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PEM Fuel Cell Durability Studies

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The durability of polymer electrolyte membrane (PEM) fuel cells is a major barrier to the commercialization for stationary and transportation power applications. For transportation applications, the durability target for fuel cell power systems is a 5,000 hour lifespan and able to function over a range of vehicle operating conditions (-40° to +40° C). However, durability is difficult to quantify and improve because of the quantity and duration of testing required, and also because the fuel cell stack contains many components, for which the degradation mechanisms, component interactions and effects of operating conditions are not fully understood. These requirements have led to the development of accelerated testing protocols for PEM fuel cells. The need for accelerated testing methodology is exemplified by the times required for standard testing to reach their required targets: automotive 5,000 hrs = ~ 7 months; stationary systems 40,000 hrs = ~ 4.6 years. As new materials continue to be developed, the need for relevant accelerated testing increases.

In this investigation, we examine the durability of various fuel cell components, examine the effect of transportation operating conditions (potential cycling, variable RH, shut-down/start-up, freeze/thaw) and evaluate durability by accelerated durability protocols. PEM fuel cell durability testing is performed on single cells, with tests being conducted with steady-state conditions and with dynamic conditions using power cycling to simulate a vehicle drive cycle. Component and single-cell characterization during and after testing was conducted to identify changes material properties and related failure mechanisms. Accelerated-testing experiments were applied to further examine material degradation.

Measurements of degradation during shut-down/start-up

Fuel cell catalysts have been shown to degrade during shut-down/start-up due to the formation of local potentials which can approach 1.5 V during the purging of hydrogen at the anode with air and with the subsequent introduction of hydrogen at start-up.[1] These local potentials create a condition under which the cathode catalyst degrades due to carbon corrosion. Measurement of carbon corrosion by NDIR from the cathode is shown in Figure 1 during three shut-down/start-up cycles for two different anode purge rates. Measured CO_2 production shows that increasing the anode purge rate decreases the carbon corrosion due to less time at localized high potentials. Integration of the of the CO_2 peaks in Figure 1 yields the total amount of CO_2 produced during the shut-down/start-up event. When the anode purge rate was increased by ~ 4x (from Figure 1a to 1b), the carbon corrosion decreased during start-up by ~ 3x, while the decrease during shut-down was ~ 2.6. The non-linearity of the carbon corrosion suggests that the anode purge rate does not linearly effect localized potentials.

In Figure 2 we see that an increase in humidification level increases the amount of carbon corrosion during start-up. However, the inverse is true during shut-down, as the carbon corrosion decreases with increasing RH, although with less magnitude. In comparing the overall effect of water on the carbon corrosion rate, the amount of CO_2 production is much greater with the presence of water, than without (compare Figure 2 with Figure 1). A 5x increase in carbon corrosion is measured for similar purge conditions wet vs. dry for shut-down ($4.9e^{-7}$ vs. $1.0e^{-7}$ moles of CO_2). While there was no detectable CO_2 for starting up dry at 80 °C, this can be compared with $1.8e^{-6}$ moles with humidified gases, which is larger carbon corrosion than observed for comparable conditions during shut-down.

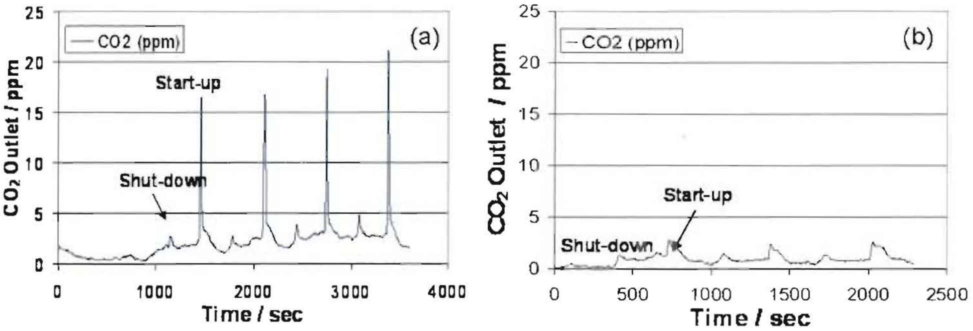

Figure 1. Anode purge rate effect during stop-start cycling on carbon corrosion with (a) Purge time (1 turn-over) = 15.0 sec (Anode:Flowrate: 100 sscm H_2, Purge: 50 sccm Air) (b) Purge time (1 turn-over) = 3.7 sec (Anode: Flowrate: 400 sscm H_2, Purge: 200 sccm Air). 50 cm^2, 25 °C

GDL hydrophobicity changes

Gas Diffusion Layers (GDLs) have been shown to lose hydrophobicity during operation.[2] An example of the loss of hydrophobicity is shown in Figure 3 as an RH fingerprint scan of aged and un-aged GDL materials. One set of GDLs was aged for ~1000 hr in 80°C DI-water with air sparge, while the other set was not aged. The two GDL sets exhibit entirely different RH sensitivities, with the un-aged GDLs showing the RH fingerprint of the "classic" hydrophobic GDL (fluoropolymer impregnation of the substrate and single-sided MPL coating. The conventional type of hydrophobic GDL is sensitive to dry conditions, showing low performance, and demonstrates excellent management of excess liquid water (high performance at high RH values in

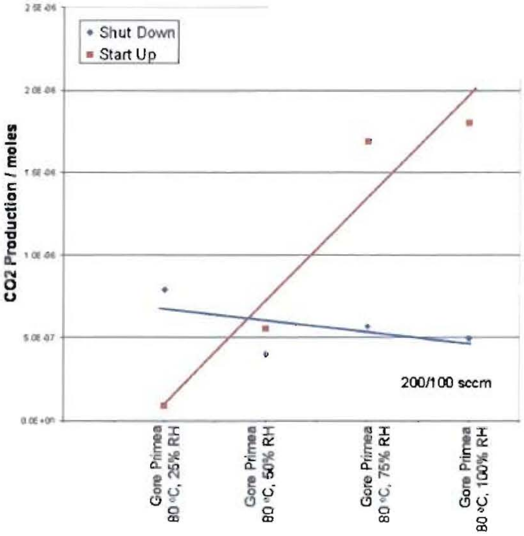

Figure 2. Amount of CO_2 produced during shut-down and star-up of a W.L. GoreTM Primea® series MEA as a function of humidification level. Anode/cathode flowrates of 200/100 sccm and 80 °C.

Fig. 3). The aged GDLs show an RH fingerprint resembling a less-hydrophobic (or even hydrophilic) GDL, characterized by higher cell performance under dry conditions and lower cell performance under wet conditions (due to flooding). Less hydrophobic and mildly hydrophilic GDLs typically exhibit less sensitivity to inlet water vapor as well, as evidenced by the flatter RH-sensitivity profile of the aged GDLs.

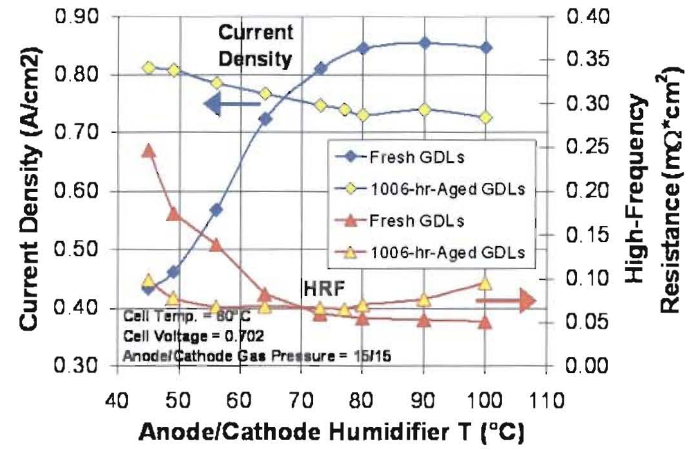

Figure 3. Comparison of RH-sensitivity scans between aged and un-aged GDLs for ~1000 hr in 80°C DI-water with air sparging.

Another method used to define the hydrophobicity and hydrophobicity loss of GDLs is by measuring single-fiber Wilhelmy and sessile drop contact angles.[2] Previous measurements have concentrated on simply aging the GDL materials with temperature, humidity (water) and either an inert or oxidizing atmosphere. As the aggressiveness of the aging conditions was elevated, the contact angles decreased, i.e. the GDLs showed loss of hydrophobicity. However, other conditions also affect the GDL material, including ionic impurities which can result from impurities in the gas stream or from other fuel cell components. Figure 4 shows dynamic sessile drop measurements for GDL materials before and after testing with NaCl during fuel cell operation. While in previous experiments, GDLs lose hydrophobicity with aging, exposure to NaCl make GDLs more hydrophobic. The exposure to NaCl also slows rate of water uptake, as evidenced by the decreased slop of the contract angle measurement versus time.

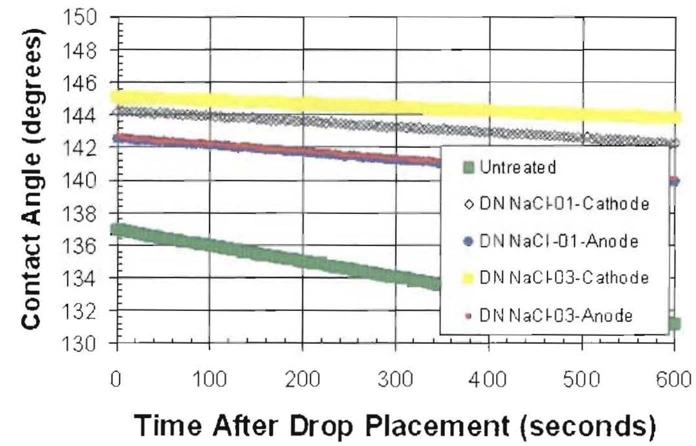

Figure 4. Contact angle changes of GDL after exposure to NaCl

Membrane degradation tests at Open Circuit Voltage (OCV)

The degradation rate and mechanism of catalyst coated Nafion 212 membrane was investigated at a series of relative humidities (RH) while holding the MEAs at OCV to accelerate the membrane degradation. Figure 5a shows membrane hydrogen cross-over with time for four different gas inlet humidities, 0, 20, 60 and 100% RH. Figure 5a shows at the un-humidified condition and at 100% RH, hydrogen crossover is constant, while at both 20% and 60% RH, hydrogen crossover increases significantly during the degradation test. Initially, hydrogen crossover at both 20% RH and 60% RH is less than that at 100% RH. However, hydrogen crossover reaches 19 mA/cm^2 after 144 hours at 60% RH and 14 mA/cm^2 after 192 hours at 20% RH. Therefore, at 60% RH, the membrane experiences the largest increase of hydrogen crossover during testing.

Figure 5b shows the OCV change with time during the same test as Figure 4a. The highest OCV was observed at 100% RH; an initial voltage drop occurred during the first period while subsequently, the OCV was stable. The rate of OCV decrease was 0.25 mV/h. For an inlet RH of 60 %, the OCV decreases significantly over the course of degradation test, with a degradation rate of 1.29 mV/h. At a lower RH of 20%, however, the degradation rate was 1.04 mV/h, which is slightly lower than that at 60% RH. At the un-humidified condition, the initial OCV is low, only 0.68V. Nevertheless, the OCV is steady during the entire test with a degradation test rate of only 0.20 mV/h. This is consistent with the previous observation that at 60% RH the membrane degradation proceeds at the highest rate.

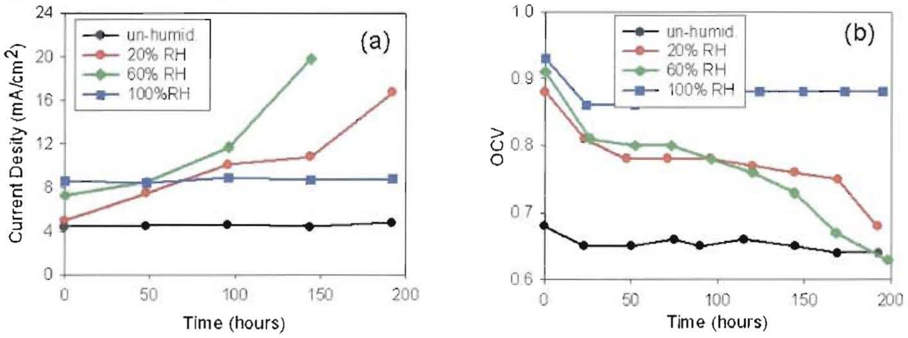

Figure 5. Gas RH effect on membrane degradation over time showing (a) hydrogen crossover and (b) open-circuit potential.

Previous studies have concluded that lowering RH significantly accelerated the membrane degradation[3,4]. This conclusion may fit the change of OCV decay when the RH is operate at 100% RH compared to 60% RH, but does not explain the membrane degradation tendency when the RH was operated at 20%, and particularly at un-humidified condition. This apparent conflict occurs because previous RH-related membrane degradation studies were performed at two RHs (low or high), or in a small range of RH. There have been no reports on the change of membrane degradation in a full range of RH. This study shows that membrane degradation rate is low at both high and low RH. The highest membrane degradation rate may appear in the mid RH ranges (40 – 60 % RH).

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