

Measurement of Electro-osmotic Drag Coefficient of Nafion Using a Concentration Cell

Ryosuke Jinnouchi*, Haruhiko Yamada and Yu Morimoto

Toyota Central R&D Labs. Inc., Nagakute, Aichi, 480-1192, Japan

*E-mail: e1262@mosk.tytlabs.co.jp

Electro-osmotic drag coefficient of Nafion 112 was measured as a function of relative humidity (RH) and temperature, using a concentration cell technique. Measured electro-osmotic drag coefficient was 0.7-1.1 in the range of RH 0.15-0.75 and 60-80 °C. The electro-osmotic drag coefficient is not dependent on RH. On the contrary, the electro-osmotic drag coefficient slightly increases with the increase in temperature.

1. Introduction

The performance of polymer electrolyte fuel cells (PEFCs) is strongly influenced by the state of hydration of the proton exchange membrane. The proton conductivity of the membrane is small under dry conditions, and large ohmic loss is caused. Then, proper control of the state of hydration of the membrane is necessary for the high performance of PEFCs.

The state of hydration is determined by the relationship between water uptake by the membrane and the water flow caused by diffusion and electro-osmosis. Electro-osmosis is the water flux accompanying the proton flux, and can be characterized by the electro-osmotic drag coefficient, which is defined as the number of water molecules moving with each proton in the absence of the concentration gradient,

$$\xi = \frac{J_{H_2O}}{J_{H^+}} \quad (1)$$

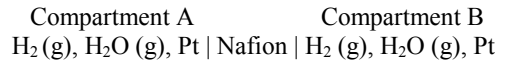
where ξ is the electro-osmotic drag coefficient, J_{H^+} and J_{H_2O} are respectively molecular fluxes of protons and water. It is significant to know the electro-osmotic drag coefficient under operation conditions of PEFCs for calculating the water distribution in the polymer electrolyte and designing fuel cells [1]. Fuller, *et al.*, measured the electro-osmotic drag coefficient of Nafion 117 under conditions with relative humidity (RH) 0.2-1.0 and 25 °C [2]. Zawodzinski, *et al.*, also measured it in order to correct the electro-osmotic drag coefficient under lower humidified conditions, i.e. RH 0.05-1.0 and 30 °C [3]. However, there is

no reliable data under the operating temperature of PEFCs, such as 80 °C.

In this study, a simple method measuring the electro-osmotic drag coefficient as a function of humidity and temperature was developed, adopting the concentration cell technique used in previous studies [2-3].

2. Experimental Methods

2.1. Theory The concentration cell technique is based on the following theory [2]. The concentration cell is constituted as:



Hydrogen gases with RH $a_{w,A}$ and $a_{w,B}$ are introduced to the compartments A and B respectively. The fluxes of protons and water can be expressed by the following equations:

$$J_{H^+} = -L_{11}c_{H^+}^2 \frac{d\mu_{H^+}}{dx} - L_{12}c_{H^+}c_{H_2O} \frac{d\mu_{H_2O}}{dx} \quad (2)$$

$$J_{H_2O} = -L_{21}c_{H^+}c_{H_2O} \frac{d\mu_{H^+}}{dx} - L_{22}c_{H_2O}^2 \frac{d\mu_{H_2O}}{dx} \quad (3)$$

where c_{H^+} and c_{H_2O} are the concentrations, μ_{H^+} and μ_{H_2O} are the electrochemical potentials, x is the distance from the edge of the membrane at compartment A, and L_{11} and L_{21} are coefficients expressed as follows,

$$L_{11} = \frac{\kappa}{F^2c_{H^+}^2} \quad (4)$$

$$L_{21} = \frac{\kappa \xi}{F^2 c_{H^+} c_{H_2O}} \quad (5)$$

where κ is the proton conductivity, F is the Faraday constant. In Eq. (2), the first term on the right hand side means the proton flux caused by the gradient of electrical potential in the membrane, and the second term means the streaming current. The first term in Eq. (3) is the electro-osmosis, and the second term is the diffusion. According to Onsager's reciprocal theorem, the two coupling coefficients are equal:

$$L_{21} = L_{12} \quad (6)$$

In the case of the open-circuit condition, the flux of protons is zero. Then, the next differential equation can be withdrawn from Eq. (2).

$$\frac{d\mu_{H^+}}{dx} = -\xi \frac{d\mu_{H_2O}}{dx} \quad (7)$$

Because the electrochemical potential of protons and water at position x are written by the following equations, using activity of water $a_w(x)$ and potential $\phi(x)$ at position x :

$$\mu_{H^+}(x) = \mu_{H^+}(0) + F\{\phi(x) - \phi(0)\} \quad (8)$$

$$\mu_{H_2O}(x) = \mu_{H_2O}(0) + RT \ln a_w(x) \quad (9)$$

Equation 7 can be rewritten as

$$F\Phi = -\xi(0) \left(\mu_{H_2O}^0 + RT \ln a_{w,A} \right) + \xi(x_i) \left(\mu_{H_2O}^0 + RT \ln a_{w,B} \right) \quad (10)$$

$$\Phi = \phi(x_i) - \phi(0) \quad (11)$$

where x_i corresponds to the membrane thickness. By differentiating Eq. (10) with $\ln a_{w,B}/a_{w,A}$, the electro-osmotic drag coefficient as a function of the cell voltage and the water activity is obtained as follows.

$$\xi(a_{w,B}) = \frac{F}{RT} \frac{d\Phi}{d \ln a_{w,B} / \ln a_{w,A}} \quad (12)$$

Eq. (12) is written by a finite differential approximation,

$$\xi(a_{w,B}) = \frac{F}{RT} \frac{\Phi(a_{w,B} + \Delta a_{w,B}) - \Phi(a_{w,B} - \Delta a_{w,B})}{\ln(a_{w,B} + \Delta a_{w,B}) - \ln(a_{w,B} - \Delta a_{w,B})} \quad (13)$$

Using Eq. (13), the electro-osmotic drag coefficient ξ can be calculated from the measured voltage of the concentration cell and RHs in the compartments A and B. The actual apparatus and methodology of the measurement are described in the following section.

2.2. Experimental The gas supplying system is shown in Fig. 1. The hydrogen gas is humidified with bubblers, mixed with the dry hydrogen gas, and after that, introduced to the cell. The total flow rate of the hydrogen gas was 5 l/min, which was sufficient to achieve uniformity in the compartments in the concentration cell. The dew point of the supplied gas at the inlets and the outlets

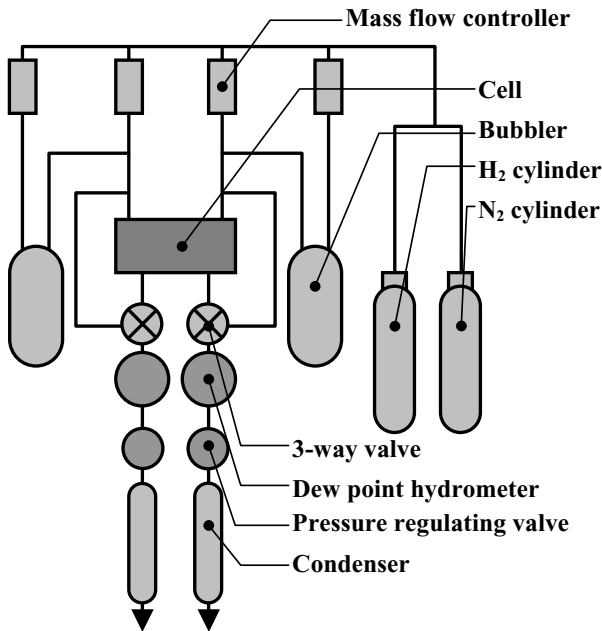


Fig. 1. Gas supplying system to the concentration cell.

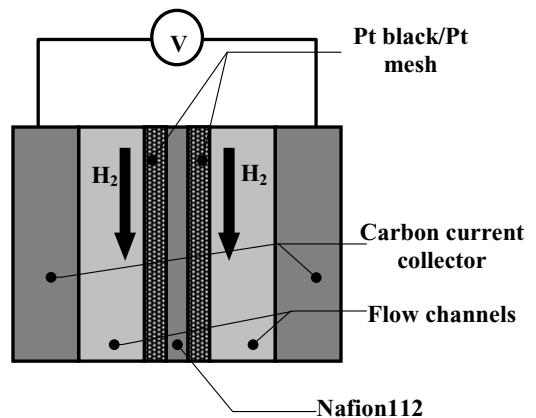


Fig. 2. Schematic figure of the concentration cell used for the measurement of the electro-osmotic drag coefficient of Nafion 112.

of the compartments was measured with dew point hydrometers. The voltage of the cell is monitored with a digital multimeter. Figure 2 shows the concentration cell. Nafion 112 was placed between two Pt black/Pt meshes. Carbon current collectors with flow channels are contacted to the Pt black/Pt mesh. The hydrogen gas was introduced to the channels and allowed to permeate to the membrane surfaces through the Pt black/Pt mesh. The apparent active electrode area was 1 cm^2 .

The experimental procedure is as follows.

- 1) Hydrogen humidified equally was supplied to the compartments for at least 30 min and the background voltage was confirmed to be stable.
- 2) The RH of hydrogen at the inlet of compartment B was lowered by 0.1, by controlling the temperature of the bubbler and the mixing ratio of the dry and humidified hydrogen gases, and the change in the voltage was measured.
- 3) The electro-osmotic drag coefficient was calculated using Eq. (13).

The procedures 1)-3) were done at various RHs and temperatures.

3. Results and Discussion

The monitored voltage of the cell is shown in Fig. 3. Stable voltage is observed both before and after the humidification change. The measured changes in the cell voltage $\Delta\Phi$ at various RHs and

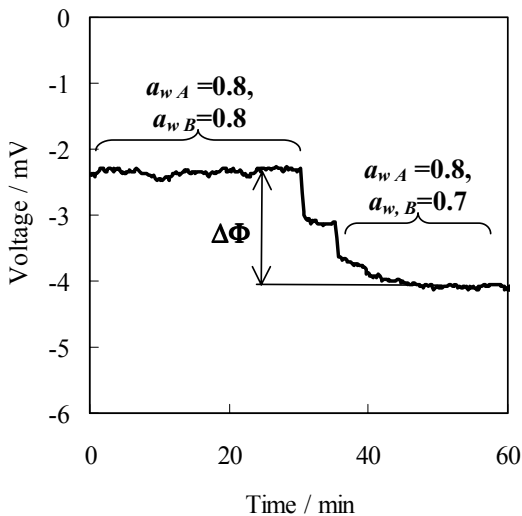


Fig. 3. Change in the voltage of concentration cell during the measurement.

temperatures are collected in Fig. 4. Plotted $\Delta\Phi$ depends on RH logarithmically. The calculated electro-osmotic drag coefficients are in Fig. 5. The electro-osmotic drag coefficient is 0.7-1.1 and not dependent on RH. The latter result agrees well with the result by Zawodzinski, *et al.* On the contrary, the electro-osmotic drag coefficient increased with the increase in temperature.

The reason for these electro-osmotic drag coefficient dependency on the RH and temperature

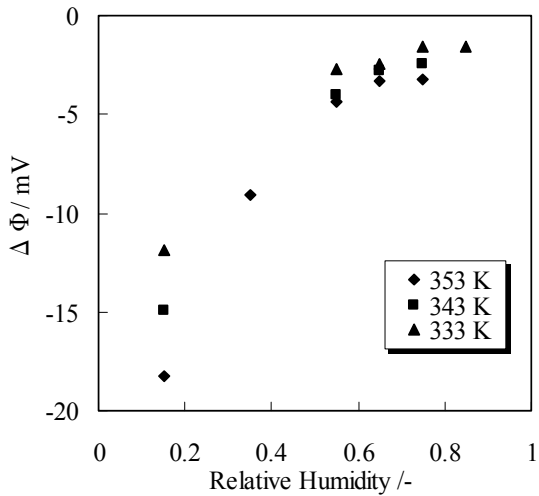


Fig. 4. Change in the voltage vs. RH.

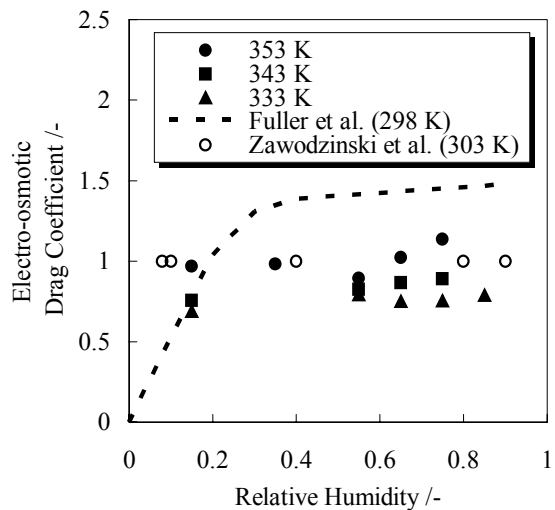


Fig. 5. Electro-osmotic drag coefficient of Nafion in various RH and temperature.

is not clear. The electro-osmotic drag coefficient seems to be determined by the interactions among protons, water and polymers, and these interactions should depend on the hydration structure [4]. For further understanding of the water transport properties of this material, therefore, it is necessary to clarify the relationship between the hydration structure and the mobility of protons and water molecules in molecular scale. Molecular simulation studies, such as molecular dynamics and dispersed particle dynamics might be useful for this objective [5-6].

4. Conclusions

Electro-osmotic drag coefficient of Nafion 112 in the range of RH 0.15-0.75 and 60-80 °C was measured using a concentration cell. Measured electro-osmotic drag coefficient was 0.7-1.1, and was not dependent on RH. On the contrary, the electro-osmotic drag coefficient slightly increased with the increase in temperature. The reason of these electro-osmotic drag coefficient dependency on the RH and temperature is not clear. Further understanding on the structure and the mobility of protons, water and polymers in molecular scale is necessary.

Symbols

$a_{w,A}$	Water activity in compartment A.
$a_{w,B}$	Water activity in compartment B.
c_{H^+}	Concentration of proton.
c_{H_2O}	Concentration of water.
F	Faraday constant.
J_{H^+}	Flux of proton.
J_{H_2O}	Flux of water.
L_{ij}	Coefficient defined as Equation 2 and 3.
R	Gas constant.
T	Temperature of the cell.
x	Distance from the edge of the membrane at compartment A.
x_t	Membrane thickness.
Φ	Voltage of the concentration cell.
$\Delta\Phi$	Change in the voltage.
ϕ	Electrical potential.
κ	Proton conductivity.
μ_{H^+}	Electrochemical potential of proton.
μ_{H_2O}	Electrochemical potential of water.
ξ	Electro-osmotic drag coefficient.

References and Notes

- [1] T. E. Springer, T. A. Zawodzinski and S. Gottesfeld, *J. Electrochem. Soc.*, **138**, 2334 (1991).
- [2] T. Fuller and J. Newman, *J. Electrochem. Soc.*, **139**, 1332 (1992).
- [3] T. A. Zawodzinski, J. Davey, J. Valerio and S. Gottesfeld, *Electrochim. Acta*, **40**, 297 (1995).
- [4] A. Eisenberg and H. L. Yeager, *ACS Symp. Ser.*, **180**, (1982)
- [5] R. Jinnouchi and K. Okazaki, *J. Electrochem. Soc.*, **155**, E66-E73, (2003).
- [6] S. Yamamoto and S. Hyodo, *Polymer Journal.*, **35**, 519 (2003).