End of project report on Degradation Processes in Hydrogen Fuel Cells

July 3, 2008

Principal Investigators

Brett Stanley (Department of Chemistry) and Tim Usher (Department of Physics), California State University, San Bernardino. Four units of assigned time were awarded to Dr. Stanley, constituting the majority of the funding. The other fraction was spent on materials and supplies.

Students Supported

Gregory Barding and Rebecca Jenkins worked on this project through the last academic year. Their materials and supplies were provided by this grant. We are very proud of both of these student researchers. Greg has finished his time on the project and is currently beginning graduate studies at the University of California, Riverside.

Introduction

Proton exchange membrane (PEM) fuel cells are one of the most popular types of fuel cells. They operate similarly to others with the electrolyte material inbetween the electrodes being a patented polymer called Nafion®, made by DuPont. This polyelectrolyte, or ionomer, is a perfluorinated substance similar to Teflon®, with side branches containing ether groups ending in a sulfonated group. This sulfonate group provides the conductivity of hydrogen ions (or protons, H^+) that are produced from hydrogen gas fuel at the anode through to the cathode where they react with oxygen to form water.

Our research has primarily focused on the effect of damaging high energy radiation on the integrity of this membrane and the performance of the fuel cell. Fuel cells on long space flights or on space stations will be subjected to significant amounts of cosmic radiation. We are able to test the effect of X-radiation with the use of an X-ray diffractometer (XRD) available in our laboratories.

Greg exposed samples of the membrane to X-rays for varying amounts of time and measured the amount of fluoride or sulfate that is emitted from them as a result of this radiation. This assumes carbon-fluorine bonds and/or carbon-sulfur bonds are broken during this exposure or subsequent reaction. The literature has shown fluoride emission results but not sulfate. Most results in the literature are with accelerated chemical degradation using Fenton's reagent, and only a few reports have been published on the effects of X-rays.

Rebecca invested a considerable amount of time to become proficient at the assembly of the membrane with the rest of the fuel cell components (the membrane electrode

assembly, MEA), testing the performance of the fuel cell by measuring voltage as a function of current by varying the resistance of the external load, disassembling the MEA, reassembling, retesting, etc. in order to achieve reproducibility. This was deemed extremely important in order to test any effect of radiation on the performance of the MEA. After reproducibility was established, she exposed membranes, and tested the resultant MEA performance.

The goal is to see what level of damage, as measured by carbon-fluorine and carbon-sulfur bond cleavage, is incurred for a given amount of X-ray irradiation, and then to relate that to any loss of performance in the MEA. From this data, one can hypothesize how much radiation a MEA can be exposed to before a significant loss of performance occurs, while correlating that loss of performance to actual polymer degradation. This could lead to knowledge of the weak link in the polymer that is susceptible to X-rays. In other words, is loss of sulfonate groups required or can a loss in tertiary structure or hydrophobicity from fluorine loss cause a performance loss? Other chemical tests for organic fragments are currently being planned, in addition to chemical degradation with Fenton's reagent. In addition, other students have spent time on this project learning electron paramagnetic resonance (EPR) spectrometry that can identify carbon radicals that may results from carbon-carbon bond rupture, and have even designed a fuel cell that can be inserted into the EPR cavity. We hope to eventually combine all of these pieces of the research project to obtain a better picture of the reactions taking place in a P.E.M. fuel cell.

Materials and Methods

Membrane Electrode Assemblies (MEAs). Two types of Nafion were studied (Ion Power, Inc., New Castle, DE). Nafion 117 represents the "first" series with a thickness of 0.17 mm. Nafion 212 represents the "second" series with a thickness of 0.12 mm. Nafion 112 was originally studied, but has since been discontinued. The difference between the first and second series is that the second series is pre-packaged inside two polymer sheets with adhesive. This type is advertised as "chem. stable" because it is more resistant to air and light oxidation during storage.

The membranes were cut into 46x46 mm squares. A 31x31 mm platinum-loaded (0.4 mg/cm^2) carbon sheet electrode (Johnson-Matthey Fuel Cells, U.K.) was placed on each side of the Nafion. This was then pressed together with collector plates imbedded in plastic housings. The holes in the collector plates allow the efficient distribution of

hydrogen and oxygen gases to the electrode sheets. The four screws are tightened so that the thickness of the MEA is 8-9 mm at each screw. The resistance of the MEA is then tested to assure at least 1 kΩ, indicating no shorts are present.
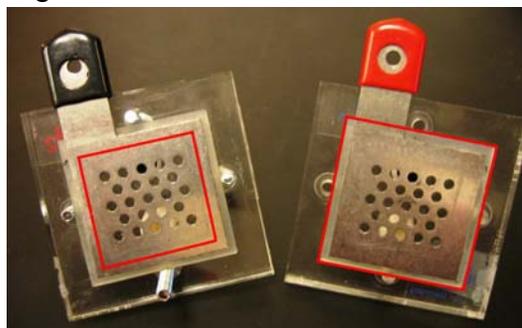
Polarization Curves. The MEAs are conditioned prior to electrical measurements by connecting to a TDI Dynaload electronic load system and holding at open circuit for 15 minutes, followed by a 0.47 Ω short for 20 minutes, followed by 10 minutes at open circuit. This was repeated three times. The polarization curve ("IV curve") was then obtained by sequentially and automatically under computer control using the g-programming code in LabView (National Instruments), decreasing the load resistance so that an open circuit voltage at 0 amps was followed until the current increased to about 0.1 A. This test was repeated three times.

Nitrogen was then flowed through the MEA for 20 minutes to dry the membrane for better subsequent handling. This was followed by 6-8 hours of air drying while still assembled before the MEA was disassembled. The entire procedure was repeated to see the assembly-to-assembly reproducibility, or the membrane was exposed to X-rays before repeating.

X-ray exposure. For the IV polarization studies, the membrane was set 33 mm from the X-ray source (a copper target) so that 13 mm^2 were exposed. The XRD (Phillips Xpert powder system) was operated at 50 mA and 40 kV in polychromatic mode. Exposure times were obtained after either 24 or 48 hours of exposure. For the fluoride and sulfate tests, the exposure was 2, 6, 10, 16, ad 24 hours on 10x30 mm membranes.

Fluoride and sulfate tests. After exposure, the membranes were soaked in 4 mL of ultrapure deionized water (Barnstead Nanopure) for 24 hours. Ion chromatography (IC, Metrohm Peak Model 760, MetroSepp 4A, 15x4 mm) was used to determine the fluoride and sulfate concentrations in a sample of this water with a suppressed conductivity detector. The eluent was 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ and the flow rate 0.7 mL/min. Standard solutions were used to calibrate peak area to concentration.
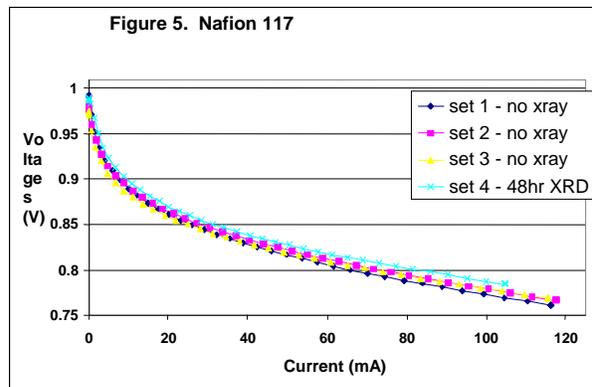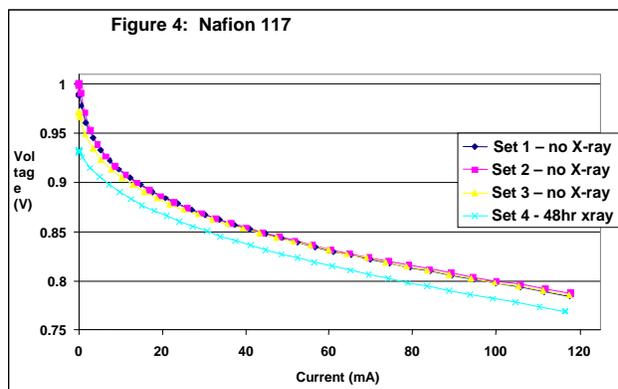
Results

IV Curves. Run-to-run reproducibility was established for a given assembly as shown in Figure 1. Assembly-to-assembly reproducibility was not as consistent as shown in Figures 2 and 3. In these data, a "set" is the average of three runs similar to what might have been obtained in Figure 1. Figure 3 shows less reproducibility than Figure 2, which were obtained on a different membrane sample.

Figure 1

Figure 2

Figure 3
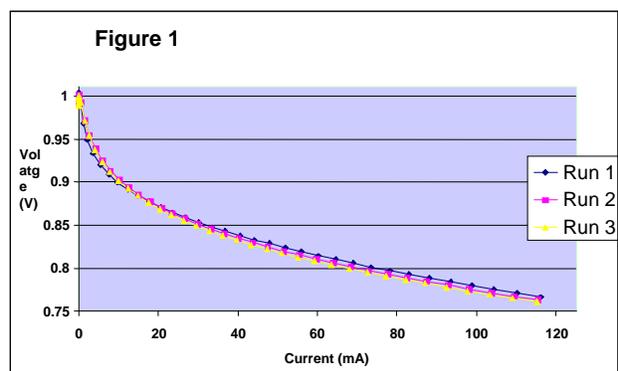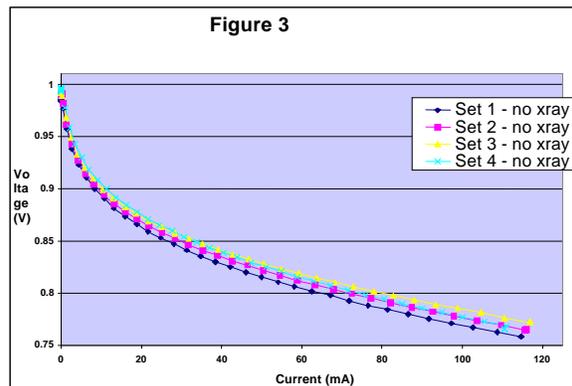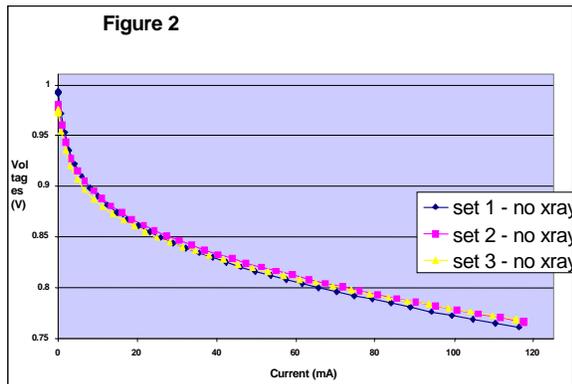
After exposure, the IV curves displayed some variability. It appeared that if the pre-exposure curves had good assembly-to-assembly reproducibility, the post-exposure curves also had high precision. If the pre-exposure curves had poor assembly-to-assembly reproducibility, the post-exposure curves had an even poorer associated precision. A consistent voltage drop in either case was not observed upon a 48 hour exposure. As shown in Figures 4 and 5 (Set 4 is an average of several IV curves), a voltage drop was often observed (Fig. 4), but sometimes no significant change was seen (Fig. 5). These results were similar for Nafion 117 and 212.

Figure 4: Nafion 117

Figure 5. Nafion 117

IC Data. Fluoride and sulfate emission from the Nafion ionomer were determined as a function of X-ray exposure. The results shown in Figure 6 (next page) indicate a fairly linear or constant emission rate for Nafion 212, with the sulfate rate being approximately 30% greater.

The results shown in Figure 7 (next page) illustrate a comparison between Nafion 212 and data obtained for Nafion 112 before it became unavailable. Although the 112 data

isn't as precise as that observed for Nafion 212, it is rather clear that the "chem. stable" ionomer undergoes significantly less degradation than the unpreserved polymer.

Figure 6: Degradation of flouride and sulfate per gram of Nafion 212 vs. time of x-ray exposure.

Figure 7: Comparison of Nafion 112 and 212 membrane sulfate degradation products.
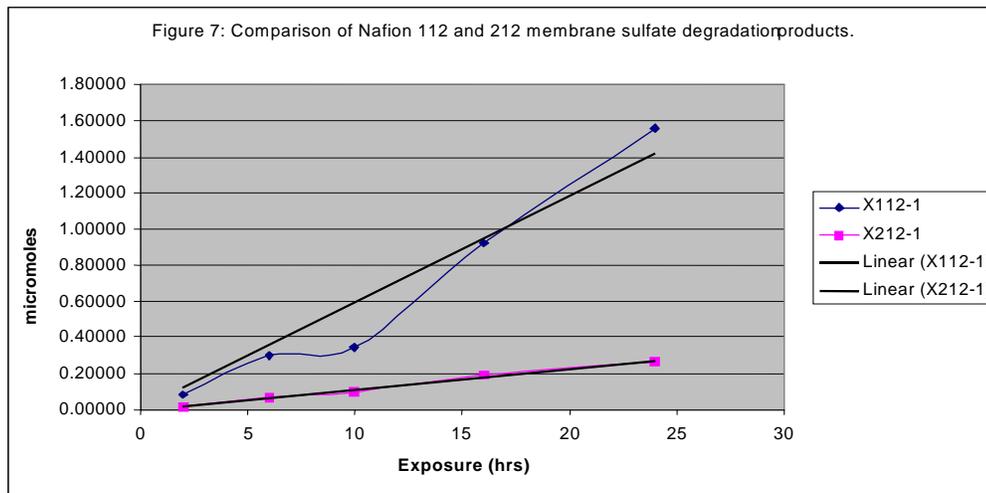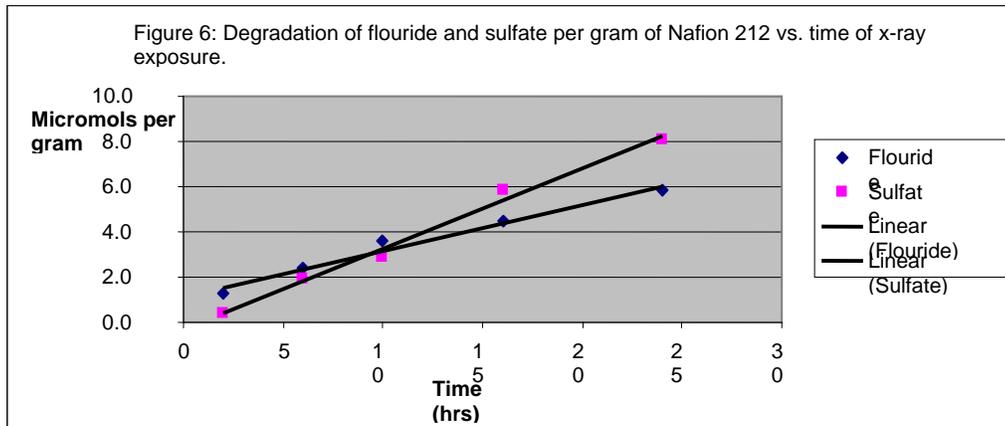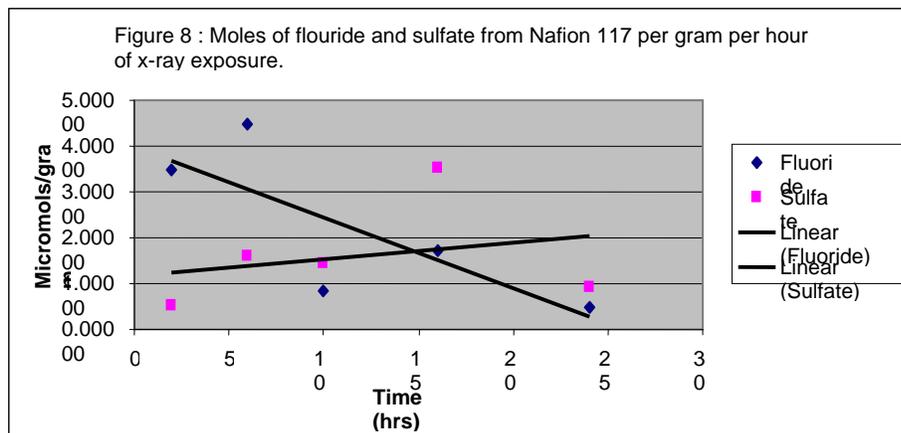
Figure 8 shows the fluoride and sulfate emission from Nafion 117 in an experiment analogous to that illustrated in Figure 6. Obviously, this experiment showed no trend.

Figure 8 : Moles of flouride and sulfate from Nafion 117 per gram per hour of x-ray exposure.

Discussion

One major challenge of this project for our student researchers is obtaining reproducible results as indicated in this report. The polarization curves inbetween disassembly/assembly cycles can be affected by a number of variables that we continue to unveil.

The measurement of the effects of X-ray degradation appear to be very sensitive. In the IC measurements, contamination is problematic due to the low (micromole) amounts being detected. One conclusion, however, is that X-ray degradation in terms of micromoles of fluoride or sulfate is low considering the high dosage occurring for many hours in these experiments. Ms. Tassano is currently performing measurements to determine precisely the radiation dosage striking the membranes. We hope to determine absorption coefficients and relate the energy absorbed to damage observed.

Visually, the student researchers note that the membranes become very brittle after 24-48 hours of exposure. It is interesting that a good polarization curve may be obtained, however the brittleness isn't noted until after further experimentation or handling is performed.

The pictures shown above illustrate that the center of the membrane broke free upon disassembly. From these observations it is apparent the physical damage is incurred. It is unlikely that this damage is caused by the loss of fluorine or sulfonate groups in the polyelectrolyte. As long as the membrane stays intact, electrical performance isn't drastically reduced as might be expected by these photos. It is probable that the physical damage is caused by other structural damage in the polymer's molecular structure.

All of the experiments discussed in the Results Section are currently being repeated to more firmly establish the trends and conclusions. In addition, experiments on the accelerated chemical degradation using Fenton's reagent are being performed. We will investigate reaction products using gas chromatography/mass spectrometry (GC/MS)

which will allow us to identify larger, organic fragments in addition to fluoride and sulfate. This will help us figure out which chemical bonds are being broken. Finally, electron paramagnetic resonance (EPR) experiments will be performed to detect radical species that may be formed as intermediates in the degradation mechanism. Initial results in this area have indicated carbon-carbon bond rupture, with a signal slowly decaying over a period of hours.