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MATERIALS RESEARCH HIGHLIGHT

Polymer electrolyte membrane (PEM) fuel cell durability

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Energy efficient, clean fuel cells have the potential to replace the vehicle's internal combustion engine. Specifically, with fast-start capability and low temperature operation, the polymer electrolyte membrane (PEM) fuel cell is the current focus for light-duty vehicles. The durability of fuel cell systems, however, has not been established. To be commercially successful, fuel cell power systems must be as durable and reliable as current automotive engines, i.e., a 5,000 hour lifespan and functionality over a range of vehicle operating conditions (-40° to +40° C ambient temperature).

Durability is one of the most critical remaining issues impeding successful commercialization of broad PEM fuel cell stationary and transportation energy applications, and the durability of fuel cell stack components remains, in most cases, insufficiently understood. Lengthy required testing times, lack of understanding of most degradation mechanisms, and the difficulty of performing *in-situ*, non-destructive structural evaluation of key components makes the topic a difficult one.

The fuel cell membrane-electrode-assembly (MEA) durability plays a vital role in the overall lifetime achieved by a stack in field applications, and is the main component of our durability study. Within the MEA's electrocatalyst layers are three critical interfaces that must remain properly intermingled for optimum MEA performance: platinum/carbon interface (for electron transport and catalyst support); platinum/Nafion interface (for proton transport); and Nafion/carbon interface (for high-activity catalyst dispersion and structural integrity). The MEA performance shows degradation over operating time, which is dependent upon materials, fabrication and operating conditions. Transient automotive operating conditions exacerbate degradation of fuel cell MEA durability and reliability. Specifically, power (or voltage) cycling simulating vehicle drive cycles increases the rate of electrocatalyst surface area loss[1-2]. Start-up/shut-down of the fuel cell can also lead to membrane degradation and carbon corrosion.

Approach to improved PEM fuel cell durability

Our approach to improved PEM fuel cell durability is to define the degradation mechanisms and to understand these mechanisms to allow design of improved fuel cell materials and components.

We have shown that the loss of electroactive platinum surface area shown during operation is due primarily to growth in platinum particle size. Cathode particle size growth is dependent on temperature, time, relative humidity, and potential. During single cell durability testing, the cathode catalyst particle size grew—with the rate of growth dependant upon test type. Testing simulated automotive drive cycles showed a greater rate of particle growth than did tests in which the cathode potential was not varied. Accelerated durability measurements showed particle size growth was accelerated at high potentials and temperature, but was decreased with lower operating relative humidity.

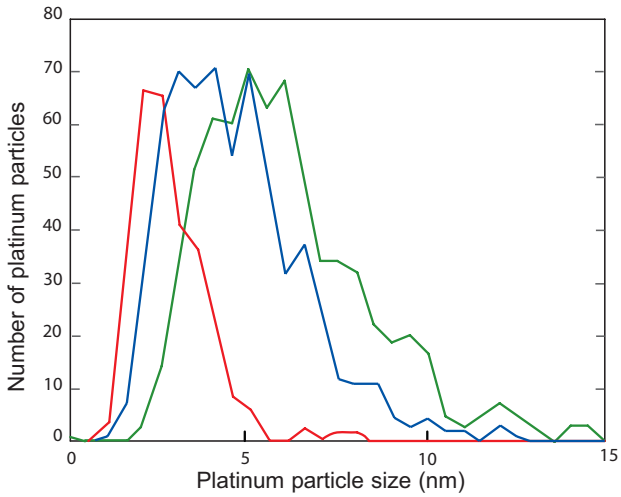

Figure 1. Transmission electron microscopy after 2,000 hours of testing with the US06 drive cycle. Initial (red curve); after testing for ~2,000 hours with the US06 Drive Cycle at:50% relative humidity (blue curve); 100% relative humidity (green curve).

Figure 1 shows the cathode platinum particle size distribution after testing utilizing an automotive drive cyclefor 2,000 hours of operation. The cathode platinum particle size showed increased particle size distribution by both X-ray diffraction and transmission electron microscopy (TEM) post-characterization. An average spherical particle size diameter of 5.0 nm was observed, however, there was a substantial particle population at significantly higher particle sizes. The particle size distribution changed from initially log normal to a bi-modal platinum particle distribution. The bi-modal distribution showed a log normal distribution coupled with

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a large shoulder at higher particle sizes.

Figure 2 shows TEM post-characterization of the bi-modal particle size distribution. The larger platinum particles are clustered in localized regions of the cathode, while other regions show smaller particle size growth.

Several candidate mechanisms appear responsible for the loss of platinum surface area. Oxidation of the platinum occurs at voltages near the peak potential of a typical drive cycle. Platinum solubility increases by approximately 2 orders of magnitude at peak drive cycle potentials compared with the solubility at lower potentials corresponding to peak power[3]. Simple Brownian motion accompanying particle coalescence is also a platinum particle growth mechanism. A theoretical investigation has been initiated to elucidate the operative mechanisms at a molecular/atomistic resolution—with the goal of providing insight for new designs mitigating the effects. To model the observed bimodal particle size distribution, particle growth has been simulated with a kinetic rate, such as would be observed due to platinum solubilizing and reprecipitation, coupled to particle coalescence by particle Brownian motion. Figure 3 shows examples of particle size distribution obtained utilizing coupled kinetic and coalescence particle growth. Modeling shows particle growth with bi-modal particle distributions, not unlike experimental measurements.

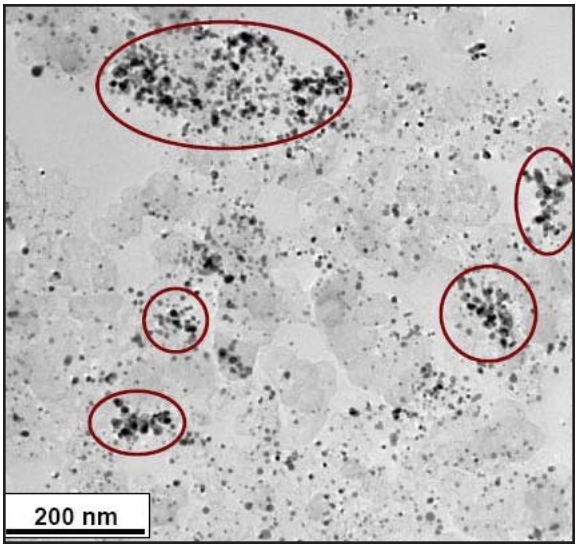

Figure 2. Transmission electron microscopy image of cathode electrocatalyst layer after 2,000 hours of testing with US06 drive cycle. Areas with high concentration of large particles are circled.

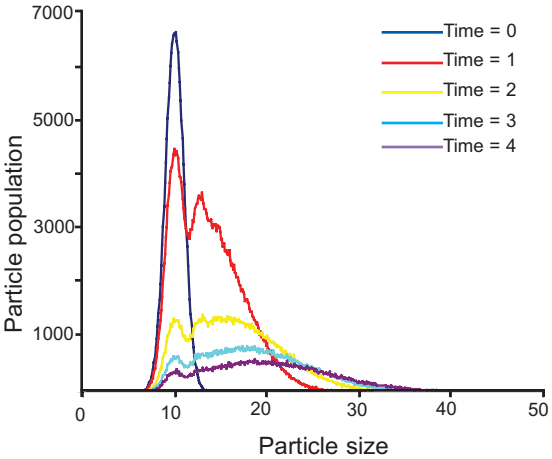

Figure 3. kinetic growth rate and particle coalescence.

Acknowledgement

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