CHARACTERIZATION OF MEMBRANE SURFACE IONIC ACTIVITY AND ITS EFFECT ON THE PERFORMANCE OF A PEM FUEL CELL

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ABSTRACT

In a Proton Exchange Membrane (PEM) fuel cell, a proton conducting membrane like Nafion® is used as the electrolyte. The proton conductivity of this membrane, which strongly affects the performance of a PEM fuel cell, depends on the characteristics of the ionic clusters both within the polymeric structure and on its outer surfaces. The bulk conductivity of these membranes has been extensively studied. However, no study has been conducted to determine the effect of the morphology and activity of the ionic clusters on the surface of these membranes on the performance of PEM fuel cells. Recent works have shown the existence of a fluorocarbon rich skin on these proton conducting membranes. There is also evidence that this fluorocarbon rich skin has a negative effect on the performance of a PEM fuel cell. Results on these works are shown here along with the development of a new surface probing microscopy technique that can be used to study the ionic activity of the membrane surface and the interaction of this surface ionic activity with the catalyst at the membrane-catalyst interface.

BACKGROUND

In a Proton Exchange Membrane (PEM) fuel cell, a proton conducting membrane like Nafion® is used as the electrolyte. The proton conductivity of this membrane, which strongly affects the performance of a PEM fuel cell, depends on the characteristics of the ionic clusters both within the polymeric structure and on its outer surfaces. The bulk conductivity of these membranes has been extensively studied [1-12]. However, no study has been conducted to determine the effect of the morphology and activity of the ionic clusters on the surface of these membranes on the performance of PEM fuel cells. Furthermore, the effects of membrane preparation and pretreatment processes (sulfonation, protonating, boiling, and drying) on the topography and activity of the ionic clusters on the membrane surface are not known. It is known, however, from water absorption, contact angle and MRI experiments that the bulk membrane and its outer surface behave differently. This difference in behavior is also known to depend on the membrane pretreatment processes [1,4-6,13]. It has been postulated that the ionic clusters that are normally found outside of the Teflon structure when the membrane is hydrated reorganize and migrate into the hydrophobic Teflon structure when the membrane becomes dehydrated, resulting in a membrane with greatly reduced surface ionic conductivity.

EXISTENCE OF A FLUORINE-RICH SKIN

Recent results from an AFM study by our group provide some support to the above theory. The atomic-force micrographs given in Figure 1 show drastic changes in the membrane topography between dry and wet conditions. Also, a study by AFM tapping and phase imaging methods by McLean et al. at DuPont showed the existence of a fluorine-rich skin covering the entire surface of Nafion membranes [14]. Note that the methods used by McLean et al. can resolve the surface and near-surface morphology of the ionic domains in Nafion membranes. However, these methods cannot determine whether the detected ionic clusters on the membrane surface are active (i.e., connected to the ionic network within the membrane to allow proton transport) and, therefore, cannot be used to study the interaction at the membrane-catalyst interface.

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Fig. 1. Atomic force micrographs of dry and wet Nafion® 112 membranes.

To determine the effects of membrane pretreatment and post-treatment and other surface modification processes on the membrane surface elementary composition, an XPS study was also conducted [15,16], and the results are shown in Table I. Note that the surface composition of a dry, as-received Nafion® 1100 membrane has lower sulfur-to-carbon ratio than those calculated from the chemical formula for Nafion® 1100, 0.024 versus 0.053. The results also show that pretreatment with sulfuric acid, which is often used to protonate the membrane, had no effect on the membrane surface composition. However, pretreatment by diluted (5%-7%) hydrogen peroxide, which is often used to clean the membrane, resulted in further reduction in the number of sulfonate groups on the membrane surface (the S:C ratio was reduced to 0.017). Also included is the XPS result for a Nafion® 1100 membrane etched by argon plasma, which shows that as the top layers of the membrane surface were removed by the plasma etching process, the new surface composition has S:C ratio closer to the calculated value (0.047 versus 0.053). Given the non-selective nature of physical etching processes we are postulating here that the plasma etching process removed the surface layer that was rich in Teflon to expose a sub-surface resembling the bulk membrane.

**Table I.** Atomic Existence Ratio from XPS for Etched and Unetched Nafion® 1100 Membranes and Membranes Treated by H₂SO₄ and H₂O₂ Solutions.

| Sample                                               | S:C Ratio |
|------------------------------------------------------|-----------|
| Unetched membrane as received                        | 0.024     |
| Membrane treated with H₂SO₄ (Protonation)            | 0.028     |
| Membrane treated with H₂O₂ (Cleaning) & H₂SO₄ (Protonation) | 0.017     |
| Membrane etched with argon plasma                    | 0.047     |
| Calculated from chemical formula                     | 0.053     |

Chemical Formula of Nafion® 1100.

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\text{Chemical Formula of Nafion® 1100.} = (\text{CF}_2\text{CF}_2)_6 - (\text{CF}_2\text{CF}_3) - O - CF_2\text{CF(CF}_3) - O - CF_2\text{CF}_2\text{SO}_3\text{H}
\]

(S to C Ratio = 1 to 19 or 0.053)
EFFECT OF SURFACE IONIC ACTIVITY ON FUEL CELL PERFORMANCE

While the chemical nature of the membrane surface is currently not fully known, preliminary fuel cell test results given in Figure 2 show that the MEA made with etched membrane show higher cell voltage over the whole current density range and higher peak current density than the one with unetched membrane. Both fuel cells had the same catalyst loading (0.25 mg Pt/cm²) and were tested under the same conditions (H₂/Air @ 1 atm & 60°C) [17]. Similarly the results in Figure 3, which shows the polarization curves of MEAs (0.59 mg Pt/cm²) with etched membranes treated and untreated with H₂O₂, support that the fuel cell performance is affected by the surface ionic activity of the membranes [18].

![Fig. 2. Performance of etched and unetched Nafion® 112 membranes untreated with H₂O₂.](image)

![Fig. 3. Fuel cell performance with etched Nafion® 112 treated and untreated with H₂O₂.](image)

It is clear from the results provided in Table I, Figures 2 and 3 that surface modification and membrane post-treatment processes can have a strong effect on the chemical properties of the membrane surface which in turn can have a significant effect on the performance of a PEM fuel cell. It should also be clear that an analytical tool that can measure the surface ionic activity of the membrane will provide information that coupled to that obtained from molecular modeling studies, will be crucial to the understanding of the effects of these treatment processes. If the topography along with the surface ionic activity of the membrane could be measured, then one could study the effects of membrane manufacturing, pretreatment and post-treatment processes on
the distribution and activity of the ionic clusters on the surface of the membrane. These surface ionic activity data and the XPS results can then be correlated with the fuel cell test data to understand how the surface pretreatment and post-treatment processes affect the performance of a fuel cell. From this understanding one can select the treatment processes and process conditions that will yield membranes with high surface activity that could be used to develop high performance MEAs for PEM fuel cells. Of special interests are the relationships between the morphology of the ionic clusters on the membrane surface and 1) the membrane hydration state, 2) the pretreatment and post-treatment processes and process variables, 3) the transport rates of protons and water across the membrane, 4) the interface between the membrane phase and the catalyst and 5) the performance of the fuel cell membrane and electrode assembly (MEA). Finding answers to these questions is the central focus of this new work.

CHARACTERIZATION OF MEMBRANE SURFACE IONIC ACTIVITY

To characterize the surface ionic activity of proton conducting membranes and determine how this property is affected by the hydration state of the membrane, the pretreatment and post-treatment processes and process conditions used, an imaging technique consisting of a tunneling/conductive atomic force microscope (TUNA/CAFM) and a miniaturized proton-exchange-membrane fuel cell. A TUNA/CAFM instead of a normal CAFM is needed because of the extremely low current occurring at the nanometer-size CAFM tip. The fuel cell is made of offset electrodes on a long strip of a proton-conducting membrane. One electrode is made of a gas diffusion layer coated with a thin layer of Pt/C/Nafion® that is hot-pressed onto one end of the membrane. This electrode is placed in a hydrogen compartment and serves as the anode (hydrogen oxidation) for the fuel cell. The conductive CAFM probe coated with platinum is used as the other electrode. This conductive CAFM probe is exposed to air and serves as the cathode (oxygen reaction) for the fuel cell. When this conductive CAFM probe contacts an ionic cluster that is in contact with the ionic network within the membrane a potential representing the electrochemical potential of the H₂/O₂ redox couple may be detected. When the conductive CAFM probe contacts the non-ionically active Teflon-rich region or ionic clusters that are isolated from the ionic network in the membrane, no potential is detected. A schematic of the experimental set-up and the imaging process is given in Figure 4. One could have the reverse arrangement in which the hot-pressed (counter) electrode acts the cathode (O₂ reduction) and the CAFM probe acts the anode (H₂ oxidation).

![Fig. 4. Visual depiction of surface probing of ionic clusters by a platinum tip.](image_url)
protons occurring at the tip (anode) and protons reduction to form hydrogen at the counter electrode (cathode) or vice versa. In this set-up, one uses a power source to force either a constant current or a constant potential between the counter electrode and the conductive CAFM tip. Depending on the polarity applied, the CAFM tip can act as either an anode or cathode, and as described before when the CAFM tip touches an ionic clusters in contact with the ionic network in the membrane the electric circuit is completed, and when the CAFM tip touches a non-conductive surface no current can be measured. With this approach a much simpler configuration can be used. See Figure 5. This approach has been tested and found to work equally well.

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\begin{align*}
\text{Pt AFM Probe} & \quad \text{(cathode)} \\
\text{Anode catalyst layer} \\
\text{Membrane} \\
\text{Proton Cluster} \\
\text{Air or Hydrogen atmosphere} & \quad \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O} \\
& \text{or} \\
& (2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2) \\
2\text{H}_2\text{O} & \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \\
& \text{or} \\
& (\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-)
\end{align*}
\]

Fig. 5. Surface probing of ionic clusters by a TUNA/CAFM using a single gas.

**Preliminary Results**

Using the setup and procedure described above we have recently obtained some preliminary results which validated the feasibility of this new imaging approach. Figure 6 shows the topography and the surface potential map of the same area of a Naftion® 112 maintained at ambient temperature, pressure and humidity for the case in which hydrogen was applied to the counter electrode and air was applied to the CAFM tip. The surface potential map in Figure 6 shows that at the conditions that the membrane was measured only a fraction of the surface was ionically active. Furthermore, the results show that there is no correlation between the topography and the surface ionic activity, an interesting and important finding.

![Topography and Surface Potential Map](image)

(a) Topography  
(b) Surface Potential

Fig. 6. Topography (a) and Surface Potential Map (b) of a Naftion 112 Membrane

**CONCLUSIONS**

Naftion membranes were found to exhibit a fluorocarbon-rich skin. The elemental composition of this skin was also found to be affected by the H₂O₂ pretreatment often used for cleaning resulting in a lower S:C ratio. Preliminary results showed that this fluorocarbon-rich sk
skin could be removed by plasma etching with argon gas resulting in a surface with higher ionic activity. Membrane-and-electrode assemblies made of etched membranes that were untreated with H2O2 showed the best performance.

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REFERENCES

1. A.V. Anantaraman and C.L. Gardner, J. Electroanal. Chem., 414, 115 (1996).
2. T.A. Zawodzinski, Jr., T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, and S. Gottesfeld, J. Electrochem. Soc., 140, 1981 (1993).
3. W.Y Hsu and T.D. Gierke, J. Membr. Sci., 13, 307 (1983).
4. Shimshon Gottesfeld and Tom A. Zawodzinski, "Polymer Electrolyte Fuel Cells," in Advances in Electrochemical Science and Engineering, R.C. Alkire, H. Gerischer, D. Kolb, and C.W. Tobias, Eds, Vol. 5, Wiley-VCH, New York, p. 256, 1997.
5. J.T. Hinatsu, M. Mizuhata and H. Takenata, J. Electrochem. Soc., 141, 1041 (1993).
6. Trung Van Nguyen and Nicholas Vanderborgh, J. Membr. Sci., 143, 235 (1998).
7. T.D. Gierke, G.M. Munn, and F.C. Wilson, J. Polym. Sci., 19, 1687 (1981).
8. S.J. Paddison, D.W. Reagor, and T.A. Zawodzinski, J. Electroanal. Chem., 459, 91 (1998).
9. S. J. Paddison, Ann. Rev. Mat. Res., 33, 289 (2003).
10. D. Marx, M.E. Tuckerman, J. Hutter, and M. Parrinello, Nature, 397, 601 (1999).
11. E. Spohr, P. Commer, and A.A. Kornyshev, J. Phys. Chem. B, 106, 10560 (2002).
12. G. Zundel and J. Fritch, Spectroscopy of salvation, in The chemical physics of solvation; R. Dogonadze, E. Kalman, A. A. Kornyshev, and J. Ulstrup, J., Eds., Elsevier Sci., Amsterdam, 1986, Vol. Part B, pp 21.
13. J.D. Seymour, S.L. Codd, J.C. Mabry, S.C. Busse and E.S. Peterson, "NMR microscopy of water and methanol distribution and dynamics in polymer electrolyte membranes," North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003.
14. R.S. McLean, M. Doyle and B.B. Sauer, Macromolecules, 33, 6541-6550 (2000).
15. Trung Van Nguyen, "Enhancement of Active Surface of Membrane and Electrode Assemblies for PEM Fuel Cells by Plasma Etching," Proceedings of VACETS Technical International Conference 2000, pp. 118-124, San Jose State University, San Jose, CA, Aug. 4-5, 2000.
16. Trung V. Nguyen, "Surface Enhancement of PEM Fuel Cell Membrane and Electrode Assemblies by Plasma Etching," AIChE 2000 Annual Meeting, Symposium on Fuel Cells, Systems and Processors I, Paper No. 4, Los Angeles, CA, November 12-17, 2000.
17. Minh Vu Nguyen, "Development of High Performance Membrane and Electrode Assemblies for PEM Fuel Cells," MS Thesis, Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, Kansas, USA, May 2003.
18. Data obtained from TVN Systems, Inc., Lawrence, Kansas, USA.

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