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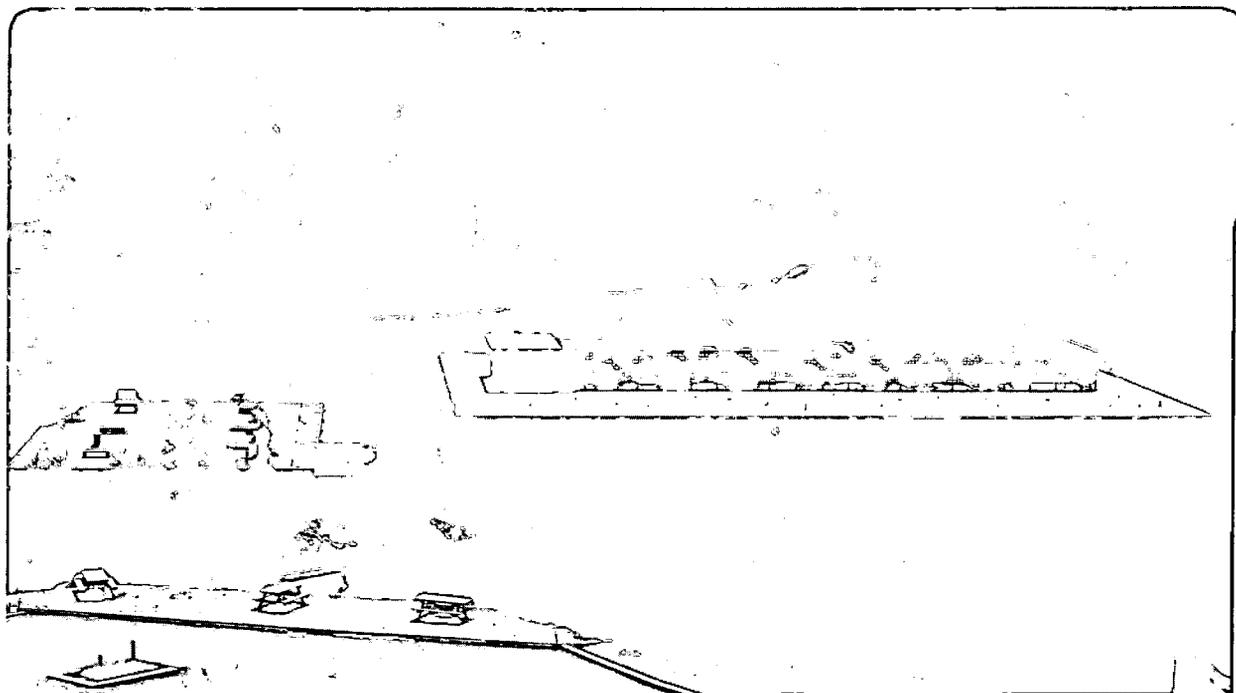
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Experimental Determination of the Transport Number of Water in Nafion[®] 117 Membrane

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October 1991



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**Experimental Determination of the Transport Number
of Water in Nafion® 117 Membrane**

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Experimental Determination of the Transport
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Abstract

The transport number of water in Nafion[®] 117 membrane over a wide range of water contents is determined experimentally using a concentration cell. The transport number of water, the ratio t_o^m/z_o , is about 1.4 for a membrane equilibrated with saturated water vapor at 25°C, decreases slowly as the membrane is dehydrated, and falls sharply toward zero as the concentration of water approaches zero. The relationship between the transference number, the transport number, and the electroosmotic drag coefficient is presented, and their relevance to water-management in solid-polymer-electrolyte fuel cells is discussed. Results are compared with other data available in the literature and with the theoretical maximum.

Introduction

A number of fuel-cell systems under development use perfluorinated ionomer membranes for both the separator and the electrolyte. Proton conductivity is strongly coupled to the hydration of the polymer, and therefore, it is vital to manage the water content in the separator of the solid-polymer-electrolyte fuel cell to maintain sufficient electrical conductivity for practical use. Cell efficiency is related to the transport properties of the membrane and may be the critical factor in load-leveling devices, for example, if the kinetics of the reactions are fast[1]. From the inception of solid polymer-electrolyte fuel cells, water-transport was recognized as a possible problem[2].

The motion of water is caused by a gradient in its chemical potential and by the movement of hydrogen ions, which is proportional to the current. The electroosmotic drag coefficient ξ ,

$$\xi = \frac{N_o}{N_+}, \quad (1)$$

is defined here as the number of water molecules moving with each hydrogen ion in the absence of concentration gradients. ξ can be related to the transference and transport numbers of water, as will be shown later. Previous work shows that for each hydrogen ion that moves across a fully hydrated membrane about three water molecules are carried along.[3] [4] [5]

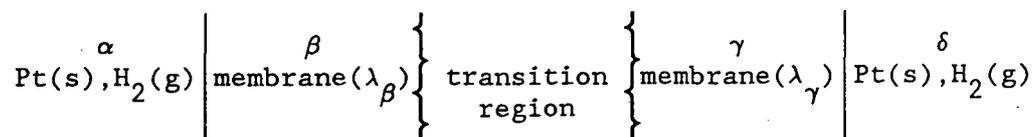
Earlier methods to determine the electroosmotic drag coefficient measured the flux of water across the membrane at constant current. The membranes were always in direct contact with liquid water, and

therefore, the water concentration in the membrane was fixed at $\lambda \approx 22$, where λ is the number of water molecules per sulfonic acid group. Changes in the pretreatment of the membranes permit limited variation in the water content of the membranes that are equilibrated with liquid water. Springer et al. [6] used this approach to measure ξ at $\lambda = 11$. The pretreatment, however, can affect the transport properties of the membrane as well. Furthermore, this method still does not allow examination of ξ at low water contents, which is critical to the modeling of fuel-cell operation.

Water content in the membrane can be controlled over a wide composition range by equilibrating the membrane with a known partial pressure of water. Our attempts to measure the flux of water from the gas phase and to eliminate concentration gradients were difficult and proved unreliable. An alternative approach using the potentials of cells with transference was developed to measure the transport number of water in ionically conducting polymers over a large range of water contents.

Theory

Transport properties can be obtained from electrochemical cells with a single electrolyte of varying concentration [7]. The cell potential depends not only on thermodynamics but also on the transport properties of the system in the transition region. The transport number of water in an ionically conducting polymer can be obtained by analyzing the concentration cell shown below.

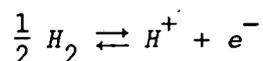


Concentration cell

The cell potential is

$$FU = F(\Phi^\delta - \Phi^\alpha) = (\mu_{e^-}^\alpha - \mu_{e^-}^\delta). \quad (2)$$

At the two electrodes, the chemical reaction



is assumed to be at equilibrium, and therefore

$$\frac{1}{2} \mu_{\text{H}_2} = \mu_+ + \mu_{e^-}.$$

The cell potential reduces to

$$FU = \frac{1}{2} RT \ln \frac{P_{\text{H}_2}^\alpha}{P_{\text{H}_2}^\delta} + \int_{y_\beta}^{y_\gamma} \nabla \mu_+ dy. \quad (3)$$

To analyze the system further we must examine the transport processes in the junction region. A gradient in chemical potential of water exists in the transition region, and diffusion occurs. The multicomponent diffusion equation,

$$c_i \nabla \mu_i = \sum_{j \neq i}^n K_{ij} (\mathbf{v}_j - \mathbf{v}_i), \quad (4)$$

describes transport in the membrane. $c_i \nabla \mu_i$ is the driving force for transport, v_i is the velocity of species i relative to some arbitrary reference velocity, and K_{ij} ($= K_{ji}$ from the Onsager reciprocal relations) are the frictional coefficients. In general, for n species there are $\frac{1}{2}n(n-1)$ independent transport properties necessary to characterize the system. The membrane is considered to be comprised of three components: water, hydrogen ions, and polymer, and therefore three independent transport properties are required. Because of the Gibbs-Duhem relationship, for n species there are only $n-1$ independent equations of the form of equation 4. The membrane velocity is set to zero, and all fluxes are referenced to it. These $n-1$ equations, together with $N_m = 0$, can be written in matrix form. With the electrochemical potential as the driving force, the multicomponent diffusion equations can be inverted to give

$$N_+ = c_+ v_+ = -L_{++} c_+^2 \nabla \mu_+ - L_{+o} c_+ c_o \nabla \mu_o \quad (5)$$

and

$$N_o = c_o v_o = -L_{o+} c_o c_+ \nabla \mu_+ - L_{oo} c_o^2 \nabla \mu_o \quad (6)$$

The L_{ij} 's ($= L_{ji}$) are related directly to the K_{ij} :

$$L_{o+} = \frac{K_{+o}}{K_{+o} K_{om} + K_{+o} K_{+m} + K_{+m} K_{om}}, \quad (7)$$

$$L_{oo} = \frac{K_{+o} + K_{+m}}{K_{+o} K_{om} + K_{+o} K_{+m} + K_{+m} K_{om}}, \quad (8)$$

and

$$L_{++} = \frac{K_{+o} + K_{om}}{K_{+o}K_{om} + K_{+o}K_{+m} + K_{+m}K_{om}} \quad (9)$$

See Newman [8] for further details. Consequently, if experiments can be devised to measure the L_{ij} , then the binary interaction coefficients can be estimated as a function of water content within the membrane. This concept is the same as the orthogonal experiments described by Pintauro and Bennion[9]. For the Nafion[®] membrane used in fuel-cell applications, the transport properties required are: the diffusion coefficient of water, the electrical conductivity, and the transport number of water. L_{++} is related to the electrical conductivity by

$$L_{++} = \frac{\kappa}{F^2 c_+^2} \quad (10)$$

From the definition of ξ , equations 5 and 6 give

$$L_{o+} = \frac{\kappa \xi}{F^2 c_+ c_o} \quad (11)$$

For the concentration cell depicted above, equation 5 can be written with the flux of hydrogen ions set to zero as

$$\nabla \mu_+ = -\xi \nabla \mu_o \quad (12)$$

Thus, if $\Delta\Phi$ represents the last term in equation 3, then we can write

$$F\Delta\Phi = FU - \frac{1}{2} RT \ln \frac{P_{H_2}^\alpha}{P_{H_2}^\beta} = \int_{y_\gamma}^{y_\beta} \xi \frac{d\mu_o}{dy} dy. \quad (13)$$

Everything in the integral is a function of water content, and therefore the equation can be integrated over the concentration. That is, the potential of the cell is independent of the shape of the concentration profile. Equation 13 becomes

$$F\Delta\Phi = \int_{\lambda_\gamma}^{\lambda_\beta} \xi \frac{d\mu_o}{d\lambda} d\lambda, \quad (14)$$

and differentiation gives

$$\xi = F \frac{d(\Delta\Phi)}{d\mu_o^\beta}. \quad (15)$$

This means that we would hold the water activity constant on the right side of the cell (γ) and vary the activity of water on the left side (β). Equation 15 then gives the value of ξ at this water activity (β).

An equivalent analysis can be made in terms of transference numbers. See, for example, Newman [8] for further information on the definitions and the details of this approach. The transference number is defined, in the absence of concentration gradients, by

$$it_i^m = Fz_i c_i (\mathbf{v}_i - \mathbf{v}_m) \quad (16)$$

and is clearly related to the L_{ij} 's or K_{ij} 's of the multicomponent diffusion equations. The current expressed in terms of transference

numbers is

$$\frac{F}{\kappa} i = \sum_i \left(t_i^m / z_i \right) \nabla \mu_i. \quad (17)$$

The ratio t_i^m / z_i , also called the transport number, is not necessarily zero for neutral species. For the Nafion[®] system, all the current is carried by the protons, and consequently the transference number of the hydrogen ions is one. At open circuit, the current is zero, and

$$\frac{\nabla \mu_+}{z_+} = - \frac{t_o^m}{z_o} \nabla \mu_o. \quad (18)$$

ξ is defined in the absence of a gradient in the chemical potential of water and therefore is related to the transference number by

$$\xi = \frac{N_o}{N_+} = \frac{t_o^m}{z_o} \frac{z_+}{t_+^m}. \quad (19)$$

Thus one obtains equation 12. Hereafter we shall use the ratio t_o^m / z_o and ξ interchangeably.

Experimental

Figure 1 shows a schematic of the concentration cell. A Nafion[®] 117 (equivalent weight = 1100, thickness 7 mils = 0.0178 cm) membrane was placed between the two chambers, suspended above solutions of lithium chloride of different compositions. At each end of the membrane there was a platinum electrode. The electrodes and the membrane were in contact with hydrogen and water vapor at ambient pressure. Sufficient

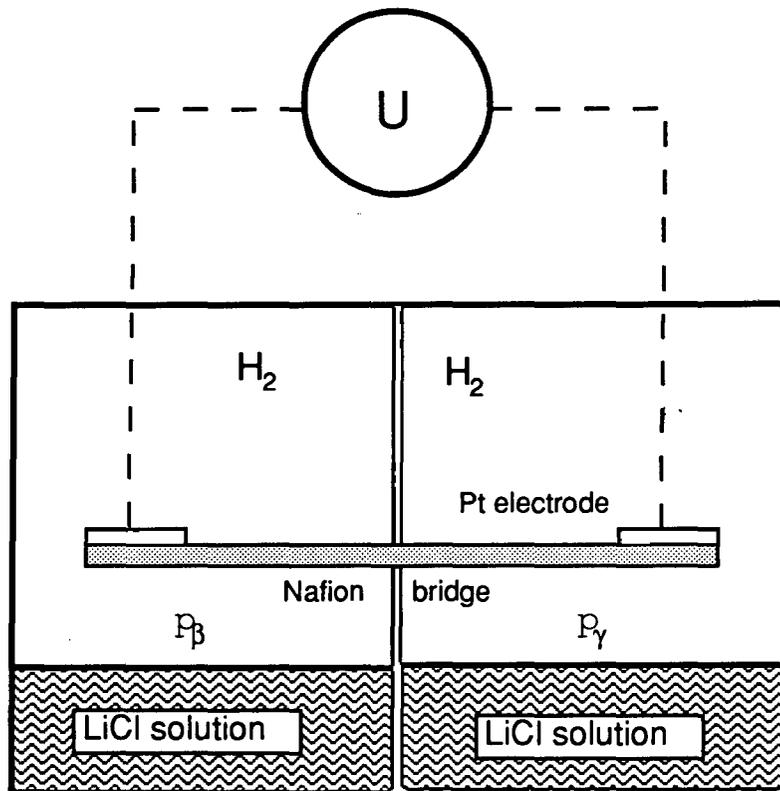


Figure 1. Schematic of concentration cell. The partial pressure of water is controlled with a lithium chloride solution. The LiCl concentration in the right side is maintained at $m=0.1$ mol/kg.

length from the barrier between the two chambers and the electrodes ensured that the activity of water in the membrane at each electrode was uniform and in equilibrium with the solution below it.

At equilibrium, the chemical potential of water is the same in the vapor phase and in the polymer electrolyte. Equation 15 becomes

$$\xi(a_o^\beta) = \frac{F}{RT} \left[\frac{d(\Delta\Phi)}{d \ln p_o^\beta/p_o^\gamma} \right] \quad (20)$$

If the potential in the form $F\Delta\Phi/RT$ is plotted against the logarithm of the activity of water, the slope of the line is equal to ξ .

The partial pressure of water in each half of the cell was controlled using a lithium chloride solution. Robinson and Stokes[10] and Gibbard and Scatchard[11] give the osmotic coefficient for a lithium chloride solution as a function of the concentration of the salt at various temperatures. The partial pressure of water is calculated from

$$\ln a_o = -\nu m M_o \phi \quad (21)$$

One side of the cell was filled with dilute lithium chloride solution, and the partial pressure of water remained constant for all experiments. Lithium chloride solutions of various concentrations were put in the other side. To minimize evaporation from the cell, hydrogen gas passed through a gas-washing bottle filled with a solution of identical composition to that in the corresponding chamber before entering the cell.

The membranes were pretreated with 1 M boiling sulfuric acid to convert to the hydrogen form, and thoroughly rinsed in deionized water.

The electrodes were fabricated from platinum mesh that was platinized with Hellige platinizing solution to ensure highly reversible reactions. The mesh was spot welded to platinum wire, which served as the electrical lead. The entire cell was placed in a water bath maintained at a constant temperature $\pm 0.1^\circ\text{C}$.

After the addition of a new solution of lithium chloride, the system was purged with nitrogen to remove oxygen from the cell, and then an equal flow of hydrogen was established to each side. The system was allowed to reach a quasi steady state; a slow relaxation of the cell occurs because of the gradient in chemical potential of water across the cell. The cell potential was measured with a Hewlett Packard model 3456A digital voltmeter, with an input resistance of greater than $10\text{ M}\Omega$. This was checked against a Keithly electrometer model 602 with an input impedance of greater than $14\text{ M}\Omega$ with identical results. The potential was measured over a period of two days, with sampling about every hour.

$\Delta\Phi$ is calculated from equation 13. The potential due to differences in hydrogen pressure, which is important at higher temperatures (see equation 3), was calculated assuming a total pressure of 1.01 bar and subtracting the partial pressure of water. The errors because of slight differences in the total pressure in the two chambers was believed to be small, but was not measured.

Results and Discussion

Figure 2 shows the measured potentials of the cell. Each line corresponds to a set of experiments with a different membrane at a given temperature. The error bars for run 4 represent the range of the meas-

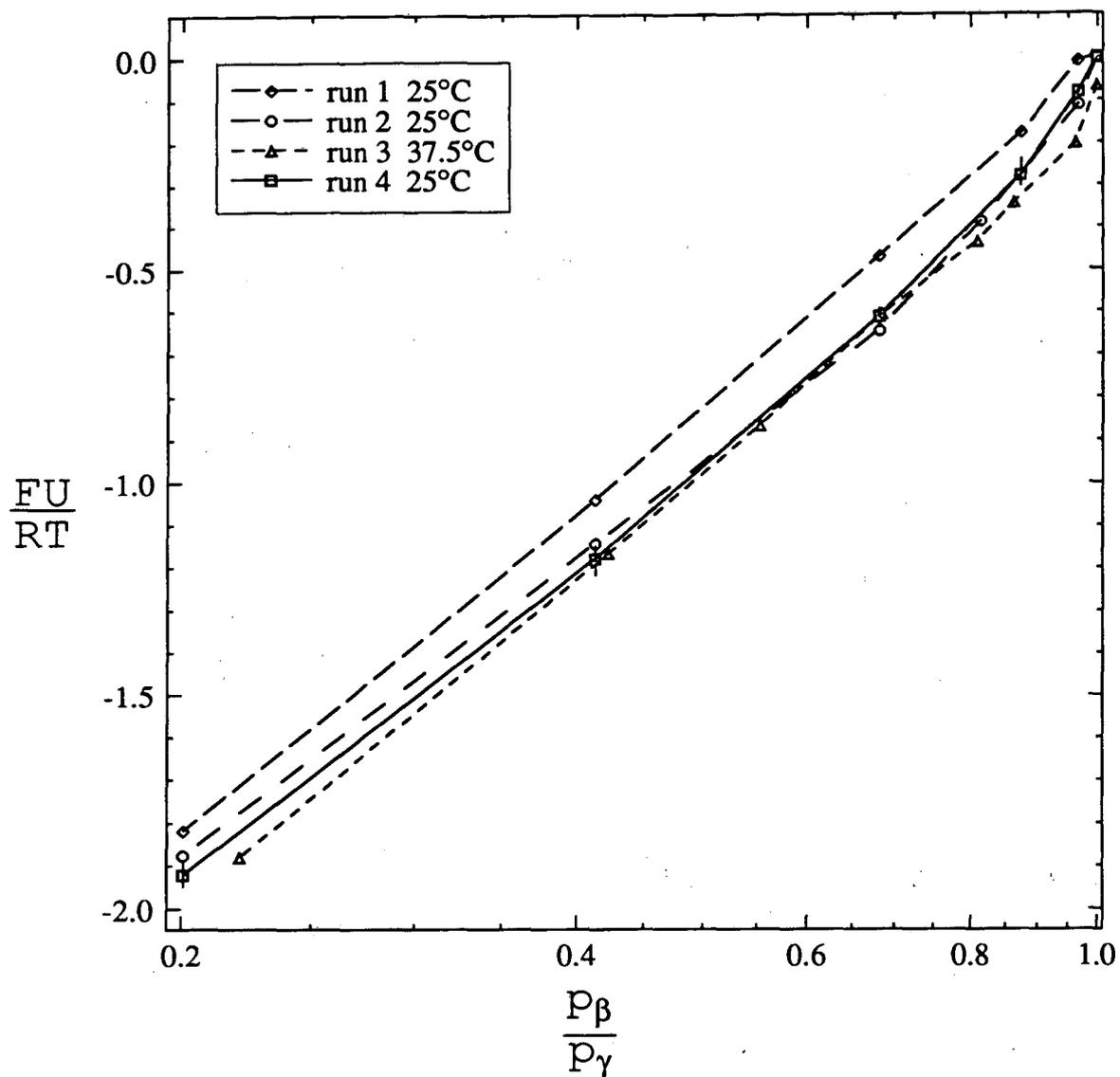


Figure 2. Measured cell potential. Each line represents a set of data with a different membrane. Data points are averaged over two days, sampling about every hour. Error bars are included for run 4 and represent the range of measured potentials.

ured potentials. The relaxation of the cell is thought to cause the variations in potential. Since a concentration gradient exists, water is transported across the membrane. The variations are larger than predicted and suggest that a perfect seal was not obtained. Nevertheless, this resulted in only a slow reduction in the magnitude of the cell potential with time.

The data were fitted with an analytic expression (as shown in figure 3), and that expression was differentiated rather than differentiating the data directly. Many functional forms were tried to fit the data, using a least-squares routine to minimize the total error. In order not to prejudice the results, we only required that the potential approach a constant as the activity of water approaches zero. A three-parameter polynomial and an exponential function gave the best results. The latter form used to interpret the data was

$$\frac{F\Delta\Phi}{RT} = A + B \exp\left[-Ca_o\right]. \quad (22)$$

The transport number of water, therefore, is

$$\frac{t_o^m}{z_o} = -BCa_o \exp\left[-Ca_o\right]. \quad (23)$$

The results are summarized in table 1. Leaks in the cell prevented making measurements at higher temperatures, although the transport number of water is not expected to vary dramatically with small changes in temperature. Runs 2 and 4 gave the most reproducible results. Improvements in the experimental technique are believed to have caused the differences between these two and the first run. The fit of data from

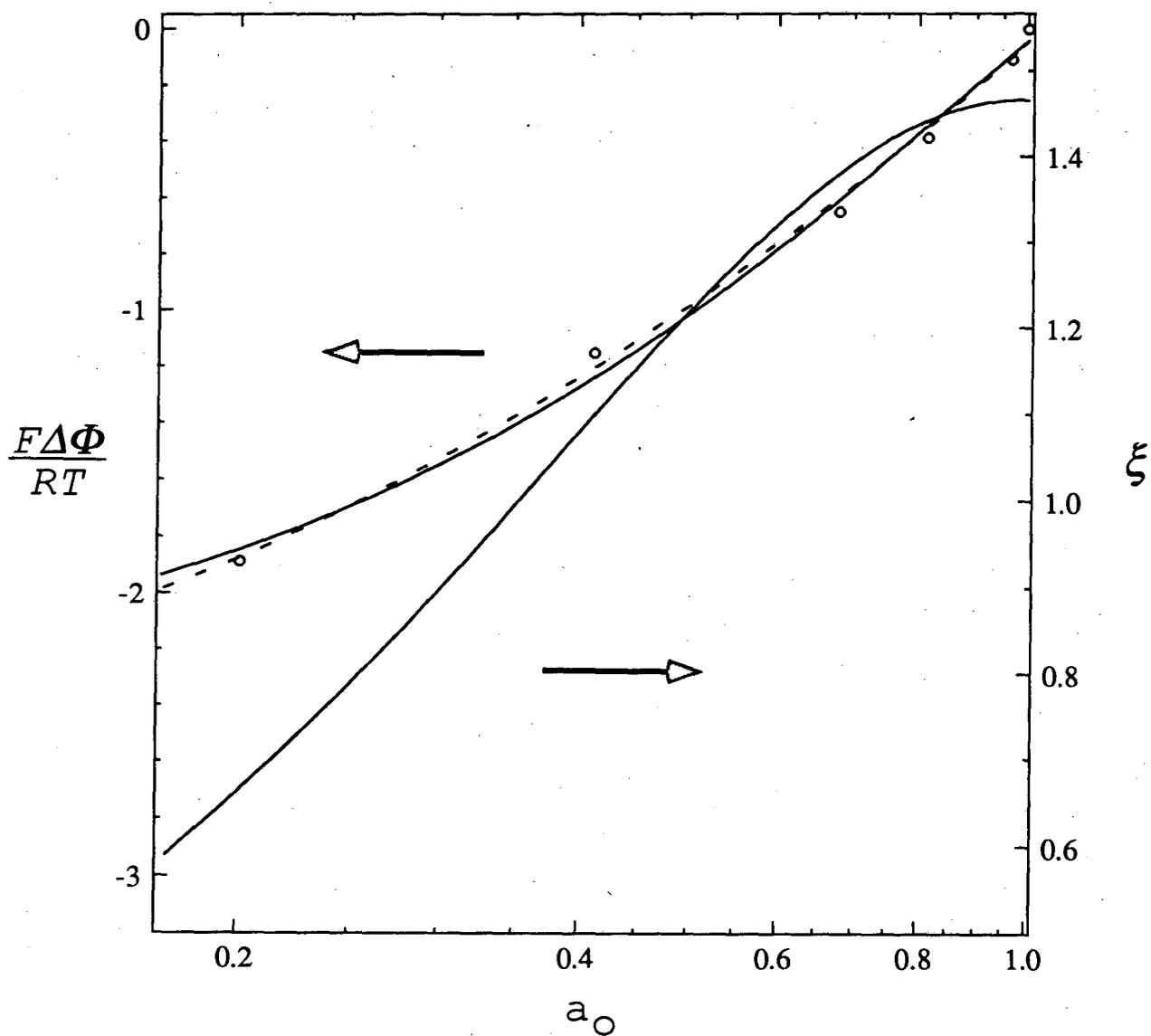


Figure 3. Experimental data for run 2, the fitted curves using equation 22 (solid line) and a second order polynomial (dashed line), and the transport number of water from equation 23.

Table 1.

run	°C	A	B	C
1	25.0	0.6165	-3.4377	1.717
2	25.0	1.3918	-3.9851	1.017
3	37.5	0.6994	-3.5519	1.454
4	25.0	1.1777	-3.9078	1.167

run 2 is shown in figure 3 for both a polynomial and an exponential fit. Since this is a derivative method, the greatest error is expected at the ends. As the concentration of water tends to zero, the transport number must also approach zero, which implies that the potential must become constant; but there is no similar asymptote as the membrane becomes fully hydrated.

To relate the transport number of water to the concentration of water in the membrane, instead of the activity of water, an adsorption isotherm is needed. This thermodynamic relationship was measured at 30°C by Zawodzinski et al.[12]. In the absence of other data, this relationship was assumed to hold at other temperatures. Figure 4 shows the results at 25°C of the present analysis; the theoretical maximum value, which is discussed below, and other data available in the literature.

At 25°C, the electroosmotic drag coefficient is about 1.4, decreases with lower water content at moderate hydration, and falls sharply as the membrane is fully dehydrated. The values are not in complete agreement with those measured at $\lambda=11$ [6]. The differences in pretreatment could cause the discrepancy. At low water contents, the value of ξ begins to drop sharply in accordance with the theoretical

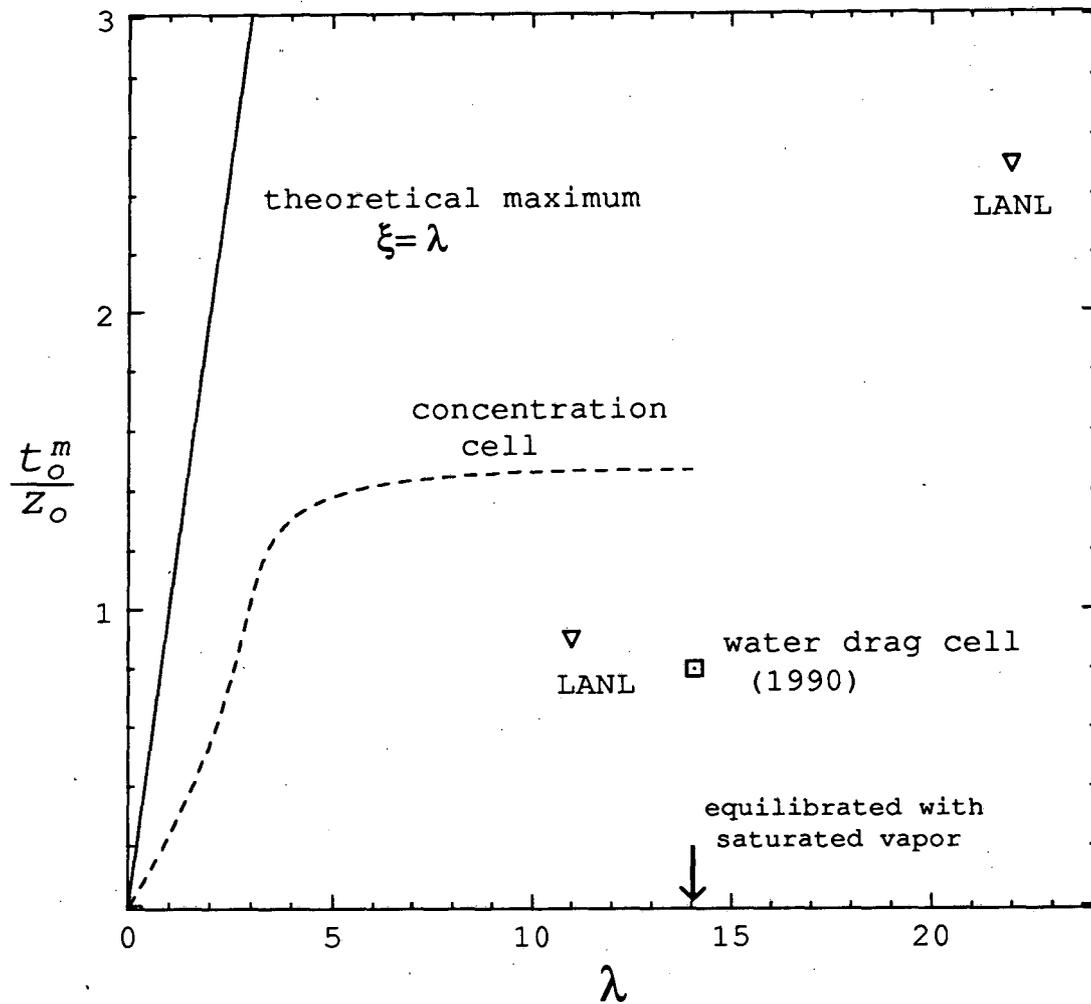


Figure 4. Transport number of water as a function of the concentration of water at 25°C. Dashed line represents the results of the present work. Triangles are values measured at Los Alamos National Laboratory [6], and the square is our unpublished result from the gas-phase flux measurements.

maximum. Physically we can picture that the first waters of hydration are tightly bound, and therefore the transport number is close to one. Only when the membrane is dehydrated does the transport number fall below one and approach zero. A membrane that has received identical pretreatment will have a different water content when exposed to liquid water as opposed to saturated water vapor. Thus, the concentration jumps from about $\lambda=14$ to $\lambda=22$ on figure 4, and we can also expect the transport properties to change abruptly as well.

The coupling between transport processes precludes one from obtaining any coefficient completely independently of the others. For an isothermal, isobaric system, with no chemical reactions, the equation of entropy production is given by

$$-\frac{1}{T} \sum_i \mathbf{v}_i \cdot \mathbf{d}_i, \quad (24)$$

which must be positive. Any experimental determination of the transport properties should be consistent with the second law of thermodynamics. Equation 4 is substituted into 24, and for our ternary system

$$(K_{+o} + K_{om}) v_o^2 - 2 K_{o+} v_o v_+ + (K_{o+} + K_{+m}) v_+^2 > 0. \quad (25)$$

Therefore, to ensure positive production of entropy

$$K_{om} + K_{o+} > 0,$$

$$K_{m+} + K_{o+} > 0,$$

and

$$K_{O+}^2 < (K_{Om} + K_{O+}) (K_{m+} + K_{O+}).$$

Finally we can conclude that

$$L_{++} > 0 \quad (26)$$

and

$$L_{oo} > 0. \quad (27)$$

These last two equations are equivalent to the requirement of the second law of thermodynamics that the conductivity and diffusivity be positive quantities.

The second law, however, makes no restriction on L_{O+} , or on the transport number of water. Although it is physically reasonable for the frictional coefficient to be positive, K_{ij} may be less than zero without violating the second law of thermodynamics. Robinson and Stokes [10] for example, discuss cation transference numbers that are negative for zinc halide systems. In these systems, the zinc is believed to be complexed with the halides to form a negative ion, which results in a negative transference number for the zinc cation. Thus, we can still argue that if the speciation is done properly we will not obtain negative transport numbers. If the speciation is correct for our system and the frictional coefficients are positive, one can conclude from equations 7 to 11 that

$$0 < \xi < \lambda \quad (28)$$

and

$$D_o > \frac{\kappa \xi}{F^2} \left(\lambda - \xi \right) \frac{d\mu_o}{dc_o}. \quad (29)$$

Equation 28 ensures that K_{om} is positive. A larger value of ξ would indicate that the interactions between water and the membrane were negative. The same result may be obtained from simple physical arguments. From the definition of ξ ,

$$\xi = \frac{N_o}{N_+} = \frac{c_o v_o}{c_+ v_+}, \quad (30)$$

for a small current density passed through the membrane and a uniform chemical potential of water, then equation 28 means that $v_o < v_+$. Violation of the inequality of equation 28 would imply that the membrane was accelerating the water rather than retarding it. The solid line in figure 4 is obtained from equation 28. Analyzing equation 29 requires data for the conductivity and diffusion coefficient of water and is not discussed further here.

The dependence of the transport number of water on concentration is needed in the modeling of fuel cells. Two assumptions that have been used are: the transport number is constant [13] and ξ proportional to λ [6]. We can integrate equation 14 and compare the predicted potential of the cell to the experimental measurements, as figure 5 shows for these two assumptions. The assumption that the transport number is proportional to λ predicts a much lower potential than was observed and is clearly not consistent with the experimental data at low water contents. Assuming the transport number of water is constant is also inconsistent with the data as well as the theoretical maximum derived earlier. The

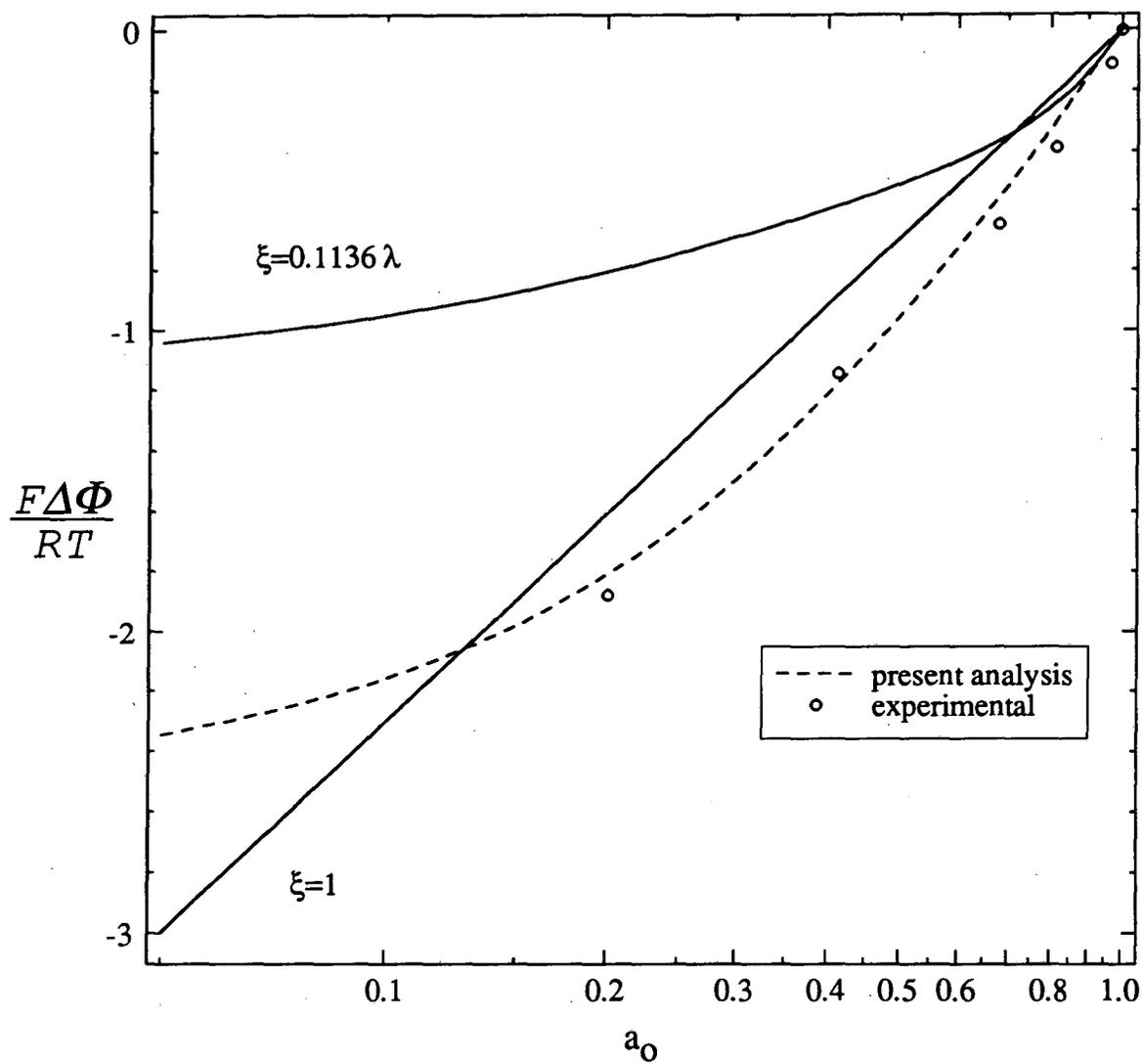


Figure 5. Comparison of the measured potential of the cell with predictions from two assumptions for variation of the transport number with concentration, as well as the present analysis.

data show that ξ must increase with the concentration of water. The results of the present analysis combine the best features of the two assumptions given above.

Acknowledgments

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List of Symbols

a_o	activity of water
A	constant in equation 22
B	constant in equation 22
c_i	concentration of species i , mol/l
C	constant in equation 22
d_i	driving force for transport of species i , N/m^3
D_o	mutual diffusion coefficient of water, cm^2/s
F	Faraday's constant, 96,487 C/eq
i	current density, A/cm^2
K_{ij}	frictional coefficient defined by equation (1), $J \cdot s/m^5$
L_{ij}	coefficient defined in equations (4 to 6), $m^5/J \cdot s$

m	molality, mol/kg
M_o	molar mass, kg/mol
n	number of species
N_i	molar flux of species i , moles/cm ² ·s
p_i	partial pressure or fugacity of species i , bar
R	universal gas constant, 8.3143 J/mol·K
t_i^m	transference number of species i
t_i^m/z_i	transport number of species i
T	temperature, K
v_i	velocity of species i , cm/s
x_i	mole fraction of species i
y	distance along membrane, cm
z_i	charge number of species i
ν	number of moles of ions into which a mole of electrolyte dissociates
λ	ratio of H ₂ O/R-SO ₃ H
κ	electrical conductivity, S/cm
μ_i	electrochemical potential of species i , J/mol
ϕ	osmotic coefficient
Φ	electrostatic potential, volts
ξ	electroosmotic coefficient

Subscripts

g	gas
m	membrane
o	water

s solid
+ hydrogen ion

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