

## V.A.4 Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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Contract Number: DE-EE0000461

Subcontractor  
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Farmington Hills, MI

Project Start Date: September 1, 2010  
Project End Date: January 31, 2015

### Overall Objectives

This project addresses the following targets from the Fuel Cells section (Table 3.14.12) of the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- <40% electrochemical area (ECA) loss in electrocatalysts using the synthesized supports tested per the General Motors (GM) protocol
- <30 mV electrocatalyst support loss in the synthesized supports after 100 h at 1.2 mV; tested using the GM protocol

### Fiscal Year (FY) 2015 Objectives

- Evaluate the suitability of titanium dioxide-ruthenium dioxide (RTO), and indium tin oxide (ITO) as conducting catalyst supports for proton exchange membrane fuel cells (PEMFCs)
- Optimize the Pt deposition method on the above catalyst supports to improve PEMFC performance and durability
- Demonstrate the performance and durability (under start-stop and load cycling protocols) of Pt deposited on RTO and ITO in a PEMFC

### Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

### Technical Targets

See the targets listed under overall objectives.

This project is conducting fundamental studies of RTO and ITO supports and catalyzed supports. A brief list of our current status is listed below:

- Initial oxygen reduction reaction (ORR) mass activity: 40% Pt/RTO: 0.160 A/mg Pt; 40% Pt/ITO: 0.160 A/mg Pt
- Loss of initial electrochemical active surface area (ECSA) activity after 10,000 cycles (load cycling protocol): 40% Pt/RTO: 34%; 40% Pt/ITO: <40% (measured in a rotating disk electrode [RDE] set-up)
- Cell voltage loss at 1 A/cm<sup>2</sup> after 10,000 cycles (load cycling protocol): 40% Pt/RTO: 6%; 40% Pt/ITO: Never measured (Pt/ITO not stable under fuel cell operating conditions)

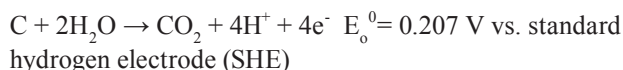
### FY 2015 Accomplishments

- We have found that the fuel cell performance of Pt/ITO was much lower than Pt/C or Pt/RTO despite the similar ORR activities found in RDE experiments. RDE stability experiments done following DOE stability protocols also revealed exceptional stability for the ITO support.
- X-ray photoelectron spectroscopy (XPS) was employed to investigate the changes occurring in Pt/ITO during PEMFC operation, and revealed the formation of indium hydroxides, which we found to be the reason for the lower performance (loss of electronic conductivity).
- NTCNA has synthesized 10% Pt/RTO catalyst with better Pt particle dispersion, ECA, and mass activity than 40% Pt/RTO catalyst due to better Pt utilization.
- NTCNA estimated, using a model, that a more appropriate ionomer/support (I/S) weight ratio of 0.3 should be employed for 10 wt% Pt/RTO to match the ionomer film coverage in 30% Pt/GKB (graphitized Ketjenblack<sup>®</sup>). Experimental results corroborated the calculations.



## INTRODUCTION

Carbon black, which is currently used as support material for the Pt in the polymer electrolyte fuel cell (PEFC) electrocatalyst can undergo corrosion under fuel cell operational conditions [1]:



This is a thermodynamically favorable reaction, but it is very slow under normal operating conditions. However, the reaction can be accelerated during voltage spikes (as high as 1.5 V) occurring during start-stop and fuel starvation [2,3]. The irreversible carbon corrosion leads to the aggregation of Pt resulting in an irreversible loss of the electrochemical active surface area (ECSA) and ORR mass activity that significantly reduce fuel cell performance. To overcome these obstacles, it is necessary to replace the carbon with high electronic conductivity, high surface area and porous support, with high corrosion resistance.

## APPROACH

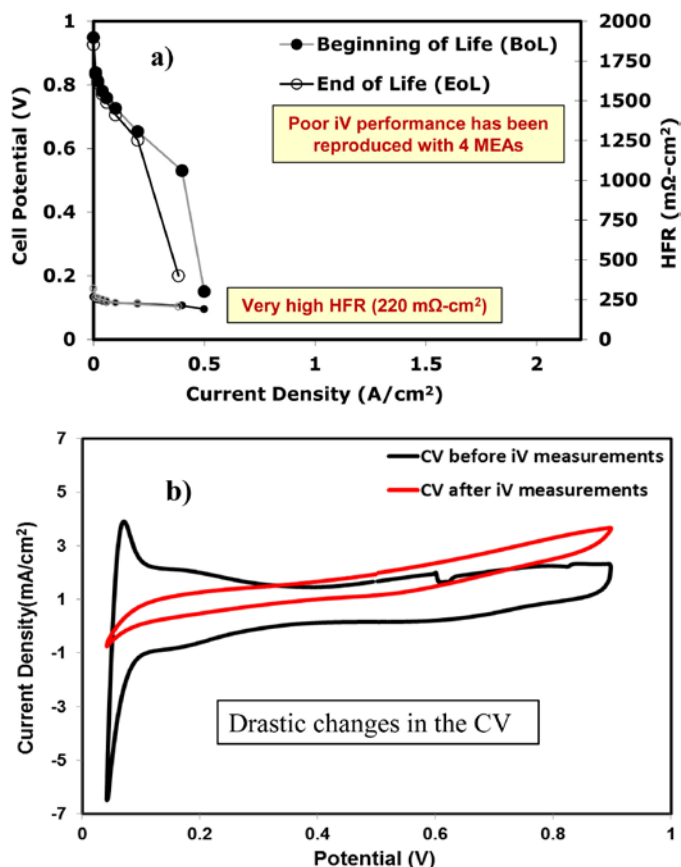
We have explored selected mixed metal oxide supports, namely RTO and tin doped ITO. Each support (RTO and ITO) was evaluated for electrochemical stability using the start-stop transient protocol (start-stop protocol: triangular wave from 1 to 1.5 V at 0.5 V/s for 10,000 cycles). Pt was deposited on stable supports and the resultant catalyst stability evaluated using start-stop protocol and load cycling protocol (rectangular wave between 0.6 V and 0.95 V with a hold of 3 s at each potential for 10,000 cycles). Membrane electrode assemblies (MEAs) were made and tested in a PEMFC to evaluate fuel cell performance for each catalyst.

## RESULTS

We have already reported (in previous annual reports) on our excellent results (RDE and MEA) with Pt/RTO and will not repeat these here. We focus here on the work we have done on Pt/ITO, and on further optimization of Pt/RTO.

### Fuel Cell Performance for Pt/ITO

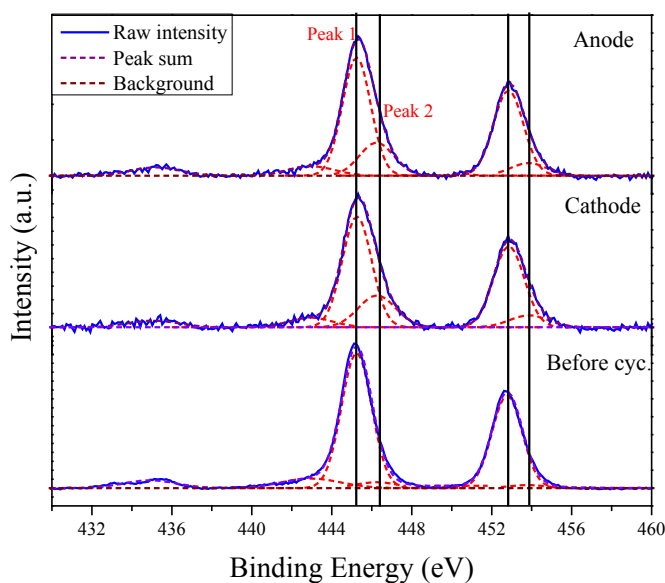
The start-stop cycling durability test was performed to determine changes between the beginning of life (BoL) and end of life (EoL) performance of Pt/ITO, and the results are shown in Figure 1a. The ink formulation that was used was the same as for the Pt/RTO samples in order to make a direct comparison with the MEA results of Pt/RTO (an I/S mass ratio of 0.9 was used). The Pt/ITO ink was successfully sprayed onto SGL 25 BCH gas diffusion layers, and four 25 cm<sup>2</sup> MEAs were made using established protocols at



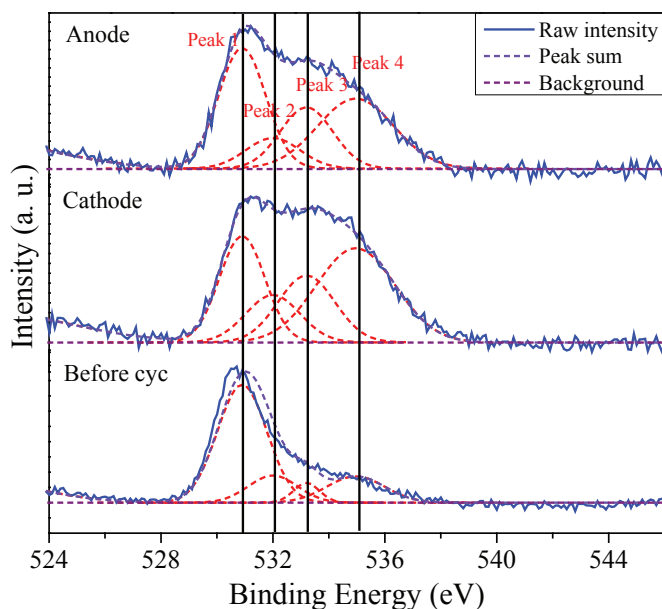
**FIGURE 1.** (a) MEA iV performance of Pt/ITO vs. Pt/C under oxygen operation; (b) CV plots of Pt/ITO before and after iV measurements. Cell conditions: H<sub>2</sub>/O<sub>2</sub>, 80°C, 100% relative humidity, 1 bar<sub>g</sub> backpressure; Pt loading: 0.35 mg/cm<sup>2</sup>.

NTCNA. The EoL performance does not appear to be significantly different than the BoL curve, indicating that the ITO support may be able to maintain its properties at its BoL state through 1,000 potential cycles from 1.0–1.5 V during the start-stop cycling. However, more importantly, we have also constantly observed (in several similar tests) that 40% Pt/ITO performs very poorly during PEMFC testing.

The high frequency resistance (HFR) was very high (220 mΩ-cm<sup>2</sup>, normally at ~60 mΩ-cm<sup>2</sup>), during all the testing, suggesting some conductivity problems with the ITO support. Furthermore, as can be seen in Figure 1b, drastic changes in the cyclic voltammograms (CV) profile (loss of H<sub>upd</sub> features and resistive behavior) was observed after minimal operation in fuel cell mode, suggesting changes in the chemical composition of the ITO support. It is possible that hydroxyl species may have formed on the ITO surface under fuel cell operating conditions during the iV curve measurements. This would explain the increase in ohmic resistance observed during MEA operation, and will be analyzed in more detail in the next section.



**FIGURE 2.** XPS fitting results for Indium  $3d_{5/2}$  before and after PEMFC performance testing (40% Pt/ITO used in the anode and cathode). Peak 1 (445 eV) was assigned to  $\text{In}^{3+}$  in the oxide (ITO); Peak 2 (446 eV) was assigned to  $\text{In}^{3+}$  adjacent to hydroxide species.



**FIGURE 3.** XPS fitting results for oxygen 1s before and after PEMFC performance testing (40% Pt/ITO used in the anode and cathode). Peak 1 (530 eV) was assigned to oxide in ITO. Peak 2 (531 eV) was assigned to oxide that is adjacent to an oxygen vacancy; Peak 3 (532 eV) was assigned to hydroxides; Peak 4 was included to account for impurities.

### XPS Analysis of Pt/ITO Before and After PEMFC Tests

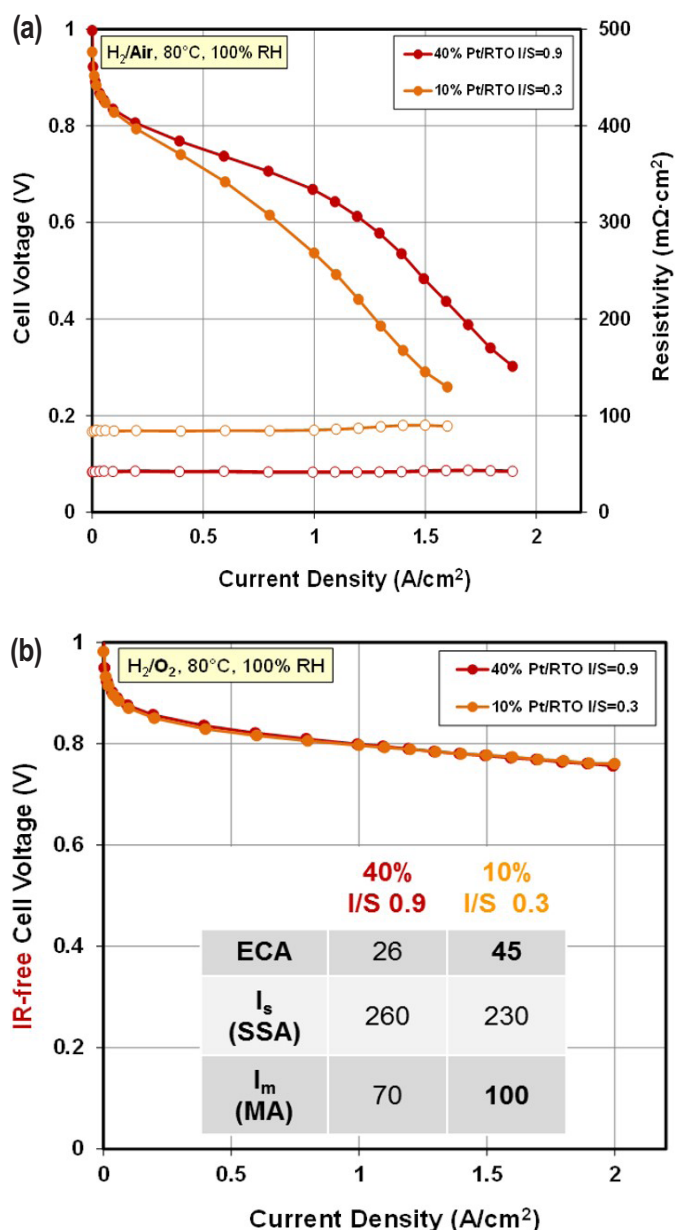
The In 3d and O1s XPS spectra of 40% Pt/ITO before and after being used in a PEMFC are shown in Figures 2

and 3. The In 3d spectrum showed the presence of a doublet peak. The In  $3d_{5/2}$  and In  $3d_{3/2}$  peaks were positioned at approximately 445 eV and 453 eV and had asymmetric shapes. The position of the In  $3d_{5/2}$  peak revealed that indium was mainly in its oxide form ( $\text{In}^{3+}$ ). The shift of In  $3d_{5/2}$  and In  $3d_{3/2}$  peaks after the catalyst was used in a PEMFC, towards higher binding energies, was a consequence of the formation of surface hydroxides and oxyhydroxides; the presence of hydroxide makes the In  $3d_{5/2}$  peak shift to approx. 446 eV [4]. The peak relative areas represent the surface concentration of each species. Fitting results showed clearly that before fuel cell operation,  $\text{In}^{3+}$  was almost entirely in the oxide form in the catalyst and that minimal indium hydroxide was present (approximately 5%). After fuel cell operation, the anode and cathode catalysts (40% Pt/ITO) were recovered and similar XPS analysis was performed. Figure 2 compares XPS fitting results for 40% Pt/ITO before testing, and at the anode and cathode after fuel cell operation (In  $3d_{5/2}$ ). Fitting results showed the presence of a peak at ~446 eV, initially assigned to  $\text{In}^{3+}$  adjacent to hydroxides, which increased after the catalyst was used in the PEMFC. According to the fitting results, hydroxide moieties on the surface of ITO increased from approximately 5%, before the catalyst was used, to 25% of the total amount of indium, once the catalyst was evaluated in the PEMFC (see Figure 2). We suspect that the presence of surface hydroxides increases the electrode resistivity (as seen in Figure 1) affecting fuel cell performance. Figure 3 shows the XPS fitting results for oxygen 1s in 40% Pt/ITO before and after being used as catalyst in the PEMFC. We found that ITO initially contained almost 100% oxide-like species, but after the catalyst was used in the fuel cell, the surface hydroxides increased to approximately 30%. The results were in agreement with the conclusions obtained from Indium 3d peak fitting.

### Pt Loading on RTO and the Appropriate Ionomer Content of the Pt/RTO

In our work we also optimized the Pt loading on RTO and the ionomer content in the Pt/RTO catalyst layer. Our calculations showed that the target Pt loading for Pt/RTO should be 10 wt% to match the Pt particle density of 30% found in Pt/GKB. 30% Pt/GKB would be a good comparison for Pt/RTO since both GKB and RTO have low surface areas and microporosity. We have also calculated that to match the ionomer film coverage in 30% Pt/GKB<sub>150m<sup>2</sup>/g</sub> electrode (I/S weight ratio of 1.3), an I/S weight ratio of 0.3 should be used for 10 wt% Pt on RTO<sub>39 m<sup>2</sup>/g</sub>.

As shown in Figure 4, the ECA for the 10% Pt/RTO sample was 45 m<sup>2</sup>/g, higher than the value obtained for 40% Pt/RTO (at only 26 m<sup>2</sup>/g). This indicates that the dispersion of Pt on the low surface area RTO support is better for the 10% sample such that more Pt active area is exposed and accessible. This is supported by the MEA PEMFC polarization curves in H<sub>2</sub>/air (as shown in Figure 4a) where the 10% Pt/RTO catalyst had a higher mass activity than the



**FIGURE 4.** H<sub>2</sub>/air and H<sub>2</sub>/O<sub>2</sub> iV performance of 10% Pt/RTO vs. 40% Pt/RTO. The 10% Pt/RTO MEA had lower iV performance due to ohmic losses (poor electronic conductivity).

40% sample. The HFR was also significantly higher for the 10% Pt/RTO. We have determined that the increase in HFR is not due to the decrease in ionomer content since several previous MEA tests has showed that decreasing the ionomer content does not lead to such drastic increases in HFR. Furthermore, the 10% Pt/RTO catalyst regardless of I/S ratio shows an HFR of around 100 mΩ·cm<sup>2</sup>, about twice as high as the typical HFR of ~55 mΩ·cm<sup>2</sup>. RTO is a mixed metal oxide consisting of RuO<sub>2</sub> and TiO<sub>2</sub> phases, and if a significant fraction of Pt particles are anchored on the TiO<sub>2</sub> phase, they could become electronically isolated.

## CONCLUSIONS

- The fuel cell performance of 40% Pt/ITO catalyst was much lower than Pt/C and Pt/RTO despite the similar ORR activities found in RDE experiments. XPS revealed the formation of indium hydroxide leading to support degradation (and loss of electronic conductivity) during fuel cell operation.
- NTCNA synthesized 10% Pt/RTO catalyst, which showed better Pt particle dispersion (transmission electron microscopy), ECA and mass activity than the originally reported 40% Pt/RTO catalyst, demonstrating better Pt utilization.
- NTCNA estimated by using a model that a more appropriate I/S weight ratio of 0.3 should be employed for 10 wt% Pt on RTO to match the ionomer film coverage in 30% Pt/GKB.

## FY 2015 PUBLICATIONS/PRESENTATIONS

- G. Wang, E. Niangar, K. Huang, D. Atienza, A. Kumar, N. Dale, K. Oshihara, and V. Ramani, *ECS Trans* (2015).

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