

V.A.7 Synthesis and Characterization of Mixed-Conducting Corrosion-Resistant Oxide Supports

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Technical Barriers

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

(A) Durability

Technical Targets

Identical to those listed under overall objectives.

FY 2014 Accomplishments

- Rotating disk electrode (RDE) testing showed that both 20% and 40% Pt/RTO had very similar mass activity (150-160 mA/mg_{Pt}), comparable to the mass activity of a commercial catalyst made by TKK, TEC10E50E-HT (~120-150 mA/mg_{Pt}).
- RDE testing of both 20% and 40% Pt/ITO showed mass activity of ~150 mA/mg_{Pt}, comparable to Pt/RTO.
- Pt/ITO was very stable under the start-up/shut-down accelerated degradation protocol. The electrochemical active surface area (ECSA) change was less than 4% over 10,000 cycles. The load cycling accelerated protocol (from 0.6 to 0.95 V vs. the standard hydrogen electrode) resulted in a loss of approximately 34% of the initial ECSA after 10,000 cycles.
- A cost model for RTO, ITO supports has been developed, and their durability benefits have been considered.



Overall Objectives

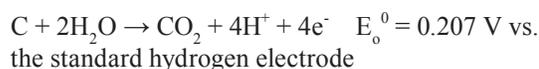
- <40% electrochemical area (ECA) loss in electrocatalysts using the synthesized supports tested per the General Motors (GM) protocol.
- <30 mV electrocatalyst support loss in the synthesized supports after 100 h at 1.2 mV, tested using the GM protocol.

Fiscal Year (FY) 2014 Objectives

- Evaluate the suitability of titanium dioxide-ruthenium dioxide (RTO), 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 titanium dioxide-ruthenium dioxide, ITO in a PEMFC.
- Prepare a preliminary cost model for new supports.

INTRODUCTION

Commercial carbon black currently used as support material for the Pt in the PEMFC electrocatalysts can undergo corrosion under fuel cell operational conditions [1]:



This thermodynamically favorable reaction is very slow under normal operating conditions but can be accelerated during voltage transients occurring during start/stop and fuel starvation. This causes reverse currents in the fuel cell, which drives the potential at the cathode to as high as 1.5 volts [2,3]. The irreversible carbon corrosion leads to the aggregation of Pt, which results in a loss of ECSA. This contributes to significant and irreversible losses in fuel cell performance. To overcome

these obstacles, it is necessary to replace the carbon with high-electronic-conductivity, high-surface-area, porous support with high corrosion resistance under fuel cell operating conditions. In this project, we are evaluating the electrochemical stability and fuel cell performance of non-carbon supports.

APPROACH

To solve the problems associated with carbon corrosion, we have synthesized and evaluated electrical conducting mixed metal oxides (ITO) as supports for PEMFC catalyst during this year. Multiple approaches were used to prepare the ITO and catalyze the ITO. A concern expressed with metal-oxide-based supports is the cost of the material compared to conventional carbon supports, which are very inexpensive. So a cost model for RTO and ITO was considered. NTCNA has prepared a preliminary cost model for these non-carbon support materials considering their durability benefits.

RESULTS

Platinum Catalyzed Indium Tin Oxide (Pt/ITO)

We have found that the best Pt/ITO (ITO synthesized by co-precipitation) catalyst resulted from the reduction of hexachloroplatinic acid in presence of ethylene glycol. The cyclic voltammograms, ECA, and specific and mass activity values for 50% and 20% Pt on ITO samples are presented in Figure 1. The mass activity values obtained for both catalysts are almost equal (140–150 mA/mg_{Pt}), and they are comparable to what we have obtained for Pt/RTO and TEC10E50E-HT, which showed mass activity values of ~120–150 mA/mg_{Pt}.

Pt/ITO was a very resistant and durable catalyst and did not degrade during the simulated start-up/shut-down

transients occurring in a PEMFC. Catalyst stability for 40% Pt/ITO (co-precipitation) was also evaluated following the same protocols (potential cycling from 1.0 to 1.5 V vs. the reference hydrogen electrode, RHE). The loss of ECSA was less than 4% after 10,000 cycles, whereas it was 40% for commercial Pt/C (Tanaka 46% Pt) after the same number of cycles (see Figure 2). The 40% Pt/ITO was also tested using the load cycling protocol (potential cycling from 0.6 to 0.95 V vs. RHE, using a square wave with a period of 6 seconds), and it was found that the loss of the ECSA for 40% Pt/ITO was about 30% after 10,000 cycles. However, the ECSA loss was 40% for commercial Pt/C (Tanaka 46% Pt) after the same number of cycles.

The fuel cell performance for a membrane electrode assembly (MEA) using Pt/ITO catalyst is shown in Figure 3. The performance was poor when compared with baseline data for 46% Pt/C (Tanaka). The maximum current density with hydrogen/air was only 100 mA/cm², whereas 1,500 mA/cm² was obtained with the 46% Pt/C commercial catalyst (at the same Pt loadings). We suspect the reason for the low performance is the low ECSA of the Pt/ITO catalyst. The ITO may also undergo structural changes under operating conditions. We are currently working to find the reasons for the low performance of ITO-based catalysts. Preliminary X-ray photoelectron spectroscopy measurements have shown that the formation of PtIn alloy and the formation of In(OH)₃ during the reduction process may affect the electrode resistivity and hence the fuel cell performance.

Cost Model for RTO and ITO Supports

The metal-oxide-based non-carbon supports may not be very cost-competitive to carbon supports when only material cost is considered, but owing to their excellent durability under automotive start-stop and load cycling accelerated tests, cost analysis of these non-carbon supports has indeed

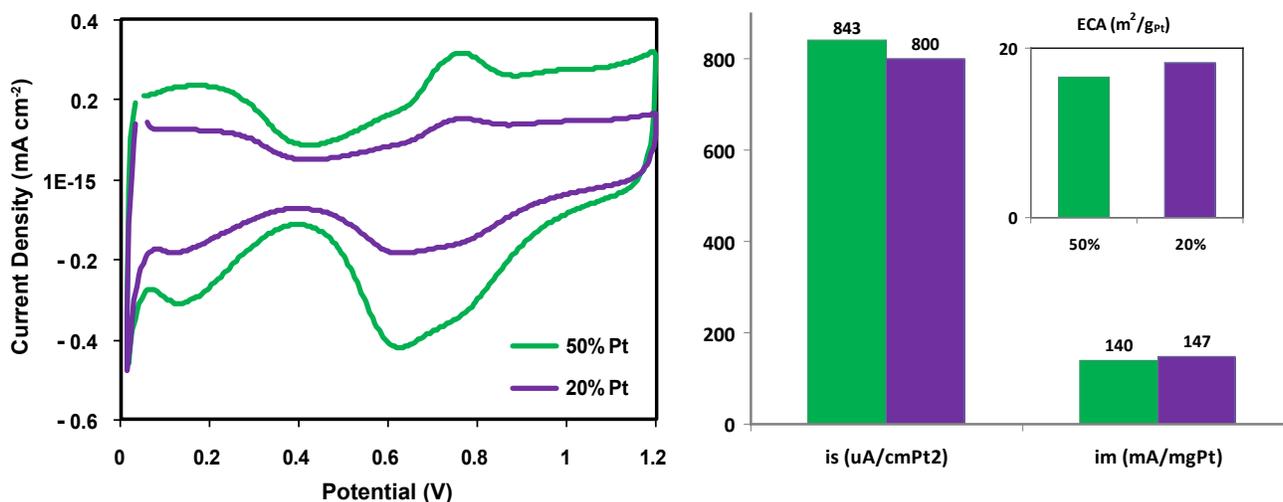


FIGURE 1. The Cyclic Voltammogram, ECA, Specific and Mass Activity Values for 50% and 20% Pt on ITO Samples

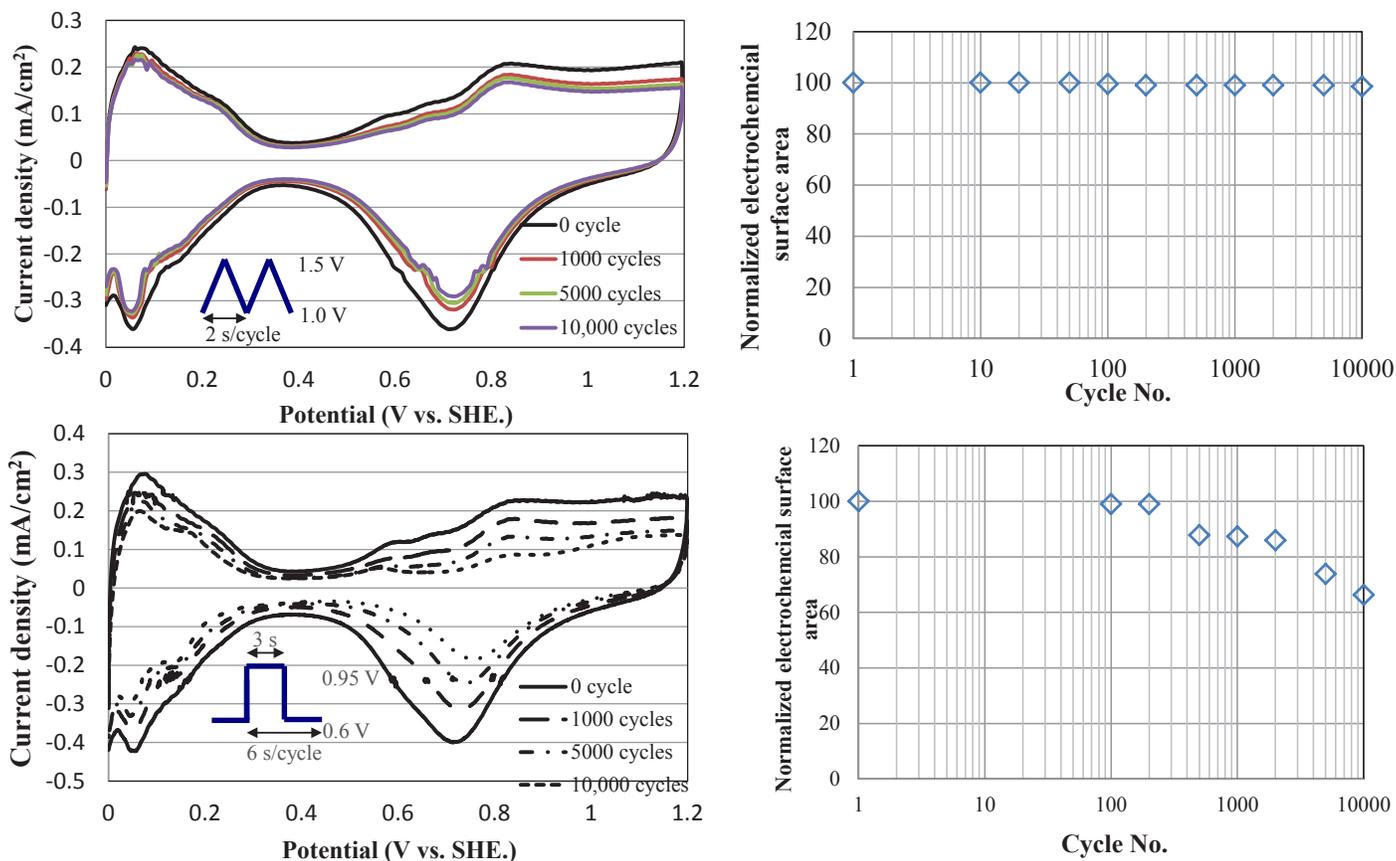


FIGURE 2. Support Corrosion Test and Platinum Dissolution Test for 40% Pt/ITO (Pt by reduction of $Pt(NH_3)_2Cl_2$ using $NaBH_4$)

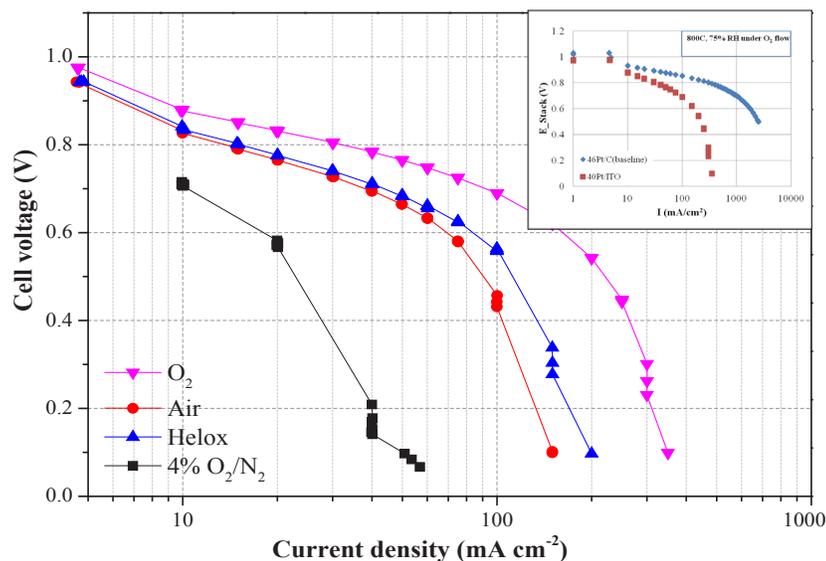


FIGURE 3. Fuel Cell Performance at 80°C for an MEA with 40% Pt/ITO Catalyst at Cathode and 46% Pt/C (Tanaka) at Anode with 30 wt% Nafion® Binder Loading

become essential. Cost modeling was done using the 2008 Pt price of \$1,100/troy oz. for comparison with the 2008 DOE fuel cell cost system. The assumptions made to simplify this model were: a) except for the cathode, the rest of the MEA was identical; b) the rated power was at 80°C, 100% relative humidity; c) all the stacks in the cell were operating identically; d) the processing costs (ink manufacturing, catalyst application, etc.) were the same.

The material costs of the cathodes are compared in Figure 4. As shown in the figure, the RTO support was more expensive than ITO and Vulcan, but the total material costs were still dominated by platinum cost. Although ruthenium is considered a precious metal, its cost (\$80-90/troy oz.) is far less than that of platinum (\$1,100/troy oz. – DOE standard). It should also be noted that ruthenium only makes up 38% of the mass of the support, while the rest is relatively inexpensive TiO_2 . This proportion can be further lowered. Furthermore, significant

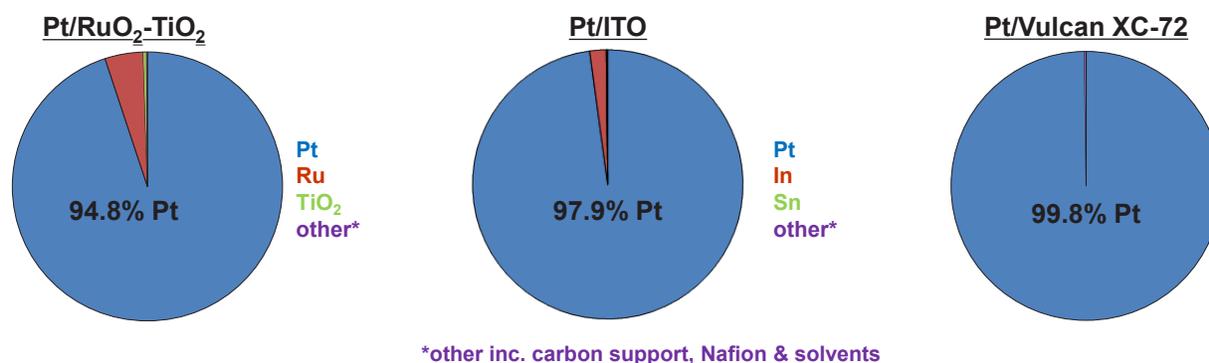


FIGURE 4. Cathode Material Cost Comparison Between Pt/Non-Carbon and Pt/Vulcan[®] XC72.

cost reduction can be achieved by reducing the cathode Pt loadings (cathode material costs were proportional to Pt loading).

The major advantage of using metal oxide supports at the cathode was their excellent resistance to degradation under start-stop cycling. This durability needs to be considered while doing the cost analysis. Based on the data obtained for Pt/RTO and Pt/Vulcan[®] XC72 under the Nissan start-stop durability cycling, a so-called “durability factor” was calculated using following equation:

$$\text{Durability Factor} = \frac{\text{Mass Activity Retention of Catalyst}}{\text{Mass Activity Retention of Pt/RuO}_2 - \text{TiO}_2}$$

Mass activity retention was chosen as a basis because the DOE target for catalyst support durability is defined in terms of mass activity. Pt/RTO retained 86% of its mass activity, while Pt/Vulcan[®] XC72 retained only 66% of its initial mass activity under Nissan start-stop durability cycling. Based on this protocol, Pt/Vulcan[®] XC72 is only 69% as durable as the Pt/RTO. After considering the durability advantages of Pt/RTO and assuming similar durability for Pt/ITO (justified thus far based on durability studies in the RDE), the preliminary cost model shows that even with almost double the Pt loading (0.35 vs. 0.18 mg Pt/cm²), Pt/RTO and Pt/ITO are only 4% and 0.5% more expensive than Pt/Vulcan[®] XC72, respectively

CONCLUSIONS

- The mass activity values obtained for both 50% and 20% Pt on ITO sample were almost equal (140-150 mA/mg_{Pt}), and they were comparable to Pt/RTO and TEC10E50E-HT.
- 40% Pt/ITO catalyst had better electrochemical stability under start-stop cycling protocol than commercial Pt/C. The loss in the ECSA was less than 4% after 10,000 cycles, whereas it was 40% for commercial 46% Pt/C (after the same number of cycles).

- Fuel cell performance when using Pt/ITO at the cathode needs to be improved. Several approaches are being used to identify the possible causes and mitigating approaches.
- After considering the durability advantages of Pt/RTO, a preliminary cost model for Pt/RTO showed that it was only marginally more expensive than Pt/Vulcan[®] XC72.

FUTURE DIRECTIONS

- Optimize the Pt deposition method on ITO and evaluate the fuel cell performance and catalyst stability in a working PEMFC. Understand how to improve MEA performance of Pt/ITO.
- Prepare MEAs with best supports to deliver to DOE for independent evaluation.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. J. Parrondo, T. Han, E. Niangar, C. Wang, N. Dale, K. Adjemian, and V. Ramani, “Pt supported on titanium-ruthenium oxide: A remarkably stable electrocatalyst for hydrogen fuel cell vehicles” Proceedings of the National Academy of Sciences, 111 (1) (2014) 45-50.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Patent Filed: “Non-Carbon Mixed-Metal Support for Electrocatalysts”

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2. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry, T.D. Jarvi, Electrochem. Solid-State Lett. 8 (2005) A273-A276.
3. H. Tang, Z. Qi, M. Ramani, J.F. Elter, J. Power Sources 158 (2006) 1306-1312.