LA-UR 91-2389

LA-UR--91-2389

DE91 016015

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE

Water Transport Properties of Fuel Cell Ionomers

AUTHOR(S)

Thomas A. Zawodzinski, Thomas Springer, John Davey,
Judith Valerio, and Shimshon Gottesfeld
(MEE-11)

SUBMITTED TO

The Electrochemical Society Proceedings of the Symposium
on Modeling of Batteries and Fuel Cells
October 13-18, 1991
Phoenix, AZ

AUG 0 , 1991

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

[illegible]

Water Transport Properties of Fuel Cell Ionomers

Thomas A. Zawodzinski Jr., Thomas E. Springer
John Davey, Judith Valerio, and Shimshon Gottesfeld
Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract

We will report transport parameters measured for several available perfluorosulfonate membranes. The water sorption characteristics, diffusion coefficient of water, electroosmotic drag, and conductivity will be compared for these materials. The intrinsic properties of the membranes will be the basis of our comparison. An objective look at transport parameters should enable us to compare membranes without the skewing effects of extensive features such as membrane thickness.

Introduction

The water transport properties of Nafion and related perfluorosulfonate ionomers are of paramount importance in the application of these materials as fuel cell electrolytes. In polymer electrolyte fuel cells (PEFC), the hydrated perfluorosulfonate ionomer membrane is the sole electrolyte in the fuel cell. The conductivity of these membranes generally decreases with decreasing water content. Thus, the maximum attainable amount of water in the membrane is desirable. During fuel cell operation, the local state of hydration of the membrane may vary due to electroosmotic drag of water by protons, the production of water at the fuel cell cathode, and diffusion of water associated with any concentration gradients.

Many reports of, for example, fuel cell performance have tended to compare membranes of different thicknesses. However, we have shown[1] that thickness is a crucial factor in determining performance due to the aforementioned competition between electroosmotic drag and back-diffusive fluxes in determining membrane water profiles. A comparison of measured values of relevant transport parameters for membranes allows us to assess the intrinsic properties of membranes, *i. e.*, those properties independent of thickness and determined by the detailed microstructure of the membrane. After all, it is in principle always possible to alter the thickness of the membrane, while the microstructure of the membrane is fixed by the chemical structure of and physical interactions among polymer chains and fixed ionic groups. Processing and pretreatment methods can also come into play, but the former is beyond the scope of the present work and the latter is kept constant in this work unless otherwise noted.

We discuss here a comparison of water uptake and transport properties of Nafion 117, Dow and Membrane C perfluorosulfonate ionomer membranes, hereafter referred to as N, D, and C respectively. Since most of our work to date has focused on Nafion 117, we use that membrane as the basis for comparison. The structure of Nafion is well known. Membrane C is 900 EW Nafion. The Dow samples used here are 800 EW and differ structurally from Nafion in that the material possesses a shorter sidechain off the PTFE backbone.

All the experimental techniques employed here have been discussed in detail in a recently submitted paper.[2]

Results and Discussion

1. Water Sorption

Water uptake by the membrane is essential to maximizing conductivity. We have measured the equilibrium amount of water taken up by the membranes immersed in liquid water and those exposed to vapor phase water of different activities. In addition, we have determined these characteristics as a function of pretreatment. In this report, we will concentrate on data obtained at 30° C, the conditions under which we have the most complete database.

During fuel cell operation, water is supplied to the membrane in the vapor phase, and thus we confine the comparison of uptake properties to uptake from the vapor phase. However, we first discuss briefly some characteristics of liquid water uptake by Nafion and the effect of changing the thermal history of the membrane on its equilibrium uptake of liquid water.

Equilibration with Liquid Water

The uptake of water by N membranes was studied for membranes prepared in several different ways. Each sample was cleaned and pretreated using our standard procedure described elsewhere.[2] Membrane samples were then dried using one of several protocols: (i) drying at room temperature under vacuum; (ii) treatment (i) followed by one hour under vacuum at 105° C; (iii) drying at room temperature over P_2O_5; (iv) treatment (iii) followed by one hour under vacuum at 105° C. Treatment (i) has been shown by Fyfe et al. to result in a membrane water content of 1 water per sulfonate (the symbol λ will henceforth be used to denote the number of water molecules per sulfonate in a polymer). Treatment (ii) causes the membrane to lose the last water molecule and completely dries the membrane. Treatment (iii) and (iv) also result in complete membrane dehydration.

The extent of rehydration of the membrane upon immersion in liquid water is strongly dependent upon the preceding drying method used. Membranes dried at room temperature imbibe roughly twice as much water as membranes exposed to elevated temperatures when both are exposed to liquid water at room temperature. The uptake upon immersion of membranes dried at 105° C is dependent on the temperature of the water in which the membrane is immersed, whereas the water content of membranes dried at room temperature is independent of the temperature of the immersion bath. These results are summarized in Table 1.

The dependence of the water uptake on dehydration conditions could have significant implications for the use of these membranes in fuel cells. In one common mode of fabrication of membrane electrode assemblies, the membrane and electrodes are hot-pressed together at 120° C. During this process, all water is lost from the membrane and the high temperature to which the membrane is exposed could cause incomplete rehydration. If less water can be taken up by the membrane thus treated, a decrease in the maximum attainable conductivity will occur since the conductivity depends roughly linearly on membrane water content (see below).

Equilibration with Water Vapor

Water supplied from the vapor phase is likely to be the principle mode of external hydration of the membrane in a PEFC. We have investigated, following Pushpa et al.[3], the sorption of water vapor of a controlled activity by Nafion and related membranes. Membrane samples were suspended above aqueous LiCl samples of various molalities. The relationship between water activity and LiCl concentration is known to the limit of LiCl solubility. Water activities in the range 0.14 - 1.0 can be accessed using LiCl solutions.

Figure 1a shows the isopiestic sorption curve for N at 30° C. The results are similar to those reported by Pushpa et al.[3] and Pineri and Scoubes[4], and indeed are quite typical of weakly cross-linked ion-exchangers, and, more generally, polymers with polar functionality. Over the entire range of water activity, the activity coefficient is greater than unity if one assumes as ideal a Raoult's Law relationship between water activity and membrane water content with λ =22 at unit activity. Two regions are discriminated: (i) a region of relatively little increase of water content with increasing water vapor activity (0.14-0.75) and (ii) a region of significantly greater increase of water content with increasing water activity. Region (i) corresponds to uptake of water of solvation of the ions in the membrane, while region (ii) corresponds to water which fills the pores and swells the polymer.

Note that the water content of the membrane in equilibrium with water vapor is not the same as the water content of a membrane in contact with liquid water. A difference in water uptake by polymers exposed to liquid versus saturated vapor phases has been observed for several polymer/solvent systems. The phenomenon was first reported in 1903 by Schroeder[5] and is thus called Schroeder's paradox. Two explanations for the phenomenon seem to us reasonable. The first, suggested by Schroeder, is that experimental difficulties (temperature gradients due to the heat of sorption, difficulty in obtaining truly saturated vapor phase, etc.) cause the observed behavior. In the present case, though the difference in sorption of water from the two phases is significantly larger than commonly observed for other polymer/penetrant systems, the isopiestic sorption curve (Figure 1a) is very steep as unit water activity is approached, and thus a small deviation from ideal conditions could lead to a large fluctuation in water content. A second explanation is that sorption from the vapor phase involves condensation of water on the strongly hydrophobic, teflon-like surface of the polymer, and thus is somewhat less favorable than the imbibition of liquid water.

The shape of the sorption isotherm for D membranes, shown in Figure 1b, is qualitatively similar to that of N, while that for C is quantitatively essentially identical to N. Quantitatively, D takes up similar amounts of water on a per equivalent basis to N at low water activities (less than 0.75). (Of course, on a weight % basis, both C and D take up significantly more water than N.) At higher water activity, D exhibits much higher water uptake in this region. As for Nafion, both C and D take up more water from the liquid than from the vapor phase. In addition to the information directly obtained form the sorption measurements, we have exploited the isopiestic equilibration technique as a simple and convenient method of controlling membrane humidification during the determination of a variety of physical properties of the ionomer such as conductivity and diffusion coefficient. The sorption isotherm has also been used in our modeling effort.

2. Diffusion Coefficient of Water

We have determined self- (or intra-) diffusion coefficients of water in membranes of various water contents using NMR diffusion and imaging methods. We can estimate a quantity approximating a mutual (or inter-) diffusion coefficient of water in these membranes by combining the self-diffusion coefficient information with the information obtained on the variation of water activity coefficients from the equilibrium sorption isotherms.

We have reported elsewhere[6] the ^1H diffusion coefficients at 30° C for N membranes in various states of hydration. These were measured using the pulsed field gradient spin-echo (PGSE) method. We have also indicated the plausibility of identifying the measured ^1H diffusion coefficient with the intra-diffusion coefficient of water in N. The diffusion coefficients thus obtained plotted, versus λ, are shown in Fig. 2. The point for the highest water content was measured using a method combining the PGSE method with imaging of a membrane immersed in liquid water. These methods are described in more detailed elsewhere. Self-diffusion coefficients vary by more than an order of magnitude over the range of water content λ=2 to 22. The self-diffusion coefficients obtained are smaller than the self-diffusion coefficient of water in water (2.5 x 10^{-6} cm^2/sec at 25° C). This is expected due at least to the increase of tortuosity of the diffusion path in the membrane. Sidechain intrusions into the ion-lined pores and the hydrophobic backbone restrict the diffusive motion of water molecules.

Self-diffusion coefficients are obtained in the absence of a concentration gradient. Diffusion in a membrane across which a concentration grad[illegible] xists, the description of which is the motivating factor behind our diffusion co[illegible] etermination, is driven by an activity gradient. In a two-component system with a [illegible] ation gradient, it is generally necessary to describe the inter-diffusion of the com[illegible] s. In the present case, the negligible mobility of the polymer matrix allows us to approximate the inter-diffusion coefficient as the intra-diffusion coefficient corrected for the variation of the activity coefficient with concentration. If we wish to use Fick's law to calculate water flux, we must include the variation of the activity coefficient in the effective diffusion coefficient. This results in our case in a much smaller variation in the value of the diffusion coefficient with membrane water content. Furthermore, the value obtained after correction is similar to that reported by Yeo and Eisenberg[7] (2 x 10^{-6} cm^2/sec at 30° C) which was calculated from the time dependence of water uptake by the membrane, an experiment which measures inter-diffusion coefficients.

We have only recently succeeded in obtaining some data on the diffusion coefficients of C and D. The diffusion coefficients of water in these materials are similar to that observed for the same membrane water content in N.

3. Electroosmotic Drag

The electroosmotic drag coefficient, the number of water molecules per proton carried across a membrane as current is passed under conditions of no concentration gradient, has been determined for the various membranes at 30° C. Since the conditions of the experiment require that the membrane be kept in direct contact with liquid water, the range of water contents for which this parameter can be measured is quite limited. The results obtained are summarized in Table 2. For a fully hydrated N membrane, 2.5 water molecules are dragged across the membrane per H+ transported, while for a partially hydrated membrane ($\lambda = 11$), the drag is only 0.9. Thus a substantial decrease in the drag is observed as the water content of the membrane is lowered.

The electroosmotic drag under conditions of full hydration measured for membranes C and D is also shown in Table 2. There is a wide range of variability observed for C, but on the whole, the drag in this membrane is similar to (or somewhat greater than) that observed in N. For the D membrane, substantially lower drag relative to N is observed. This could give this material a substantial advantage in terms of water management in fuel cells (see below and reference 1).

4. Conductivity

We have determined the conductivity of the membranes when immersed and partially hydrated. For immersed membranes, the temperature dependence of the conductivity was also probed. In Fig. 3, the conductivity of N at 30° C is plotted versus the membrane water content. The conductivity decreases roughly linearly with water content. The value of the conductivity at $\lambda = 14$, 0.07 S/cm, agrees with the value previously reported by Rieke *et al.*[8] An Arrhenius plot illustrating the temperature dependence of the conductivity over the temperature range 25-90 C of immersed N, D, and C samples is shown in Fig. 4. Note that the water content of the membranes is constant over this temperature range. The conductivity of membranes C, D is only marginally improved (10-20%) over that of Nafion. Somewhat more improvement might be expected based on the lower equivalent weights of C and D. The slight difference actually observed is particularly notable for D, which has much higher water content under these conditions than either of its competitors. The conductivity of C and D under partial hydration conditions is currently under investigation and will be presented in the oral delivery of this paper.

Conclusions

In spite of reported differences in performance of fuel cells using these membranes, their uptake and transport properties reported here are fairly similar. The difference in performance can be explained in large part by the thickness of the readily available form of the membrane (D is typically thinner than C, and both are thinner than Nafion 117; most of the difference between fuel cells based on D and N is erased if a 2-mil Nafion membrane is used). If water management in the fuel cell were not a problem, the advantage of a thinner membrane would simply lie in the linear variation of the resistance contribution of the membrane to the observed overall fuel cell resistance. A nonlinear advantage is gained by thinner membranes due to the nature of the fluxes trading off to produce the observed water profile. The Dow membrane does seem to have better electroosmotic drag characteristics, and thus may contribute to improved water management. We hope that the combination of relevant experimental measurements with modeling will provide further insight into water management.

References

1. T. Springer, T. A. Zawodzinski Jr., and S. Gottesfeld, in press, *J. Electrochem. Soc.*

2. T. A. Zawodzinski Jr., C. Derouin, S. Radzinski, R. J. Sherman, T. Springer, and S. Gottesfeld, submitted to *J. Electrochem Soc.*

3. K.K. Pushpa, D. Nandan, R. M. Iyer, *J. Chem. Soc. Faraday I*, **84**, 2047 (1988).

4. M. Escoubes, M. Pineri, in *Structure and Properties of Ionomers*, M. Pineri and A. Eisenberg, eds., Reidel, Dordrecht, 1987, p. 341.

5. P. Schroeder, *Z. Phys. Chem.* **45**, 75 (1903).

6. T. A. Zawodzinski Jr., M. Neeman, L. Sillerud, and S. Gottesfeld, in press, *J. Phys. Chem.*

7. S. C. Yeo, A. Eisenberg, *J. Apple. Poly. Sci.* **21**, 875 (1977).

8. P. C. Rieke, N. E. Vanderborgh, *J. Mem. Sci.* **32**, 313 (1987).

Table 1

Water Uptake of Nafion® 117 Immersed in Liquid Water

	Water Uptake (H_2O/equivalent)			
	Drying Method			
Water Temperature	1	2	3	4
27° C	21.3	11.3	21.0	12
65° C	21.0	15.2	----	----
80° C	20.7	15.9	----	----

1) Dried under vacuum, Room Temperature

2) Dried under vacuum, 105° C

3) Dried over P_2O_5, Room Temperature

4) Same as (3), followed by 1 hour at 105° C

Table 2

Water Drag by Protonic Current

Membrane	Measured Drag $H_2O/H+$, 30° C
Nafion® 117, 22 H_2O/SO_3H	2.5 - 2.9
Nafion® 117, 11 H_2O/SO_3H	0.9
Membrane C	2.6 - 4.[illegible]
Dow Membrane	1.5

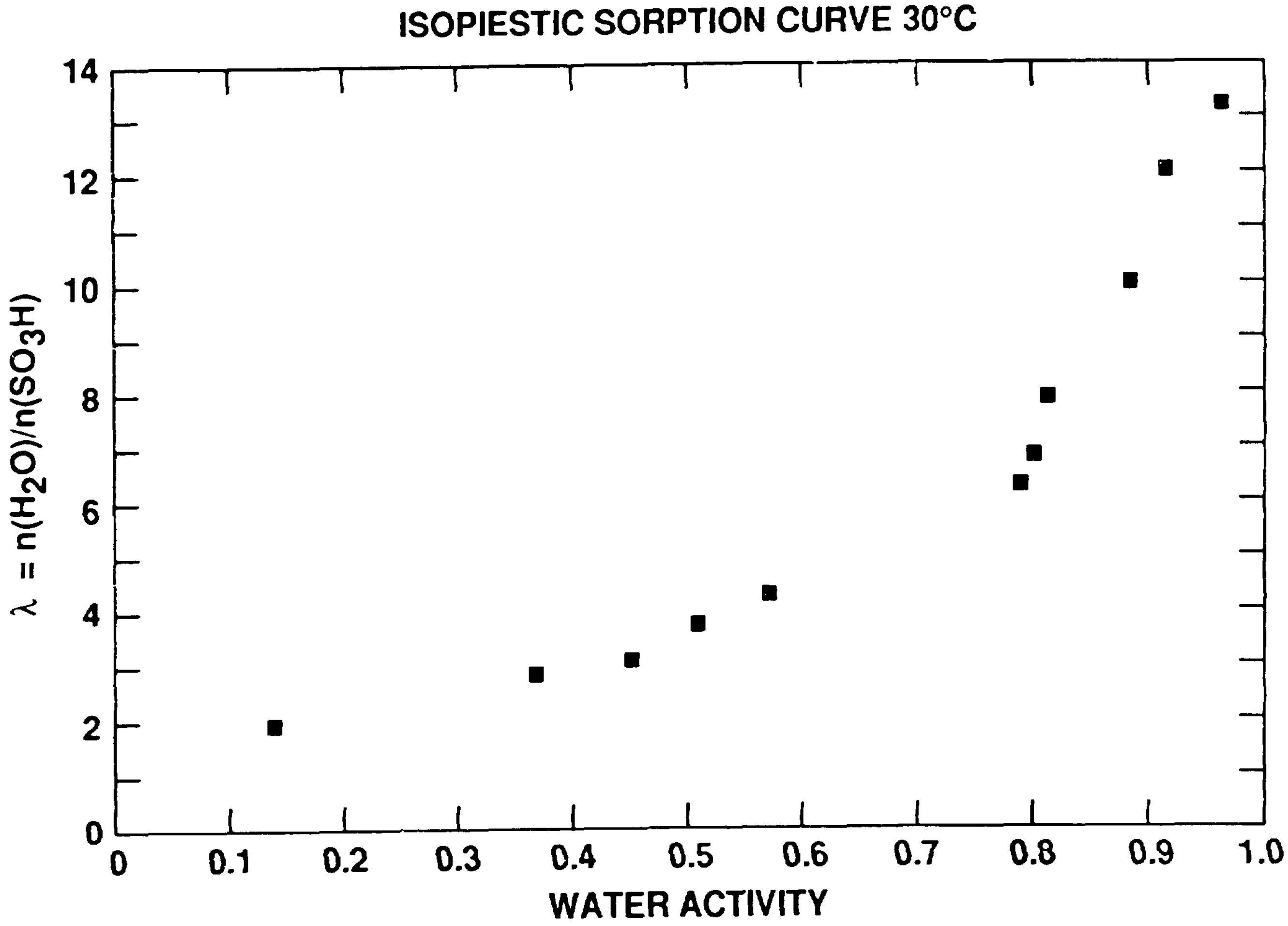

Figure 1a. Isopiestic sorption curve for water in Nafion 117.

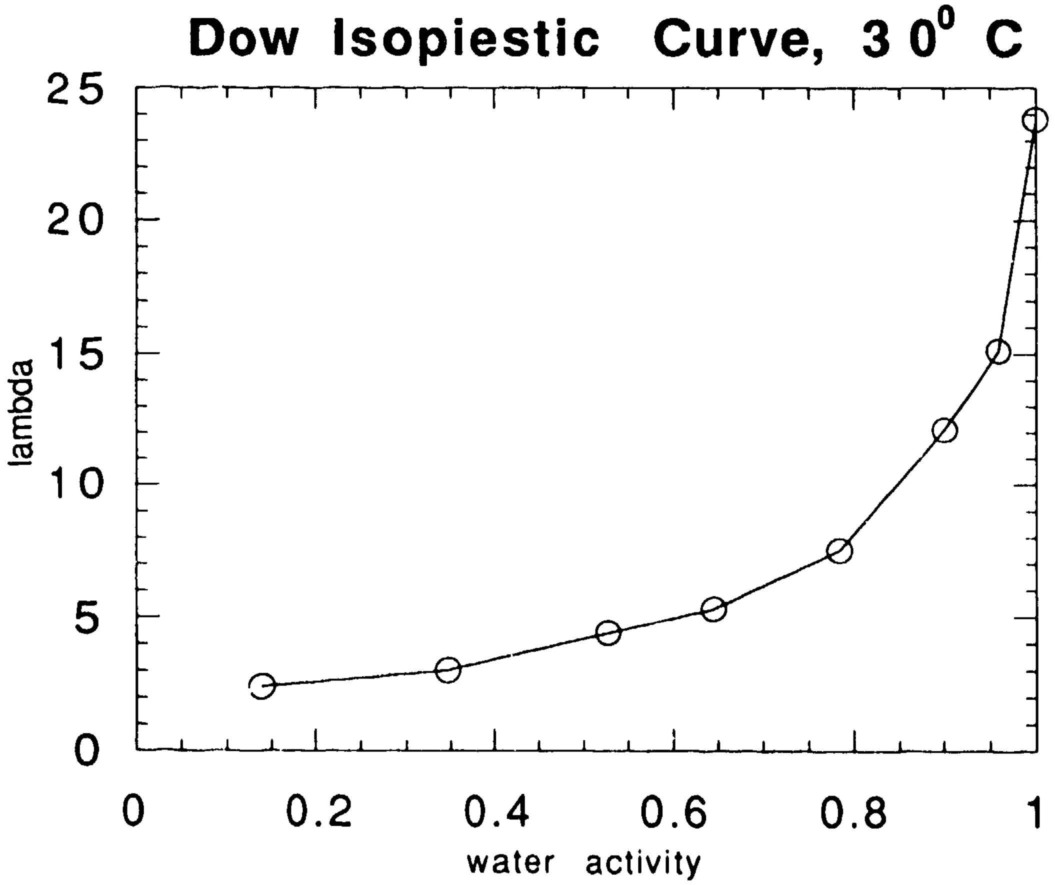

Figure 1b. Isopiestic sorption curve for water in Dow membrane.

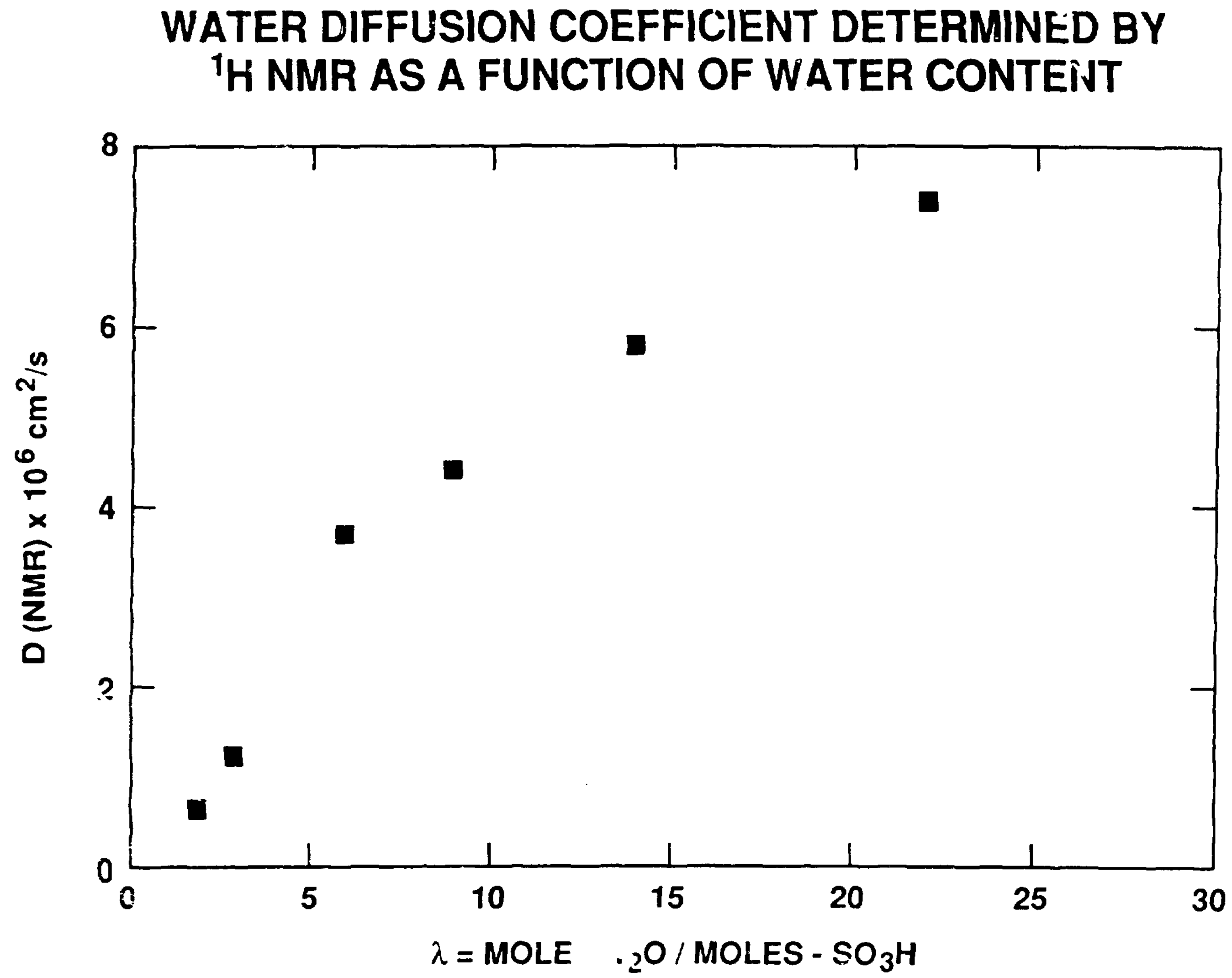

Figure 2. Diffusion coefficient of water in Nafion 117 at 30° C as a function of extent of membrane hydration.

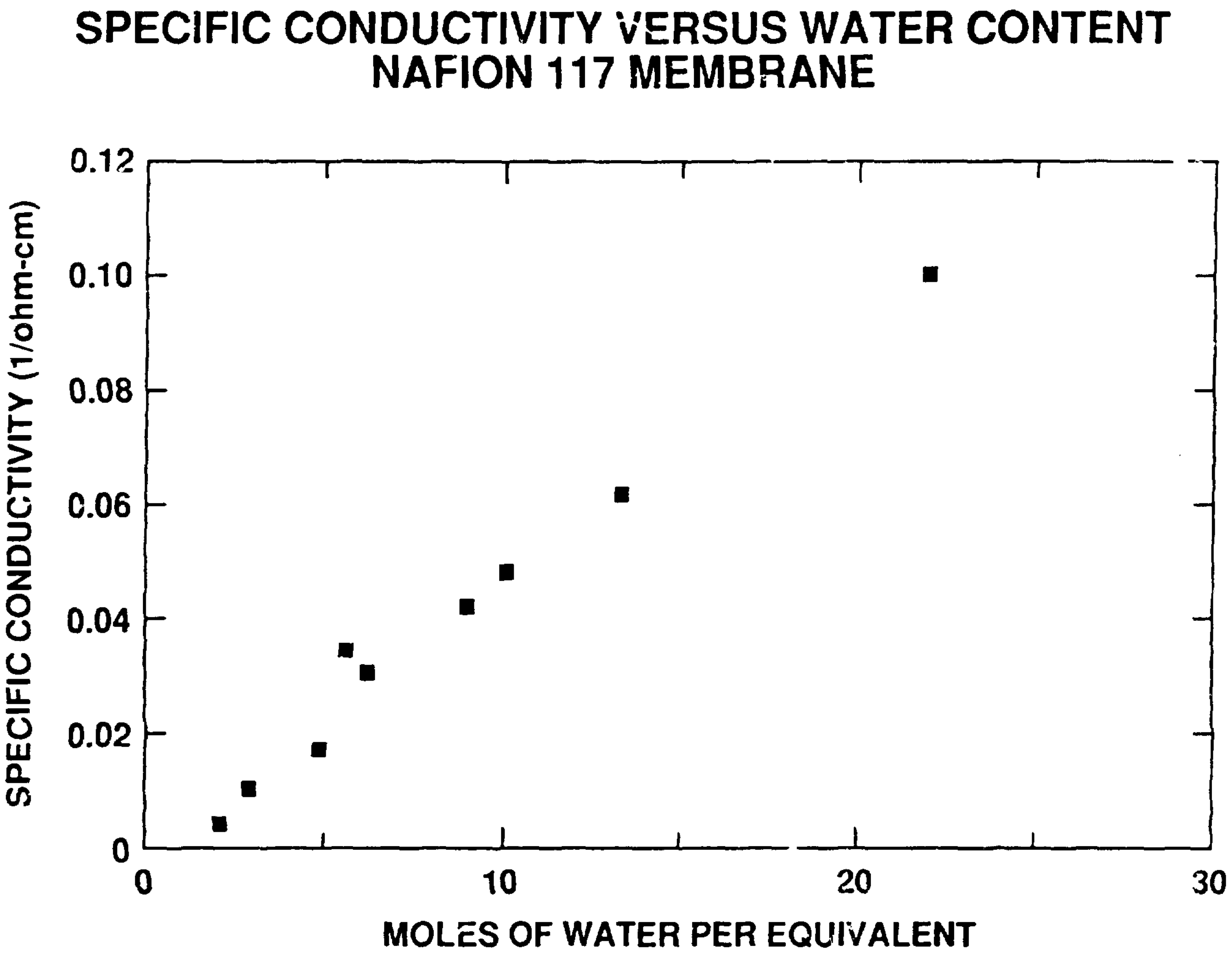

Figure 3. Conductivity of Nafion 117 membrane as a function of state of membrane hydration.

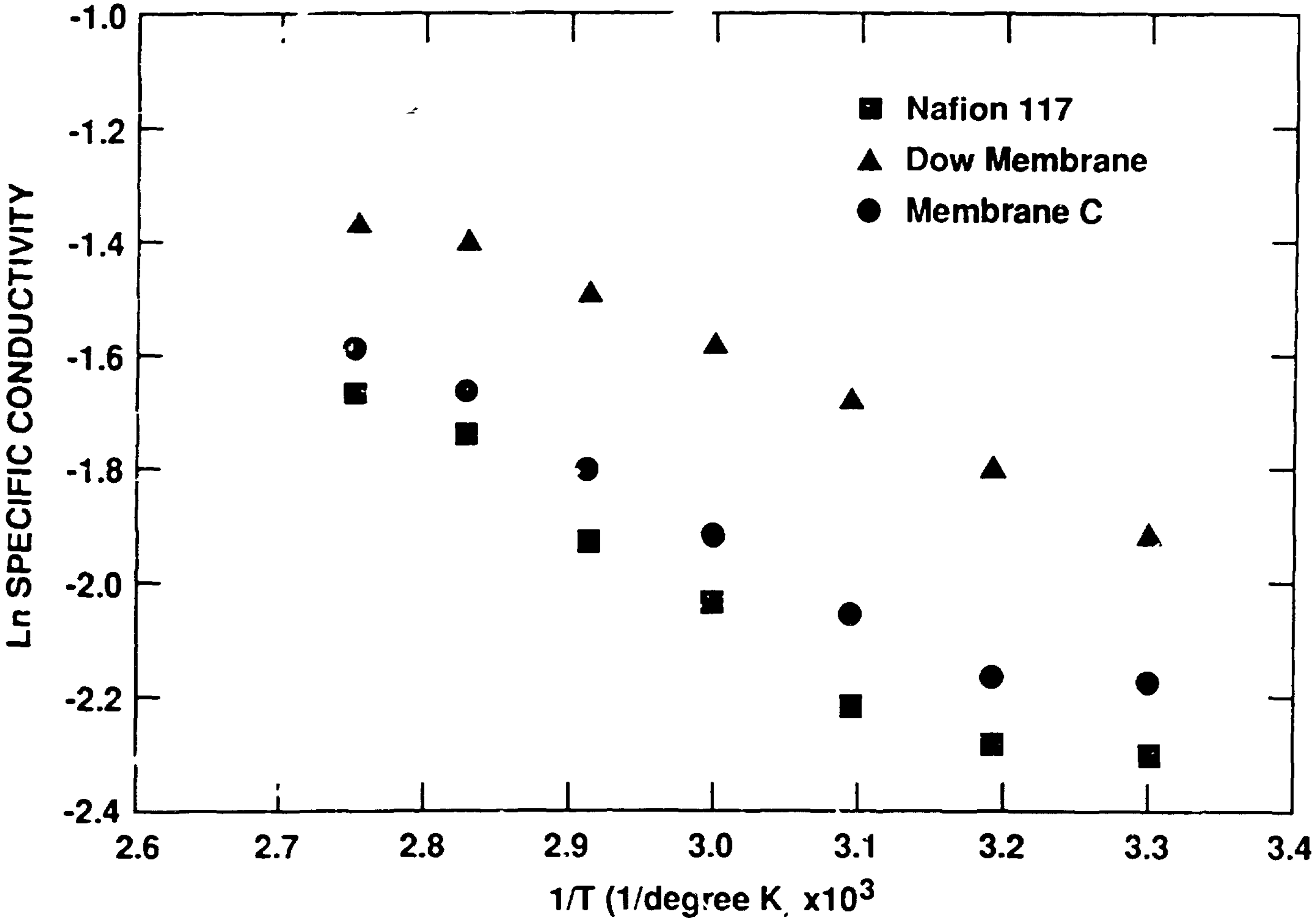

Figure 4. Conductivity of Nafion 117, Dow and Membrane C immersed in water as a function of temperature.