Published in final edited form as:

Langmuir. 2013 February 26; 29(8): . doi:10.1021/la304418p.

CHARGE-BASED FORCES AT THE NAFION-WATER INTERFACE

Ronnie Das* and Gerald H. Pollack

Department of Bioengineering, University of Washington, Seattle, WA 98195

Abstract

Interfacial water lying next to hydrophilic surfaces has been shown to be spectroscopically, mechanically, and electrically distinct from bulk water. Interfacial water has also been shown to exclude negatively- and positively-charged microspheres, and has thus become known as the “exclusion zone.” Measurements have demonstrated that exclusion zones exhibit a negative electrical potential on the order of -100 mV relative to bulk water, with a corresponding distribution of positive protons in the bulk water region beyond the exclusion zone. This separation of charge is hypothesized to create an electrostatic force between the exclusion zone and the proton-enriched zone beyond. To test this hypothesis, a hydrophilic Nafion ring was attached to the tip of a deflectable ribbon-like force sensor. The sensor was designed to obstruct the flow of protons from one side of the lever to the other, so that any proton-based force would remain unilateral. pH-sensitive dye measurements confirmed that the protons were largely confined to one side. When the lever assembly was exposed to water, the sensor deflected toward the protons. Over a period of 20 min, deflection amounted to approximately $20\text{ }\mu\text{m}$, corresponding to a force of approximately $22\text{ }\mu\text{N}$. Hence, electrostatic forces are confirmed. If exclusion zones exist ubiquitously at hydrophilic surfaces, including biological surfaces, then the resulting electrostatic forces may play significant roles in many biological phenomena including adhesion and protein folding.

I. INTRODUCTION

Charged surfaces are centrally important to many natural processes. These processes include the gecko’s ability to climb up vertical faces to evade predators, the *Stenocara* beetle’s capacity to harvest drinking water out of desert air, and the honeybee’s collection of pollen from flowers. As unrelated as these examples may appear, a common feature is the involvement of surface water films^{1–3}.

In the last decades, advances in instrumentation have sparked a renewed interest both in the nature of charged surfaces and in the role of the interfacial water nearby^{4–12}. Spectroscopically^{4–6}, mechanically^{7–10} and electrically^{11–12} distinct from bulk water, the interfacial water first studied by theoreticians in the mid-19th century^{13–18} has become amenable to study by diverse methodologies. These range from boundary layer observations along biological surfaces^{19–21} to the study of hydrated polymers^{11–12,22–27}. Recently, surface measurements have demonstrated how largely different the mechanical properties of interfacial water can be from bulk water^{4,8,10,12}. Such investigations have shown that interfacial water is ordered^{4–5,7–8,11–12} and that the interfacial zone may span up to hundreds of micrometers from a surface^{4,8,12,19–22}.

An increasingly popular tool for studying interfacial water is the polymer Nafion. Next to that hydrophilic polymer, the ordered water has been found to exclude microspheres, other nanoparticles, and dyes for distances up to 200 – 300 micrometers²³. Because of this

Corresponding author: Ronnie Das, Telephone number: 1.858.361.6692, rdas@u.washington.edu.

exclusionary feature, the interfacial water zone has been called the exclusion zone^{11–12}. Previous measurements have demonstrated that exclusion zones commonly possess a negative electrical potential relative to bulk water¹¹, while the bulk water situated beyond the exclusion zone region is concentrated with protons²⁸. Thus, some separation of charge appears to occur between the exclusion zone and the bulk water region beyond.

Although charge separation is well characterized in some solids, including the P-N junction between semiconductor crystals, charge separation in aqueous solution is more complex due to the multiplicity of charge carriers ordinarily present in water (including water dipoles) and their diverse range of mobilities. Nevertheless, the charge separation leads naturally to the hypothesis that the separated charge may create a significant electrostatic force. Here we describe the testing of this hypothesis.

II. METHODS

Two primary experimental approaches were employed. The first approach was aimed to confirm that a separation of charge occurs between the exclusion zone and the bulk water, as reported earlier^{12,28}. This objective was achieved by measuring the proton distribution in the bulk water using pH-sensitive dye. The second approach made use of a simple mechanical sensor to directly measure the hypothesized electrostatic force-based deflection when an exclusion-zone-generating Nafion tube was attached to the tip of the sensor. Finally, both approaches were combined to measure proton distributions during sensor deflection and correlate measured experimental force data with calculations based on electrostatic interactions.

pH-Sensitive Dye

To measure the proton distribution in the bulk water beyond the exclusion zone, universal pH-sensitive dye (Science Lab, Universal Indicator Solution, Catalog #SLU1051) was added 1:50 v/v to 850 μL of ultrapure water (Barnstead, Inc., D3750 Nanopure Diamond Water, ρ 18 $\text{M}\Omega \cdot \text{cm}$). The solution was then pipetted into a glass chamber containing a 500- μm long Nafion tube (PermaPure, LLC, Nafion tube, Model #TT-030, nominal outer diameter = 840 μm).

The chamber was constructed from glass microscope slides attached together using UV-curing glue. Four pairs of stacked slides formed the sides of the chamber and were glued together at their edges. A coverslip was glued to the bottom to create a chamber $2.5 \times 1.5 \text{ cm}$ in area with a height of 2 mm.

To set up an exclusion zone we used a Nafion tube, as specified above. Nafion is a copolymer consisting of a sulfonated polytetrafluoroethylene (Teflon) chain. The Nafion tube was held upright and in place by a platinum wire that acted as a mechanical scaffold (figure 1a). Lighting from below illuminated the chamber as it was filled (figure 1b–c) and a digital camera (Scion Corporation, Inc., Color Digital Camera, Model #CFW-1312C) recorded images of the chamber at 1 fps.

pH-dye was also added (1:50 v/v) to each of several identical chambers containing acid solutions of pH 0–7 in order to produce a calibration correlating the intensity of red color (corresponding to high proton concentrations) to pH value (measured with a standard pH meter). Red color is the product of the pH-dye's chemical constituents that react to low pH (acidic) solutions. Therefore, a second set of calibrations was also performed with the previous acid titrations, but at different pH-dye concentrations (1:100, 1:200 and 1:400 v/v). These calibrations determined the smallest concentration of dye that continued to produce a

measurable red color and consequently, and would yield an estimate for the concentration of protons in the bulk water.

Mechanical Deflection Approach

To test the hypothesis that electrostatic force exists between the exclusion zone and the bulk water, we used the apparatus diagrammed in figure 2a. A Nafion tube $\sim 200\text{ }\mu\text{m}$ long was glued (KrazyGlue) to the tip of a silver, ribbon-like cantilever. The tube created an exclusion zone with protons in the bulk water beyond. The ribbon-like cantilever had a high aspect ratio: the large face attached to the Nafion sample was as wide as the tube was long, and practically as high as the chamber fluid in which the assembly was placed. These features were expected to restrict most protons to one side of the cantilever. Hence if electrostatic attraction between the negative exclusion zone and the positive bulk were of significant magnitude, the cantilever would bend toward that positive bulk, and the deflection would be measured optically (figure 2b).

The ribbon-like cantilever was made from a $75\text{-}\mu\text{m}$ diameter silver wire (A-M Systems, Inc., silver wire #785500). The wire was fed between two metal rollers, which flattened the wire into a ribbon-like shape. Ribbon length was cut to 5 mm. Ribbon width and thickness were measured optically and averaged 220 ± 5 and $31 \pm 3\text{ }\mu\text{m}$, respectively. Measured ribbon stiffness was $1061 \pm 84\text{ pN/nm}$. A stationary beam, situated parallel to the cantilever, served as a reference. The reference beam consisted of a stiff 26G hypodermic needle, 7 mm long and $450\text{ }\mu\text{m}$ in diameter. The needle's luer-lock connector was cut off, so that the end of the needle could be superglued into the ribbon holder in the same fashion as the ribbon-like sensor.

Once assembled, the mechanical sensor assembly was placed in the middle of the chamber (figure 2c). The chamber was the same as the one used for the previously described experiments, and the same volume of water was added slowly, over a period of one minute, in order to minimize any disruptive effects of turbulence. Measurement and reference beam positions were recorded in a movie at 5 fps using a LabVIEW-controlled camera (Edmund Optics, 1/2" CMOS Color USB Camera, Model #EO-3112C). A MATLAB-based algorithm measured and analyzed beam positions in the movie and plotted their positions over time. Control experiments consisted of the same experimental procedures, but without an attached Nafion tube.

III. RESULTS

pH-Sensitive Dye

To measure proton distribution, a volume of water containing pH-dye was added to the chamber containing the vertically oriented Nafion tube, the latter held stationary by a wire inserted into the tube. A dye-free exclusion zone soon began forming at the tube's outer surface. The exclusion zone was similar to those observed in previous studies, where the excluded substances were microspheres¹¹⁻¹². pH-dye in the bulk water immediately began turning red, denoting low pH and a high concentration of protons. Over 5 min (figure 3), the dye-free exclusion zone had grown to approximately $300\text{ }\mu\text{m}$ (and remained approximately steady thereafter), while the proton-rich region beyond the exclusion zone had grown approximately ten times thicker as a result of diffusion, and continued to grow into the surrounding bulk.

Based on the pH-dye calibration, the pH value at the very boundary of the exclusion zone at 5 min was approximately 2.3. pH values farther from the exclusion zone were higher; i.e., proton concentrations were lower. By using a spectrum of dye concentrations, properly calibrated, ranging from 1:400 to 1:50, v/v, we could measure the range of pH values over

the entire chamber. At 5 min, those pH values yielded a total number of protons ranging, in different experiments, from 8×10^{13} to 2×10^{15} .

Mechanical Deflection Measurements

Following the addition of water to the Nafion-beam assembly, the sensor began deflecting away from the stationary reference beam. Figure 4a shows selected movie frames taken during a representative run. At 20 min, deflection was 25 to 30 μm . Corresponding records of beam positions over time are plotted in figure 4b-top. Approximately 75% of the maximum recorded deflection occurred within the first 90 s of adding the water (figure 4b-top); deflection continued for the duration of the experiment.

Corresponding records without a Nafion tube attached to the beam are plotted in figure 4b-bottom. The sensor remained relatively static, varying in position by no more than 1 – 3 μm throughout the experimental run.

Experiments, both with and without a Nafion tube attached to the sensor, were repeated ten times each. A point-by-point mean and standard deviation were calculated and plotted in figure 5a. The deflection (figure 5a, green) was significantly greater than the control, when no Nafion tube was attached (figure 5a, blue). Measured deflection data were then converted to values of force in figure 5b using the ribbon's stiffness coefficient. At the end of the 20 min runs, the measured force averaged $22 \pm 2 \mu\text{N}$ ($n = 10$).

Many natural processes exhibit exponential behaviors; therefore the force data of figure 5b were fit with a double exponential function (figure 5b in red overlay). Using the “fminsearch” root-finding method in MATLAB, the program calculated the ideal coefficients ($A = 11$, $b_1 = 3.2$, $b_2 = 0.2$) for the exponential function. A correlation coefficient of $R^2 = 0.98$ reflected a reasonable fit.

Proton Blockage and Electrostatic Force Magnitude

We next checked the extent of proton restriction to one side of the ribbon. This feature would permit electrostatic force to develop mainly on one side of the ribbon. This experimental condition was realized through the ribbon's large aspect ratio, where its largest face was as wide as the height of the Nafion tube, and practically as high as the water in the chamber. Thus, the ribbon could largely obstruct proton diffusion to the side without the Nafion (called the “blocked” side).

To confirm that proton efflux was essentially unilateral, pH-dye (1:50 v/v in water) was pipetted into chambers containing the ribbon with the attached Nafion tube. Within 90 s, an asymmetric proton distribution was visible (figure 6). The asymmetry persisted over time.

Proton distributions over time were quantitatively analyzed using a MATLAB program (figure 7). An intensity profile was obtained along a line perpendicular to the ribbon and passing through the tube's axis (figure 7a-top). The profile was divided into two segments, corresponding to the “blocked” and “unblocked” sides, and plotted as a function of distance from the Nafion tube (figure 7a-bottom). Initially, the intensity values were distributed on both sides of the ribbon (figure 7b-top); however, by 100 s, intensities were more heavily weighted on the unblocked side (figure 7b-bottom).

Next, we used the dye intensity data to compute force. To do so, pH-dye profile magnitudes were converted to local pH values, and thus proton concentrations. This conversion was done at time points throughout the course of deflection. Proton concentrations were then entered into an equation for computing electrostatic force.

To compute the electrostatic force, the standard expression for Coloumbic force was modified to account for charge on both sides of the sensor. Thus,

$$F_{\text{net}} \sim (q_{- \text{ unbl}} q_{+ \text{ unbl}} / r_{\text{unbl}}^2) - (q_{- \text{ bl}} q_{+ \text{ bl}} / r_{\text{bl}}^2)$$

where F_{net} is the net force, $q_{- \text{ unbl/bl}}$ is the total negative charge of the exclusion zone on the unblocked/blocked side, $q_{+ \text{ unbl/bl}}$ is the total positive charge of the proton-rich bulk on the unblocked/blocked side, and $r_{\text{ unbl/bl}}$ is the separation between the unlike charges on the unblocked/blocked side. Since exclusion zones adjacent to Nafion tubes were dye-free, and hence presumably proton free, all protons were presumed to lie in the bulk water zone beyond the exclusion zone. If the protons are generated by the exclusion zone, then the total positive charge in the bulk is assumed equal to the total negative charge of the exclusion zone. Hence

$$F_{\text{net}}(t) \sim \sum [q_{i+ \text{ unbl}}^2 / r_{i \text{ unbl}}^2] - \sum [q_{i+ \text{ bl}}^2 / r_{i \text{ bl}}^2]$$

where $F_{\text{net}}(t)$ is the net force at time frame t and $q_{i+ \text{ unbl/bl}}$ is the charge magnitude located at a distance $r_{i \text{ unbl/bl}}$ from the Nafion tube on the unblocked/blocked side at time frame t . The calculated electrostatic force was averaged across three experiments and plotted in red (figure 8). Measured force from figure 5b was plotted in green for comparison.

The time course of calculated force roughly tracked with the time course of measured force initially. Both traces reached a peak between 20–30 s, a period during which the measured force reached approximately half of maximum. The calculated force then dropped and eventually returned towards zero. Thus, electrostatic forces can account for the initial bending of the ribbon; however, additional factors seem necessary to explain the force developed beyond that time (see Discussion).

IV. DISCUSSION AND CONCLUSION

Many hydrophilic materials nucleate exclusion zones in the adjacent water^{11–12,22}. One such material is Nafion, a charged, hydrophilic polymer whose exclusion zone excludes colloids, microspheres, and at least several solutes^{11–12,22,28–29}. We used that polymer to study the electrostatic forces developed between the negative charges in the exclusion zone and the positive charges lying in the region beyond the exclusion zone, presuming that an understanding this charge-separation phenomenon might provide insight into the long-range ordering of water at hydrophilic surfaces. Here, we tested the hypothesis that a significant electrostatic force develops between those two regions. We were able to confirm a significant attractive force.

To test this hypothesis, an apparatus was designed to characterize the exclusion zone phenomenon through measurements of pH and mechanical force. Exclusion zones visibly excluded universal pH-sensitive dye (figure 3). This permitted measurements of the exclusion zone width, and simultaneously provided an indicator of proton concentration distribution in the proton-rich bulk water region (figure 3).

Force between the negatively charged exclusion zone and the positively charged bulk water was measured through the deflection of a ribbon-like force sensor, onto whose tip was mounted a Nafion tube (figure 2b–c). As the Nafion tube hydrated, an exclusion zone formed on the tube's outer surface. (The exclusion zones that ordinarily form next to tube's

inner surface were precluded by the supporting wire inside the tube.) Interfacial (exclusion-zone) water remains tightly bound to Nafion's molecular structure^{25–27}; therefore, Nafion and its exclusion zone act as a unit. This negatively charged unit evidently attracts the bulk-water protons sufficiently to bend the mechanical sensor (figure 4b-top). Deflection experiments showed a significant force, on the order of 20 μN , between the exclusion zone and the bulk water. This finding confirms our hypothesis that an attractive force develops between the exclusion zone and the proton-rich bulk water.

The ribbon-like geometry of the mechanical sensor allowed us to infer that the measured attractive force was electrostatic. The large area of the sensor obstructed proton diffusion to the side of the ribbon that did not contain the Nafion tube (figures 6, 7); as a result of this asymmetry, the negatively charged Nafion-plus-exclusion zone was attracted principally in one direction. At 90 s, when force attained approximately 75% of the maximum (figure 5b), protons in the bulk water extended more than 2.5 times farther on the unblocked side than on the blocked side (figure 6 at 90 s; figure 7b-bottom). Given this asymmetric distribution, a plausible explanation for the attractive force is an electrostatic interaction between the exclusion zone and the protonated bulk water region beyond.

The deflection force, calculated from pH-dye intensity profiles, correlated well with the measured force for the first 25 s (figure 8); it then diverged significantly. Convective proton diffusion may have been responsible for the divergence: protons diffused to regions not necessarily sampled in the one-dimensional profile, yielding non-meaningful results. Future work will take into account the impact of that (somewhat unpredictable) diffusion pattern. Nevertheless, the two traces followed a similar time course for the first period of time.

Another aspect of the results is that the deflection did not reach steady state even at 20 min (figure 5a). To determine the likely time to reach steady state, a double exponential function was fit to the force data (figure 5b). Based on the fitting coefficients, a steady state is projected to occur in just over 2 hr.

Further to the point above, preliminary observations were made on dye distribution over long periods of time. Three experimental runs were carried out with pH-dye and Nafion tubes. The tubes were left overnight. During that time the proton-rich region filled the entire chamber and the dye continued to turn to a darker red. Whether deflection would continue for such long time periods is unclear. Any followup experiments done on these time scales would need to deal with evaporative effects, which could be significant over long periods and small chambers..

Possible Artifacts

Because long-range electrostatic forces are not ordinarily expected in aqueous solutions, we considered a number of possible artifacts.

Sensor mechanical polarization—To fabricate ribbon sensors, a roller apparatus was used. The resulting ribbons might in theory have had a preferential bending direction, similar to a bimetal strip. Fabricated ribbons were therefore cut into sister pieces. A Nafion tube was attached to one piece, and another Nafion tube was attached to the opposite side of its sister piece. Separate experiments were then conducted using both assemblies. Levers bent in the same direction in the two assemblies, confirming that mechanical polarization could not have been a significant factor.

Weight of hydrated Nafion tube—The density of dry Nafion (1.91 g/cm^3) is nearly twice that of water. As Nafion hydrates, it absorbs at least 20% of its dry weight of water. Therefore, a possible artifact could have been the bending of the ribbon as the weight of the

Nafion tube increased. Countering any such sensor “droopage” in the edge-on direction was the sensor’s high transverse stiffness, resulting from its ribbon-like geometry and high aspect ratio. Since any such droopage should be greatest in air, where no buoyant force is present, ribbon positions in air were monitored with a camera for periods as long as 20 minutes to compare dry and hydrated tubes. The hydrated Nafion tubes were obtained by immersing the assembly into the water bath for 10 min, and then carefully removing the assembly. No downward deflection was detectable. Furthermore, we checked downward deflections in the experimental chamber. By tracking the tube’s two edges within consistent focal planes, we could confirm that vertical translation was undetectable. Thus, we found no evidence of droop.

Thermal gradients—Another possible source for the measured deflection may be rooted in thermal gradients developed at the tip of the ribbon sensor. At the tip, one side of the silver ribbon is exposed, while the other is covered with an attached Nafion tube. In air at room temperature (18 – 19 °C), both the Nafion tube and silver ribbon are in thermal equilibrium. When the water bath (approximately 20 °C) is infused into the chamber, the small temperature difference means that the ribbon must adopt a new thermal equilibrium. Silver conducts heat much faster than Nafion: their thermal conductivities are 0.5 and 760 W/m*K, respectively. Hence, the attached side of the ribbon may absorb less heat than the unattached side and thereby cause the ribbon to contract in the direction of the measured deflection.

To test for the presence of these thermal gradients, thermocouples were placed at several locations: near the tip of the sensor; in the surrounding water environment; and at the chamber boundary. All thermocouples were kept at the same vertical level as the Nafion tube, i.e. midway between the air-water interface and the chamber bottom. For the duration of the experiment, the measured temperatures did not change within the resolution of the thermocouple (1 °C). In three experiments, a higher resolution (0.1° C) IR camera was employed to record the radiant energy emitted from the entire chamber as the water was added. No thermal gradients exceeding 0.3° C could be visualized between the ribbon tip and other regions of the chamber during the course of the 20 min experiments. Differences on the order of 1 °C were visualized near the beam holder, which protruded out of the bath into the air. However, these thermal differences were found far (~1.5 cm) from the area where deflection was measured. We therefore could find no evidence of thermally driven mechanical deflection.

Ruling out these potential artifacts lent confidence that the deflection was indeed the result of electrostatic forces.

Electrostatic Forces in Nature

The results obtained here imply that separated charges in aqueous solutions may exert significant force. Such forces are unexpected. A common presumption is that large-scale separated charges do not exist in nature; or, if they do, they must act over short range only. However, the exclusion-zone phenomenon demonstrates that charges are indeed naturally separated, and that those separated charges can create substantial force. Those electrostatic forces may be sufficient to explain various adhesion phenomena, for example the ability of caterpillars and geckos to walk vertically on walls.

An obvious question arises: Why don’t the negatively charged exclusion zone and the proton-rich region simply collapse and neutralize one another? The reason may lie in the molecular structure of exclusion-zone water. Spectroscopic studies of the interfacial water next to the Nafion surface^{26–27,29} have demonstrated that the water at the interface exhibits a distinct, ice-like structural organization^{4,26–27,29} water molecules are neither organized in a

fully ordered arrangement as in ice, nor are they free water molecules exhibiting random O-H bond stretching. The arrangement is intermediate. This water is tightly bound to the Nafion's molecular structure^{24–26}, resisting evaporation even under intense vacuum²⁵. Therefore, the exclusion zone appears to be a separate phase of matter distinct from bulk water, and one that cannot simply collapse and neutralize the bulk water. Hence, the charges remain separated.

The separated charges also have implication for cells and tissues. A recent study compared exclusion zones to the unstirred layers^{20–21} that are found to envelop biological tissues and cells. With thicknesses of hundreds of microns up to millimeters, those unstirred layers may be similar to exclusion zones¹⁹. In other words, the slow diffusion zones long noted to exist around cells and tissues might arise from the same ordered ice-like water that creates the exclusion zone^{4–6,26–27}.

The separated charges may also impact protein interactions, in a similar way that charge separation impacts the P-N interface between two adjacent semiconductor crystals. In the latter case, diffusion of electrons (and hence separation of charge) from one crystal to the other is balanced by an opposing electric field in the interfacial area known as the depletion zone. The depletion zone is considered the lowest energy state of the interface. Analogously, proton diffusion from the exclusion zone may be balanced by the developed electrostatic force between the interfacial and bulk water regions, as measured in this study. If exclusion zones are intracellularly ubiquitous³², then charge separation may be a general phenomenon that occurs spontaneously at biological interfaces. Mechanical forces such as those measured here may therefore play an important role in cellular processes, including protein folding and transport, as well as more macroscopic processes such as adhesion and water harvesting².

A next step in investigating this charge-based force phenomenon is to determine its degree of generality. Nafion surfaces may suffice as a reasonable model for biological surfaces such as intracellular proteins, since that polymer is both charged and hydrophilic. It will be of interest to see whether other hydrophilic materials, including those biological in nature, exhibit similar electrostatically driven mechanical deflections.

Acknowledgments

Financial support was provided by an NIH Transformative R01 Award and the 2012–2013 University of Washington College of Engineering Donald W. and Joan P. Baker Endowed Fellowship. We also would like to acknowledge Jeff Magula for his help with machining, Rainer Stahlberg and Mark Fauver for extensive discussions, and Federico Ienna, Mina Rohani and Ariel Meyra for manuscript review and discussion.

References

1. Pesika NS, Zeng H, Kristiansen K, Zhao B, Tian Y, Autumn K, Israelachvili J. Gecko adhesion pad: a smart surface? *J Phys Condens Matter*. 2009; 21:4641321–4641326.
2. Garrod RP, Harris LG, Schofield WC, McGettrick J, Ward LJ, Teare DO, Badyal JP. Mimicking a *Stenocara* beetle's back for microcondensation using plasmachemical patterned superhydrophobic-superhydrophilic surfaces. *Langmuir*. 2007; 23:689–693. [PubMed: 17209621]
3. Vaknin Y, Gan-Mor S, Bechar A, Ronen B, Eisikowitch D. The role of electrostatic forces in pollination. *Plant Syst Evol*. 2000; 222:133–142.
4. Yalamanchili MR, Atia AA, Miller JD. Analysis of interfacial water at a hydrophilic silicon surface by in-situ FTIR/internal reflection spectroscopy. *Langmuir*. 1996; 12:4176–4184.
5. Ostroverkhov V, Waychunas GA, Shen YR. New information on water interfacial structure revealed by phase-sensitive surface spectroscopy. *Phys Rev Lett*. 2005; 94:0461021–0461024.

6. Asay DB, Kim SH. Evolution of the adsorbed water layer structure on silicon oxide at room temperature. *J Phys Chem B*. 2005; 109:16760–16763. [PubMed: 16853134]
7. Horn RG, Israelachvili JN. Direct measurement of structural forces between two surfaces in a nonpolar liquid. *J Chem Phys*. 1981; 75:1400–1411.
8. Israelachvili J. Direct measurements of forces between surfaces in liquids at the molecular level. *Proc Natl Acad Sci U S A*. 1987; 84:4722–4724.
9. Houston JE, Michalske TA. The interfacial-force microscope. *Nature*. 1992; 356:266–267.
10. Goertz MP, Houston JE, Zhu X-Y. Hydrophilicity and the viscosity of interfacial water. *Langmuir*. 2007; 23:5491–5497. [PubMed: 17408290]
11. Zheng J, Pollack GH. Solute exclusion and potential distribution near hydrophilic surfaces. *Water and the Cell*. 2006
12. Zheng JM, Chin WC, Khijniak E, Khijniak E Jr, Pollack GH. Surfaces and interfacial water: evidence that hydrophilic surfaces have long-range impact. *Adv Colloid Interface Sci*. 2006; 127:19–27. [PubMed: 16952332]
13. Helmholtz H. *Pogg Ann*. 1853; 89:211.
14. Gouy G. *J Phys*. 1910; 9:457.
15. Chapman DL. *Philos Mag*. 1913; 25:475.
16. Stern OZ. *Electrochem*. 1924; 30:508.
17. Hiemenz PC. *Principles of Colloid and Surface Chemistry*. Marcel Dekker. 1977
18. Overbeek, JThG. Recent developments in the understanding of colloid stability. *Adv Colloid Interface Sci*. 1977; 58:408–422.
19. Green K, Otori T. Direct measurements of membrane Unstirred Layers. *J Phys*. 1970; 207(1):93–102.
20. Clegg JS. Intracellular water and the cytomatrix: some methods of study and current views. *J Mol Cell Biol*. 1984; 99:167–171.
21. Pollack, GH.; Clegg, J. *Phase Transitions in Cell Biology*. Springer; 2008. Unexpected linkage between unstirred layers, exclusion zones and water.
22. Zheng JM, Pollack GH. Long-range forces extending from polymer-gel surfaces. *Phys Rev E*. 2003; 68:0314081–0314087.
23. Heitner-Wirguin C. Recent advances in perfluorinated ionomer membranes: structure, properties and applications. *J Memb Sci*. 1998; 120:1–33.
24. Majsztrik P, Bocarsly A, Benziger J. Water permeation through Nafion membranes: the role of water activity. *J Phys Chem B*. 2008; 112:16280–16289. [PubMed: 19053672]
25. Goswami S, Klaus S, Benziger J. Wetting and absorption of water drops on Nafion films. *Langmuir*. 2008; 24:8627–8633. [PubMed: 18611043]
26. Kunimatsu K, Bae B, Miyatake K, Uchida H, Watanabe M. ATR-FTIR study of water in Nafion membranes combined with proton conductivity measurements during hydration/dehydration cycle. *J Phys Chem B*. 2001; 115:4315–4321. [PubMed: 21446705]
27. Basnayake R, Peterson GR, Casadonte DJ Jr, Korzeniewski C. Hydration and interfacial water in Nafion membrane probed by transmission infrared spectroscopy. *J Phys Chem B*. 2006; 110:23938–23943. [PubMed: 17125361]
28. Chai B, Yoo H, Pollack GH. Effect of radiant energy on near-surface water. *J Phys Chem B*. 2009; 113:13953–13958. [PubMed: 19827846]
29. Chai BH, Zheng JM, Zhao Q, Pollack GH. Spectroscopic studies of solutes in aqueous solution. *J Phys Chem A*. 2008; 112:2242–2247. [PubMed: 18298105]
30. Osada Y, Gong J. Stimuli-responsive polymer gels and their application to chemomechanical systems. *Prog Polym Sci*. 1993; 18:187–226.
31. Hazlewood CF, Nichols BL, Chamberlain NF. Evidence for the existence of a minimum of two phases of ordered water in skeletal muscle. *Nature*. 1969; 22:747–750. [PubMed: 5786190]
32. Pollack GH. *Cells, Gels and the Engines of Life*. Ebner and Sons. 2001

Figure 1. pH-dye distribution measurement. a) A Nafion tube was held upright in the chamber by a bent platinum wire. The magenta lines are artifact and were left over markings denoting where to cut the glass slides during chamber fabrication. b–c) Top view of the area before and after pH dye was pipetted into the chamber.

Figure 2. Experimental schema. a) Schematic of Nafion tube attached to a ribbon-like beam sensor designed to deflect in the presence of charge-based force. b) Image of sensor assembly. c) Image of the full assembly.

Figure 3. pH-dye color distribution beyond the exclusion zone of a Nafion tube. Movie frame was taken at 5 min after pH dye-containing water was pipetted into the chamber. A dye-free zone (approximately 300 μm thick) zone appears as a clear, yellow-white ring (see arrow) around the darker Nafion tube. In the bulk water, a high concentration of protons was observed (denoted by the red color).

Figure 4.

Representative experiment showing time course of ribbon deflection. a) The pink rectangle defines the recorded area and is expanded below to show individual movie frames. The pink arrows are drawn for reference. b) Position history of the sensor and reference beams (top). Orange arrows correspond to time points of the movie frames in 4a. Bottom panel shows traces when the sensor did not contain a Nafion tube.

Figure 5.

Summary of mechanical results. a) Point-by-point average (bright green trace) and one standard deviation (dark green traces) of ten mechanical deflection records obtained with a Nafion tube attached to the sensor. Blue traces represent experiments with no Nafion tube attached. b) Double exponential fit to the measured force data of Figure 5a, $R^2 = 0.98$.

Figure 6.

Representative proton distribution near the ribbon sensor. Most protons, indicated by red color, were restricted to the side of the ribbon containing the Nafion tube. The tail-like formation seen at 90 s appeared in some experimental runs; when present, it remained on one side of the ribbon.

Figure 7. Proton distributions on both sides of the mechanical sensor. a) Schematic of measurement, and sample distribution of red-color intensity. b) Red color intensity distribution obtained at 10 s (top) and 100 s (bottom) into the experiment.

Figure 8. Calculated and measured force. The magnitude of the calculated force depends on relative permittivity of the exclusion zone, which is unknown; therefore the units of the calculated force were arbitrarily kept in C/m^2 .