PEM Fuel Cell Catalyst Layer Structure Degradation During Carbon Corrosion

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The durability of PEM fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications. One of the major degradation involves the electrocatalyst, including the catalyst support and changes in the catalyst layer and has been studied in some detail [1], yet is not completely understood. The carbons typically used as the support for Platinum catalysts in proton exchange membrane fuel cells (PEMFCs) are vulnerable to electrochemical corrosion, especially during potential excursions generated by startup/shutdown cycling and local anode starvation [2].

The cost of the noble metal used in catalysts makes this a crucial area that requires improvement in durability. The catalyst degradation is due to a combination of degradation mechanisms, with operating conditions and An example of the localized localized effects. degradation is demonstrated in Figure 1 after testing utilizing a simulated Drive Cycle Test prescribed by DOE/Fuel Cell Tech. Team [3]. TEM post-analysis shows significant thinning of the catalyst layer by about 30% (A \rightarrow B) which can be due to loss of carbon through carbon corrosion or due to compaction and loss of void volume. The thinned cathode catalyst layer shows localized changes (C \rightarrow D) and shows a structure of "bands" of graphite oxide, partially oxidized carbon and relatively unchanged HSAC (High Surface Area Carbon). These bands are primarily direction with respect to the membrane.

To rapidly evaluate materials we employ Accelerated Stress Tests (ASTs); to evaluate the cathode support material, a potential hold of the cathode at 1.2V was used. Figure 2 shows changing elemental composition of the carbon in the catalyst layer as a function of time at the corrosion potential. An increase in the graphitic content of the carbon is observed, likely due to the loss of amorphous carbon material due to carbon corrosion. In addition, an increase in oxygen content of the catalyst layer is observed compared with fresh samples; this is likely formation of surface oxides.

To reduce degradation due to corrosion of the support material, different carbon supports have been employed, but typically at the cost of lower initial performance. Figure 3 shows a Waterfall Plot for three types of carbon, (E – High Surface Area Carbon, HSAC, V – Vulcan, Ea – graphitized) plus a case where graphitized carbon was mixed with High Surface Area Carbon to prevent the loss of catalyst layer porosity and retain higher performance.

References

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- 3. U.S. Department of Energy: DE-FOA-0000360, Appendix F – MEA/Stack Durability Protocol

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Figure 1. TEM of carbon structure of catalyst layer and MPL before (A,C) and after (B,D) Drive Cycle testing.



Figure 2. Compositional changes of the catalyst support carbon as a function of AST testing time.



Figure 3. Waterfall Plot of mass activity and ECSA for catalyst support carbons (a) E carbon (High Surface Area), (b) Vulcan carbon and (c) Ea (graphitized) carbon. Initial and final performance after carbon corrosion AST.