

Using Electron Microscopy to Investigate Degradation of Candidate PEM Membranes due to Exposure to Fenton's Reagent

S.C. Weakley-Bollin* and M. Sulek*

*Ford Motor Company, Research and Innovation Center, PO Box 2053, MD 3182, Dearborn MI 48121

Polymer Electrolyte Membrane (PEM) fuel cells are currently being investigated for use as clean, efficient power sources. However, current fuel cell materials are not durable enough to be economical for commercialization. Chemical and/or mechanical degradation of the membrane can reduce ionic conductivity and increase reactant crossover, lowering the output of the cell and decreasing cell lifetime [1]. One suggested degradation mechanism is the free radical attack of the membrane due to reactions between peroxide and small amounts (ppm) of impurities, like Fe^{+2} , that can be found in the cell [2].

In this experiment, two different types of perfluorinated membranes from different manufacturers were exposed to 26 ppm Fe^{+2} in 30% H_2O_2 (Fenton's reagent) at 70 °C for 20 hours. Following exposure, the membranes were characterized optically and with a JEOL 6300F Scanning Electron Microscope (SEM). In addition to examining the membrane surface, cross-sections were prepared by sandwiching the membrane between two pieces of Mylar film for support, using Gatan G-1 epoxy to attach the membrane to the Mylar. The samples were then microtomed with a diamond knife using a Leica Ultracut for examination in the SEM.

After exposure, some sections of the membranes remain clear, while others become opaque, with either a white or yellow hue (Figure 1). Examination in the SEM showed that the clear areas of the membrane showed very little damage, while the surfaces of the opaque areas of both membranes were covered in bubbles (Figure 2). Some of these bubbles are split either on the top or along the sides. The bubbles are likely due to the formation of CO_2 and HF gases from the reaction of the peroxide with the membrane material which is catalyzed by the Fe^{+2} present in the solution. The affected surfaces of both Membranes A and B appear to be similar, although Membrane B appears to have a wider size distribution and higher density of bubbles compared to Membrane A. Cross-sections of the membranes reveal two very different morphologies (Figure 3). Membrane A has both the larger sized (~30-40 μm) bubbles that are seen on the surface plus a significant amount of smaller porosity (< 1 μm) in the middle of the membrane that is not seen on the surface. This porosity is also found in areas of the membrane before any large bubbles occur. Membrane B does not have any of the numerous smaller pores that were observed in Membrane A, but contains large bubbles and cracks not only on the surface, but through the core of the membrane. Swelling of both membranes is also visible in the cross sections.

Exposing the membrane to Fenton's reagent is an aggressive test which can quickly provide information about the degradation of the membranes. Further work is necessary to determine the mechanism(s) causing the observed porosity and consequently how best to mitigate its occurrence.

[1] Kinumoto, et. al., *J. of Power Sources*, *in Press*.

[2] Aoki, et.al., *Electrochemistry Comm.*, **7** (2005).



Figure 1: Optical image of example membrane after exposure (rectangle indicates an example of an area where a cross-section would be taken)

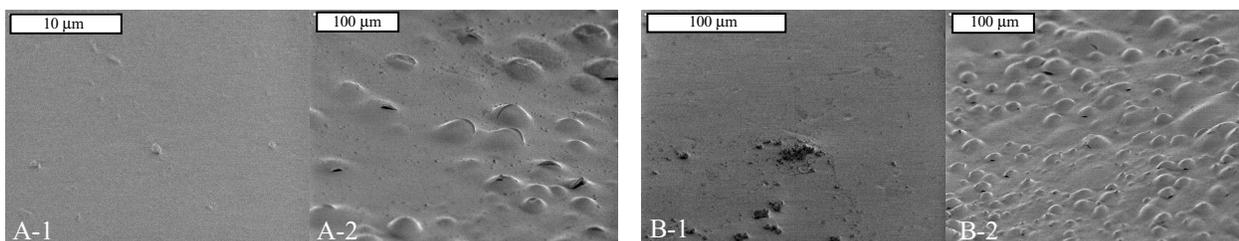


Figure 2: Secondary electron images (SEIs) of the surface of Membranes A and B in unaffected (1) and affected (2) areas ($E_0 = 1 \text{ keV}$)

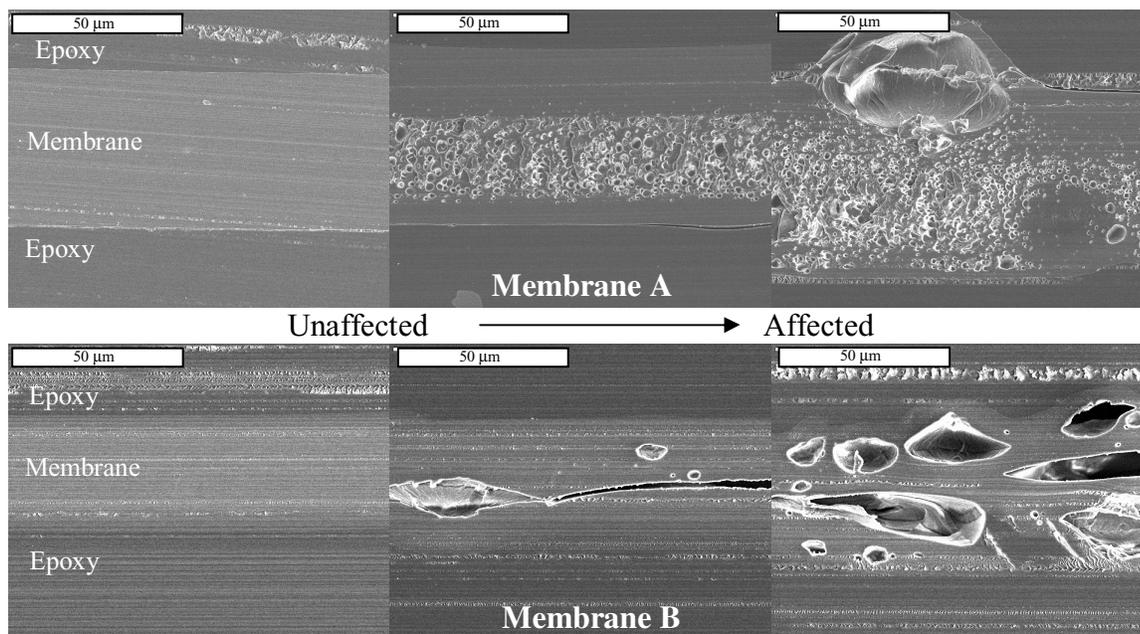


Figure 3: SEIs of cross-sections of Membrane A and B from unaffected to affected areas ($E_0 = 5 \text{ keV}$)