DURABILITY ISSUES AT THE POLYMER ELECTROLYTE MEMBRANE AND THE ELECTROCATALYST INTERFACE WITH NON-FLUORINATED IONOMERS

Lei Zhang, Vivek S. Murthy and Sanjeev Mukerjee
Department of Chemistry and Chemical Biology, Northeastern University
360 Huntington Ave. Boston, MA 02115

ABSTRACT

Different modes of degradation and aging processes that result in either chemical or morphological alteration in the polymer electrolyte membranes (PEM) during the course of fuel cell operation are of paramount importance of commercial acceptance. The effect of radicals on the PEM durability is of particular interest since a common feature of many hydrocarbon-based membranes is that the building block consists of sulfonic acid substituted aromatic rings, which are much more sensitive to radical attack than the Teflon-like backbone in perfluorinated sulfonic acid type materials. In this work, we attempt to provide answers to the hydroxyl radical initiated durability issues at the polymer electrolyte-electrode interface by analyzing the performance of some novel non-fluorinated membranes using a newly designed durability evaluation method which enables analysis under fuel cell-operating conditions. This method is able to separate the membrane evaluation process into cathode and anode half cell processes for individual analysis of their respective interfacial degradation.

INTRODUCTION

Understanding factors effecting the long term durability of polymer electrolyte fuel cells to a large measure depends on the longevity of the polymer electrolyte-electrode assembly (MEA) interface, which constitutes the very core of the electrochemical conversion device. Operational parameters such as potential window, transitions in relative humidity, fuel and oxidant distribution gradients can severely affect MEA durability. From the perspective of the membrane, these can be manifest as both chemical and morphological alterations of the polymer electrolyte membranes. In this context, the radical initiated chemical attack of the membrane is of special interest as this relates to both choice of appropriate membrane chemistry as well as determining the source (which electrode, anode or cathode under a multitude of cell operating conditions) and factors related to its generation. It is generally believed that in a working PEMFC, the most likely initiators of membrane chemical decomposition are hydroxy (HO•) and hydroperoxy (HOO•) radicals generated at the membrane and electrode interface. Both HO• and HOO• are very reactive with polymers and contribute to their degradation. Especially hydroxyl radical, one of the most reactive chemical species known, has been found being able to gradually break Nafion's® perfloro polymer chains over long term [1]. On the basis of experimental evidence, there are two points of view about the location of the radical-initiated membrane degradation. One assumes that radicals such as HO• and HOO• arise formed at the anode (H2) side of the MEA because the oxygen can diffuse through the membrane and be incompletely reduced at the surface of anode...
catalyst\textsuperscript{2-5}; the other supports the cathode (O\textsubscript{2}) side degradation mechanism, i.e., oxygen reduction at the cathode proceeding through a peroxide intermediate – \textit{H}_{2}\textit{O}_{2}, which can react with trace metal ions in the membrane or carbon support to form destructive hydroxyl radicals \textsuperscript{6-9}.

A proper understanding and localization of the membrane chemical deterioration in fuel cell is expected to provide useful information on designing and preparing of novel membrane materials as well as preventing PEMFC degradation by selective precautions. Experimentally two methods have been used in prior PEM degradation studies. One is referred to as “Fenton test”, in which the membranes of interest are put into a Fenton’s reagent (typically 3\% \textit{H}_{2}\textit{O}_{2} aqueous solution mixed with up to 4ppm Fe\textsuperscript{2+}) at 68°C \textsuperscript{10}. However such a test is independent of fuel cell operating parameters (such as operating potential, relative humidity etc) and largely exempt from effect of choice of different MEA preparation methods and choice of electrocatalysts. An alternative approach that makes more practical sense is to run long-term fuel cell test and conduct post mortem analysis to study the changes in membrane properties. However testing fuel cells for such lengthy periods (at least hundreds of hours) is time-consuming and hence very expensive; further, the contributions to loss of durability from other fuel cell components could become dominant and hence the results suspect. This investigation attempts to provide answers to these durability issues (specifically radical initiated PEM degradation) at the polymer electrolyte-electrocatalysts interface by analyzing the performance of sulfonated poly(arylene ether sulfone) and sulfonated poly(ether ether) ketone, as representative examples of new polymer electrolyte membrane materials which have the potential for elevated temperature operation (110 to 140°C, instead of the conventional 70-85°C for the typical perfluorinated sulfonic acids). Attempt was to design experiments wherein fuel cell operating conditions form an integral part of the measurements. We hope that by means of this method it is possible to separate the stability characteristic of the electrocatalyst-membrane into individual contributions as cathode and anode interface.

**EXPERIMENTAL**

**Membrane Preparation**

The sulfonated poly(arylene ether sulfone) polymers (SPES-40, Structure1) in this work were prepared in-house in accordance with methodology described elsewhere, detailed synthesis conditions and membrane properties have been reported earlier \textsuperscript{11,12}. Membranes were obtained by casting filtered 10wt\% polymer in N-methylpyrrolidone (NMP) solution onto a clean glass substrate followed by drying in vacuum at 100°C for 48 hours. Nafion\textsuperscript{®} 1135 membrane is bought from Ion Power, Inc.

Nafion\textsuperscript{®} membrane was cleaned by boiling in 3\% \textit{H}_{2}\textit{O}_{2} in 1 M \textit{H}_{2}\textit{SO}_{4} respectively at 80°C for 2hours. SPES-40 membranes were boiled at 80°C in 1 M \textit{H}_{2}\textit{SO}_{4} for 2hours to ensure full protonation. After acid treatment, the membranes were washed in deionized water at 80°C for 1hour, then rinsed and stored in deionized water.
Design and Setting Up of the Durability Test

Experimental Apparatus. Durability experiment was performed using a fuel cell hardware modified based on a “high throughput screening fuel cell assembly”. The design allows for testing an array MEA with 25 testing spots. Figure 1 shows the fuel cell assembly. Its key components include an electronically conducting flow field block and an electronically insulating array block on the opposite sides of the MEA. The array block has 25 sensors glued into the block; each sensor has a flow field side facing one of the testing spots on the array MEA and a pin jack on the other side used for electrical connection. Detail descriptions of this device can be found in reference [13]. The heating control and gas supplies to this fuel cell were built in-house that enable the cell to run at ambient pressure and constant temperature up to 50°C. Gases were passed through humidification bottles kept at a temperature of 20°C higher than that of the fuel cell in order to ensure the MEA’s were well humidified (100% relative humidity). The MEA’s in this work were customized for the purpose of durability tests. As shown in Figure 2, the MEA comprises one piece membrane of interest with a size of approximately 11cm x 11cm. Attached to one side of the membrane is a common counter electrode (CE), on the other side, the testing area of the MEA was divided into five testing units. Each unit consisted of a strip of electrode (working electrode, WE), and two disk electrodes for building the dynamic hydrogen reference electrode (DHRE) of this unit. This design enabled a simultaneous evaluation of five WE samples in each run under same operating conditions. A multi-channel Arbin (BT2000) Testing System (Arbin Instruments, TX) was employed to conduct the experiments.

Anode Side Durability Test. The test was conducted in the aforementioned fuel cell device running with pure hydrogen and pure oxygen at ambient pressure. As shown in Figure 3-(a), humidified hydrogen was passed through the catalyzed working electrodes and reference electrodes side of the MEA, and humidified oxygen was passed through the non-catalyzed counter electrode side. After full humidification of the MEA, the working electrodes were either held at the typical anode operating potential of PEMFC (0.1-0.2 V, vs. RHE) or left in open circuit potential condition for varied periods of time. After the test, membrane at the interface with the working electrodes was subjected to mortem analysis. The results were then compared with corresponding properties of the membrane before the test.
Cathode Side Durability Test. Figure 3-(b) shows the cathode durability test arrangement. The cell was operated on pure oxygen and pure nitrogen at ambient pressure. Humidified oxygen was passed through the working and reference electrode side of the MEA; humidified nitrogen was passed through the counter electrode side. The counter electrode process in this case was therefore oxygen evolution using the aqueous environment as the source of oxide formation. The reference electrode used was a solid-state dynamic hydrogen electrode (DHRE)\[14\]. After the full hydration of MEA, the potential of the working electrodes was held (vs DHRE) at 0.4–0.5 V, which is the lower limit of working potential of PEMFC cathode, for the same period of time as in the anode durability tests. When finished, the membrane at the interface with the working electrode was taken out for analysis.

MEA fabrication. Working electrodes were selected from 20%Pt/C electrode (E-Tek, Somerset, NJ) or 20% Pt/Co and 20% Pt/Fe electrode made in-house (NEU), for reference electrode a 30%Pt/C electrode (E-Tek) was used; counter electrode for anode side durability test was non-catalyzed carbon gas diffusion electrode (GDL) by E-Tek, for cathode degradation test a thin platinum foil (0.025mm in thick) was used. To prepare the 20% PtCo and 20% PtFe electrodes, a mixture of appropriated amount of the catalyst powder, 5 wt% ionomer (same as the testing membrane) in NMP solution and water was blended ultrasonically for 30minutes. The resulting catalyst ink was then brushed on the E-Tek carbon gas diffusion electrode. The electrode thus obtained was dried in a vacuum oven at 60°C overnight. For all the other commercial electrodes, a thin layer of corresponding ionomer were painted before experiment by brushing 5% ionomer in NMP solution on the electrode surface (for an approximate loading of 9 mg/cm²) then drying in the oven. The MEA was prepared by hot-pressing the electrodes to the polymer membrane.

Characterization Techniques. After the durability experiment, the MEA was uninstalled from the cell, and the working electrodes were carefully peeled away from the MEA. Anhydrous ethanol was used to facilitate the peeling process. The membrane samples with a size of 1cm × 5 cm were then washed thoroughly with deionized water before post mortem analysis. All FT-IR (ATR) spectra were collected from 64 scans at 4cm⁻¹ resolution. Dry nitrogen gas was purged around the sample during the measurement to eliminate moisture in the air. Proton conductivities were determined from the water vapor equilibrated membrane samples at 30°C using a four-probe conductivity cell setup described in our prior publication[15]. Intrinsic viscosity was chosen as a qualitative parameter reflective of changes in molecular weight of the membranes. The polymer solution was measured according to the single point method developed by Solomon and Ciuta[16] with an Ubbelohde viscometer in a 25°C water bath, using 1% lithium bromide in N-methylpyrrolidone (1%LiBr / NMP) as the solvent.
RESULT AND DISCUSSION:

Effect of Radical Initiated Degradation on Membrane Properties

A representative analysis on the membranes before and after a durability test is discussed below. It was obtained with the cell operated in the cathode half cell mode with three different electrocatalysts at the interface between the working electrode and the membrane. Polarization potentials used for the WE samples were 0.4 and 0.5 V, with the cell temperature varied between 30 and 50°C and a constant pressure of 1 atm. These tests involved a fixed time period of 72 hours (hence the term accelerated durability test). Figure 4 compares the FT-IR spectrums of SPES-40 membrane before and after degradation test. The readily observable differences in the two spectrums are at the 1005cm⁻¹ and 1022cm⁻¹ band. The band at 1005cm⁻¹ is due to a ring vibration of p-substituted aryl ether v(Ph-O-Ph). The band at 1022cm⁻¹ can be assigned to the symmetric stretching of sulfonate group v₄(SO₃⁻). The lowering of the v(Ph-O-Ph) intensity in the tested SPES-40 sample relative to those in the sulfonated group v₄(SO₃⁻), suggested a likely breaking of ether link between two aromatic rings in specific blocks of the polymer chain due to radical attack. Further evidence confirming the decomposition of SPES-40 is given by the reduced intrinsic viscosity hence lower molecular weight in the tested sample. Our experimental results indicating the scission at the ether linkage (see scheme 1) is in agreement with a prior report using EPR measurements[17], which clearly indicates that the point of highest susceptibility is the non-fluorinated biphenyl ring close to the ether linkage. Extent of these chain scission is provided by the comparison of the relative changes in intrinsic viscosity (which us a direct probe of the chain scission) and proton conductivity (which measures the effect of these changes). After the addition of HO⁻ to the sensitive sites, the ultimate scission of the ether link may be caused by ipso-attack of HO⁻ to the -OR group.

Figure 5 compares the SEM pictures of SPES-40 membrane before and after above-mentioned durability test. The radical-initiated degradation caused significant membrane surface morphological alteration in SPES-40 membrane. This is further confirmed by the SEM images in Figure 6, which shows SEM pictures before and after peeling the
electrode (WE) from the membrane sample, thus eliminating artifacts in the picture due to the peeling process.

Similar durability experiments were also performed with Nafion® 1135 samples. As expected, no significant changes in membrane proton conductivity and FT-IR spectrums (not shown here) were observed after such a short period (72 hours) of testing. The use of non-fluorinated membranes of the type SPES-40 constitutes therefore an accelerated method for evaluating choice of materials used at the polymer electrolyte-electrode interface.

Based on present results the likely modes of radical initiated decomposition in the samples were proposed. However, detailed degradation mechanism can not be clarified until the radical species and decomposition products of the polymers are identified. Advanced experimental setup and more sophisticated detection methodologies including in-situ radical sensing and ex-situ chemical analysis such as release water monitoring etc., have to be undertaken in the future.

Comparing of the Cathode and Anode Side Durability Tests

Table 1 shows the data of the cathode side degradation tests with SPES-40 and Nafion®1135 membranes at ambient pressure, cell temperatures of 30°C and 50°C with fully humidified O2/N2. The membrane samples were obtained after holding the potential of the working electrodes in the MEA at 0.4 and 0.5 V for 72 hours each. To investigate the effect of various electrocatalysts on the stability of the membrane at the membrane/electrocatalyst interface, three types of working electrodes were used they included 20%Pt/C, 20%PtCo/C and 20%PtFe/C were employed. The intrinsic viscosities and proton conductivities of the

![Figure 5: SEM pictures of SPES-40 membrane before and after cathode side degradation test.](image)

(a) Blank SPES-40
(b) Degraded

![Figure 6: Comparison of the SEM images of SPES-40 membrane before and after MEA processing. Image (b) was obtained by first hot-pressing the membrane to electrode using same MEA preparing method applied to the SPES-40 sample for durability test, then peeling off from the electrode for SEM study.](image)

(a) Blank SPES-40
(b) Degraded

348 Electrochemical Society Proceedings Volume 2004-21
membranes were measured before and after the degradation test, the changes (in percentage) comparing pre and post treated samples indicate the extent of degradation as shown in Table 2. Several key points merge from these results, which can be summarized as follows: (i) degradation of the SPES-40 samples are more severe in the tests conducted at 0.4 V as compared to 0.5 V; (ii) the SPES-40 samples in contact with 20%Pt/C during the durability test show more degradation than with 20% Pt/C and 20% PtCo/C working electrodes; (iii) SPES-40 samples obtained from the tests at 50°C degraded more than those at 30°C; (iv) no detectable degradation occurred in Nation® 1135 membranes. In these “cathode side” durability tests, selection of these experimental conditions, i.e., the polarization voltages and the materials for working electrodes, were inspired by our earlier studies wherein the peroxide formation at the Pt/C and Pt alloy/C electrocatalysts were investigated in liquid electrolyte interface. Here using RRDE method it was shown that varying amounts of hydrogen peroxide intermediate could be generated during the oxygen reduction process between Pt and Pt alloys (Figure 7). These intermediates will attack not only the polymer electrolyte membrane but also the ionomer component within the active layer, which will result in a dramatic decrease in cell performance.

Table 1: Comparison of membrane properties before and after cathode side durability test

| Cathode Durability Test | T °C | WE @ Potential | $\eta_{\text{before}} - \eta_{\text{after}}$ | $\sigma_{\text{before}} - \sigma_{\text{after}}$ |
|-------------------------|-----|----------------|-----------------|-----------------|
|                         |     |                |                 |                 |
| SPES-40                 | 30°C| 20%Pt/C @ 0.4V | 17%             | 35%             |
|                         |     | 20%Pt/C @ 0.5V | 6%              | 10%             |
|                         | 50°C| 20%Pt/C @ 0.4V | 24%             | 44%             |
|                         |     | 20%Pt/C @ 0.5V | 8%              | 14%             |
|                         |     | 20%PtFe/C @ 0.4V | 47%       | 55%             |
|                         |     | 20%PtCo/C @ 0.4V | 38%       | 42%             |
| Nation® 1135            | 50°C| 20%Pt/C @ 0.4V | -               | 0               |
|                         |     | 20%Pt/C @ 0.5V | -               | 1%              |

Note:
- [\eta]: Intrins ic viscosity (dL g⁻¹); $\sigma$: Proton conductivity (S cm⁻¹)

Table 2: Comparison of membrane properties before and after anode side durability test

| Anode Durability Test | T °C | WE @ Potential | $\eta_{\text{before}} - \eta_{\text{after}}$ | $\sigma_{\text{before}} - \sigma_{\text{after}}$ |
|----------------------|-----|----------------|-----------------|-----------------|
|                      |     |                |                 |                 |
| SPES-40              | 30°C| 20%Pt/C @ 0.1V | 3%              | 10%             |
|                      |     | 20%Pt/C @ 0.2V | 5%              | 8%              |
|                      | 50°C| 20%Pt/C @ 0.1V | 4%              | 6%              |
|                      |     | 20%Pt/C @ 0.1V | 6%              | 8%              |
|                      |     | 20%Pt/C @ 0.1V | 3%              | 7%              |
| Nation® 1135         | 50°C| 20%Pt/C @ 0.1V | -               | 2%              |
|                      |     | 20%Pt/C @ 0.2V | -               | 1%              |

Note:
- [\eta]: Intrins ic viscosity (dL g⁻¹); $\sigma$: Proton conductivity (S cm⁻¹)
circuit potential for 72 hours. Same types of working electrodes as the cathode side tests were used. Under given experimental conditions, no significant degradation in SPES-40 and Nafion®1135 samples were detected, which may be attributed to the short testing time (72 hours). The present results cannot rule out the possible occurrence of degradation at anode side in longer period of testing. More research needs to be done in the future.

CONCLUSIONS

In this work the issue of radical-initiated membrane degradation at the electrocatalyst/electrolyte interface in PEMFC was studied by means of a newly designed durability test method. This method is able to separate the membrane degradation process at the cathode and anode interface so that two formerly proposed PEM degradation mechanisms can be evaluated respectively without interference. Under experimental conditions (30-50°C, 1 atm, testing duration 72 hours), deterioration in SPES-40 samples was observed after the cathode side durability test, particularly at 0.4 V vs. DHRE; PtFe/C initiated more serious deterioration than PtCo/C and Pt/C. This sensitivity of peroxide originated PEM degradation with choice of operating voltage and electrocatalyst has the potential of major impact on interfacial stability, especially for the application of non-fluorinated membranes and novel electrocatalysts in PEMFC, and those PEMFC devices running in discontinuous modes. No significant membrane degradation was found in the anode side durability test under similar conditions as the cathode side test. Advanced investigations are necessary in the future.

REFERENCE

1. P. Maletzky, R. Bauer, J. Lahnsteiner, and B. Pouresmael, Chemosphere, 38, 2315, 1999
2. A. B. LaConti, M. Hamdan, and R. C. McDonald, Mechanisms of membrane degradation, in Handbook of Fuel cells-Fundamental, Technology and Applications, ed. W. Vielstich, H. A. Gasteiger, and A. Lamm, p. 647, John Wiley & Sons, Ltd., 2003.
3. F. N. Buchi, B. Gupta, O. Haas, and G. G. Scherer, Electrochimica Acta, 40, 345, 1995
4. G. G. Scherer, Berichte der Bunsen-Gesellschaft, 94, 1008, 1990
5. H. Wang and G. A. Capuano, J. Electrochem. Soc. 145, 780, 1998
6. Q. Guo, P. N. Pintauro, H. Tang, and S. O’Connor, J. Membr. Sci., 154, 175, 1999
7. J. Yu, B. Yi, D. Xing, F. Liu, Z. Shao, Y. Fu, and H. Zhang, Physical Chemistry Chemical Physics, 5, 611, 2003
8. H. Ericson, T. Kallio, T. Lehtinen, B. Mattsson, G. Sundholm, F. Sundholm, and P. Jacobsson, J. Electrochem Soc., 149, A206, 2002
9. M. Watanabe and H. Uchida, Solid polymer electrolyte composition for fuel cells, US 5766787 1998
10. A. B. LaConti, M. Hamdan, and R. C. McDonald, Handbook of Fuel cells-Fundamental, Technology and Applications, in, ed. A. Lamm, p. 647, John Wiley & Sons, Ltd., 2003.
11 F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, and J. E. McGrath, *J. Membr. Sci.*, **197**, 231, 2002

12 W. Harrison, 'Synthesis and characterization of sulfonated poly(arylene ether sulfone) copolymers via direct copolymerization: candidates for proton exchange membrane fuel cell', Doctorial Disseration, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 2002.

13 R. Liu and E. S. Smotkin, *J. Electroanal. Chem.*, **535**, 49, 2002

14 A. Parthasarathy, C. R. Martin, and S. Srinivasan, *J. Electrochem. Soc.*, **138**, 916, 1991

15 C. Ma, L. Zhang, S. Mukerjee, D. Ofer, and B. Nair, *J. Membr Sci.*, **219**, 123, 2003

16 O. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6**, 683, 1962

17 G. Hubner and E. Roduner, *J. Mater. Chem.*, **409**, 1999

18 V. S. Murthi, R. C. Urian, and S. Mukerjee, *J Phys. Chem. B*, **108**, 11011, 2004