SHORT COMMUNICATION

The contact angle between water and the surface of perfluorosulphonic acid membranes

T. A. ZAWODZINSKI Jr., S. GOTTESFELD
Electronics Research, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
S. SHOICHET, T. J. McCARTHY,
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, U.S.A.

Received 21 January 1992; revised 21 April 1992

Recently studies aimed at clarifying the effect of perfluorinated sulphonic acid membrane surface properties on their behaviour in fuel cells were initiated. These polymers generally consist of a poly(tetrafluoroethylene) (PTFE) backbone with sulphonate-terminated sidechains. A primary influence of membrane surface properties in fuel cells could be through surface effects on membrane hydration. The difference in the timescale for membrane equilibration with water in liquid and vapour phases may be explained by the effect of surface properties on membrane hydration. A membrane of thickness 178 μm equilibrates with liquid water within, at most, a few tens of seconds [1], whereas it takes much longer for this membrane to completely equilibrate with vapour phase water [2, 3]. (This is not simply because of the low concentration in the gas phase; a simple calculation shows that, at 1 atm vapour pressure, the membrane would be saturated with water in less than a second if the process were limited by the number of collisions of gas-phase water molecules with the membrane surface.) This difference in hydration dynamics may cause the apparent difference in equilibrium water uptake by ionomers from liquid and saturated vapour phases [3]. Surface effects may also account for the differences in water diffusion coefficients measured by (i) classical vapour-phase sorption methods, which involve transport of isotopically labelled water into, across, and out of a membrane sample, and (ii) NMR methods, which probe transport within the membrane. The vapour-phase sorption measurement yields apparent water diffusion coefficients significantly lower [4] than those determined by NMR [5]. The self-diffusion coefficients measured by the sorption method are weakly dependent on membrane water content while those measured by NMR depend strongly on water content. A hydrophobic membrane surface could control the flux observed in the sorption experiment and likely acts as a barrier to water transport into, and possibly out of, the membrane. Our work described here aims to determine whether or not such a hydrophobic 'skin' exists. We report here on water contact angles measured on the perfluorosulfonate ionomer membranes to obtain some information on the hydrophilicity of the ionomer surface.

2. Experimental details

Water contact angles were measured with a Rame-Hart telescopic goniometer with the droplet size controlled by a Gilmont syringe. Typical droplet volume was on the order of 10 μl, though of course the droplet size was varied in the experiment. The water was house distilled water which was redistilled using a Gilmont still. The advancing angle was measured as water was added to a droplet spreading over the membrane surface; it is the angle at the air/water/membrane interface between the horizontal and the tangent to the advancing drop. The receding angle at this interface was measured as water was withdrawn from the surface back into the syringe. Droplets were contacted with the membrane at several different spots on each membrane sample to obtain a series of advancing/receding contact angle pairs. All measurements reported here were carried out at ambient temperature (25–30 °C).

Contact angles were taken on membranes which had equilibrated with water vapour of known activity before and during the measurement in order to characterize more precisely the membrane dependence of the water contact angle on the membrane water content. This was accomplished by equilibration of the membrane samples with aqueous LiCl solution of known water activity in a sealed cuvette. Each pre-equilibrated membrane sample was mounted flat with double side tape on top of a hollow cylinder of Teflon placed in the cuvette. A small puncture was made through the parafilm sealed top of the cuvette immediately prior to the experiment, and the syringe was introduced through this hole. The contact angle for the sample was then measured as described above.

3. Results and discussion

3.1. *Measurements on immersed membranes*

Initially, the measurements were carried out on prehydrated membrane samples freshly removed from liquid water. As noted in the experimental section, the advancing/receding contact angle pairs were each obtained from a series of droplets exposed to different positions on the membrane. The results are summarized in Table 1. Because no attempt was made to control the atmosphere surrounding the membrane sample during the measurement, the membrane dried out with time after immersion. The time was not precisely noted, but some idea of the rate of change of membrane hydration is given by the total elapsed

0021-891X

Table 1. Contact angles (30 °C) for water on perfluorosulphonic acid membranes

Sample	*Contact angles (Advancing/Receding)**
Prehydrated Nafion® 117	87/27, 84/35, 94/29, 94/34, 99/35 (20 min)
Dry Nafion® 117	116/30, 115/? (5 min)
Prehydrated membrane C	85/32, 84/34, 88/32, 93/36 (15 min)
Dry membrane C	113/40, 113/42, 107/45 (15 min)
Prehydrated Nafion® 115	86/35, 83/33, 83/33, 85/37, 87/40 (10 min); After 10 more min.: 103/45
Prehydrated Dow	78/25, 81/24, 92/29.5, 88/32, 92/35 (15 min)

*The advancing/receding angle pairs are listed in order of increasing time from start of the experiment, providing a qualitative idea on the variation of the contact angles with time. Measurement times were not exactly noted, but total elapsed times are noted in the Table.

Table 2. Contact angles (30 °C) for water on Nafion® 117 membranes of controlled water content

Water content	P_{H_2O}/P_{H_2O}	*Contact angle (Advancing/Receding)*
0 H_2O/SO_3H	0	116/30
2 H_2O/SO_3H	0.14	115/0
4 H_2O/SO_3H	0.58	114/0
9 H_2O/SO_3H	0.82	107/0
14 H_2O/SO_3H	1.00 (vapour)	98/14

times listed in Table 1. Under such conditions, the advancing contact angle is characteristic of the surface when in contact with some level of water vapour in air, while the receding angle is characteristic of the surface of a fully hydrated membrane; prior to the receding angle measurement, the membrane is exposed to a liquid water droplet for a time sufficient to allow substantial uptake of water by the membrane surface layer, reaching a level characteristic of an immersed membrane. For the prehydrated and emersed sample, the first advancing angle measured was 87° and the first receding angle was 27°. The hysteresis between the advancing and receding contact angles is likely the result of several factors. The membrane surface may consist of an irregular array of hydrophobic and hydrophilic 'islands'. The hydrophobic component of the membrane surface, i.e., the PTFE groups, affects the contact angle by 'pinning' the water drop back from advancing whereas the hydrophilic component of the membrane, i.e. the sulphonate-terminated side-chains, tends cause a lower value of the receding contact angle relative to the advancing angle. When the membrane surface is in contact with water, the hydrophilic sulphonic acid moieties near the surface reorient such that they are exposed to the water, thus hydrophilizing the surface by increasing the proportion of the surface covered by hydrophilic islands. Such reconfiguration of the surface would be more facile following a significant water uptake due to the plasticizing effect of water on the polymer. An additional factor contributing to the significantly lower value for the receding contact angle is the penetration of liquid water into the outer polymer layers, causing the water droplet to be retracted across a hydrous surface. There are only weak trends in the values of receding angles reported in Table 1. Also, the receding angles were more difficult to estimate (Section 3.2). Therefore, we have primarily concentrated on the contact angle hysteresis instead of attempting to interpret the receding angle data.

Water droplets were contacted with the Nafion® 117 membrane surface over the course of approximately 5 to 30 min from the membrane immersion. The contact angles changed with time after immersion as summarized in Table 1. As the initially wet sample dries out under ambient conditions, the advancing contact angle continuously increases, indicating that the drier membrane has a more hydrophobic surface. Membranes dried over P_2O_5 prior to contact angle determination exhibited advancing contact angles similar to the contact angle of water on PTFE (116°) [5]. The advancing angles increase toward this extreme even as the membrane simply dries out in air at room temperature, as shown in Table 1. The receding angles for dry membranes were difficult (and sometimes impossible) to obtain accurately since the membrane tended to deform as the water droplet was withdrawn. Indeed, so strong was the affinity of the island of wet membrane under the droplet for the water droplet that it often detached and collapsed on the membrane surface rather than being taken back into the syringe. Membrane deformation during receding angle measurements also occurred in some cases for partially hydrated membranes. We thus use these receding angle data in only the most qualitative sense.

Immersed samples of other ionomeric membranes behaved in a similar fashion. Data for emersed samples of Membrane C (Chlorine Engineers Co., Equivalent Weight (EW) = 900, dry thickness = 5 mil), Dow XUS 13204.10 Developmental Fuel Cell Membrane (EW = 800, 4 mil dry thickness), and Nafion® 115 (EW = 1100, dry thickness = 5 mil) membranes were also obtained. The only difference in the data obtained for these membranes relative to Nafion® 117 was that the prehydrated, emersed Dow membrane initially exhibited a lower advancing contact angle. This result is in accordance with the very high water content of the immersed Dow membrane. The results for other membranes are also summarized in Table 1.

3.2. *Measurements on samples in contact with water vapour of known activity*

In order to obtain a more complete picture of the water/vapour/ionomer interface, particularly with respect to the water content dependence of the interface hydrophobicity, we performed experiments with controlled humidification conditions about the membrane. The results for Nafion® 117 membrane samples are summarized in Table 2. The contact angles indicate that the membrane surface is hydrophobic, even in contact with saturated water vapour. The samples with the lowest water contents exhibited advancing angles indistinguishable from those of completely dried membranes; however, some decrease in the apparent hydrophobicity of the membrane surface is observed as water is added from the vapour to the polymer. The very slight effects on surface hydrophilicity of as much as 9 H_2O/SO_3H (Table 2) can be understood remembering that, in membranes of low water content, the water essentially solvates only sulphonic acid moieties, whereas only in highly hydrated membranes water swells the polymer and behaves in a similar fashion to water in aqueous solutions. Furthermore, hydrophilic moieties may randomly reorient near the surface because the polymer is significantly plasticized as water is added to it. The membrane surface may reorganize to attain a close match to the dielectric properties of the medium to which it is exposed, a phenomenon suggested for other polymeric systems [7]. Air saturated with water vapor contains only 3–4 mol % water at ambient temperatures, while liquid water is of course a quite polar dielectric medium. This dependence of the surface state of the membrane on its surrounding medium also explains why the advancing angles obtained for emersed membranes are more similar to the advancing angles of the vapour-equilibrated membranes than to the receding angles of the emersed membranes. Once immersed and exposed to water vapour, the membrane is essentially the same as a vapour-equilibrated membrane, though with a higher water content.

4. Conclusion

It may be concluded that a substantial barrier to water uptake by membranes exposed to water vapour probably exists because of the rather hydrophobic membrane surface. The advancing contact angle for a membrane equilibrated with saturated water vapour is particularly high. The hydrophobicity of the membrane surface in contact with water vapour may be of practical importance in polymer electrolyte fuel cells because, particularly with certain humidification schemes, the sole external source of water is vapour carried with the gas streams into the fuel cell. Ionomeric membrane conductivity depends strongly on water content in the membrane, and thus on the efficiency of the specific humidification scheme employed in the cell. The results shown in Table 2 indicate that surface hydrophobicity could play an important role in the dynamics of ionomeric membrane hydration, and thus in determining overall polymer electrolyte fuel cell performance. The present work provides baseline data on the surface properties of perfluorosulphonic acid membranes.

References

[1] T. A. Zawodzinski Jr., C. Derouin, S. Radzinski, R.J. Sherman, V. T. Smith, T. E. Springer and S. Gottesfeld, *J. Electrochem. Soc.*, in press.

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

[3] T. A. Zawodzinski Jr., F. Garzon, V. T. Smith and S. Gottesfeld, paper presented at the 178th Meeting of the Electrochemical Society. Seattle, WA, October, 1990, Abstract number 117.

[4] H. R. Zelsmann, M. Pineri, M. Thomas and M. Escoubes, *J. Appl. Poly. Sci.* **41** (1990) 1673.

[5] T. A. Zawodzinski Jr., M. Neeman, L. Sillerud and S. Gottesfeld, *J. Phys. Chem.* **95** (1991) 6040.

[6] J. Brandrup and E. H. Immergut (eds), 'Polymer Handbook', 2nd ed., Wiley, New York (1975).

[7] J. D. Andrade, D. E. Gregonis and L. M. Smith, in: 'Surface and Interfacial Aspects of Biomedical Polymers', Vol. 1, (edited by J. D. Andrade), Plenum, New York (1986) Chapter 7, section 4.7, and references therein.