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INFLUENCE OF MEMBRANE-ELECTRODE INTERFACE ON LONG-TERM PERFORMANCE OF DIRECT METHANOL FUEL CELLS

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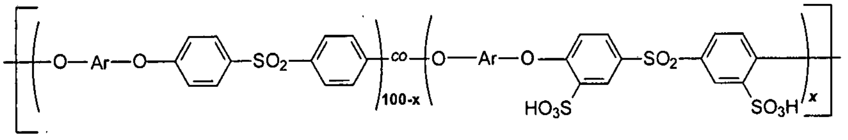
INTRODUCTION

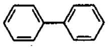
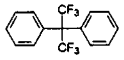
Long-term stability of direct methanol fuel cells (DMFCs) is one of the most critical requirements for the successful launch of this technology to commercial market. When a DMFC is operated for extended periods of time, performance decreases continuously. The performance decay in continuous operation of DMFCs is caused by several different attributes, such as surface oxidation of platinum at the cathode, loss of catalytic active surface area, interfacial failure between membrane and electrode, changing hydrophobicity of backing layers or ruthenium crossover. Among those attributes, the interfacial incompatibility between membrane and electrode becomes more important when alternative polymer electrolyte membranes (PEM) are used with Nafion-bonded electrode. In earlier work, we demonstrated that the direct methanol fuel cells (DMFCs) using alternative fully aromatic hydrocarbon based PEMs initially outperformed the DMFCs using industrial standard Nafion membranes.[1] Nonetheless, the longer-term performance of the alternative system deteriorated rather faster probably due to the interfacial incompatibility.[2]

In this presentation, the effect of interfacial incompatibility of membrane electrode assemblies (MEAs) on long-term DMFC performance is presented in a systematic manner. A series of disulfonated poly(arylene ether) copolymers having different ion exchange capacity and fluorine content was prepared. The effects of chemical structure of the PEMs on interfacial compatibility and long-term performance were investigated and compared with Nafion control membrane-electrode assembly.

EXPERIMENTAL

Materials - The disulfonated poly(arylene ether sulfone) copolymers were obtained from Hydrosize, Inc. and Virginia Tech., where those copolymers were synthesized by copolymerization of sulfonated aromatic dihalides, aromatic dihalides, and one of two structurally distinct bisphenols.[3,4] Figure 1 shows the chemical structures for the protonated form of the copolymer, used in this study.



where, Ar =  (biphenol) and/or  (6F)

When the biphenol unit is 100 % the polymer is referred to as BPSH-X, when the hexafluoro bisphenol A (6F) unit is 100 % the polymer is referred to as 6F-X, for mixtures of the two, the name is 6FyBPSH-X where y is the % of Ar groups that are 6F in the polymer. X is the degree of disulfonation.

Figure 1. Chemical structure and nomenclature of disulfonated poly(arylene ether sulfone) copolymers

Fuel cell testing - Long-term DMFC performance was performed at a cell voltage of 0.5 V up to 700 h. Typically, 0.5 M methanol was fed at the anode with a flow rate of 1.8 ml/min and 500 sccm air was fed at the cathode at the ambient pressure. The temperature of the cathode humidifier was set 15°C higher than the cell temperature, 80°C. *In-situ* high frequency resistance, HFR, was measured at 2 kHz during life test, because this frequency was found to minimize capacitive contributions. The life test was stopped at periodic intervals to evaluate cell degradation. During these stops of the life test, the cell was disconnected from the methanol feed and humidified air for at least 12 h to allow complete platinum reduction at the cathode and removal excess water from the catalyst layers. DMFC polarization curve were obtained before and during the life test, using the same anode and cathode feed conditions as the life test.

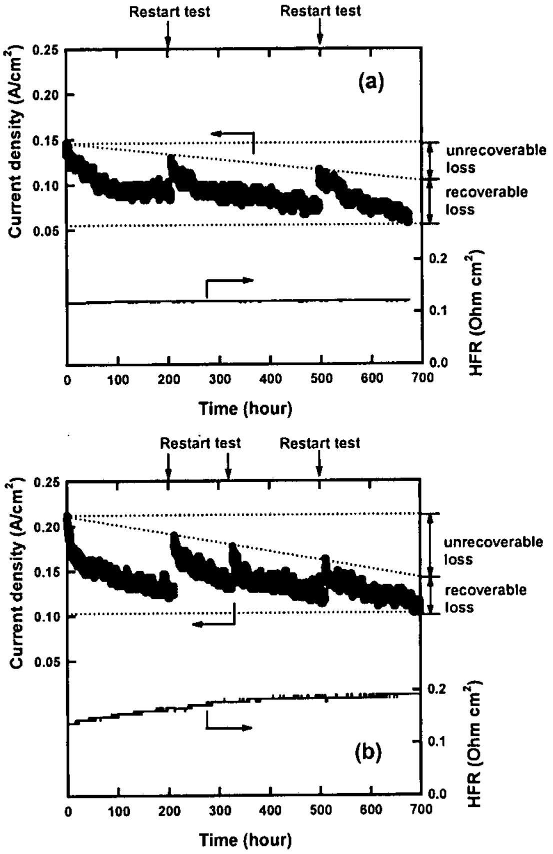


Figure 2. Change of current density and high frequency resistance (HFR) of (a) the Nafion 1135 MEA (PEM thickness: 90 μm) and (b) the BPSH-35 MEA (membrane thickness: 65 μm) during a 700 hour life test at 0.5 V.

RESULTS AND DISCUSSION

Figure 2 demonstrates the current density change with time for the Nafion 1135 and BPSH-35 MEAs at a fixed cell potential of 0.5 V. The current density for both MEAs decreased significantly in continuous cell operation. However, some portion of the current loss was recovered after stopping and restarting the life test. By connecting the highest attainable current density after restarting the test, an estimate of the unrecoverable performance loss is separated from the recoverable loss. The unrecoverable performance loss is more critical because it will ultimately limit the DMFC lifetime, regardless of operating conditions, while the recoverable one can be minimized by adjusting operating parameters. Figure 2 shows that the BPSH-35 MEA had a considerably greater unrecoverable performance loss than the Nafion 1135 MEA (i.e. approximately 70 vs. 40 mA/cm^2 loss after 700 h operation). This greater unrecoverable performance loss is also reflected in the increasing HFR, which is not apparent in the Nafion 1135 MEA.

Figure 3 compares the polarization curves for the BPSH MEAs as a function of degree of disulfonation after 200 h life test. All BPSH MEAs exhibited a meaningful performance loss accompanied by an increasing HFR during the life test. The performance decrease and HFR gain showed a clear trend, increasing in severity with the degree of disulfonation of the polymer. These results indicated that the BPSH membrane with lower disulfonation had better interfacial compatibility and therefore a slower decay in performance and slower increase in HFR.

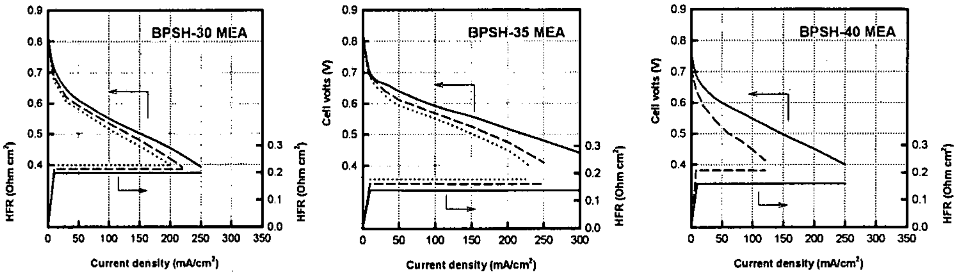


Figure 3. Effect of degree of disulfonation of the BPSH copolymers on polarization curve after 200 h life test; solid line: initial; dash line: after 200 h; dot line: after 700 h.

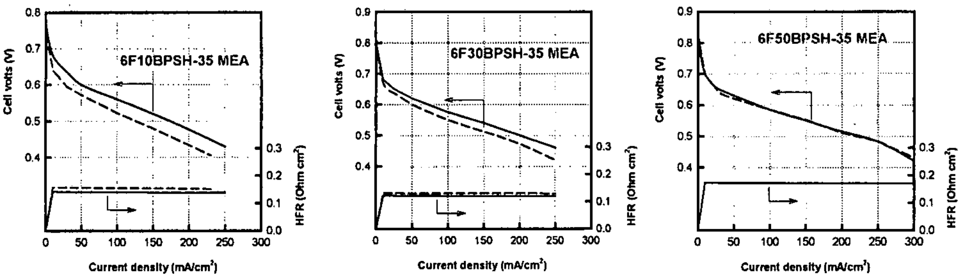


Figure 4. Effect of fluorine content of copolymers on polarization curve after 120 h life test; solid line: initial; dash line: after 120 h.

Experiments involving sulfonation level were followed by investigation into the effect of fluorine content within the backbone. In order to understand the influence of chemical structure on interfacial compatibility and long-term performance, a modification of chemical structure of the BPSH membrane was performed by replacing biphenol moiety with 6F. The level of disulfonation in these polymers was fixed at 35 %, and polymers with 10, 30 and 50% 6F monomer were compared. The polarization curves of these MEAs initially and after relatively short-term life tests (~120 h) are shown in Figure 4. The initial performance for all 6F containing copolymer MEAs were comparable to the BPSH-35 MEA (the current density was between 170 to 220 mA/cm^2. at 0.5 V). The slight difference of the cell performance could be due to the membrane thickness variation, which influences on methanol crossover and ohmic losses. Still, the data in Figure 4 clearly demonstrate that the performance loss and HFR gain after the life test decreased, as the 6F moiety in the BPSH-35 membrane increased. In fact, the 6F50BPSH-35 MEA did not show any current density loss and HFR gain after 120 h life test. This result demonstrate that the interfacial compatibility and the long-term performance was greatly improved by introduction of the 6F moiety. Further, this improvement in durability was accompanied by no decrease in initial performance producing a much improved DMFC MEA.

CONCLUSIONS

The influence of the membrane-electrode interface on long-term performance of direct methanol fuel cells was investigated. The interfacial degradation over time was measured by HFR increase and DMFC performance losses under fully hydrated cathode conditions. The HFR gain for disulfonated poly(arylene ether sulfone) membranes increased with increasing the degree of disulfonation and decreasing fluorine content in the copolymer backbone, and thus, improved long-term performance could be obtained with high fluorinated and modest degree of disulfonated copolymers.

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