Anal. Chem. **2002,** *74,* 4794−4799

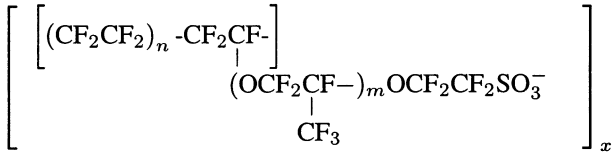
Density of Nafion Exchanged with Transition Metal Complexes and Tetramethyl Ammonium, Ferrous, and Hydrogen Ions: Commercial and Recast Films

Kristi J. Oberbroeckling, Drew C. Dunwoody, Shelley D. Minteer, and Johna Leddy*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

The densities of commercial Nafion 117 and cast Nafion 1100 films were determined by the hydrostatic weighing method for films fully exchanged with hexaammineruthenium(III), tris(2,2′ bipyridyl)ruthenium(II), tetramethylammonium, ferrous, and hydrogen ions. Films were pretreated in either water or concentrated nitric acid prior to cation exchange. All densities ranged between 1.65 and 2.19 g/cm^3. Excluding the proton-exchanged films, the average density is 1.90 ± 0.14 g/cm^3, well in excess of the 1.58 g/cm^3 commonly employed for Nafion. The density of acid-pretreated Nafion 1100 was constant at 1.95 ± 0.03 g/cm^3 for all cations except the proton. A simple, empirical model based on the Coulombic interaction between the intercalated cation and the sulfonate sites of the Nafion characterizes density for the commercial Nafion 117 films. A modified version of the model is appropriate for water-treated Nafion 1100. Water content of the films and implications for characterizing modified electrodes are discussed.

Nafion (E.I. du Pont de Nemours and Co., Inc.) is one of the most commonly used cation exchange polymers. As a membrane, Nafion 117 is used as a separator in electrochemical cells, such as fuel cells. It is also available as a suspension in water and alcohols, here denoted as Nafion 1100. The suspension is used to coat surfaces including electrodes to make sensors and modified electrodes. The structure of Nafion, shown below, consists of a



Structure of Nafion where m is usually 1; $5 \leq n \leq 7$

fluorocarbon backbone and side chains that terminate in the anionic sulfonate exchange site. The polymer segregates into hydrophilic and hydrophobic domains. The Nafion 117 membranes are heat processed and are viewed as having an inverted micellar configuration. Cold-cast Nafion 1100 films are thought to have the opposite configuration with a fluorocarbon core shrouded in ion exchange sites. Although the properties of Nafion are often discussed in terms of the hydrophobic and hydrophilic domains,[1−3] here it is the electrostatic interactions between the sulfonate group and the exchanged cations that dictate the density of Nafion.

Density is a basic materials property. It is the basis for calculating the thickness and volume of Nafion films as well as the concentration of exchange sites and intercalated cations. Inaccuracies in the density will impact the most basic characterizations of the material. Throughout the literature, the density of Nafion is taken as 1.58 g/cm^3, a value extracted by other researchers from an early and excellent paper by Mauritz et al.[4] The density was extracted by extrapolating trend lines on a figure that contained no data points. Although the density was determined by Takamatsu and Eisenberg[5] for alkali metal-exchanged membranes in the following year (1979) and the density was shown to be in the range of 1.860 and 2.177 g/cm^3 for 1155 equivalent weight membranes, the ubiquitous 1.58 g/cm^3 persisted. More recently, densities for alkali metal cation-exchanged membranes (1100 equivalent weight) have been reported by Garcıa-Fresnadillo et al.[6] The densities of Nafion 117 and films cast from Nafion 1100, both cold cast and heat annealed, have been determined for as-received and proton-exchanged films in water and acetonitrile.[7,8] The densities exceed 1.58 g/cm^3. Since this report in 1996, a density of 1.58 g/cm^3 persists in the literature.[9−13]

* To whom correspondence should be addressed. Phone: 319-335-1720. Fax: 319-335-1270. E-mail: johna-leddy@uiowa.edu.

(1) Mauritz, K. A.; Hora, C. J.; Hopfinger, A. J. In *Ions in Polymers;* Eisenberg, A., Ed.; Advances in Chemistry Series 187; American Chemical Society: Washington, DC, 1980; pp 124−154.
(2) Gierke, T. D.; Hsu, W. Y. The Cluster-Network Model of Ion Clustering in Perfluorosulfonated Membranes. In *Perfluorinated Ionomer Membranes*;; Yeager, H. L., Eisenberg, A., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982; pp 283−307.
(3) Yeager, H. L. Transport Properties of Perfluorosulfonated Polymer Membranes. In *Perfluorinated Ionomer Membranes*; Yeager, H. L., Eisenberg, A., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982; pp 41−63.
(4) Mauritz, K. A.; Hora, C. J.; Hopfinger, A. J. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1978**, *19*, 324.
(5) Takamatsu, T.; Eisenberg, A. *J. Appl. Polym. Sci.* **1979**, *24*, 2221−2235.
(6) Garcia-Fresnadillo, D.; Marazuela, M. D.; Moreno-Bondi, M. C.; Orellana, G. *Langmuir* **1999**, *15*, 6451−6459.
(7) Zook, L. A.; Leddy, J. *Anal. Chem.* **1996**, *68*, 3793−3796.
(8) Zook, L. A.; Leddy, J. In *Nafion−Cold Cast, Thermally Processed, and Commercial Films: Comparison of Density, Water Content, and Equivalent Weight*; Leddy, J., Vanýsek, P., Porter, M. D., Eds.; New Directions in Electroanalytical Chemistry II, 99-5; The Electrochemical Society, Inc.: Pennington, NJ, 1999; pp 217−224.

10.1021/ac025586h CCC: $22.00
Published on Web 08/15/2002

Here, densities are reported for academically interesting cations with a range of charges, sizes, and hydrophobicities. Nafion 117 and cold-cast films of Nafion 1100 are evaluated following either water or acid pretreatments. Densities again exceeded 1.58 g/cm^3. An empirical electrostatic model successfully correlates the density with the size and charge of the intercalated cation. The hydrophobicity of the cations has little effect on the density. The electrostatic model is appropriate for Nafion 117 and water-treated Nafion 1100 films. The acid-treated Nafion 1100 films are better modeled by a constant density of 1.95 ± 0.03 g/cm^3. The implications of film history and inaccurate density values in characterizing modified electrodes are also considered.

EXPERIMENTAL SECTION

Film Preparation and Cation Exchange. Commercial films of Nafion 117 and cast films formed from suspension of Nafion 1100 (Aldrich) were studied. Films of Nafion 1100 (Solution Technology, Inc.) were cast by pipetting 20 mL of a 5% Nafion suspension into square polypropylene weighing boats (7 cm × 7 cm) and allowing the solvents to evaporate on the benchtop. When solvents were evaporated more quickly in the hood, less pliable films were formed, which were prone to fragmentation. The weighing boats were lightly covered to prevent airborne particles from disrupting film formation. Films formed in two to four days and had a thickness of ∼0.2 mm. Films were placed in a vacuum desiccator for 1 h and then peeled from the weighing boats.

Cast Nafion 1100 and commercial Nafion 117 were cut into squares approximately 2.5 cm × 2.5 cm. A small hole was cut into one edge to facilitate suspension of the film during density determination. Film preparation is similar to that used previously.[7,8] Films were pretreated in either water or concentrated nitric acid by soaking for 48−72 h. Films were water rinsed and blotted dry. High-purity water (18 MΩ Milli-Q (Millipore)) was used. Films were exchanged with the appropriate cation by soaking the film in a 50- or 100-mL solution containing ∼5 mM cation. The exchanged species were tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate, hexaammineruthenium(II) chloride, iron(II) perchlorate hexahydrate, and tetramethylammonium tetrafluoroborate. For all but the Fe^{2+}, the selectivity of the ions over proton is highly favored[14] and the cation fully replaces the protons in the films. Films were exchanged for 48−72 h before density measurements were made to ensure equilibrium exchange.

Density Measurements. The hydrostatic weighing method was used to determine density.[15] The sample mass, m, is found by weighing the hydrated sample once it is briefly blotted dry. The sample is rewetted, blotted, and suspended in a beaker of water, and weight, W, is found. The weight of the suspension system and the beaker absent the sample is also determined as W_0. The volume of water displaced by the sample is determined with the density of water, $d_W = 0.9982$ g/cm^3. With correction for the density of air ($d_A = 0.001\,29$ g/cm^3), the measured density is found. The values of d_W and d_A are appropriate for 20 °C and 760 mmHg.

$$d_{meas} = \frac{m}{(W - W_0)/d_W} + d_A \qquad (1)$$

The protocol used here was the same as used previously,[7,8] with the following modification. A fish hook and small lead weight were found to suspend the sample more stably than the wire used previously. For each film, m, W, and W_0 were each determined three times. Except as noted, each density is calculated based on at least three films for each cation.

Molecular Modeling of Density. Densities of the cations were determined by dividing the molecular weight of the ion by the ionic volume. All ionic volume calculations were performed using Gaussian 98W on a Dell Optiplex Pentium II PC. The LANL2DZ basis set was used for all calculations. Ion structures were solvated in water using the Onsager model reaction field calculation and optimized before volume calculations were performed.

Table 1. Densities for Nafion 117 and Recast Nafion 1100

	Nafion 117		recast Nafion 1100	
cation	water treated	acid treated	water treated	acid treated
$Ru(NH_3)_6^{3+}$	2.19 ± 0.11	2.16 ± 0.10	2.13 ± 0.08	1.95 ± 0.07
$Ru(bpy)_3^{2+}$	1.92 ± 0.13	1.81 ± 0.07	1.91 ± 0.12	1.98 ± 0.21
Fe^{2+}	1.90 ± 0.19	1.90 ± 0.06	1.77 ± 0.06	1.96 ± 0.21
TMA^+	1.92 ± 0.06	1.81 ± 0.05	1.75 ± 0.03	1.92 ± 0.09
H^+	1.83 ± 0.10	1.76 ± 0.14[a]	1.65 ± 0.02	1.77 ± 0.19
H^+ from ref 7	1.77 ± 0.10	2.05 ± 0.17	1.40 ± 0.15	1.67 ± 0.14

[a] Two replicates.

RESULTS

Density. The results of the density determinations are listed in Table 1. The densities for the protonated films are in agreement with the values determined previously in this laboratory.[7,8] The values found for protonated films do not differ from those found in ref 7 at the 98% confidence level; at the 90% confidence level, values for all but the water-treated Nafion 1100 do not differ. The density found previously for the water-treated Nafion 1100 seems low compared to values determined here and in refs 5 and 6. Water treatment should not displace any exchanged cations, and as the commercial Nafion suspension is neutralized with alkylammonium ions, a density similar to that for TMA^+ is anticipated. The density of 1.65 g/cm^3 found here is more appropriate than that we found previously.[7]

The results in Table 1 range between 1.65 and 2.19 g/cm^3. All values are well above the commonly employed value of 1.58 g/cm^3. For all the intercalants except proton, the average density is 1.90 ± 0.14 g/cm^3. Interestingly, for all exchanged species except proton, the density for the acid-treated, recast Nafion 1100 films is invariant. The average density for these films is 1.95 ± 0.03 g/cm^3.

(9) Komura, T.; Yamaguchi, T.; Sato, H.; Shimatani, H.; Takahashi, K. *Electrochim. Acta* **2001**, *46*, 3579−3588.
(10) Marayama, J.; Inaba, M.; Katakura, K.; Ogumi, Z.; Takehara, Z. *J. Electroanal. Chem.* **1998**, *447*, 201−209.
(11) Sanmatıas, D.; Benito, D.; Navarro-Laboulais, J.; Garcıa-Jareño, J. J.; Vicente, F. *Electrochim. Acta* **1999**, *45*, 767−808.
(12) Agra-Gutiérrez, C.; Suárez, M. F.; Compton, R. G. *Electroanalysis* **1999**, *11*, 16−22.
(13) Ganesan, V.; Abraham John, S.; Ramaraj, R. *J. Electroanal. Chem.* **2001**, *502*, 167−173.
(14) Szentirmay, M. N.; Martin, C. R. *Anal. Chem.* **1984**, *56*, 1898−1902.
(15) *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D., Hilton, C. L., Eds.; Interscience: New York, 1966; Vol. 1, p 557.

Table 2. Water Volume Fraction v_w (H_2O/RSO_3^-) and Average v_+ for Nafion 117

	Nafion 117		recast Nafion 1100		
cation	water treated	acid treated	water treated	acid treated	average v_+
$Ru(NH_3)_6^{3+}$	−0.05 (−2)	−0.03 (−1)	0.00 (0)	0.16 (6)	0.12 ± 0.01
$Ru(bpy)_3^{2+}$	0.16 (9)	0.26 (16)	0.17 (9)	0.11 (5)	0.30 ± 0.02
Fe^{2+}	0.21 (8)	0.21 (8)	0.33 (14)	0.16 (5)	0.03 ± 0.00
TMA^+	0.19 (7)	0.28 (13)	0.34 (17)	0.19 (7)	0.10 ± 0.01
H^+	0.28 (11)	0.34[a] (15)	0.43 (22)	0.33 (14)	0.02 ± 0.00

[a] Two replicates.

For acid- and water-treated Nafion 117 and water-treated Nafion 1100, the proton-exchanged films are least dense and the $Ru(NH_3)_6^{3+}$-exchanged films are the most dense. Excluding Fe^{2+} in Table 1, the densities decrease down the columns. The average density for the proton-exchanged films is 1.75 ± 0.08 g/cm^3 whereas the average for $Ru(NH_3)_6^{3+}$ is 2.11 ± 0.11 g/cm^3. The average densities of the remaining three cations range between 1.85 and 1.91 g/cm^3.

Water Content. The water content of the film is approximated from d_{meas} and the densities of the fluorocarbon (d_{CF} = 2.15 g/cm^3), the water (d_w = 1.00 g/cm^3), and the cation (d_+). The density of poly(tetrafluoroethylene) (i.e., Teflon) is used to approximate d_{CF}. The cation densities were found by molecular modeling; the resulting cation densities (g/cm^3) are 0.914 ($Ru(NH_3)_6^{3+}$), 0.979 ($Ru(bpy)_3^{2+}$), 0.94 (Fe^{2+}), 0.985 (TMA^+), and 1.226 (H_3O^+). For volume fractions of the fluorocarbon (v_{CF}), water (v_w), and cation (v_+), $1 = v_{CF} + v_+ + v_w$. This assumes an ideal mixture where there is no change of volume on mixing of the components. The film density is then approximated as $d_{meas} = v_{CF}d_{CF} + v_+d_+ + v_wd_w$. For a fully exchanged film, electrostatic interactions between the intercalant and the sulfonate groups determines that $z \times \text{moles}_+ = \text{moles}_{CF}$, where z is the charge on the cation. That is, $zv_+d_+/MW_+ = v_{CF}d_{CF}/1100$. The molecular weight of the cation is MW_+ and that of the fluorocarbon is taken as 1100. (Note that throughout the paper, 1100 g/mol is used as the equivalent weight of Nafion. This is the nominal equivalent weight. For recast Nafion 1100 films, recent studies[16] yield an equivalent weight of 996 ± 24 g/mol.) Water volume fractions are listed in Table 2. Although the Fe^{2+} films are not fully exchanged, the value of MW_+/z for Fe^{2+} is small such that the calculation based on full exchange is reasonable approximation. The number of waters per sulfonate, $1100v_wd_w[18v_{CF}d_{CF}]^{-1}$, is cited in the table in parentheses.

A density of 1.58 g/cm^3 for a proton-exchanged film corresponds to v_w = 0.49 and 29 waters per sulfonate. All values of v_w determined here fall well below 0.49 and range effectively between 0 and 0.43. The slightly negative water content for the $Ru(NH_3)_6^{3+}$ films is zero within the limitations of the measurement and reflects the high level of film dehydration. Consistent with the densities, the $Ru(NH_3)_6^{3+}$ films are most dehydrated and the protonated films are most hydrated. For the acid-treated Nafion 1100 films exclusive of the proton, the average volume fraction of water is 0.15 ± 0.03. For all but the $Ru(NH_3)_6^{3+}$, the number of waters per sulfonate ranges between 5 and 22. It is also noted that for each cation v_+ is fairly constant across all classes of films, as shown in the table. The ratio MW_+/z is important in determining v_+ as well as the density. This reflects the ratio of radius to z that determines the density of these films, as discussed below.

DISCUSSION

Electrostatic Model for Predicting Density. The measurements yield densities consistent with films containing less water than anticipated by a density of 1.58 g/cm^3. The distance between the sulfonates of the Nafion and the exchanged cations is reduced with less shielding by intercalated water. This enables electrostatic interactions that can drive the densification of the film.

The properties of ionic crystals are anticipated by the electrostatic interactions between the anions and the cations. It was found empirically that electrostatic models are useful in predicting the densities of the Nafion 117 films. The electrostatic potential energy between two charges is defined as

$$E\ (\text{J/mol}) = z_1z_2e^2N_0/4\pi\epsilon_0\epsilon r \qquad (2)$$

where z_1 and z_2 are the charges, $e = 1.602 \times 10^{-19}$ C is the charge on an electron, N_0 is Avogardro's number, $\epsilon_0 = 8.854 \times 10^{-12}$ $C^2N^{1-}m^{-2}$ is the permittivity of free space, ϵ is the dielectric constant, and r is the distance of separation between the two charges. When the charges are attracted, $E < 0$. When the charges are condensed into an ionic crystal, an additional term, the Madelung constant A, is introduced to account for the attractive and repulsive interactions between the cationic and anion charges of the crystal.[17] Equation 3 is then expressed as

$$E\ (\text{J/mol}) = z_1z_2e^2AN_0/4\pi\epsilon_0\epsilon r \qquad (3)$$

The Madelung constant can be calculated directly if the crystal structure is known. If the structure is not known, the Kapsutinskii approximation[18] can be used. For a crystal where ν is the number of ions per unit formula, $A \cong 0.874\nu$. For the interaction between a cation of charge z with a sulfonate, $\nu = 1 + z$.

Measurements by Paddison et al.[19] have shown that the high-frequency dielectric constant of Nafion ranges between 4 and 20

(16) Chen, T.-Y.; Leddy, J. *Langmuir* **2000**, *16*, 2866−2871.

(17) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row Publishers: New York, 1972; p 60.

(18) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W.B. Saunders Co.: Philadelphia, PA, 1977; p 290.

(19) Paddison, S. J.; Reagor, D. W.; Zawodinski, T. A. *J. Electroanal. Chem.* **1998**, *459*, 91−97.

Table 3. Properties of the Exchanged Species

cation	charge z	r (nm)	fully exchanged?	E pot. energy (kJ/mol)
$Ru(NH_3)_6^{3+}$	3	0.34 [23]	yes	-142.9
$Ru(bpy)_3^{2+}$	2	0.70 [24]	yes	-41.7
Fe^{2+}	2	0.30 [21]	no	-76.7
TMA^+	1	0.23 [21]	yes	-30.4
H^+	1	0.45 [21]	yes	-19.4

with the values changing as a function of hydration. For 5−13 waters/sulfonate, the dielectric constant ranges between 11 and 20. For the simple purpose of demonstrating a correlation between the density and the electrostatic interactions between the charges, the dielectric constant is approximated here as 20 consistent with the 5−22 waters/sulfonate found for all intercalants but $Ru(NH_3)_6^{3+}$ (see Table 2). It is of note that significant ion pairing occurs in systems with dielectric constants below 20.[20] For a 0.1 M solution of a 1:1 electrolyte (tetrabutylammonium picrate), at a dielectric constant of 20, only ~38% of the electrolyte is dissociated. At higher concentrations, the ion pairing is more extensive. The molar concentration of cation in Nafion of equivalent weight 1100 is approximated as $10^3 d_{meas}/(1100z)$; for a proton, the concentration is ~1.5 M. For the species examined here, the concentrations range between 0.22 and 3.66 M. Thus, in the high-concentration environment of Nafion, the extent of ion pairing will be high, and this is conducive to strong binding between the cations and sulfonates.

Equation 3 provides a method for calculating density of Nafion 117 for a given cation provided its charge and diameter are known and the Nafion is fully exchanged with only that cation. See Table 3 for values of E calculated from eq 3, where $\epsilon = 20$ and r is taken as $0.5(r_+ + r_-)$. The radius of the sulfonate, r_-, is taken as 0.35 nm based on the radii[21] of similar ions, NO_3^- (0.3 nm), ClO_3^- (3.5 nm), and HSO_3^- (0.4−0.45 nm), and the diameter of the fluorocarbon side chain binding the sulfonate to the Nafion backbone[22] (0.41 nm).

The model predicts densities for the cations examined here as well as alkali metal cations[5,6] in commercially available membranes (e.g., Nafion 117). A modification of the model is suggested for water-treated Nafion 1100. For acid-treated Nafion 1100, the density is invariant at 1.95 ± 0.03 g/cm^3. These are discussed below. Except as noted, Fe^{2+} is not included in the statistical analysis as it is not fully exchanged into the Nafion under the conditions of these measurements.

Nafion 117. For water-treated Nafion 117, the correlation between density and the potential energy is shown in Figure 1a. Linear regression yields a relationship between d_{meas} and E of $d_{meas} = -(2.7 \pm 0.3) \times 10^{-3}E + (1.81 \pm 0.02)$ for $r^2 = 0.975$. For acid-treated Nafion 117, the correlation between d_{meas} and E shown in Figure 1b is shown by regression to be $d_{meas} = -(3.2 \pm 0.2) \times 10^{-3}E + (1.70 \pm 0.01)$ for $r^2 = 0.993$. The slope and intercepts for the water- and acid-treated films are similar. The regression did not include Fe^{2+}, but results for Fe^{2+} are shown on both plots in Figure 1. For the acid-treated system, Fe^{2+} is better represented by the electrostatic model than for the water-treated Nafion 117. The electrostatic interactions of the intercalant with the sulfonates of the Nafion characterize the densities for the commercial Nafion 117 films.

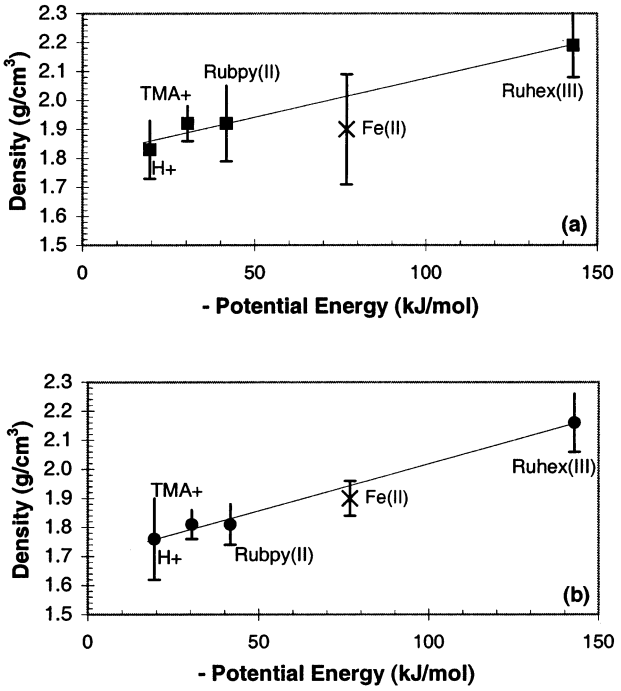


Figure 1. Correlation of density with electrostatic potential energy for commercial Nafion 117 (a) water and (b) acid treated. The fully exchanged species (all except Fe^{2+}) are included in the regression analysis.

The electrostatic model also allows prediction of the density of Nafion 117 membranes exchanged with alkali metal ions. In the work of García-Fresnadillo et al.,[6] the densities of Nafion 117 exchanged with hydrogen, lithium, sodium, and potassium cations were measured. The sample preparation differed from that used here as the films were washed in methyl alcohol. Densities are reported for membranes equilibrated in water, methyl alcohol, and chloroform. For a dielectric constant of 20, the electrostatic potential energy for Nafion exchanged with lithium, sodium, and potassium are, respectively, −25.6, −30.4, and −37.4 kJ/mol for radii[21] of 0.30, 0.23, and 0.15 nm. For water-equilibrated Nafion 117, density for lithium-, sodium-, and potassium-exchanged films is linearly correlated with E as $d_{meas} = -(0.0145 \pm 0.0009)E + (1.35 \pm 0.03)$ for $r^2 = 0.996$. For Nafion equilibrated in chloroform, the density of the four exchanged species is characterized as $d_{meas} = -(5.5 \pm 0.5) \times 10^{-3}E + (1.87 \pm 0.01)$ for $r^2 = 0.99$. For methanol-equilibrated films, the density is not a linear function of electrostatic potential energy.

Takamatsu and Eisenberg[5] reported measured densities for alkali metal-exchanged Nafion 1155 (1.26 mm thick) in 1979. The hydrostatic weighing method was used to measure the density of water-immersed commercial Nafion 1155 film containing lithium, sodium, potassium, and cesium. The densities ranged between 1.860 and 2.177 g/cm^3. The electrostatic model again yields a linear relationship between density and electrostatic

(20) Laitinen, H. A.; Harris, W. E. *Chemical Analysis*, 2nd ed.; McGraw-Hill Book Co.: New York, 1975; pp 67−68.
(21) Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675−1678.
(22) Zook, L. A.; DeJohn, M. D.; Leddy, J. Aggregation of Ionomer and Carbon Blacks during MEA Preparation: Model to Characterize Particle Size and Catalyst Accessibility. In *Second International Symposium on Proton Conducting Membrane Fuel Cells*; Gottesfeld, S., Fuller, T., Halpert, G., Eds.; The Electrochemical Society, Inc.: Boston, MA, 1998; Vol. 98-27, pp 10−22.

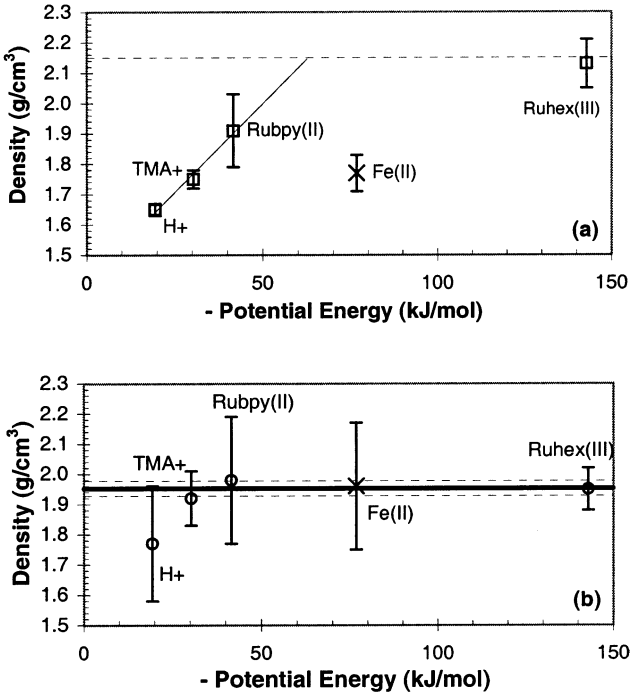


Figure 2. Correlation of density with electrostatic potential energy for commercial Nafion 1100 (a) water and (b) acid treated. For (a), the density can be represented as linearly correlated with potential energy (solid line) for densities less than that of fluorocarbon (dotted line). For (b), the densities for all the exchanged species except proton are best represented by the average density of 1.95 ± 0.03 g/cm

potential energy ($d_{meas} = -(0.020 \pm 0.0.003)E + (1.33 \pm 0.09)$ for $r^2 = 0.97$).

Nafion 1100: Water Treated. The density of water-treated Nafion 1100 is plotted as a function of E in Figure 2a. The data are not well fit linearly across the full range of E; an alternative interpretation is suggested. The density of $Ru(NH_3)_6^{3+}$ is the same as pure fluorocarbon, as indicated by the broken line. It is unlikely that the density of the exchanged films would substantially exceed that of the fully dehydrated film. For measured densities less than that of the fluorocarbon, the variation of d_{meas} with E is linear, as shown by the solid line ($d_{meas} = -(0.012 \pm 0.001)E + (1.41 \pm 0.05)$ for $r^2 = 0.98$). The results suggest that the electrostatic model may be appropriate for $E \gtrsim -62$ kJ/mol, where the line for the electrostatic potential energy intersects the line for the density of fluorocarbon. Thus, for $E \gtrsim -62$ kJ/mol, the density of fluorocarbon (2.15 g/cm^3) may be the better estimate.

The data for Fe^{2+} are not included in these analyses as the density of the Fe^{2+} in the water-treated Nafion 1100 falls substantially below the other values and ferrous ion is not fully exchanged under the experimental conditions. The behavior of Fe^{2+} in the water-treated Nafion 1100 is analogous to that for the water-treated Nafion 117.

Nafion 1100: Acid Treated. The data for the acid-treated Nafion 1100 are shown in Figure 2b. As discussed above, the density of these films is constant at 1.95 ± 0.03 g/cm^3, exclusive of the proton-exchanged material. The solid line on the plot is the average value, and the dotted lines are the standard deviation. For these systems, the density is well represented by the average value. The data for Fe^{2+} are also well represented by the average value. As for the Nafion 117, the Fe^{2+} data are more closely in line with the fully exchanged intercalants when the films are acid treated. It is not clear why the acid-treated Nafion 1100 films have such a narrow range of densities. It is possible that the acid treatment in some manner sets the structure and the hydration level before the intercalant is added. The experimental conditions are such that the films should be completely exchanged by all the cations except Fe^{2+}, so it is not clear why any structure set by protons would persist once the exchange is completed and the protons displaced.

The data in Figure 2b may be fit to an electrostatic model similar to that for water-treated Nafion 1100. If TMA^+ and proton are taken as below the average line of 1.95 g/cm^3 and species with $E \lesssim -35$ kJ/mol as on the average line, then the slope through TMA^+ and proton is 0.014 and the intercept is 1.50 g/cm^3. The slope and intercept are similar to those for water-treated Nafion 1100, but there are insufficient data to make a judgment as to whether the model is appropriate. For $E \lesssim -30$ kJ/mol, the density of 1.95 ± 0.03 g/cm^3 is an excellent model.

Implications for Characterization of Modified Electrodes. Suspensions of Nafion 1100 are commonly used to modify electrode surfaces. For a cationic or neutral intercalant, the films are often characterized voltammetrically. For a simple homogeneous film, a common characterization of the film is in terms of the extraction coefficient, κ, and a diffusion coefficient, D. The extraction coefficient is the ratio of concentration of the intercalant in the film relative to that in solution. For steady-state techniques such as rotating disk voltammetry,[25] the steady-state current is proportional to $\kappa D/\ell$, where ℓ is the thickness of the film. For transient techniques such as cyclic voltammetry and chronoamperometry, the current is proportional to $\kappa D^{1/2}$ provided the diffusion length is confined to the film. If ℓ is known, then the steady-state and transient data can be combined to separate κ and D.

Density is used to calculate ℓ, and if ℓ is miscalculated, κ and D will be in error. Let $b = d_{real}/d_{assumed}$, where d_{real} is the real density of the film and $d_{assumed}$ is the density used in the calculation. The most common value in the literature for $d_{assumed}$ is 1.58 g/cm^3. Then, for real values of κ_{real} and D_{real}, and values found by calculation using the assumed density ($\kappa_{assumed}$ and $D_{assumed}$), $D_{assumed}/D_{real} = b^2$ and $\kappa_{assumed}/\kappa_{real} = b^{-1}$. For all intercalants but proton, the densities found here for Nafion 1100 range between 1.75 and 2.13 g/cm^3. If the assumed density is 1.58 g/cm^3, the D_{real} is misestimated by 23 and 82% and κ_{real} is misestimated by 10−35%. These discrepancies may contribute to the inconsistencies often observed for Nafion-modified electrodes when transient and steady-state data are combined to determine extraction and diffusion coefficients.

CONCLUSION

The densities of Nafion 117 and Nafion 1100 are well in excess of the commonly employed value of 1.58 g/cm^3. Correspondingly, the water content of the films ranges between 0 and 43 vol %.

(23) Zuckerman, J. J., Ed. *Inorganic Reactions and Methods*; VCH: Deerfield Beach, FL, 1986; Vol. 15.
(24) Chance, B.; DeVault, D. C.; Frauenfelder, H.; Marcus, R. A.; Schrieffer, J. R.; Sutin, N. *Tunneling in Biological Systems*; Academic Press: New York, 1979; p 206.
(25) Gough, D. A.; Leypoldt, J. K. *Anal. Chem.* **1979**, *51*, 439.

Often the properties of Nafion are discussed in terms of the hydrophobic and hydrophilic interactions in the film,[2,26] but from the results here, a simpler model based on size and charge is more appropriate for describing density. The electrostatic potential energy description implies that density and water content are set by Coulombic attraction between the sulfonates and the intercalated cations. The model works across a wide range of cations for the Nafion 117 films, whether acid or water treated. Its application is restricted for water-treated Nafion 1100 films to densities of <2.15 g/cm^3. The density of the acid-treated Nafion 1100 films is constant at 1.95 ± 0.03 g/cm^3, exclusive of the proton-exchanged material.

Regressions of data to the electrostatic potential energy model are summarized in the Discussion section under Nafion 117. Note that whereas the regressions are consistent with a linear relationship between density and electrostatic potential energy, the slopes and intercepts vary with the nature of the cations and the film preparation protocols. As has been discussed previously, the density determined for Nafion is dependent on the history of the film.[5] This suggests that the best protocol for determining density for films formed under a given preparative protocol is to determine the density of the films for a series of representative intercalants. If the electrostatic potential energy model is appropriate, then it should be predictive for other intercalants. The preparative conditions of water and acid treatment used in this study are not uncommon and may provide direct access to densities of Nafion films. Certainly, the constant density of 1.95 g/cm^3 found for acid-treated Nafion 1100 films where $E \lesssim -30$ kJ/mol is easily accessible.

(26) Eisenberg, A.; Yeager, H. L. *Perfluorinated Ionomer Membranes;* American Chemical Society: Washington, DC, 1982; p 283.

ACKNOWLEDGMENT

The financial support of the Department of Defense, Maryland Procurement, is most gratefully acknowledged.

Received for review February 18, 2002. Revised manuscript received June 17, 2002. Accepted June 25, 2002.

AC025586H