Wetting and Absorption of Water Drops on Nafion Films

Sharonmoyee Goswami, Shannon Klaus,[†] and Jay Benziger*

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263

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Water drops on Nafion films caused the surface to switch from being hydrophobic to being hydrophilic. Contact angle hysteresis of >70° between advancing and receding values were obtained by the Wilhelmy plate technique. Sessile drop measurements were consistent with the advancing contact angle; the sessile drop contact angle was 108°. Water drop adhesion, as measured by the detachment angle on an inclined plane, showed much stronger water adhesion on Nafion than Teflon. Sessile water and methanol drops caused dry Nafion films to deflect. The flexure went through a maximum with time. Flexure increased with contact area of the drop, but was insensitive to the film thickness. Methanol drops spread more on Nafion and caused larger film flexure than water. The results suggest that the Nafion surface was initially hydrophobic but water and methanol drops caused hydrophilic sulfonic acid domains to be drawn to the Nafion surface. Local swelling of the film beneath the water drop caused the film to buckle. The maximum flexure is suggested to result from motion of a water swelling front through the Nafion film.

Introduction

Nafion is a unique copolymer that finds extensive use as an ion conducting membrane in fuel cells and other applications.[1–6] It blends a hydrophobic backbone of tetrafluoroethylene (TFE), with side chains containing exceptionally hydrophilic sulfonic acid groups.[2,7,8] Disparity between hydrophilic and hydrophobic groups induce microphase separation giving rise to unusual physical and mechanical properties. Because of its utility as an ion conducting membrane in environments where water exists as a both a liquid and vapor it is important to understand how liquid water interacts with Nafion surfaces.

Nafion is a commercial product of DuPont. A number of papers have been published regarding Nafion's structure (see ref 1 and references therein). It is generally accepted that the polymer microphase separates into hydrophobic and hydrophilic domains.[7] The microstructure of Nafion is envisioned as sulfonic acid groups that cluster to form a hydrophilic microphase surrounded by a continuous hydrophobic TFE phase.[9] Water is absorbed into the hydrophilic domains solvating the acid groups causing the polymer to swell. In this paper we present a series of experiments aimed at understanding the nature of the liquid water/Nafion surface interactions.

Experimental Section

Wetting of Nafion was measured by Wilhelmy plate, sessile drop contact angle and adhesion to an inclined surface.[10] Similar experiments were carried out with Teflon for comparison. Wilhelmy plate measurements were done with a bottom hanging analytic balance (Ohaus Model ARO640). Strips of Nafion and Teflon 2.5 cm × 2.5 cm × 0.0127 cm were suspending from a bottom weighing hook. A mass was clipped to the bottom of the strips to keep them from curling. The balance was tared with the suspended substrates in place. A beaker with fresh DI water placed below the sample and the advancing contact angle was measured by raising the beaker in increments of 635 μm every 20 s and recording the mass. It was necessary to limit the equilibration time at each position because water absorbs into Nafion. The diffusion front for water is estimated to move 100 μm/min so we attempted to advance the liquid/solid contact faster than the water absorption front.[11] After the sample had been submerged by 15 mm the beaker was sequentially lowered and the receding contact angle measured. The data for the receding contact angle measurement was corrected for the mass of water absorbed by the Nafion. We assumed the film was uniformly hydrated after the advancing measurement and no water desorbed during the receding measurements. This resulted in a simple linear correction to the mass of the film. The measurements were repeated with at least three different samples. Advancing and receding contact angle measurements were also made for Nafion films soaked in water. Nafion 1110 films were soaked in DI water at room temperature for 24 h. The films were removed from the water, mounted with the clip to the balance. They were tamped dry with a tissue, the balance tared and then the contact angle measurement proceeded as outline above. We do not report any results for measurements of membranes presaturated with methanol. Excessive membrane distortion and methanol evaporation resulted in large variations with the Wilhelmy plate measurements.

Nafion films had a tendency to curl or be pushed sideways by the water as the films were submerged, which limited to accuracy of the contact angle measurements to ±5°. To avoid the effects of film deformation measurements were carried out with thin Nafion films coated onto stiff substrates. Nafion solutions (5 wt % 1100 equivalent weight Nafion in mixed alcohol solvents from Ion Power) were air-brushed to a loading of 0.2 mg Nafion/cm^2 onto carbon paper (Toray paper from E-TEK Division of De Nora N.A., Inc.) and 79 μm thick α-alumina strips. The Nafion films (~1 μm thick) were annealed to 160 °C after deposition. This produced a nonporous coating of Nafion on the substrate. Advancing and receding contact angle measurements were obtained with these samples.

Sessile drop measurements were obtained with water drops placed on Nafion and Teflon films. Nafion films with dry thicknesses of 51 (Nafion 112), 127 (Nafion 115) and 254 μm (Nafion 1110) were

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* To whom correspondence should be addressed. E-mail: benziger@princeton.edu.

[†] Currently at the University of Missouri.

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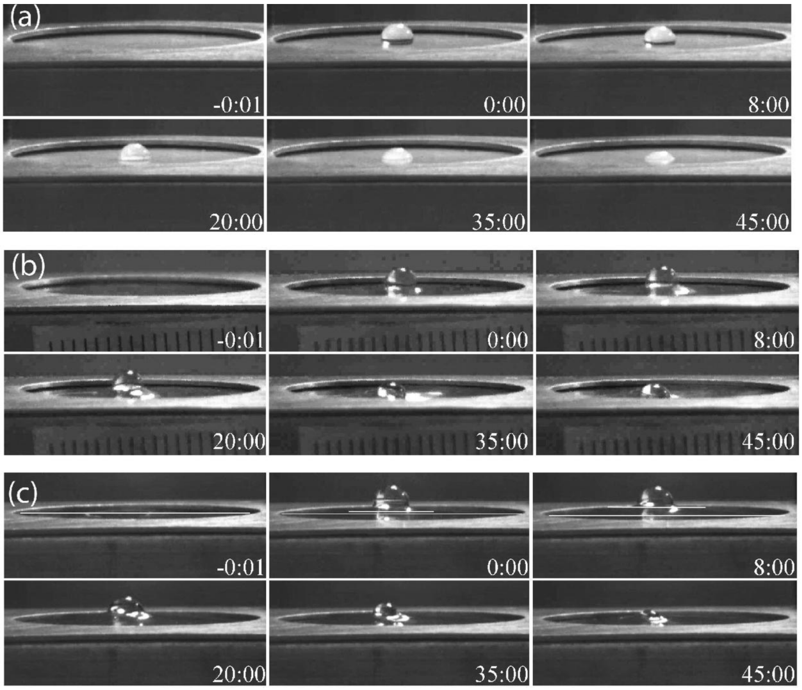

Figure 1. Time sequence of water drops evaporating from the surface of (a) Teflon, (b) hydrated Nafion and (c) dry Nafion films. These films were constrained. The complete video sequences of these three experiments can be view at http://pemfc.princeton.edu/data.html.

Table 1. Contact Angles for Nafion and Teflon

liquid/ substrate	advancing contact angle	receding contact angle	sessile drop contact angle
water/Teflon	110	95	110
water/Nafion	105	25	105
water/Nafion on Carbon	110	40	110
water/Nafion on Alumina	107	30	105
octane/Teflon	20	15	>15
octane/Nafion	25	15	>15
methanol/Teflon			20
methanol/Nafion			20

tested. Unconstrained disks 12 mm in diameter were dried at 70 °C in a vacuum oven and stored in a desiccator at room temperature until use. Additional samples were also stored above liquid water for >24 h and tested. The unconstrained samples were laid on a glass substrate in front of a video camera and water drops of 3, 5 or 10 μL were placed on the substrate. The drop and the Nafion substrate were filmed from just before the drop was placed on the substrate until the drop had evaporated.

The adhesion of water to Teflon and Nafion was measured with an inclined plane. Strips of Teflon and Nafion were clipped to a glass slide and mounted on a rotatable stage. The Nafion was soaked in liquid water for 24 h and stretched onto the glass slide. Drops of water were placed on the films and the films were rotated from horizontal toward vertical. The contact diameter of the drop and the angle where the drop detached from the film surface were recorded. The interfacial adhesive energy was determined from the gravity force necessary to detach the drop.

The unconstrained Nafion samples buckled almost immediately after the water drops were placed on the surface. The samples flattened out again after the water drop evaporated; however the buckling was not always uniform. To quantify the buckling a frame was made that constrained a Nafion film. The film was clamped in place with a free area 24 mm in diameter as seen in Figure 1. Water drops were placed at the center of the film. The samples bowed uniformly up when water drops were placed at the center and the films returned to flatness after the drops evaporated. The frame holding the Nafion sample was placed on an analytic balance interfaced to a computer. The mass of the sample as a function of time was recorded from placement of the drop until the mass returned to its initial value. Video images of the Nafion film were collected and time stamped during the placing of the water drop and its evaporation. Experiments were carried out with drops of deionized water and methanol.

Results

The advancing and receding contact angles for Nafion and Teflon films obtained by the Wilhelmy plate measurements are summarized in Table 1. There was little difference between the values obtained by the free-standing film compared to the values obtained from a Nafion film deposited on carbon paper or alumina; the small differences in the receding contact angles were probably due to different surface roughness and distortion of the free-standing films. Teflon had an advancing contact angle of 110° and a receding contact angle of 95°. The Teflon surface was nonwetting for water in both the advancing and receding modes. The advancing contact angle for Nafion was 105−110°, close to that observed for Teflon. In contrast the receding contact angle

Table 2. Nafion Deformation by Water, Methanol and Octane on Nafion

liquid/drop volume (μL)	film thickness (μm)	contact diameter of drop (mm)	maximum film flexure (mm)	time to maximum flexure (s)
octane 10 μL	127	24	0	no flexure
water 10 μL	50	2.6 ± 0.4	1.1 ± 0.3	300 ± 50
water 10 μL	127	3.2 ± 0.4	1.2 ± 0.3	550 ± 50
water 10 μL	254	3.2 ± 0.4	0.9 ± 0.3	750 ± 100
water 5 μL	127	2.7 ± 0.4	0.7 ± 0.3	450 ± 75
water 20 μL	127	3.8 ± 0.4	1.5 ± 0.5	600 ± 75
methanol 10 μL	127	7.6 ± 0.6	2.1 ± 0.4	100 ± 25

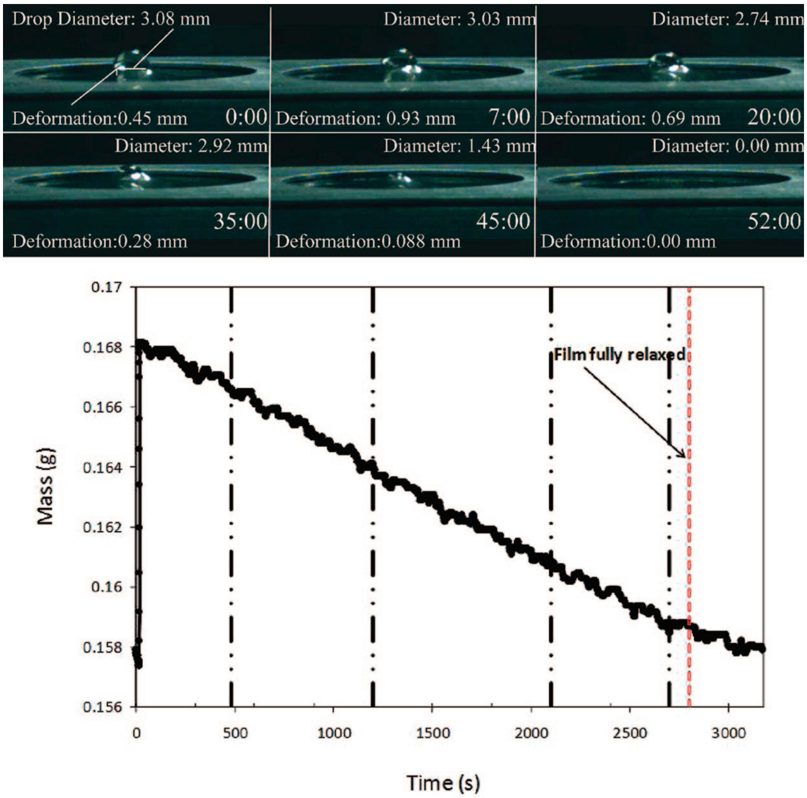

Figure 2. Placement and evaporation of a water drop on a dry Nafion 115 film. The time shown is in minutes, and the times at which the images are given with respect to the mass remaining are demarcated by the dashed black lines on the graph. The time sequence shows the rapid buckling of the film after placement of the water drop, followed by a long period of time while the drop evaporated with little change in the buckling of the film, and finally the disappearance of the drop with the film returning to its original flatness.

Table 3. Adhesive Energy for Water and Methanol on Teflon and Nafion

liquid/solid	V_{drop} (μL)	D_{drop} (mm)	critical angle for drop detachment	interfacial adhesion (dynes/cm)	interfacial adhesion from Wilhelmy plate
water/Teflon	10	4.0	no detachment		
water/Teflon	20	5.1	no detachment		
water/Teflon	40	7.6	20°	57	25
water/Teflon	60	8.8	15°	55	25
water/Nafion	10	4.0	no detachment		
water/Nafion	20	5.2	no detachment		
water/Nafion	40	7.4	no detachment		
water/Nafion	60	10.4	55°	148	91
water/Nafion	100	11.0	25°	120	91

for Nafion was between 20° and 30°; water was strongly wetting Nafion in the receding mode. Nafion went from being hydrophobic (Teflon-like) in the advancing mode to hydrophilic in the receding mode.

Figure 1 shows 10 μL sessile drops as a function of time on 127 mm films of Teflon (a), Nafion equilibrated at water activity unity (b), and dry Nafion (c). These were obtained in weighing chamber of the analytic balance with a constant flow of dry air to keep the humidity close to zero. In the dry environment the water drops evaporated. Sessile water drops on Teflon and hydrated Nafion appear similar. The drops initially have a contact angle of 105−110°. As the drops evaporated they did not retain their spherical shape. The drop circumference appeared to be pinned until the later stages of evaporation. The circumferential pinning was more noticeable with Nafion where the area of the drop only receded when evaporation was almost complete. Both Teflon and hydrated Nafion films remained nearly flat from the time the water drop was placed on the surface until the drop evaporated.

Placing a sessile drop of water on a dry Nafion film caused it to bend. Flexure began immediately when a drop of water is placed a dry film. The film flexure increased for 200−1000 s, went through a maximum and then decreased. The flexure of the dry Nafion film by water shown in Figure 1 can be most readily identified by examining the location of the constraining plate. In Figure 1a and b the Teflon and hydrated Nafion films show no movement relative to their interface with the constraining plate. In contrast, the interface between the Nafion film and the constraining plate cannot be seen after the water drop is place onto the Nafion film. A 10 μL water drop placed on an unconstrained 127 μm thick Nafion films, 12 mm diameter, bowed 2−3 mm. The deformation was 1−1.5 mm with constrained 24 mm diameter film as seen in Figure 1c. The time to maximum deformation and the maximum film deformation for Nafion 112, 115 and 1110 are summarized in Table 2.

Sessile drop experiments were also carried out with octane and methanol on Teflon and Nafion. Octane almost completely wetted both Teflon and Nafion (contact angle of less than 15°).

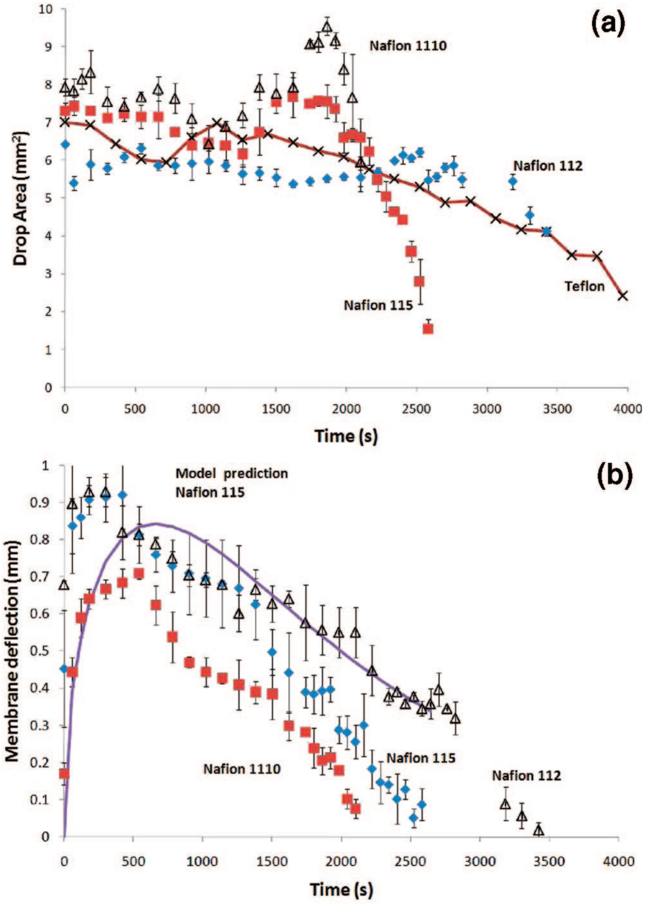

Figure 3. Water drops on Nafion membranes: (a) Drop area as a function of time and (b) Membrane deflection as a function of time. The solid line in (b) is the model prediction for Nafion 115.

Octane drops did not deform either the Teflon or Nafion films. Methanol showed intermediate wetting of both Teflon and Nafion; the wetting angle was approximately 20° on both Teflon and Nafion. Methanol drops spread out on Nafion, in contrast to water drops which remained nearly spherical (Figure 6 shows the difference of drop shape for 10 μL drops of water and methanol). Methanol drops on Nafion caused greater film deformation than water drops. The film flexure was faster with methanol as well.

Water and methanol evaporate in dry air; at room temperature a 10 μL drop of water on Teflon evaporated in 4000 s, a 10 μL drop of methanol on Teflon evaporated in 400 s. On Teflon the disappearance of the drops coincided with complete mass loss. The water and methanol drops placed on dry Nafion disappeared in less time than on Teflon and before complete mass loss. Both water and methanol were absorbed into the film; absorbed solute continued to desorb after the surface drop disappeared. A sequence of images and the mass versus time for a sessile water drop on Nafion115 (127 μm thick) are shown in Figure 2. A 10 μL water drop placed on the film increased the mass by 10 mg. The mass decreased linearly with time as the drop evaporated. The Nafion film began to buckle immediately and went through a maximum flexure ca. 500 s; the flexure slowly declines with the membrane flattening out after 2500 s. (Videos of these experiments are available on our Web site at http://pemfc.princeton.edu/data.html). A 10 μL water drop on Nafion 115 disappeared almost 1000 s before all the water had evaporated (see Figure 2). After the drops have disappeared the films flatten out returning to their "original" shape in approximately 100 s, well before all the water evaporated.

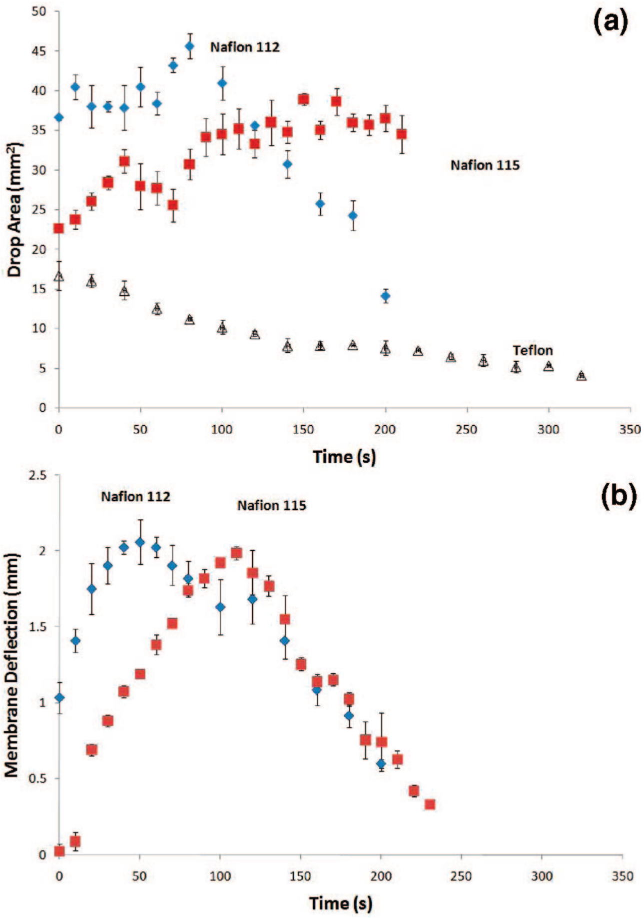

Figure 4. Methanol drops on Nafion membranes: (a) Drop area as a function of time and (b) Membrane deflection as a function of time.

During the drop evaporation and film deformation we monitored the drop size (area of the drop) and the film flexure (change in elevation of center point of the film relative to its starting point). Figures 3 and 4 are representative data for both water and methanol drops. The data points in Figures 3 and 4 were obtained from the video images. The images from three drops were averaged for each data set. Drop area was nearly constant until a short time before the drop disappeared. Film deformation stops about 100 s after the drop disappeared. Evaporation continues after the drop disappeared and the film was no longer deformed. Film deformation was fast followed by a slower decline. The maximum film flexure appeared to be independent of film thickness, but the time for the maximum deformation increased with increasing film thickness. The effect of film thickness on the maximum deformation was more apparent for methanol drops as seen in Figure 4.

Adhesion energies for water and methanol on Teflon and Nafion are summarized in Table 3. The adhesion force is found from the gravitational force required to detach a drop. If the gravitational force is less than the adhesive force the drop will not detach regardless of the angle of the film relative to gravity. The adhesion energy of the liquid per unit area is the adhesive force of detachment divided by the contact perimeter, as given by eq 1. The expression at the center in eq 1 is the adhesive energy based on the contact angle hysteresis.[12–15] Only when the equality

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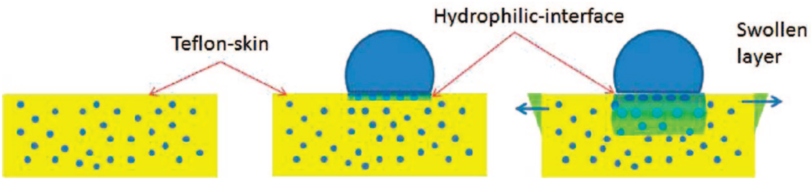

Figure 5. Schematic of restructuring of the Nafion surface by exposure to liquid water. A dry film has the hydrophilic groups distributed throughout the continuous hydrophobic TFE matrix (a). Placing a drop on the surface causes the hydrophilic domains to move to the surface to contact the water drop (b). The water diffuses into the film causing the film to swell underneath the drop. This creates a differential expansion between a top wet layer and a bottom dry layer (c). The wet layer is under compression from the dry layer and the dry layer is under tension from the wet layer.

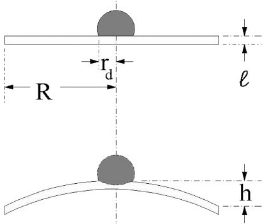

Figure 6. Schematic of Nafion deformation by addition of a water drop. Within seconds of placing the drop on the film with thickness ι and initial radius *R* the film buckles rising by a height *h*.

constraint in eq 1 is satisfied will the drop detach. Even for hydrophobic surfaces like Teflon, water drop sizes must be greater than 30 μL for the gravitational force to satisfy the inequality in eq 1 and detach.

$$\text{adhesion energy} = \gamma(\cos\theta_r - \cos\theta_a) \geq \frac{m_{\text{drop}} g \sin\phi_{\text{detachment}}}{2\pi r_{\text{drop}}} \qquad (1)$$

The adhesive energy for the water drops to both Teflon and Nafion determined by experiment are greater than predicted by contact angle hysteresis predicted by eq 1. The important result in Table 3 is that the difference in adhesive energies between Teflon and Nafion are consistent with the difference in contact angle hysteresis observed by the Wilhelmy plate measurements. Both the Wilhelmy plate measurement and the adhesion energy indicate a large hysteresis of the surface of Nafion after exposure to liquid water.

Discussion

The two key results from these measurements of water on Nafion surfaces are

1. Nafion surfaces changed from hydrophobic to hydrophilic when exposed to liquid water. The advancing contact angle of water on Nafion was 110°, approximately equal to that for poly(tetrafluoroethlyene). The receding contact angle of water on Nafion was <30°. The adhesion energy of water drops also show the Nafion surface is hydrophilic.
2. Liquid water and methanol drops caused Nafion films to deform. The maximum deformation occurred within 100−500 s. Film deformation disappeared rapidly after the drop has disappeared from the surface of the film.

The contact angle of water on Nafion from the Wilhelmy plate method and sessile drop measurements has previously been reported by several investigators.[16–20] Zawodzinski et al. and Yu et al. both reported a substantial contact angle hysteresis. Those studies also reported some differences in advancing contact angle between hydrated and dry Nafion films, but the contact angle hysteresis was seen for both cases. Those studies suggested that the surface flipped from hydrophobic to hydrophilic when exposed to liquid water. Kim et al. used surface wetting by different liquids to evaluate the surface properties of Nafion; they also concluded that the surface composition changes due to exposure to liquid water.[20] McLean and co-workers employed AFM to image the surface of Nafion and concluded that the surface had a thin fluorine rich “barrier” covering the surface.[21]

Several investigators reported the contact angle for sessile drops changed as a function of time due to drying.[16,18,19] The photos of Yu et al. even show buckling of a dry Nafion film when a water drop is placed on the film.[19] However, no one seems to have made any effort to quantify the flexure of the film.

The surface composition of Nafion can have a major impact on the transport of water through Nafion membranes. Weber and Newman pointed out that a surface skin of “teflon” could alter the transport of water at the membrane/gas interface.[22] Recently Benziger and co-workers have shown that water permeation through Nafion membranes and water absorption by Nafion films are both controlled by interfacial mass transport and not diffusion.[11,23] Those results point out the importance that the interfacial compostion can have.

Teflon and Nafion showed similar contact angles by sessile drop and in the advancing mode with a Wilhelmy plate. However, they showed dramatically different contact angles by the receding mode of the Wilhelmy plate. The adhesive forces of water drops were much greater for Nafion than Teflon; this is consistent with the large contact angle hysteresis seen with the Wilhelmy plate. The contact angle hysteresis and the adhesive force suggest that the Nafion surface changed from hydrophobic to hydrophilic when contacting liquid water or methanol.

The unusual behavior of Nafion can be rationalized by molecular rearrangements at the polymer-fluid (gas or liquid) interface to minimize the surface energy. When Nafion is exposed to a gas interface the surface energy is minimized by presenting a hydrophobic poly(tetrafluoroethylene) interface to the gas. In contrast when the surface is exposed to liquid water the hydrophilic sulfonic acid groups are drawn to the surface. This restructuring is summarized schematically in Figure 5 a and b. Water will also associate with the sulfonic acid groups drawn to the surface so there will be swelling of the surface region. The propagation of this swelling region is what causes the film to buckle. The final

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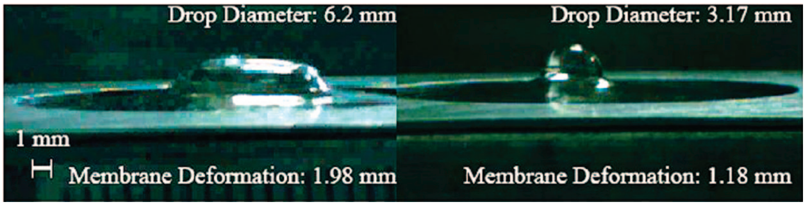

Figure 7. Deformation of Nafion 115 from a 10 mL drop of methanol and water, respectively. The deformation occurred in ~50 s in methanol, and 6 min in water after placing the drop on the surface (maximum deformation shown).

composition of the surface will depend on the bulk composition of the Nafion. Elastic energy is spent in deforming the polymer to pull the sulfonic acid groups to the surface. The composition will depend on the balance of the interfacial energy gain offset by the elastic energy of deformation.

The perimeter of the water drops did not change until the drop was nearly completely evaporated. We thought this was indicative of the contact angle hysteresis seen with the Wilhelmy plate measurements. However, a similar result was found with Teflon. Panwar et al. also reported similar pinning of the water contact line during evaporation from glass and polycarbonate surfaces.[24] The pinning of the contact line perimeter is the result of contact angle hysteresis and is not unique to Nafion.

Surface restructuring between hydrophobic and hydrophilic surfaces have been seen in poly(2-hydroxyethyl methacrylate) (PHEMA), which possess a mixture of hydrophobic and hydrophilic groups along a flexible backbone.[25,26] Sum frequency generation spectroscopy showed that the surface of PHEMA is comprised on hydrophobic methyl groups when exposed to air, but rapidly restructured to expose the hydrophilic hydroxyethyl methacrylate groups when the polymer is exposed to liquid water.[27] Similar results have been obtained with poly(*n*-octyl methacrylate) (POMA).[28] These transitions in PHEMA and POMA are reversible and rapid, similar to the reversible transition seen with Nafion. The large difference that the two microphase domains have with water drives the restructuring of the surface composition. Segregation of hydrophilic domains to the Nafion/water interface has also been suggested to affect transport of water across Nafion membranes.[22,29]

The most dramatic result from the experiments reported here was the large deformation of the Nafion films associated with the sessile drop. There are reports of adsorbed layers causing film deformation.[30–33] Those who work with Nafion know that it swells and deforms when exposed to water. But we have not seen any attempts to quantify the rate and magnitude of Nafion film deformation when exposed to water or methanol.

Figure 2 shows that deformation of the dry Nafion film after placing a water drop at the center of the film; a schematic of the deformation is shown in Figure 6. Water absorption swells Nafion. Placing a drop on one side of the film causes a differential expansion across the membrane. The local swelling creates a stress field; the dry side of the film that is under tension, while the wet side is under compression. The rate and magnitude of the deformation is a complex problem that depends on the elastic properties of Nafion, the rate of water diffusion in Nafion and the rate of polymer stress relaxation of Nafion. The mechanical and transport properties are all dependent on the local water content.[23,34]

We present here a simple semiquantitative model to explain the magnitude and rate of the deformation. A schematic of the buckling of the film due to the water drop is shown in Figure 6.

Water transport and the mechanical response are assumed to occur independently (i.e., it is assumed that water absorbs and then the film relaxes in response to the water absorption). Water transport in Nafion is by frontal movement between a water swollen region and an unswollen dry region. The frontal movement can be approximated by equation 2 where D is the diffusion coefficient, l_{Nafion} is the membrane thickness and l_{wet} is the thickness of the water saturated part of the film.

$$\frac{l_{wet}}{l_{Nafion}} = \left(1 - \exp\left(-\frac{D}{l_{Nafion}^2}t\right)\right) \qquad (2)$$

The diffusion coefficient has been determined from water permeation studies;[11] an approximate value of 2×10^{-7} cm^2 s^{-1} will be used here.

In a typical experiment the Nafion film is 0.05−0.25 mm thick, the film diameter is 24 mm and the drop diameter is 3 mm. During the 3600 s while the water drop evaporates the water diffusion distance, $\sqrt{Dt}$, is <0.6 mm. This is sufficient for water to diffuse transverse through the Nafion film, but lateral diffusion is not significant relative to the drop size. Hence the swelling of the polymer film from water or methanol drop can be viewed as disk of radius r_{drop} that grows in thickness l_{wet} with time.

The mechanical stress field in the Nafion film can be approximated from a two layer model. The top layer has thickness l_{wet} and is expanded by a length $\varepsilon_{wet} = (r_{drop})\delta/R$, where δ is the linear expansion coefficient for water or methanol absorption, r_{drop} is the radius of the drop and R is the radius of the film. The linear expansion of Nafion from water uptake is 20%.[8,35–38] The bottom layer has a thickness $l_{Nafion} - l_{wet}$. The total stress across the Nafion film must be zero so the top layer is in compression and the bottom layer is in tension. The Nafion will deflect because of the differential stress. The top layer can be treated as a composite, a dry ring surrounding a wet disk. The effective elastic modulus can be found from the elastic moduli of the dry Nafion (E_{dry}) and wet Nafion (E_{wet}) as given by eq 3.

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$$E_{effective} = \frac{2E_{dry}\dfrac{R-r_{drop}}{R}}{1+\dfrac{E_{wet}}{E_{dry}}\dfrac{r_{drop}}{R-r_{drop}}} \tag{3}$$

The differential strain between the top layer and the bottom layer is given by equation 4.

$$\Delta\varepsilon = \varepsilon_{wet} - \varepsilon_{dry} = (\delta r_{drop})\left(\frac{l_{wet}}{l_{Nafion}}\right) \times \left\{\frac{\left(1+\dfrac{E_{wet}}{E_{dry}}\left(1+\dfrac{\delta r_{drop}}{R}\right)\right)}{1+\dfrac{E_{wet}}{E_{dry}}\left(1+\dfrac{\delta r_{drop}}{R}\right)\dfrac{l_{wet}}{l_{Nafion}-l_{wet}}}\right\} \tag{4}$$

The differential strain gives rise to deflection of the film. The height of the deflection increases with the differential strain as given by eq 5.

$$h = \sqrt{2\Delta\varepsilon R r_{drop}} \tag{5}$$

The deflection goes through a maximum when the water has penetrated approximately halfway through the film (the distance depends on the ratio of the elastic modulus of wet and dry Nafion). Beyond that point the amount of compression from the bottom half of the film decreases, so the film is expanded but the differential expansion across the film is reduced.

The wet film thickness can be evaluated as a function of time using eq 2 and substituted into eq 4 to determine the differential strain as a function of time, and finally the height of the flexure versus time can be evaluated. The film deformation data shown in Figure 3 has been fit to model using $(E_{wet}/E_{dry})=0.5$ and $D = 2 \times 10^{-7}$ cm^2/s. The rise and fall of the deflection as a function of time are captured by this simple model. The maximum deflection corresponds to the water front penetrating to the midplane of the Nafion film. The model indicates that the deflection increases with the differential strain. Increasing the drop size, which increases the differential strain, caused greater deflection. The maximum deflection height is independent of film thickness, but the time to achieve maximum deflection increases with film thickness—both trends were verified experimentally.

The model presented here indicates that the rate of the deflection should increase with diffusivity. The diffusivity of methanol in Nafion is greater than water. Figure 4 shows the deflection of the Nafion film occurred faster with methanol. The methanol drops also spread more resulting in greater strain and greater deformation. This is illustrated in Figure 7 which compares the deformation of Nafion from 10 μL drops of water and methanol.

Very little buckling was observed with fully hydrated films. When the film was fully hydrated there is no driving force to absorb water and swell the film. However, we frequently saw small deformation of the thin hydrated films. This may be attributed to water desorbing from the bottom surface of the film creating a differential stress. Water diffusion through the film from the drop eventually restores the water through the central cylinder of the film and the film relaxes to being flat. In the initial stages of our work with sessile drops we did not control the ambient humidity and saw large difference in the membrane deformation. Our experience suggests that the surface of Nafion exposed to any gas phase (even high humidity) will be hydrophobic and is changed to hydrophilic when exposed to liquid water. The sessile drops advancing and receeding contact angles will show the similar hysteresis. However, the film deflection is the result of the differential swelling resulting from water absorption. Membranes equilibrated at intermediate relative humidities will be uniformly partially swollen. A liquid water drop placed on the suface will result in absorption and flexure of the film, but the magnitude of the deformation will be reduced.

Conclusions

Adsorption of water onto Nafion surfaces causes the surface to switch from being hydrophobic to being hydrophilic. Liquid water draws sulfonic acid groups to the surface of Nafion. This structural change produces a large contact angle hysteresis for water with Nafion. Water and methanol absorb into Nafion films underneath liquid drops creating a differential stress which deforms the Nafion film. The flexure caused by drop adsorption increases with drop size and decreases with film thickness. Methanol drops produces larger film buckling than water. The results indicate that liquid drops can change the surface composition of Nafion and cause substantial deformation of thin Nafion films.

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