Mechanism of Pin-hole Formation in Membrane Electrode Assemblies for PEM Fuel Cells

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The most common failure mode of polymer electrolyte membrane (PEM) fuel cells is gas cross over caused by pin-hole formation in membrane electrode assemblies (MEAs). Possible reasons for pin-hole formation are the flaws introduced in MEAs during materials processing or the conditions imposed during operation of the fuel cell. In this paper the formation of pin-holes is correlated to the fuel cell operation that results in mechanical and chemical membrane failure modes.

The pin-hole formation mechanism was studied with MEAs that had a similar catalyst loading and different membrane types and thicknesses. Ex-situ and in-situ methods were used for this study. The ex-situ tests included measurements of MEA mechanical degradation in an oxidative environment and heat of ignition [1]. MEA durability tests were performed in fuel cells at different operating conditions. The reactant gases used were hydrogen and oxygen. The MEA failure analyses were carried out with an Olympus BX 60 optical microscope and Cambridge 120 scanning electron microscope. Chemical analysis was done with an IXRF EDS microanalysis system.

The results of the MEA aging in oxygen showed that mechanical properties did not degrade over the 1000h test. The cone calorimeter test [1] demonstrated that heat necessary to ignite the MEA was almost two orders of magnitude higher than the heat generated in fuel cell.

The microstructure analyses of MEAs that failed during fuel cell testing indicated that there were both mechanical and chemical causes for the pin-hole formation. The majority of pin holes appeared in MEA areas where the membrane thickness was drastically reduced. The thickness reduction was as high as 75% at these spots as presented in Fig. 1. The thin areas coincided with the stress concentration points, indicating that membrane creep was responsible for pin-hole formation.

In addition to the pin-holes created by creep, some of the holes detected had particles precipitated within the membrane (Fig. 2). The EDS chemical analysis revealed that the contaminant composition involved strontium and oxygen The mechanism of pin-hole formation in the presence of contaminants is due to blistering, a well known chemical failure mechanism of plastics [2]. Voids that surround particles in membranes enlarge continuously during fuel cell thermocycles, creating a path for gas mixing.

The weak spots in a membrane created by either mechanical or chemical failure mode, allow gas mixing. The chemical reaction of hydrogen and oxygen generates enough heat to melt the polymer, burn the catalyst and form a pin-hole in the MEA.

Reference:

[1] ASTM E-1354-97 “Standard Test method for Heat and Visible Smoke Release Rates for Materials and Products using Oxygen Consumption Calorimeter”.

[2] J. Scheirs, “Compositional and Failure Analysis of Polymers”, (John Wiley & Sons, Ltd., New York, USA, 2000), pp 683.

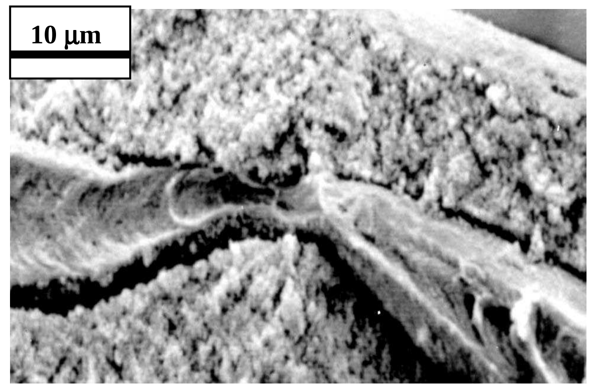

Figure 1: At the stress concentration point MEA thickness was reduced by 75% due to creep, creating a pin hole.

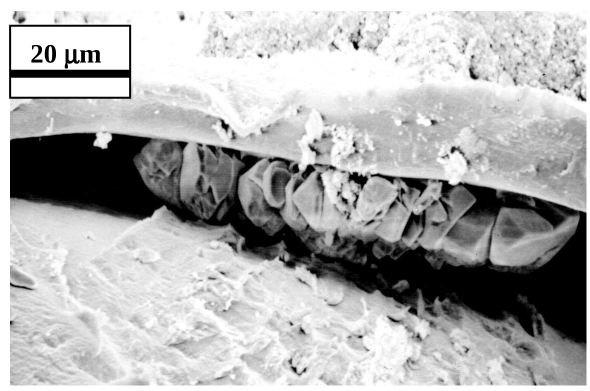

Figure 2: Contaminant particles precipitated within membrane, caused blistering, and pin hole formation.