsorbed intermediates e.g., CO and/or impurities, and significantly enhance electrochemical performance by increasing the catalyst activity. In PEM (proton exchange membrane) fuel cells, it is particularly critical to manage the water content in the polymer electrolytes to maintain sufficient proton conductivity and avoid cathode flooding and anode dehydration.

The motion of water through a polymer electrolyte in a methanol/air fuel cell can be ascribed according to concentrated solution theory to the gradient in the chemical potentials of water and methanol, and to water drag due to the movement of protons (proportional to the DC current). This latter water drag is referred to as the “electro-osmotic drag” and is quantified in term of the electro-osmotic drag coefficient,
\[ \xi = N_{\text{H}_2\text{O}} / N_{\text{H}^+} \], indicating the number of water molecules moving with each proton in the absence of concentration gradients.

The electro-osmotic drag coefficient in Nafion® membrane electrolyte has been previously determined by measuring the flux of water across the membrane at constant current and fixed water concentration in the membrane by exposing the membrane on both sides to liquid water\(^5,6\). In another study, the electro-osmotic drag coefficient has been determined over a wide range of water content by measuring the open-circuit potential of a concentration cell\(^7\). The water content in the Nafion® 117 was controlled by equilibrating the membrane with various partial pressures of water. Both measurements\(^5,6,7\) were carried out at room temperature and the electro-osmotic drag coefficient in Nafion membrane electrolyte was determined to be about 1 ~ 3.

This study describes a different approach for the measurement of the electro-osmotic drag coefficient which is particularly suited for higher temperature where water is a vapor. The electro-osmotic drag coefficient of water in polymer electrolytes was determined here as a function of water vapor activity, current density, and temperatures up to 200 °C.

**EXPERIMENTAL**

Nafion®117 membranes (acid form, DuPont, film thickness of 0.018 cm and equivalent weight 1100) were first boiled in distilled water for 4 hours, then treated in 10% hydrogen peroxide (H\(_2\)O\(_2\)) at 80 °C for 12 hours to oxidize organic impurities in the membrane, and subsequently boiled in distilled water again for 4 hours. The membranes were eventually equilibrated with 85% phosphoric acid (H\(_3\)PO\(_4\)) at 150°C for 12 hours.

Following phosphoric acid equilibration, the samples of the Nafion®/H\(_3\)PO\(_4\) membrane electrolyte were stored in phosphoric acid until use. This treatment yields a phosphoric acid content, measured after withdrawing the membrane from the solution and lightly squeezing and wiping off its surface with a blotting paper, equivalent to \(\approx 2\) moles of phosphoric acid per mole of sulfonic acid in the membrane. Nafion samples treated in this way remain conductive at temperatures in excess of 100°C without resorting to pressurized conditions\(^1\).

PBI (polybenzimidazole) membrane samples, which were cast from a solution of the polymer in dimethylacetamide (membrane thickness of \(\sim 0.009\) cm and repeat unit weight 308), were first boiled in distilled water for several hours to remove impurities, and then doped by immersion in 71% phosphoric acid for at least 16 hours at room temperature. This treatment yields a phosphoric acid content of about five phosphoric acid molecules per polymer repeat unit.
For the purpose of the electro-osmotic drag coefficient measurement, two E-TEK gas diffusion electrodes were hot-pressed on both sides of Nafion®/H₃PO₄ or PBI membrane electrolytes at 130 ~ 150 °C. The diameter of the E-TEK electrode was 1.27 cm corresponding to an area of about 1.27 cm².

The electro-osmotic drag coefficient was measured in a specially designed closed volume cell, shown in Figure 1. The cell consists of two chambers, a 2200 cm³ reservoir and a 175 cm³ small chamber, separated by the membrane electrolyte with the E-TEK gas diffusion electrodes placed on both sides. The apparatus was placed inside an oven and connected to a gas manifold system so that the temperature, pressure and composition of the gas phase in contact with the sample could be controlled.

Initially, both chambers were evacuated at the prescribed temperature, and then filled with hydrogen to the desired pressure. Finally, sufficient liquid water and/or methanol was injected into the reservoir via a septum to yield a water and/or methanol vapor partial pressure that was significantly higher than that in the small chamber. The pressure change (increase) in the small chamber was monitored by a MKS pressure transducer within the oven, and the results (in the absense of current) used to determine the permeability coefficient.

When both the reservoir and the small chamber were at equal hydrogen and water vapor pressures, the two E-TEK gas diffusion electrodes were connected to a PAR Model 173 potentiostat/galvanostat and a stable DC current was passed through the membrane. Hydrogen was consumed at the reservoir side (oxidation) and generated at the small chamber side (reduction). As protons were transported across the membrane, water was also dragged through the membrane from the anode to the cathode. The pressure change in the small chamber, due to the contribution of hydrogen generated on the cathode and the water dragged across the membrane along with the protons, was monitored by the MKS pressure transducer within the oven. The pressure versus time results were used to determine the electro-osmotic drag coefficient. After the measurement, the cell was evacuated again and filled with hydrogen and water and/or methanol vapor for the next run.

RESULTS AND DISCUSSION

In the osmotic drag measurements outlined above, the back diffusion of hydrogen can be neglected since the permeability of hydrogen is much less than that of water \( (P_m(H_2O)/P_m(H_2) > 30 \text{ in PBI}^9) \). Assuming that the water and/or methanol vapor and hydrogen follow the ideal gas law, the molar flux of water vapor passed across the membrane from anode to cathode, \( N_{H_2O} \), is given by:

\[
N_{H_2O} = \frac{P_m(H_2O) \cdot I \cdot t \cdot A}{R \cdot T \cdot M_{H_2O}}
\]
\[ N_{H_2O} = \xi \frac{I}{FA} - \frac{P_m(P_{s,H_2O} - P_{R,H_2O})}{V_{STP}h} \]  

where \( F \) and \( I \) are Faraday's constant and the total current passed across a membrane of thickness \( h \) and an area \( A \), respectively. \( P_m \) is the permeability of water, which was determined from the initial permeability measurement. \( V_{STP} \) is the standard molar gas volume. \( P_{s,H_2O} \) and \( P_{R,H_2O} \) are the water partial pressures in the small chamber and the reservoir (cathode side and anode side), respectively. \( \xi \) is the electro-osmotic drag coefficient defined as the number of water molecule dragged by each proton. The first term on the right represents the flux of water dragged by the migrating protons, i.e. due to the effect of electro-osmotic drag coefficient \( \xi \), the second term is due to the back diffusion of water resulting from the increase in the water partial pressure in the small chamber during the measurement. The pressure rise in the small chamber, \( dP_{s,H_2O} \), due only to water vapor transport between time \( t \) and \( t+dt \) is:

\[ dP_{s,H_2O} = \frac{RT}{V_s} \left( \xi \frac{I}{F} - \frac{AP_m(P_{s,H_2O} - P_{R,H_2O})}{V_{STP}h} \right) dt \]  

where \( R \) and \( T \) are the gas constant and temperature. \( V_s \) is the volume of the small chamber. The initial condition for equation (2) is:

\[ t = 0, \quad P_{R,H_2O} = P_{s,H_2O} = P_{0,H_2O} \]  

Using the ideal gas law, at constant temperature a mass balance of water vapor between the small chamber and the reservoir can be written as:

\[ V_s(P_{s,H_2O} - P_{0,H_2O}) = V_R(P_{0,H_2O} - P_{R,H_2O}) \]  

where \( V_R \) is the volume of the reservoir. Substituting equation (4) into (2) yields:

\[ dP_{s,H_2O} = \frac{RT}{V_s} \left( \xi \frac{I}{F} - \frac{AP_m(V_s/V_R + 1)(P_{s,H_2O} - P_{0,H_2O})}{V_{STP}h} \right) dt \]  

Solving Equation (5) for the change in the partial pressure of water in the small chamber and applying initial condition (3) yields:

\[ \Delta P_{s,H_2O} = \frac{IV_{STP}h}{FAP_m(V_s/V_R + 1)} \left( 1 - \exp\left( -\frac{RTAP_m(V_s/V_R + 1)}{V_sV_{STP}h}t \right) \right) \]
The electro-osmotic drag coefficient, $\xi$ can be determined by fitting the experimental data to Equation (6).

Typical data from an experiment using a Nafion®/H$_3$PO$_4$ membrane are shown in Figure 2. Curve 1 represents the pressure change in the receiving small chamber. Line 2 represents the calculated pressure rise from hydrogen transported due to the current, $I$. Curve 3 (correlated by line 4) represents the pressure rise in the small chamber due only to water vapor transport and is obtained by subtracting line 2 from curve 1. The solid line 4, which yields the electro-osmotic drag coefficient, represents the curve fit of Equation (6) to the pressure increase due to water vapor transport (curve 3).

The electro-osmotic drag coefficients of water in Nafion®/H$_3$PO$_4$ membrane electrolyte measured and calculated by the procedure discussed above are shown in Figure 3. The water vapor activity was changed by either maintaining a constant temperature of 125°C and varying the water partial pressure, or by maintaining a constant water partial pressure around 46.6 kPa and varying the temperature from 125 to 185°C. The results indicate that the electro-osmotic drag coefficient in Nafion®/H$_3$PO$_4$ membrane electrolyte is a strong function of water content in the membrane electrolyte, since the water content increases as the water vapor activity increases and the water vapor activity alone controls the amount of water sorbed in the membrane. At the same water vapor activity, identical electro-osmotic drag coefficients of water is expected regardless of the change of the temperature. The electro-osmotic drag coefficient varied from 0.2 to 0.6 over the range of water vapor activity studied. These values are significantly lower than those expected from the hydration number of the proton and less than the corresponding room temperature values that have been previously reported in the literature. At 30°C, it has been reported that the electro-osmotic drag coefficients for water equilibrated Nafion membrane was between 1 to 3. The small electro-osmotic drag coefficient obtained here may indicate that instead of a simple proton migrating mechanism, conductivity by a Grotthus proton hopping mechanism may take place under the present conditions.

As another check on the validity of our experiment, several trials were run with varying current densities. Figure 4 shows that the electro-osmotic drag coefficients remain essentially constant for various levels of applied current density.

In PBI membranes, the results show that the pressure change due to water (the total pressure change in the small chamber minus the pressure change due to the hydrogen) is near zero (Figure 5), implying that the electro-osmotic drag coefficient is near zero in PBI membrane electrolyte.

Several trials were run at different water and methanol vapor partial pressures, different phosphoric acid doping levels in the PBI membranes and at different current densities. Table 1 shows that the electro-osmotic drag coefficients are essentially zero in
each case. There is some scatter in the data shown in Table 1. This may be due to changes in the structure of PBI membrane which probably occurs during the measurement processes (crystallization in the absence of water and/or the formation of pyrophosphoric acid in the system) and measurement errors. However, the near zero water electro-osmotic drag coefficient found here reflects the dense, non-porous nature of the phosphoric acid doped PBI membrane and indicates that the conductivity mechanism in the PBI membrane is different from that in the Nafion®/H₃PO₄ membrane electrolyte. The near zero water electro-osmotic drag coefficient also implies that PEM fuel cells with PBI membranes should lessen the difficulties associated with water redistribution that are observed in conventional PEM fuel cells employing Nafion or other perfluorosulfonic acid polymer electrolytes. This result is consistent with the relative insensitivity to the humidification conditions that has been observed during fuel cell tests with doped PBI membranes².

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Table 1. Osmotic drag Measurement in phosphoric acid doped PBI membrane

| DC current mA/cm² | H₃PO₄ Content mol% | P_{H₂O:CH₃OH} kPa | H₂O:CH₃OH | Drag coefficient |
|-------------------|--------------------|---------------------|------------|-----------------|
| 40                | 480                | 40                  | 1:0        | 0               |
| 40                | 480                | 28.8                | 1:0        | 0.039           |
| 40                | 480                | 70                  | 1:0        | 0.025           |
| 47                | 480                | 61.3                | 1:0        | 0.028           |
| 55                | 480                | 34.7                | 1:0        | 0               |
| 40                | 310                | 36                  | 1:0        | 0               |
| 40                | 310                | 26.7                | 1:0        | 0               |
| 40                | 500                | 44                  | 4:1        | 0.09            |
| 40                | 500                | 52.5                | 2.08:1     | 0.085           |
| 40                | 500                | 44.9                | 2:1        | 0.073           |
| 40                | 500                | 45.6                | 1:1        | 0.034           |
| 40                | 500                | 44.3                | 1:0        | 0.059           |
| 40                | 500                | 43.6                | 10:1       | 0.08            |
| 40                | 500                | 44.7                | 7.6:1      | 0               |
| 40                | 500                | 37.9                | 6.7:1      | 0               |
| 40                | 500                | 44                  | 1:0        | 0               |
| 40                | 500                | 44.9                | 5:1        | 0               |
| 40                | 500                | 48.9                | 3.6:1      | 0               |
| 40                | 500                | 46.9                | 2:1        | 0               |
| 40                | 500                | 35.7                | 1:1        | 0               |
| 40                | 500                | 32.3                | 0:1        | 0               |

All measurement were carried out at 150 °C and about 54 kPa hydrogen partial pressure in the cell.
Figure 1. Schematic diagram of the electro-osmotic drag measurement cell, consisting of a 2200 cm$^3$ reservoir and a 175 cm$^3$ small chamber.
Electro-osmotic drag coefficient measurement in Nafion®/H₃PO₄ polymer electrolyte at 125°C. The pressure change in the small chamber is indicative of the electro-osmotic drag coefficient. (1) Total pressure change in the small chamber. (2) Expected pressure change in the small chamber due to H₂ electrolysis based on i = 40 mA/cm². (3) Pressure change due to water drag, (=curve 1 - curve 2). (4) Results fitted to Eq. 6 with ξ = 0.45. Electrode area is 1.27 cm².
Figure 3. The electro-osmotic drag coefficient, $\zeta$, in the Nafion®/H$_3$PO$_4$ polymer electrolyte at various water vapor activities. The activity was varied by changing the temperature maintaining $P_{H_2O} \approx 46.7$ kPa and by varying the water vapor pressure maintaining a temperature of 125°C. Error bars represent estimation of accumulated errors from experimental measurements and equipment sensitivity.

Figure 4. Electro-osmotic drag coefficient, $\zeta$, in the Nafion®/H$_3$PO$_4$ polymer electrolyte at various current densities maintaining $P_{H_2O} \approx 46.7$ kPa and a temperature of 125°C. For error bars description see Figure 3 caption.
Figure 5. Electro-osmotic drag coefficient measurement in PBI doped with 480 mol% H$_3$PO$_4$ at 155°C. The pressure change in the small chamber is indicative of the electro-osmotic drag coefficient. (1) Total pressure change in the small chamber. (2) Expected pressure change in the small chamber due to H$_2$ electrolysis based on $i = 55$ mA/cm$^2$. (3) Pressure change due to water drag (=curve 1 - curve 2). Electrode area is 1.27 cm$^2$. 