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MEA Design For Improved Cathode Durability Under Startup Shutdown Automotive Conditions

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A novel MEA design solution - an "intelligent switch" to provide protection of the cathode catalyst layer from degradation caused by startup/shutdown events is proposed (1). This unique approach adapts gas sensor-type materials (2) that exhibit several orders of magnitude change in resistance depending on its gas environment (1) in PEM fuel cell anodes. The high resistance of the new layer in air environments prevents corrosion loop currents. In hydrogen environments, the layer becomes conductive and fuel cell performance is minimally hindered. In-situ fuel cell test results demonstrate a successful reduction in cathode peak potentials during startup events leading to reduced performance degradation in startup/shutdown stress tests. This strategy of preventing corrosion loop currents is compatible with various catalyst types and with different catalyst loadings. The approach enables MEA design to minimize air/air start/stop degradation and provides a pathway for the use of alternative catalyst options.

Introduction

Automotive fuel cell stacks are required to operate under challenging dynamic conditions and last for 5000 hours (3). For Proton Exchange Membrane Fuel Cells (PEMFC) in automotive applications cost, durability and performance are the key development drivers. Meeting one requirement is often at cost of another. The catalyst material is a key contributor. Strategies to enable lower catalyst loading or higher activity catalyst without lowering durability are needed to enable commercialization. Startup/shutdown cycling has been identified as a key durability stressor for the cathode electrode (4) and a novel method to reduce cathode degradation will be the focus of this paper. As the catalyst loading is decreased, the impact of startup/shutdown stressors on degradation becomes increasingly significant. Membrane Electrode Assembly (MEA) design advancements are necessary to enable lower catalyst loadings and thereby enable cost reduction with minimal burden to system design and operational strategy.

Yu et al. recently conducted a detailed review focusing on mechanisms and mitigation of performance degradation due to startup/shutdown stressors (4). Some startup/shutdown mitigation strategies which have been considered are alternative catalyst supports and system-enabled solutions such as load during startup, shutdown with hydrogen stored on both sides of the MEA , hydrogen purging to the anode during

startup and shutdown, cathode exhaust gas recycling during startup and shutdown, and an auxiliary load to consume residual gases at shutdown, but most of these approaches have the disadvantage of lower performance, additional cost and/or system complexity.

In this paper, a new strategy is proposed to reduce high cathode peak potentials. A selectively conducting oxide discrete layer is added in the MEA as shown in figure 1b. The selectively conducting oxide material added to the MEA assembly has the special characteristic to be conductive in the presence of hydrogen but resistive in an air environment. Gas sensitive materials are used in the sensor industry but they usually operate humidity-free and in a temperature range between 300°C and 750°C (5, 6), which is well outside the conventional PEMFC operational window. It has been found that similar materials can be successfully applied to PEM fuel cell.

Startup/Shutdown Processes

Reiser et al. (7) first proposed the corrosion current mechanism, which suggest that upon startup or upon shutdown damaging loop currents lead to high cathode potentials. Subsequent experimental measurements and modeling calculations estimate these cathode potentials may range from 1.4 to 1.75V (4, 7-11). Within the context of this paper, "startup" refers to a situation where within a fuel cell assembly, hydrogen flows through air filled anode channels while simultaneously air flows through cathode channels, prior to application of load. Similarly "shutdown" refers to the removal of load application, followed by the cessation of reactant supply. After a period of time, air infiltrates into the anode channels filling them with air.

Figure 1a depicts the theorized startup process under a conventional PEMFC environment. The key reactions expected at the high potential region of the cathode are:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \qquad E_o = 0.207V \qquad [1]$$

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad E_o = 1.229V \qquad [2]$$

Although the carbon oxidation occurs at a low potential it is not kinetically preferred in a fuel cell operating under normal conditions (12, 13). In the presence of the high cathode potentials, the likelihood of the carbon oxidation increases. The presence of platinum can also promote carbon corrosion.

Figure 1b depicts the theorized function of the gas selective oxide design. For this example the selectively conducting oxide layer is depicted as a discrete layer on the microporous layer of the anode GDL (gas diffusion layer) but alternatively it could be placed in different locations as long as the catalyst layer is protected from the corrosion current.

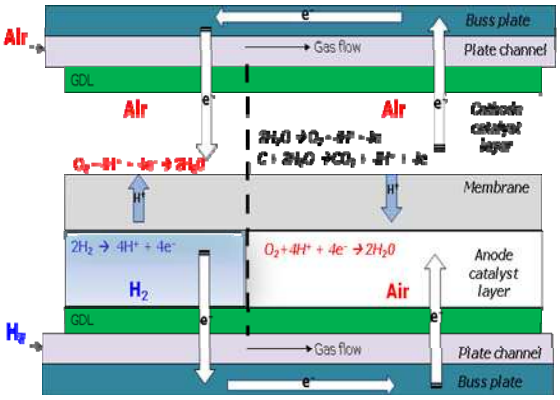

Figure 1a. Pictorial Schematic of Corrosion Currents under startup

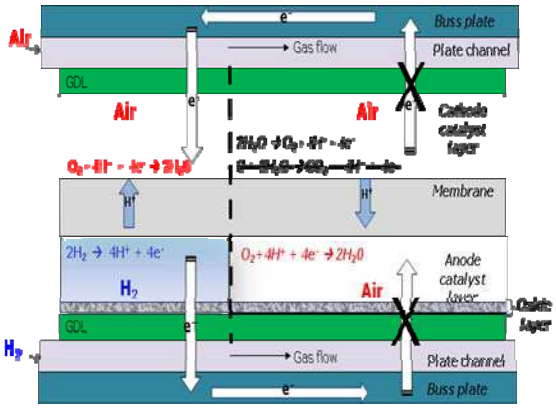

Figure 1b. Pictorial Schematic of Corrosion Currents under startup with a Selectively Conducting Oxide layer in the MEA Assembly

Experimental

Selective Conducting Oxide Layer Preparation

Selectively conducting oxide coated samples were prepared by preparing the selectively conducting oxide powder into a slurry. Inks were mixed to reduce agglomerate size. These selectively conducting oxide inks were then coated onto a substrate and then heat treated. Four types of selectively conducting oxides were considered for this study: Oxide A, B, C and D with two types of GDLs and two main types of CCMs.

Fuel cell testing

MEA designs were evaluated in two configurations. In the first stage, MEAs were evaluated in-situ, in a small scale cell with either 5 or 50cm^2 active areas. Second-stage evaluations were conducted in full automotive cell dimension, 20 cell stack configuration.

Characterization

Sample layer thicknesses were measured by SEM (Scanning Electron Microscope). Samples were cut with a scalpel. Pieces were mounted in epoxy and polished. Samples were examined with 400X magnification and an average of 400 points was used to determine the thicknesses.

Results and Discussions

Design Requirements

The ideal selectively conducting oxide structure would have no negative performance impact on fuel cell operation. For the normal operation there would be no loss in performance but under startup/shutdown conditions the selectively conducting oxide layer would be highly resistive in the air portion to protect against high cathode potentials.

The critical property is the magnitude of the resistance change between the conductive "on" state, in hydrogen and the resistive "off" state, in air. A new requirement, "switching capability", for the selectively conducting oxide material, will be defined as:

$$\text{Switching Capability} = \text{Log}\left(\frac{\text{Resistance in Air}}{\text{Resistance in Hydrogen}}\right) \quad [3]$$

The exact requirement will not be fully determined but based on experience a switching capability of 4 is targeted.

For simplicity of measurement, an in-plane resistance measurement was employed. It is assumed that the resistance properties of the selectively conducting oxide are isotropic. The selectively conducting oxide layer was prepared by coating on a non-conductive substrate. The sample was placed on an in-house, in-plane resistance apparatus. The entire measurement assembly was transferred into a sealed vessel. Dry target gas environments were supplied to the vessel while measurements were made. Nitrogen was supplied to the vessel between hydrogen and air measurements in order to flush out residual gases.

Figure 2 shows the resistance of the three examples of selectively conducting oxides. Table 1 shows a summary of the switching capability for the measured selectively conducting oxides. Oxide B and Oxide C show a switching capability of 6 with rapid and reversible switching capability. Oxide A shows an initial switching capability of approximately 5 and is reversible but the switching time is significantly slower from the high resistivity condition to conductive state. Figure 2 shows that material selection determine switching capability and the speed of switching.

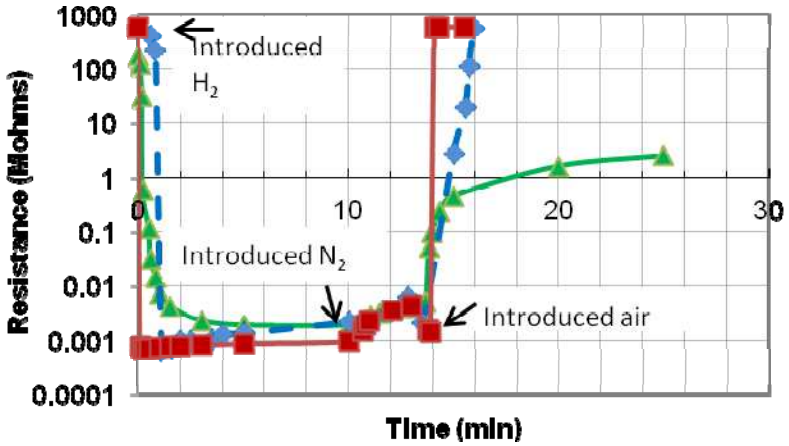

Figure 2. In plane resistance of ▲ Oxide A, ◆ Oxide B and ■ Oxide C.

TABLE I. Calculated Switching Capacity for Selectively conducting oxides

Sample	Switching Capability
Target	4
Oxide A	5.0
Oxide B	5.8
Oxide C	5.9

Fuel Cell Performance

Selectively conducting oxide coated GDL samples were assembled into MEAs and evaluated in a 5cm^2 single cell. In an operating fuel cell, the selectively conducting oxide would be exposed to humidity, which may compromise the gas switching capability of the gas selective materials (5, 6). In order to evaluate the switching capability under humidity, the selectively conducting oxide coated GDL was used in two configurations. In the first configuration--the desired configuration, the selectively conducting oxide layer was coated on the anode GDL. In a second configuration, the selectively conducting oxide coated layer was coated on the cathode GDL. The catalyst coated membrane position in the MEA was constant for both tests. In Figure 6, results were compared against the same MEA design without any selectively conducting oxide layer, the baseline.

When the selectively conducting oxide layer was added to the baseline design as an anode, the selective oxide layer environment is hydrogen rich. Hydrogen adsorbs onto the oxide surface and reduces it, making it electrically conductive. This is the "on" state for the intelligent switch in the selectively conducting oxide layer. Ideally, the addition of the selectively conducting oxide layer should be invisible to performance under normal fuel cell operation. Conversely, if the selectively conducting oxide layer is coated on the cathode GDL, it is exposed to an air environment. Oxygen will act as an oxidizer for the selectively conducting oxide layer, increasing the electrical resistance. This is the "off" state for the intelligent switch in the selectively conducting oxide layer. For the oxide

materials evaluated in Figure 2, there are several orders of magnitude change in resistance between the "on" state and the "off" state of the intelligent switch of the selective oxide layer. A cathode GDL with the selective oxide layer should perform very poorly when operated in a fuel cell under normal conditions.

Figure 3 shows the polarization results of the various designs when the oxide is on the anode GDL or the cathode GDL. For the selectively conducting layer coated on the anode GDL, a 15-40 mV performance loss is observed at 1.5 A/cm^2 which is greater than desired but in the right order of magnitude. When the selectively conducting oxide coated GDL is used as a cathode, the oxide the performance loss is drastic, as intended. Reduced performance could also be due to reduced oxygen diffusivity from the selectively conducting oxide layer.

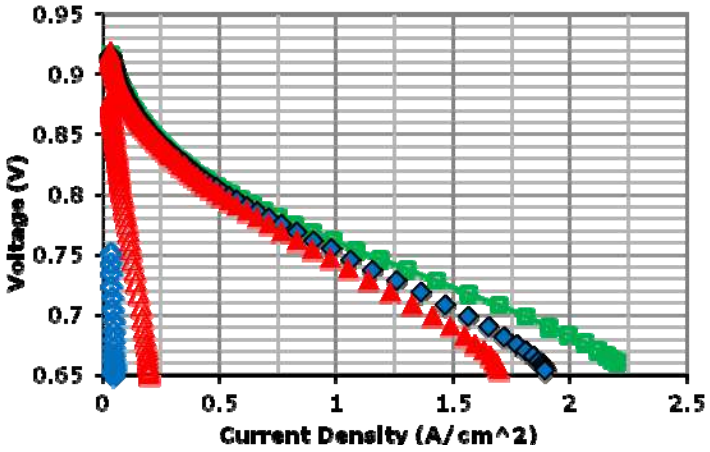

Figure 3. Polarization Curves @ 68°C and 100% RH of □ Baseline (no oxide), ▲ Oxide A coated GDL as an anode, △ Oxide A coated GDL as a cathode, ◆ Oxide B coated GDL as an anode, ◇ Oxide B coated GDL as a cathode

If the selectively conducting oxide layer is functioning as designed, there should be a suppressed cathode voltage peak under startup or shutdown conditions. In-situ reference electrodes were then used to measure the cathode peak potential under startup events. A small stack with 50cm^2 MEAs was assembled with MEAs which contained the selectively conducting oxide design and MEAs which did not. A start up event was simulated by introducing hydrogen into the air filled anode channels while the reference electrode half cell potential voltage traces were recorded. Figure 4 shows the voltage trace for an MEA without selectively conducting oxide and an MEA with selectively conducting oxide coating. A 200mV drop in cathode peak potential was observed for the MEA with the selectively conducting oxide.

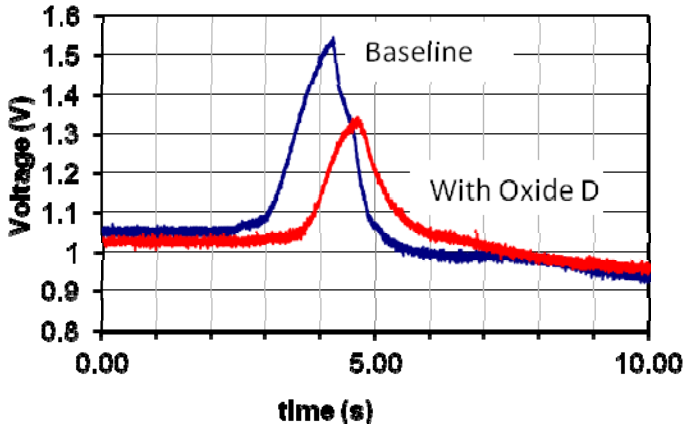

Figure 4. Cathode reference electrode results for Baseline (without oxide) and Oxide D

The selectively conducting oxide layer was now built into a full scale active area automotive, 20–cell stack. A startup/shutdown accelerated stress test (AST) was used to evaluate the impact on durability to quickly assess the impact of the selectively conducting oxide layer addition. Figure 5 shows the steady state performance measured at 1.0A/cm^2 during the startup/shutdown cycling, which illustrates that the selectively conducting oxide design showed a clear improvement in durability roughly doubling the cycling lifetime of the stack. Following the completion of the startup/shutdown AST, the cathode catalyst layer thicknesses were assessed for signs of cathode electrode damage.

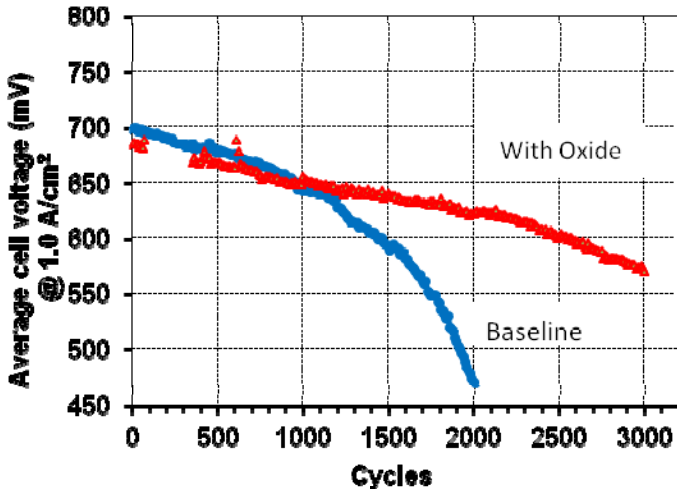

Figure 5. 20-cell stack steady-state performance at 1.0 A/cm^2 measured during startup/shutdown AST for Baseline (without oxide) and Oxide layer design

Failure Analysis

SEM analysis was performed on untested BOL (Beginning of Life) MEAs and on degraded MEAs removed from the stacks to determine the changes in cathode catalyst layer thickness. Samples were cut at regular intervals along the active area and analyzed. Cathode catalyst layer thicknesses were reported terms relative to the percentage of the original (BOL) thickness for the untested sample.

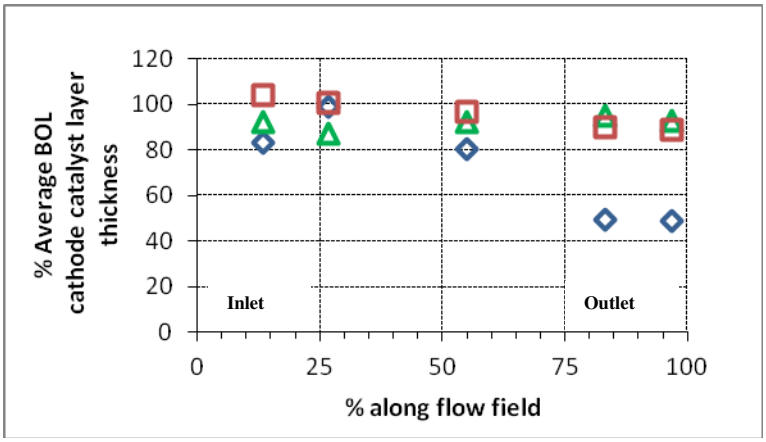

Figure 6. Change in Cathode catalyst layer thickness along length of cell
◇ Baseline (2000 cycles) △ Oxide stack (2000 cycles) □ Oxide stack (3000 cycles)

Figure 6 shows the change in the cathode catalyst layer thickness due to carbon corrosion for the baseline design (without oxide) and the selectively conducting oxide design after 2000 and 3000 startup/shutdown cycles respectively. After 2000 cycles, the baseline design has experienced 50% loss of the cathode catalyst layer thickness at the outlet while even after 3000 cycles, the selectively conducting oxide design shows approximately 10% loss in the cathode catalyst layer thickness.

Catalyst Loading Durability Evaluations

Various Pt/C catalyst loadings were evaluated under the subscale startup/shutdown AST with and without the selectively conducting oxide protection to quantify the benefit in terms of catalyst loading. Figure 7 shows that the selectively conducting oxide layer improved the durability of all designs and for this CCM design, enabled a 30-40% catalyst layer loading reduction while still maintaining the same degradation rate.

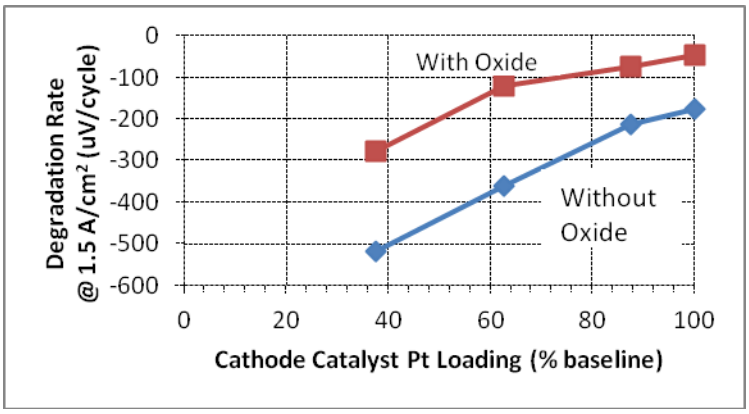

Figure 7. Subscale Startup/Shutdown durability evaluations for different loaded Pt/C based CCM with and without selectively conducting oxide protection

Alternative Catalyst Durability Evaluations

High activity carbon supported catalysts are often susceptible to carbon corrosion. Application of the new selectively conducting oxide layer, shown to protect the carbon support, could potentially enable the use of high activity materials. Figure 8 shows a small scale assessment of the selectively conducting oxide benefit for a platinum based catalyst on a robust carbon support as compared to a high performing/less durable PtCo/C alloy. The increase in startup/shutdown durability is substantial. The Pt/C based design has roughly doubled the number of cycles before failure. The PtCo/C design is projected to extend to roughly a seven fold increase in the number of cycles to failure.

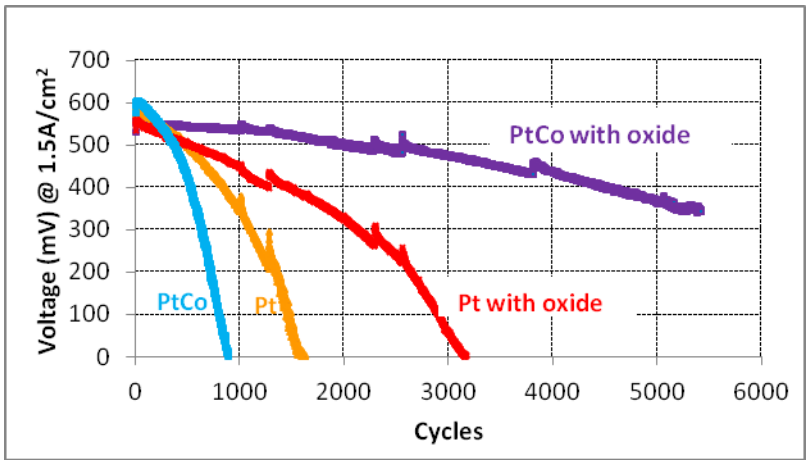

Figure 8. Performance @ 1.5A/cm^2 during subscale startup/shutdown durability evaluations for Pt/C based CCM or PtCo/C based CCM with and without selectively conducting oxide protection

Conclusions

A novel approach is proposed to prevent startup shutdown degradation by minimizing destructive corrosion currents. The selectively conducting oxide layer acts as an "intelligent switch"; conductive in the presence of hydrogen and resistive in the presence of air. In-plane resistance measurements verified that selectively conducting oxides studied had the required switching capability to provide good operating performance and still provide startup/shutdown protection. Reference electrodes demonstrated a successful suppression of the cathode peak potential under startup/shutdown stressors with the new design. In-situ evaluations showed that performance losses under operation were slightly higher than desirable but demonstrated improved durability under startup/shutdown AST's. SEM measurements of the cathode catalyst layer thickness verified that carbon corrosion was significantly reduced. The baseline design showed ~50% loss of cathode layer thickness at the outlet after 2000 startup/shutdown stressor cycles while after 3000 cycles the selectively conducting oxide design has only lost ~10% cathode catalyst layer thickness at the outlet. Pt/C catalyst loadings could be to reduced 30-40% while maintaining the same degradation rate under startup/shutdown cycling. Higher activity/less durable catalysts also showed significant durability benefits when the selectively oxide layer was incorporated into the MEA design. This unique approach empowers an MEA design solution to minimize performance losses linked to startup/shutdown events and enables alternative catalyst options without burdening the system structure or operation strategies.

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