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Inhomogeneous Degradation of Polymer Electrolyte Membrane in PEM Fuel Cells

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Membrane durability is one of the technical barriers for the commercialization of polymer electrolyte membrane (PEM) fuel cells. Membrane embrittlement (a form of mechanical weakening) can lead to the frequently observed "sudden death" behavior of PEM fuel cells. It is the objective of this study to explore the fundamental mechanisms of the mechanical weakening of perfluorosulfonic acid (PFSA) based electrolyte membranes during the accelerated degradation test.

Chemical degradation of PFSA membrane does not necessarily results in the loss of mechanical toughness. For example, it has been observed that PFSA membrane in liquid phase Fenton test, if conducted in mild conditions (low concentration of H_2O_2 with low concentration of Fe (II) catalyst), can lose a significant amount of fluorine account (>30%) over time but still maintains its mechanical ductility.[1] However, it has also been found that accelerated membrane degradation test conducted in cell at open circuit voltage (OCV), high temperature, and low RH usually results in chemical degradation of PFSA membrane (as indicated by high fluoride emission) together with a drastic reduction of membrane mechanical toughness [2]. These contrasting results lead the authors to believe that localized or inhomogeneous membrane decay is responsible for the embrittlement or the mechanical weakening of the membrane. Liquid phase Fenton test results in uniform decay of the membrane; in-cell OCV test likely promotes localized membrane decomposition, which later can act as mechanical defects that are responsible for the brittle fracture of the membrane.

To confirm the hypothesis, the authors have recently conducted in-cell OCV test using bilayer MEAs [3]. Each bilayer MEA consists of two pieces of one-side catalyst coated PFSA membrane stack together back-to-back. The tests were conducted at open circuit voltage, 80ºC and 30%RH. Pure hydrogen and air were used for one set of OCV tests, 4% hydrogen (balance nitrogen) and air were used for another set of OCV tests. The cell diagnostic tests (polarization curve, hydrogen crossover rate, catalyst electrochemical area) were conducted before and after OCV hold. After the OCV test, the two layers in each bilayer MEA were separated into an anode-side membrane and a cathode-side membrane, and their mechanical properties were evaluated separately. Scanning electron microscopy, Raman and FTIR were also used to characterize the morphology and chemical composition of the PFSA membranes after the accelerated test.

One major finding of the study was revealed by mechanical testing of the membrane after OCV test. Stress-strain curves of the bilayer membrane after 50 hrs of OCV test with pure hydrogen and air are shown in Figures 1 and 2. The results indicate that the cathode-side membrane lost mechanical integrity more than the anode-side membrane. Interestingly, the OCV test conducted using 4% hydrogen and air showed the opposite trend, the mechanical strength of the anode-side membrane is severely degraded instead of the cathode-side membrane. Another finding is that the OCV decay behavior is affected by the hydrogen partial pressure. At low hydrogen partial pressure, cell voltage remained high (~0.96 V) over 137 hrs of OCV hold; however, under pure hydrogen, the cell voltage reduced to 0.8V in just about 50 hrs [3].

The experimental results clearly indicate that the degradation of the membrane occurs non-uniformly through the thickness direction of the membrane. The results show that mechanical defects primarily form within one layer of the bi-layer MEA. The location of the "defect" band is affected by the partial pressure of reactants used in the OCV hold test. This behavior is probably related to the platinum band formation in the membrane.[4]

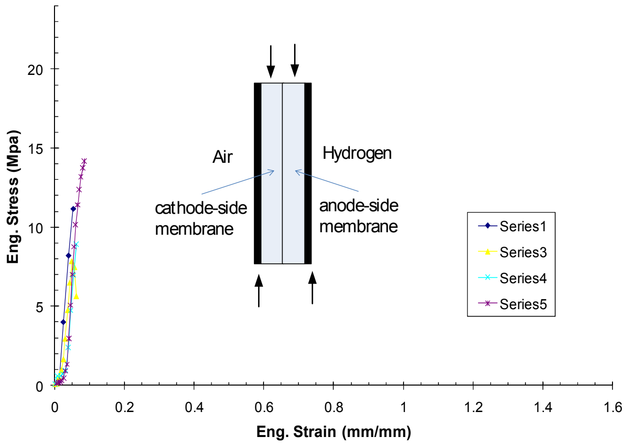

Figure 1. Residual mechanical properties of cathode-side membrane [3].

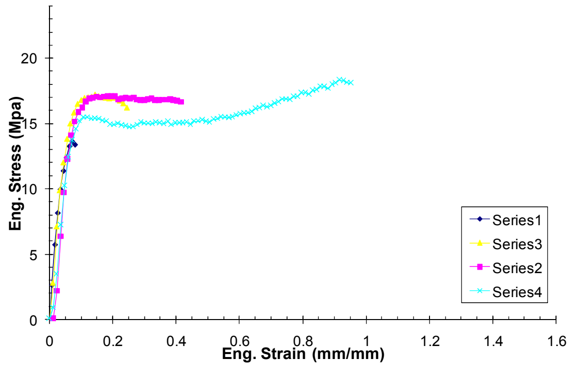

Figure 2. Residual mechanical properties of anode-side membrane [3].

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