Water-Sorption and Transport Properties of Nafion 117 H

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SYNOPSIS

The density and dimensional changes of Nafion 117 H have been measured as a function of the water content. Swelling of Nafion commences at N ($\equiv$ mol ratio water to hydrogen ion) $\sim$ 1.9. Some anisotropy of dimensional changes was observed. Water-sorption isotherms obey Henry's Law with a nonzero intercept indicating some water retention. The diffusion coefficient of water in Nafion and the electrical conductivity of Nafion are strong functions of the water content. The latter is exploited for the development of a humidity sensor.

INTRODUCTION

The materials known as perfluorinated ionomers have applications in the electrochemical industry[1] and in the development of fuel cells[2,3] and electrochemical sensors.[4,5] These applications have resulted from the high degree of chemical inertness, good ionic conductivity, and the availability of the materials as thin film.

A well-known example of the materials is Nafion (DuPont), which is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether. The material comprises a chemically inert hydrophobic "backbone" ($-CF_2-CF_2-$) with hydrophilic ionic groups ($-SO_3^-H^+$), which permit water sorption and ionic conductivity.

As a corollary to the development of electrochemical sensors utilizing this material,[4] measurements of water sorption, density, and dimensional changes, the diffusion coefficient of water and the electrical conductivity of Nafion H 117 have been made. This article reports the results of these measurements and describes a humidity sensor exploiting the strong dependency of the electrical conductivity of Nafion upon the water concentration.

EXPERIMENTAL

Material

Nafion H 117 (DuPont) was pretreated with boiling nitric acid solution and boiling water to remove impurities. A sample was dehydrated under vacuum (0.01–1 Pa) at 150°C for ~24 h. The material so treated is referred to as dry. The equivalent weight was determined to be 1098 ± 4.1 by back titration of hydrogen ion following exchange from the Nafion with 2*M* sodium chloride solution.

Density and Thickness

The density of the Nafion was determined by the hydrostatic weighing method,[6,7] utilizing distilled water for immersion of the sample. To eliminate effects due to progressive water sorption by the Nafion, mass/time curves were extrapolated to time zero, at which the specimen was immersed. Nafion specimens of various water contents were obtained by drying the specimen as described above: immersion in water followed by partial redrying.

Thickness measurements of the Nafion were made simultaneously with multiple layers of the Nafion using a micrometer. Typically, three measurements were made at different locations.

Water Sorption

The sorption of water by Nafion in the temperature range 25–100°C was determined by three methods:

1. By continuous measurement of the weight of a sample of Nafion in contact with a known water-vapor pressure using the Cahn microbalance. The sample was suspended inside a quartz vessel situated inside a furnace and dried as noted earlier. The temperature was

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Journal of Applied Polymer Science, Vol. 50, 1445–1452 (1993)
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lowered to the desired value and the Nafion exposed to progressive increments of water-vapor pressure to the maximum attainable in the equipment, $P^0_{H_2O} = 3.2$ kPa (23.8 mmHg) at 25°C. The sample of Nafion was subsequently exposed to progressive decrements of water-vapor pressure.

2. By measuring the weight increases of a dry sample of Nafion after isopiestic equilibrium[8] with lithium chloride solutions of known concentration and water activity.[9]
3. By measuring the weight increase of a dry sample of Nafion after immersion in pure water. Additional data were obtained by equilibration of a sample of water-saturated Nafion, with air of known humidity utilizing the equipment constructed for measurement of the electrical conductivity (see below).

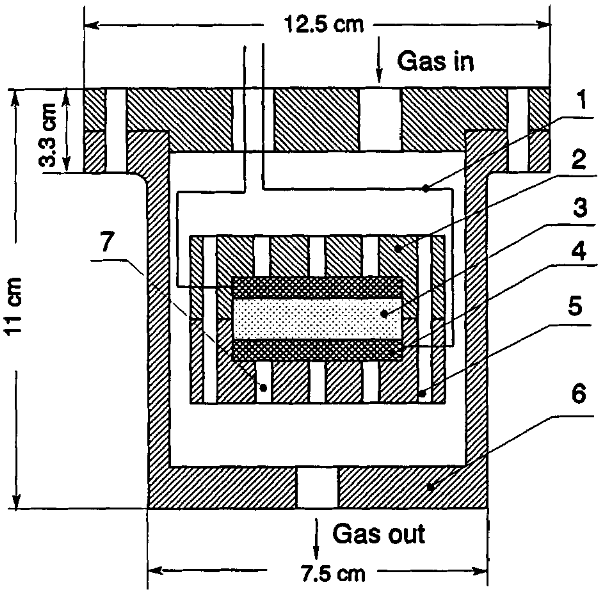

Figure 1 Assembly for electrical conductivity measurements: (1) lead wire; (2) plexiglass flanges; (3) Nafion disc; (4) platinum gauze; (5) clamping bolts; (6) plexiglass vessel; (7) gas access ports.

The electrical conductivity of Nafion was measured with a YSI model 31A conductance bridge (Yellow Spring Instrument Co., Yellow Springs, OH). Measurements were made at 50 Hz and 1 kHz in the temperature range 23–90°C.

A chemical procedure was used to deposit platinum metal in the surface of a Nafion disc.[10] A Nafion disk (~3 cm diameter) was immersed in a solution of 0.01*M* tetramine platinum chloride hydrate for 1 h and washed with distilled water, followed by immersion in a solution of sodium boron hydride (3 g/L). After deposition of the platinum metal, the disc was boiled in dilute nitric acid (1*M*) to remove Na^+ ions and finally boiled in distilled water. To eliminate edge effects, a disc of the plated Nafion (2.5 cm) was cut from the larger disc. The depth of platnium deposition within the Nafion was examined by energy dispersive X-ray analysis on a scanning electron microscope.

The plated Nafion disc was clamped between platnium gauzes (100 mesh) using plexiglass flanges with gas access ports (see Fig. 1). Platinum wires were welded to the gauzes for connection to the conductivity bridge. The test assembly was mounted in a small plexiglass vessel through which air of known humidity was passed. The plexiglass vessel containing the Nafion test assembly was mounted in a temperature-controlled oven (see Fig. 2). Dry air from a cylinder was partially humidified as shown in Figure 2.

Additional measurements were made with a potentiostat programmed to apply a square wave voltage (±2.0 V). The current was sampled just prior to the step change of voltage.

Density and Dimension Changes

The results of density measurements and fractional thickness change as a function of the water content of Nafion are shown in Figures 3 and 4, respectively. Clearly, the density progressively decreases and the material swells as water is absorbed.

Assuming additivity of the volumes of dry Nafion and water in the wet Nafion, the following relation for the density of the wet Nafion ρ may be derived[7]:

$$\rho = \frac{\rho_{H_2O}\rho_0(1 + f_m)}{\rho_{H_2O} + f_m\rho_0} \qquad (1)$$

where ρ_{H_2O} and ρ_0 are the densities of water and dry Nafion, respectively, and f_m is the mass ratio of water to Nafion. The water content of the Nafion may also be expressed in terms of the mol ratio of water to hydrogen ions, N:

$$N \equiv \frac{n_{H_2O}}{n_{H^+}} = \frac{m_{H_2O}/18}{m_0/1098} = 61.0 f_m \qquad (2)$$

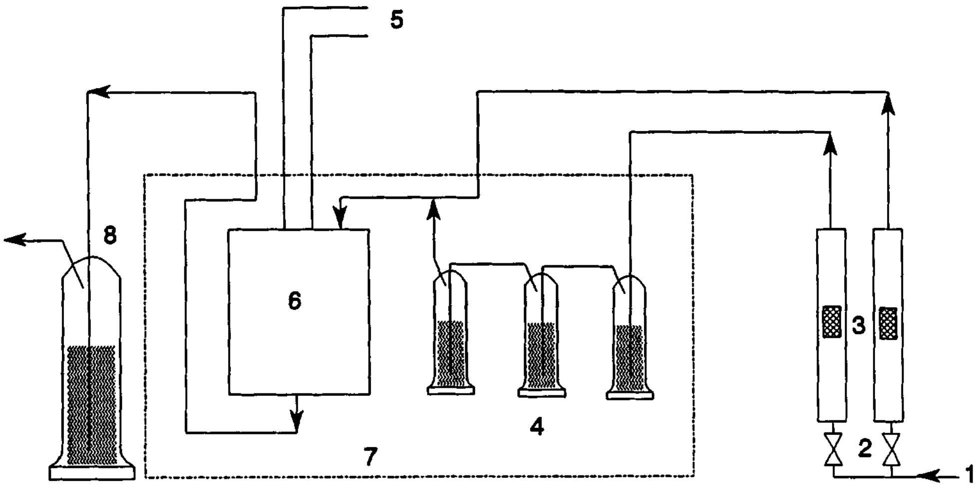

Figure 2 Humidity and temperature control system for conductivity measurements: (1) dry gas from cylinder; (2) flow control valves; (3) rotometers; (4) humidifiers in oven; (5) lead wires; (6) assembly of Figure 1; (7) oven; (8) flow indicator.

where m_0 is the mass of dry Nafion of equivalent weight equal to 1098 as noted earlier.

A plot of eq. (1) is included in Figure 3 with $\rho_0 = 2.05$ g/cm^3. It is evident that the assumption of additivity of the volumes of dry Nafion and water is valid within the limits of experimental error.

The density of Nafion may also be written in terms of the fractional diameter, δ_d, and thickness, δ_l, changes:

$$\rho = \frac{\rho_0(1 + f_m)}{(1 + \delta_d)^2(1 + \delta_l)} \quad (3)$$

where $\delta_d \equiv (d - d_0)/d_0$ and $\delta_l \equiv (l - l_0)/l_0$, and d, l, d_0, and l_0 are the diameter and thickness of the Nafion at the water content, f_m, and the diameter and thickness of the dry Nafion disc, respectively. Equation (3) in conjunction with the measurements of δ_l (Fig. 4) permit estimation of δ_d; the results of these calculations are included in Figure 4. It is seen that the fractional diameter change is somewhat less than the fractional thickness change. The ratio $\delta_d/\delta_l = 0.564 \pm 0.040$.

Water-sorption Isotherms

Water-sorption data, obtained by the methods described, are presented in Figure 5 as plots of the mol ratio $N = n_{H_2O}/n_{H^+}$ in the Nafion vs. the water-pressure ratio, p/P^0, where p and P^0 are the water-

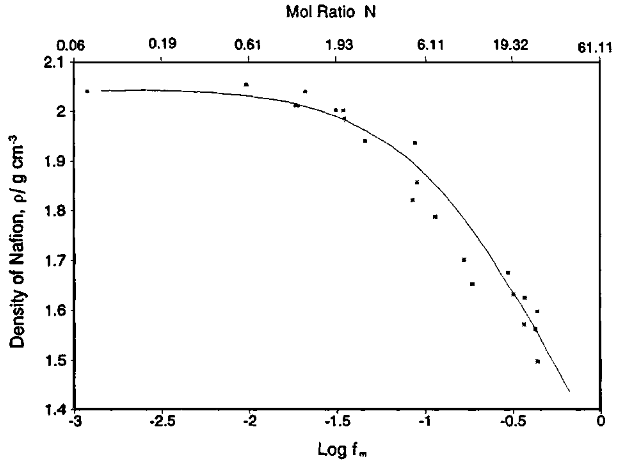

Figure 3 Density of Nafion as function of water content: (X) experimental data; (–) eq. (1).

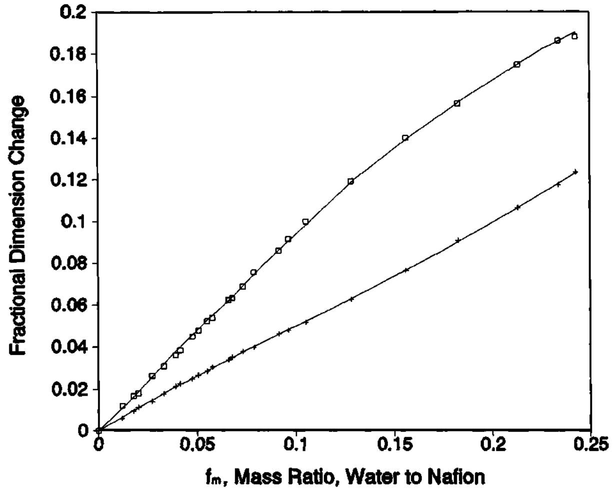

Figure 4 Fractional dimension changes of Nafion as function of water content: (□) thickness; (+) diameter.

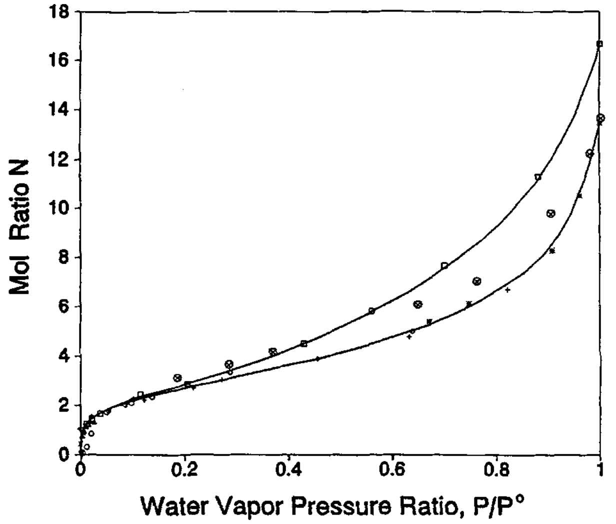

Figure 5 Water-sorption isotherms of Nafion 117 H: (+) 25°C; (O) 50°C; (x) 100°C; (⊕) 25°C, Ref. 11.

vapor pressure and saturation water-vapor pressure at the temperature of the experiment, respectively. Data obtained by the three methods showed good agreement. A small hysteresis effect was noted; for a given water pressure ratio, a slightly higher equilibrium water content of the Nafion was observed from a desorption experiment. This was particularly noticeable at very low water pressure ratio ($p/P^0 < \sim 0.05$). However, data from the microbalance at these levels of water activity were obscured by oscillations of the balance. Data obtained by sorption or desorption are not distinguished in Figure 5. Data obtained by Pushpa et al.[11] at 25°C are included in Figure 5; these data differ slightly from those obtained in this investigation.

It is clear from Figure 5 that the water content of Nafion increases with increasing water-pressure ratio of the gas phase and with increasing temperature. At unit water-pressure ratio, $N = 13.5$, 16.7, and 23.1 at 25, 50, and 100°C, respectively.

Plots of p vs. N show that Henry's Law

$$p = H(N - N_0) \qquad (4)$$

is obeyed over a wide range with a nonzero intercept, N_0. This indicates that some water is retained relative to the "dried" Nafion. The same phenomenon was observed by Duplessix et al.,[12] from studies with Nafion H 120. Values for the constants H and N_0 as a function of temperature are summarized in Table I. It is evident that the amount of retained water decreases with increasing temperature.

According to thermodynamic principles,[13]

Table I Sorption of Water by Nafion H: Henry's Law Constants and Retained Water

Temperature (°C)	H (kPa)	N_0 (mol H_2O [mol H]$^{-1}$)
25	0.592	1.58
50	1.430	1.26
100	5.800	0.87
20	0.368	2.20 (Ref. 12)

$$\frac{\partial \ln H}{\partial(1/T)} = -\left[\frac{h_{(H_2O,g)} - h_{(H_2O,\mathrm{Naf})}}{R}\right] \qquad (5)$$

where h_{H_2O} represents the molar enthalpy of water in the gas phase and Nafion as indicated. Plots of ln H vs. $1/T$ obtained in this work and from the data of Escombes and Pineri[14] are shown in Figure 6. The two sets of data show good linearity but different slopes, corresponding to $\Delta h_{H_2O} = 28.2$ and 39.8 kJ/mol, respectively. Escombes and Pineri, from their microcalorimetric studies, found Δh to be a function of N, in the range 16.7 to 52.3 kJ/mol, with the higher values at low concentrations of water ($N < \sim 4$). The average values noted above, determined using eq. (5), fall within this range. The low values of $\Delta h_{(H_2O)}$ relative to that for the $H_2O_{(g)} \rightleftarrows H_2O_{(l)}$ equilibrium have been interpreted by Escombes and Pineri as due to an endothermic contribution corresponding to the expansion of the clusters inside the organic phase. This expansion is evident from Figure 3.

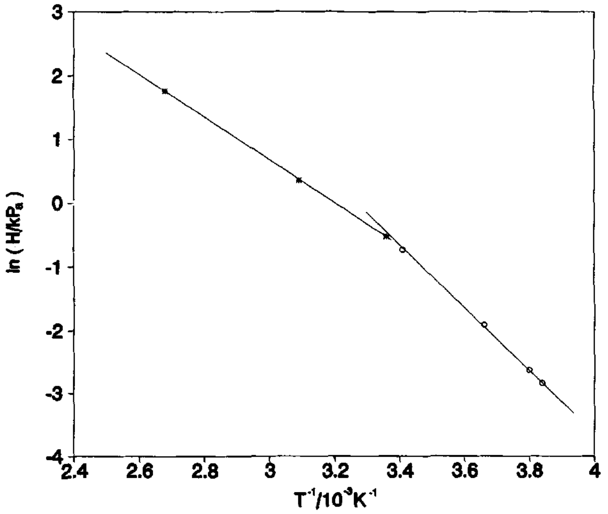

Figure 6 Plot of ln (Henry's Law constant) vs. reciprocal temperature: (x) this work; (⊙) Ref. 14.

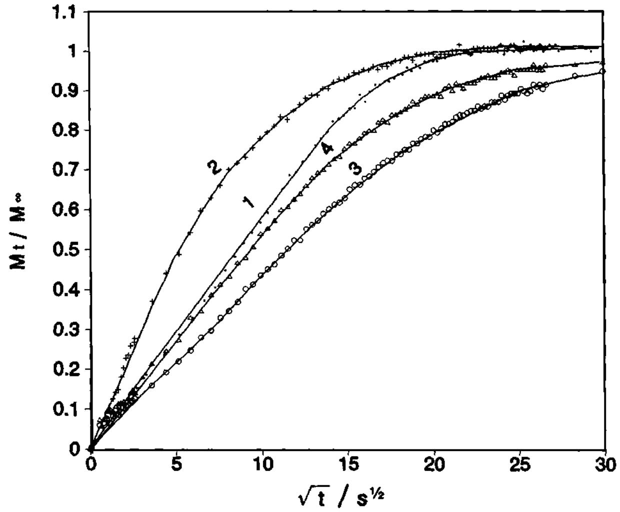

Figure 7 Typical water-sorption data at 25°C. Water-vapor pressure range (in mmHg): (1) 2.17–6.50; (2) 6.88–2.44; (3) 15.2–19.7; (4) 19.7–15.3.

Diffusion Coefficient of Water

Water-sorption experiments conducted with the Cahn microbalance permitted determination of the diffusion coefficient D of water in Nafion by means of the following equation[15]:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2} \qquad (6)$$

where M_t and M_∞ are the masses of water absorbed by the Nafion at time t and at equilibrium with the prevailing water-vapor pressure, respectively, and l is the membrane thickness. Some typical curves of M_t/M_∞ as a function of $t^{1/2}$ are shown in Figure 7. The data show good linearity to $M_t/M_\infty \sim 0.5$. Diffusion coefficient data were obtained from these curves at 25, 50, and 100°C. Diffusion coefficients obtained by this sorption method are related to the mutual diffusion coefficient D_v by the following equation[15]:

$$D = D_v(1 - f_v)^2 \qquad (7)$$

where f_v is the volume fraction of water in the Nafion. Equation (7) has been developed for the case in which there is no overall volume change in mixing, which has been verified as noted earlier. It may be shown that

$$1 - f_v = \frac{\rho_{H_2O}}{\rho_{H_2O} + f_m\rho_0} \sim \frac{1.0}{1.0 + 0.0336\bar{N}} \qquad (8)$$

where $\bar{N}$ is the mean mol ratio, n_{H_2O}/n_{H^+} for each experiment. The diffusion coefficients so obtained are presented in Figure 8.

It is evident from Figure 8 that the diffusion coefficient of water in Nafion is a strong function of the water content. Furthermore, D attains a maximum value at $\bar{N} \sim 4$ at 25°C. Experimental restrictions with the microbalance precluded measurements at the higher water concentrations at 50 and 100°C. Hence, no maximum in D was observed at these temperatures. The above noted restrictions precluded detailed analysis of the temperature dependency of D. At the relative pressure $p/P^0 = 0.1$, $N = 2.1$, the activation energy for water diffusion $E \sim 20$ kJ/mol is estimated utilizing the Arrhenius equation. However, only data at 25 and 50°C are available for the estimate. Data at lower water concentrations are too scattered to permit a reliable estimate.

Several studies of water diffusion in Nafion H have been reported. These studies have usually involved immersion of dry Nafion in liquid water, though there have been some investigations utilizing water vapor. All experiments were conducted over a wide water concentration range. From water-immersion experiments, Yeo and Eisenberg[16] gave

$$D = 6.0 \times 10^{-3}\exp(-20.2 \times 10^3/RT)\ \text{cm}^2/\text{s} \qquad (9)$$

The data of Takamatsu et al.[17] and Eisman[18] are in close agreement. The activation energy for water diffusion (20.2 kJ/mol) is similar to the approximate value ($\sim$23 kJ/mol) obtained in this work.

Diffusion coefficient data obtained from experiments involving water vapor are substantially lower than predicted by eq. (9). Takematsu et al.[17] reported $D = 0.2 \times 10^{-7}$ cm^2/s (sorption) and $D = 1.11 \times 10^{-7}$ cm^2/s (desorption) at 23°C. These data are similar in magnitude to data obtained in this work (Fig. 8). From eq. (9), D equals 16.3×10^{-7} cm^2/s at 23°C. The larger value of D derived from a desorption experiment noted by Takematsu et al. was frequently noted in this work. It is suggested that this variability of the diffusion coefficient is a consequence of the two-phase structure of Nafion, comprising hydrophilic and hydrophobic regions and the dimensional changes accompanying water sorption. In particular, the swelling that accompanies water sorption will induce uptake of liquid water in an immersion experiment, resulting in an apparently high diffusion coefficient, as determined from the weight change.

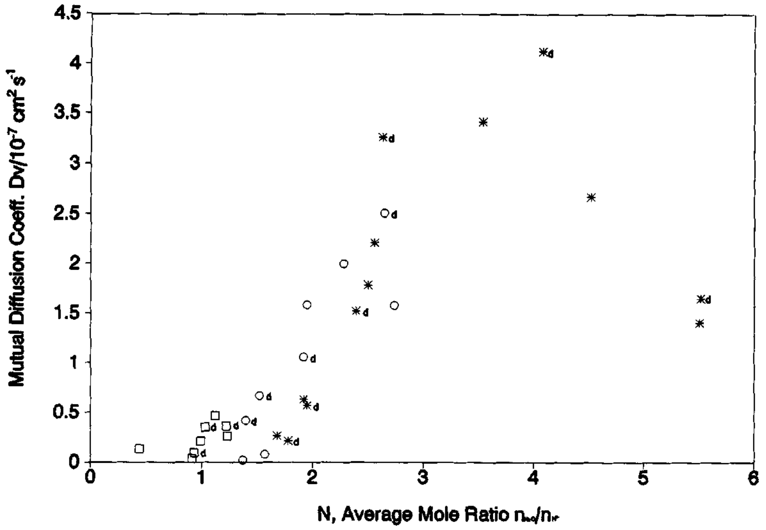

Figure 8 Water-diffusion coefficients in Nafion: (x) $t = 25°C$; (⊙) $t = 50°C$; (□) $t = 100°C$; $d \equiv$ desorption expt.

The water-concentration dependency of D evident in Figure 8 may be attributed to ionic clustering in Nafion swollen with water. Several workers[16,19] have reported that the cluster size increases with water content; Gierke and Hsu[20] formulated a cluster-network model to describe transported processes in Nafion. They showed that ion transport in Nafion is controlled by percolation in which process the connectivity of ion clusters is critical. Barrie[21] also discussed the concentration dependency of D from a thermodynamic viewpoint. Finally, it may be noted that the form of the concentration dependency of D observed in this work (Fig. 8) is such that the rate of desorption will differ from the rate of absorption.[22]

Electrical Conductivity of Nafion

The results of electrical conductivity (σ) measurements with Nafion 117 H as a function of the water content N are presented in Figure 9. X-ray analysis indicated that the platinum metal deposit was virtually coincident with the surface of the Nafion. It is clear that σ is a strong function of N, as expected; the influence of temperature on σ is small over the range studied (23–90°C). At water saturation $\sigma \sim 1 \times 10^{-2}\ (\Omega\ \mathrm{cm})^{-1}$; as $N \rightarrow 0$, $\sigma < 1 \times 10^{-9}\ (\Omega\ \mathrm{cm})^{-1}$.

Electrical conductivity measurements with Nafion Na reported by Hsu et al.[23] have been interpreted in terms of percolation theory. According to this theory, a threshold value, f_{v0}, exists for the volume fraction, f_v, of the aqueous phase in the polymer below which ion flow is impossible. Above this threshold, the conductivity conforms to a simple power law:

$$\sigma = \sigma_0 (f_v - f_{v0})^n \qquad (10)$$

where σ_0 and n are constants.

From the definition of f_v and with the additivity of volumes of water and Nafion verified earlier,

$$f_v = \rho_0[(61.1\rho_{H_2O}/N) + \rho_0]^{-1} \qquad (11)$$

From Figure 3, the onset of swelling of the Nafion occurs at $N \sim 2.0$. Hence, the threshold value f_{v0} would be expected to be ~ 0.063 from eq. (11). Analysis of the experimental conductivity data in

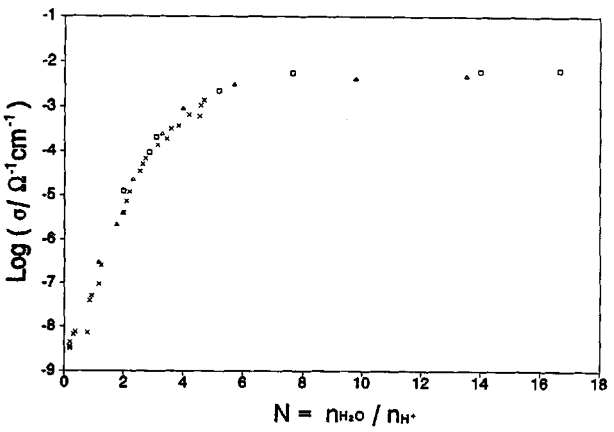

Figure 9 Electrical conductivity of Nafion 117 H: (△) $t = 23°C$; (□) $t = 50°C$; (x) $t = 100°C$.

terms of eq. (10) with $0.05 < f_{v0} < 0.09$ ($1.6 < N < 3.0$) yields the regression equation, with correlation coefficient $r = .98$. The threshold value $f_{v0} = 0.06$ ($N = 1.9$) and

$$\sigma = 0.125(f_v - f_{v0})^{1.95} \qquad (12)$$

For Nafion Na, Hsu et al.[23] found $\sigma_0 = 0.16\ \Omega^{-1}\ \mathrm{cm}^{-1}$, $f_{v0} = 0.10$ and $n = 1.5$. For a given value of $f_v - f_{v0}$, the conductivity of Nafion Na is slightly larger than is the conductivity of Nafion H.

Development of a Humidity Sensor

The strong dependency of the electrical conductivity of Nafion upon the water content, noted in the previous section, suggests utilization of Nafion for the construction of a monitor for water in, e.g., gas mixtures. A sintered glass disc (2.5 cm diameter, ~ 0.2 cm thick) was immersed in 5% Nafion solution, followed by air-drying of the solvents. A thin film of Nafion was thereby deposited on the glass particles of the disc. Platinum black–Nafion slurry was applied to each side of the disc and stainless-steel gauzes were clamped to the sides to act as current collectors. The experimental assembly was similar to that described for the measurement of electrical conductivity (see Figs. 1 and 2).

The results of a typical experiment are presented in Figure 10 as a plot of the measured current as a function of time for various water-vapor pressures in the equilibrating air. The range of water-vapor pressure utilized in the experimental work was 187 Pa (1.40 mmHg, dew point ~ −13°C) to 610 Pa (4.58 mmHg, dew point 0°C). It is seen that the sensors showed rapid response to a step change of gas humidity (90% response time < 1 min) with good reproducibility. Continuous operation for over 400 h at constant gas humidity gave the standard deviation of the current as 3.7%. Hence, the long-term stability is satisfactory. As expected, the sensor constructed with sintered glass as a substrate for the Nafion film showed a much more rapid response to humidity change than did sensors constructed with the Nafion membrane.

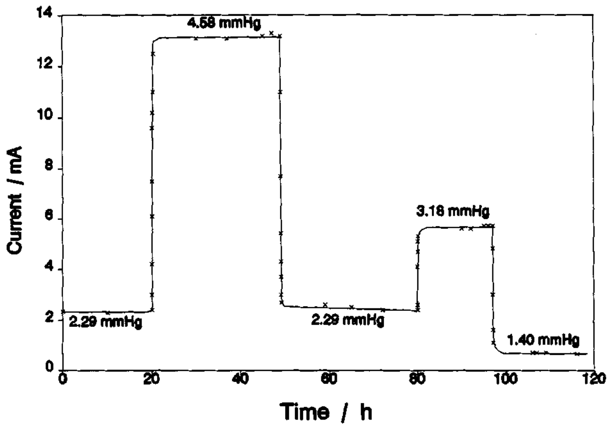

Figure 10 Response of humidity sensor. Numerals are water-vapor pressure in equilibrating gas.

CONCLUSIONS

1. The absorption of water by Nafion 117 H is accompanied by a progressive decrease in density for $N \equiv N_{H_2O}/n_{H^+} > \sim 1.9$. The fractional increase in thickness is greater than the fractional increase in the other dimensions.
2. Water-sorption isotherms have been measured at 25 and 50°C by equilibration with water vapor. For a given relative pressure, p/P^0, the amount of water sorbed increased with temperature. Water-sorption isotherms obey Henry's Law with a nonzero intercept.
3. The enthalpy of sorption of water by Nafion 117 H is 28.2 kJ/mol. This is within the range of published values.
4. The diffusion coefficient of water in Nafion 117 H is a strong function of the water content. A maximum value for D occurs at $N \sim 4.0$ at ambient temperature. The diffusion coefficients determined in this work by equilibration with water vapor are much lower than values determined by immersion of Nafion in liquid water.
5. The electric conductivity of Nafion 117 H is a strong function of the water content. The data have been interpreted in terms of percolation theory. An attempt was also made to interpret the diffusion coefficient data in terms of percolation theory. This was unsuccessful.
6. A humidity sensor, utilizing Nafion 117 H deposited in sintered glass, has been developed. The sensor showed good responsiveness to water-vapor pressure change and good long-term stability.

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Received November 16, 1992
Accepted January 29, 1993