

V.A.8 Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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- Prepare a preliminary cost model for new supports.

Technical Barriers

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

(A) Durability

Technical Targets

The specific technical targets that we were trying to address during this year in this project were the following:

- Synthesis of non-carbon catalysts supports and Pt catalysts (supported on those supports) that lead to less than 40% ECA loss during potential cycling following the GM protocol.
- Synthesis of non-carbon supports that result in less than 30 mV polarization losses after 100 h at 1.2 V (tested per the GM protocol).
- These targets were taken from the 2007 Multi-Year Research, Development, and Demonstration Plan.

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.
- These targets are taken from the 2007 Multi-Year Research, Development, and Demonstration Plan.

Fiscal Year (FY) 2013 Objectives

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

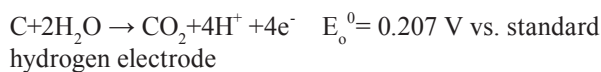
FY 2013 Accomplishments

- We have demonstrated that ITO synthesized using the co-precipitation method possessed the following properties: 1) high electrical conductivity (1-3 S/cm); 2) better electrochemical stability than carbon; and 3) better catalyst stability than Pt/C catalysts when subject to potential cycling (10,000 cycles from 0.6 to 0.95 V).
- ITO was also synthesized using two other strategies (epoxide initiator and supercritical CO₂ methods) in order to get materials with higher surface area, and both showed similar electrochemical stability as ITO synthesized using the co-precipitation method.
- ZIOs have shown better electrochemical stability than carbon (start-stop stability test). The conductivity (around 0.1 S/cm) and Brunauer-Emmett-Teller (BET) surface area were still low but efforts are in progress to improve these properties.
- A cost model for RTO supports has been developed and their durability benefits have been considered.



INTRODUCTION

In recent years, fuel cells have been demonstrated as feasible devices to convert chemical energy to electrical energy with high power density, high efficiency, and zero carbon dioxide emissions. However, one of the main issues delaying its commercialization is the durability of the electrocatalysts. The commercial carbon black currently used as support material for the Pt in the electrocatalyst 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 electrochemical active surface area (ECSA). This contributes to significant and irreversible losses in fuel cell performance. This is a critical factor in delaying the adoption of fuel cell technologies by the automobile industry. In order to overcome these obstacles, it is necessary to replace the carbon support with a high electronic conductivity, high surface area, porous material, with high corrosion resistance under fuel cell operating conditions. In this project, we are working on the synthesis and characterization of the electrochemical stability of non-carbon supports.

APPROACH

To solve the problems discussed in the previous section, we have synthesized and evaluated two kinds of non-carbon supports. The first was ITO which possesses good electrical conductivity for a PEMFC catalyst support. We have used three methods to synthesize high surface area and electrochemically stable ITO: co-precipitation, epoxide initiator, and supercritical CO₂ drying methods. Each support was evaluated for electrochemical stability using start-stop transient (cycling from 1 to 1.5 volts at 0.5 V/s for 10,000 cycles) protocols. Pt was deposited onto the supports that showed good stability during start-stop cycling protocol. Start-stop protocol and load cycling protocol (changing the electrode potential using a rectangular wave between 0.6 and 0.95 volts with a hold of 3 seconds at each potential for 10,000 cycles) were used to examine the stability of the catalyzed supports. The second non-carbon support evaluated

during this year was ZIO. So far, the biggest criticism for metal oxide-based supports is the cost of the material compared to conventional carbon support, which is very inexpensive. To address this concern, a cost model for RTO was developed. NTCNA has prepared a preliminary cost model for these non-carbon support materials considering their durability benefits.

RESULTS

ITO was synthesized using three different procedures: co-precipitation, supercritical CO₂, and epoxide initiator methods. Those methods were intentionally selected to get metal oxides with high surface area, a key characteristic needed for a catalyst support when depositing Pt onto it. The electrical conductivity and BET surface areas are shown in Table 1.

The pseudo capacitance loss for ITO prepared by these three different methods was less than 10% over 10,000 cycles compared with the 230% change observed for Vulcan XC-72 carbon. These results (see Figure 1) are promising and suggest that ITO is a very resistant and durable catalyst support and does not degrade during start-up/shut-down transients in PEMFCs. Catalyst stability for 40% Pt/ITO (co-precipitation) was also evaluated following the same protocol (1.0 to 1.5 V potential cycling). The loss in the ECSA was less than 20% after 10,000 cycles, whereas it was 40% for commercial Pt/C (Tanaka 46% Pt) after the same number of cycles (see Figure 2a). The Pt/ITO was also tested using load cycling protocol (0.6 to 0.95 V) and this result showed similar loss in the ECSA to commercial Pt/C (Tanaka, 46%) after 10,000 cycles (Figure 2b).

ZIOs were synthesized by co-precipitation, using silica-templates, and epoxide initiator methods. The materials were annealed at 400 or 800°C in air for three hours to allow zirconium atoms to dope the indium oxide lattice. The BET surface area and electronic conductivity of zirconium doped indium oxide were 40-50 m²/g and around 0.1 S/cm (see Table 2). The BET surface areas are still low but we are currently working to improve the surface area of the materials by making them into aerogels (alcogels dried using supercritical CO₂ to maintain the porous structure). Figure 3 shows the results of the stability test for the supports subjected to start-stop protocol and its comparison with Vulcan carbon, zirconium indium oxide, 10% ZrO₂ and 90% In₂O₃ by molar ratio, annealed at 800°C (ZIO [1:9 mol]/800°C/co-precipitation) was the most stable among the materials assayed.

TABLE 1. Properties of ITO Catalyst Supports

	Vulcan XC-72	Commercial ITO	ITO 1 co-precipitation	ITO 2 supercritical drying	ITO 3 epoxide initiator
BET (m ² /g)	207 ± 4	30 ± 2	45 ± 2	72 ± 2	41 ± 1
Conductivity (S/cm)	31 ± 5	0.6 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.9 ± 0.1

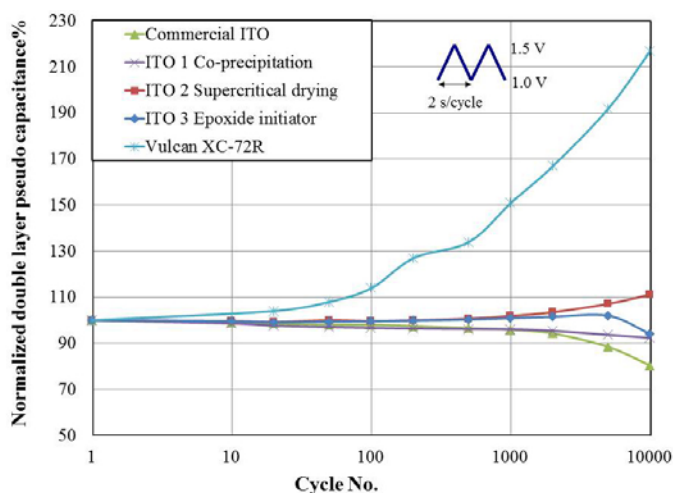


FIGURE 1. Electrochemical stability under start-stop cycling protocol for ITO catalyst supports.

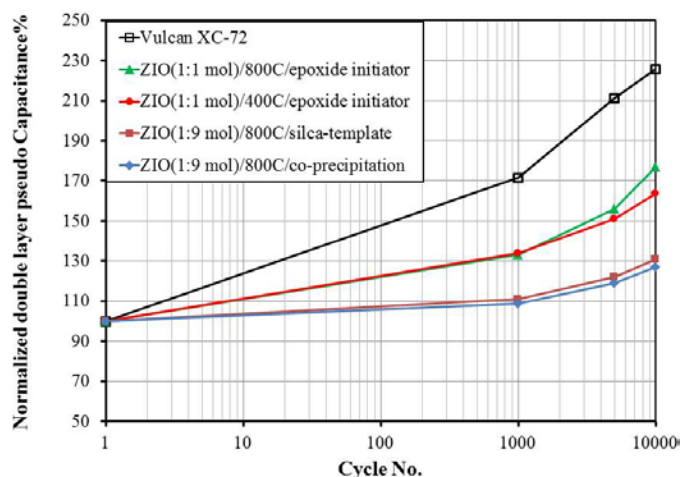


FIGURE 3. Electrochemical stability under start-stop cycling protocol for ZrO_2 - In_2O_3 mixed oxides.

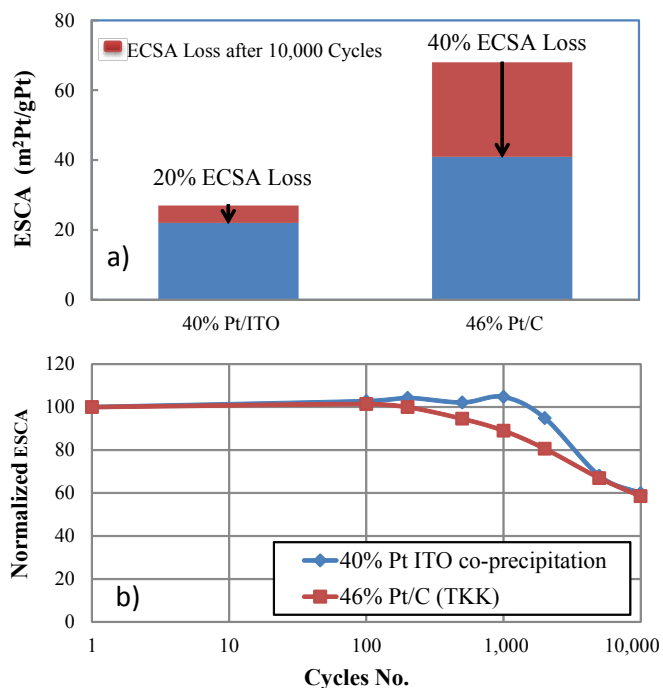


FIGURE 2. Comparison of the electrochemical stability of ITO (co-precipitation) and commercial Pt/C (loss of ECSA) under a) start-stop and b) load cycling protocols.

Cost Model for RuO_2 - TiO_2 : Though the RTO support is more expensive compared with carbon, the total catalyst cost is still dominated by platinum. Material costs of the carbon and non-carbon-based catalysts are compared as shown in Figure 4. 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 . The major advantage of using metal oxide support at the cathode is its excellent resistance

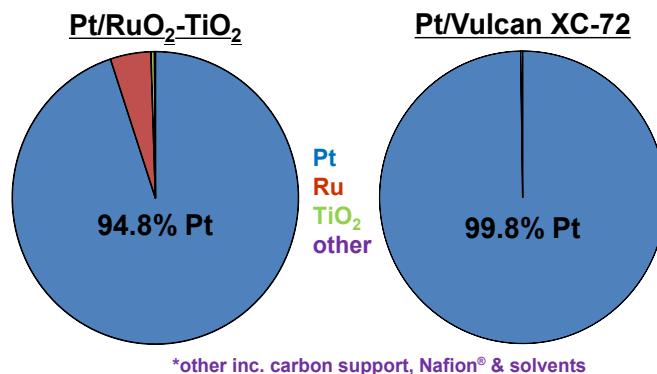


FIGURE 4. Cathode material cost comparison between Pt/non-carbon and Pt/Vulcan XC-72.

TABLE 2. Properties of ZIO Catalyst Supports

Material	BET Surface Area (m^2/g)		Electrical Conductivity (S/cm)	
	Annealed at 400°C	Annealed at 800°C	Annealed at 400°C	Annealed at 800°C
ZIO (1:9 mol)/co-precipitation	37	17	0.07± 0.01	0.09± 0.01
ZIO (1:9 mol)/silica-template	38	18	N/A	N/A
ZIO (1:1 mol)/epoxide initiator	50	7	N/A	N/A

N/A – not available

to degradation under start-stop cycling. This durability needs to be considered while doing the cost analysis. Based on the data obtained for these two cathode materials, Pt/RTO and Pt/Vulcan XC-72 under the start-stop durability cycling test, a “durability factor” was calculated using following equation:

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

Pt/RTO retained 86% of its mass activity while Pt/Vulcan XC-72 retained only 66% of its initial mass activity under start-stop durability cycling. Based on this protocol, Pt/Vulcan XC-72 is only 69% as durable as the Pt/RTO. When this factor is taken into account, and given the fact that the platinum costs dominate overall catalyst cost, there was minimal difference in electrocatalyst costs between Pt/C and Pt/RTO.

CONCLUSIONS AND FUTURE DIRECTIONS

- We have shown that ITO and ZIO had better electrochemical stability than carbon under start-up and shut-down potential cycling protocol.
- After considering the durability advantages of Pt/RTO, the preliminary cost model shows that Pt/RTO is only slightly more expensive than Pt/Vulcan XC-72.

The future directions for the next FY are:

- Optimize the deposition of Pt on non-carbon supports to get higher ESCA and oxygen reduction reaction activities.
- Synthesize high surface area metal oxides by drying of alcogels using supercritical CO₂.
- Evaluate the conductivity and electrochemical stability of hafnium-doped indium oxide.
- Synthesize functionalized mixed metal oxides with proton conductivity.
- Complete the cost model.
- Prepare membrane electrode assemblies with best supports (catalyzed) to deliver to DOE.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Chih-Ping Lo, Guanxiong Wang, Amod Kumar, Vijay Ramani, “TiO₂-RuO₂ electrocatalyst supports exhibit exceptional electrochemical stability” *Applied Catalysis B: Environmental* **140–141** (2013) 133–140.
2. Chih-Ping Lo, and Vijay Ramani, “SiO₂-RuO₂: A Stable Electrocatalyst Support” *ACS Applied Materials and Interfaces*, **4**, (2012) 6109–6116.
3. Guanxiong Wang “Ruthenium Titanium Oxide (RTO) electrocatalyst supports exhibit exceptional start-stop durability” 223rd ECS Meeting, Toronto, Ontario, Canada. May 2013.

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