

# V.D.10 Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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Farmington Hills, MI

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## Technical Targets

This project addresses the following technical targets:

- <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 hrs at 1.2 mV; tested per the GM protocol.
- These targets are taken from Table 3.14.12, Multi-Year Research, Development and Demonstration Plan.

## FY 2012 Accomplishments

- Demonstrated that the synthesized RuO<sub>2</sub>-TiO<sub>2</sub> (TRO) catalyst supports possessed the following properties: a) excellent electrical conductivity (~22 S/cm), b) excellent electrochemical stability, and c) comparable fuel cell performance with Pt/C baseline. Start-stop stability tests for stand alone supports and membrane electrode assemblies (MEAs) were performed by potential cycling of the cell between 1 V to 1.5 V vs. the normal hydrogen electrode (NHE) for 10,000 cycles. Tests performed both at IIT and Nissan Technical Center, North America (NTCNA) and have confirmed support durability.
- Tests at NTCNA have confirmed that using the ruthenium-titanium oxide (RTO) supports synthesized and catalyzed at IIT, the beginning of life performance is exactly equal to end of life performance in an MEA that has been subjected to severe start-stop cycling (1-1.5 V, 10,000 cycles). This is in sharp contrast to baseline Pt/C catalyst that shows significant performance deterioration.
- Indium tin oxide (ITO) aerogels with high surface area (283±2 m<sup>2</sup>/g) have been synthesized using a supercritical drying technique. The annealed ITO possessed higher stability than carbon.
- Functionalized silica aerogel with different levels of sulfonic acid functionalization were synthesized. These materials have demonstrated varying degrees of proton conductivity and thermal stability proportional to the loading of sulfonic acid functional group.

## Fiscal Year (FY) 2012 Objectives

- To develop and optimize innovative non-carbon mixed conducting materials that will serve as corrosion resistant, high surface area supports for anode and cathode electrocatalysts.
- Concomitantly facilitate the lowering of ionomer loading in the electrode (by virtue of surface proton conductivity of the electrocatalyst support), thereby enhancing performance.

## Technical Barriers

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

(A) Durability



## Introduction

While Pt supported on carbon is the most commonly used electrocatalyst for polymer electrolyte fuel cells (PEFCs), the

carbon support has limitations with respect to its durability during excursions to high electrode potentials that arise during startup and shutdown sequences and during fuel starvation. The issue of carbon corrosion is a major technical barrier. Carbon corrosion facilitates the agglomeration of Pt particles and dissolution of Pt from the support, which leads to a loss in the ECSA of the electrode [1]. To address this issue, the development of non-carbon mixed-conducting catalyst support materials is explored. Desirable properties of these alternative materials include (i) high electrical conductivity; (ii) high surface area; and (iii) high electrochemical stability. In addition, it is hypothesized that fuel cell performance can be enhanced by utilizing non-carbon catalyst supports that conduct protons on their surface. The addition of sulfonic acid functionalities on the support surface should permit lowering the ionomer content in the electrode, thereby enhancing gas transport to the catalyst site without compromising on the efficacy of ion transport.

## Approach

To achieve the objectives discussed above, two classes of non-carbon support have been synthesized. The first class of support involves the development of a RuO<sub>2</sub>-TiO<sub>2</sub> structure. TiO<sub>2</sub> was used as core matrix and was further functionalized with a layer of RuO<sub>2</sub> to introduce electronic conductivity. A similar approach was also pursued in parallel, using silica or functionalized silica as the high surface area matrix. The second class of support involved the synthesis of conductive metal oxides by doping. The metal oxide aerogels with high surface area such as ITO, and metal-doped TiO<sub>2</sub> were prepared using the supercritical drying technique. The electrochemical stability of non-carbon support and Pt/non-carbon support were measured under accelerated start-stop and load cycling test protocols and compared with that of commercial XC-72R carbon and baseline Pt/C (TKK TEC10E50E).

## Results

The non-carbon supports and catalysts were prepared using a wet-chemical synthesis procedure. These materials were characterized by X-ray diffraction, transmission electron microscopy, and Brunauer-Emmett-Teller (BET) surface area analysis. Their electrical conductivity and electrochemical properties such as stability, ECSA, electrocatalytic activity, and fuel cell performance were also determined.

The stability of the non-carbon supports and catalysts was evaluated in rotating disk electrode (RDE) and single-cell MEA as a function of cycle number using accelerated start-stop and load cycling durability protocols provided by NTCNA. The start-stop cycling test was conducted by cycling the electrode potential between 1.0 V to 1.5 V vs. NHE (triangular wave form) at a scan rate of 500 mV/s to simulate the startup-shutdown transients in an operating

PEFC. Load cycling was conducted by cycling the electrode potential between 0.6 V to 0.95 V vs. NHE (rectangle wave form) with 3 seconds hold at each potential to simulate full load-no load transients in an automotive drive cycle. The stability of the support was quantified by measuring the change in capacitance (including double layer and pseudo capacitance) calculated at 0.4 V with potential cycling. The stability of the catalyzed support was evaluated by monitoring the change in ECSA, and performance.

## RuO<sub>2</sub>-TiO<sub>2</sub> (TRO)

TRO powders in hydrous (TRO-a) and anhydrous (TRO-h), ITO, and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> were prepared. The electrical conductivity and BET surface area are summarized in Table 1, with Vulcan XC-72 as the baseline. The amorphous ITO with high surface area (283±2 m<sup>2</sup>/g) was successfully prepared with supercritical drying technique. To increase the electrical conductivity, the ITO was further annealed at 820°C.

**TABLE 1.** Properties of Supports

	Vulcan XC-72	TRO-a	TRO-h	ITO	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>
BET (m <sup>2</sup> /g)	207±4	33±4	97±8	41±1 <sup>a</sup>	91±5
Electrical conductivity (S/cm)	31±5	21±5	10±3	1.9±0.1	~10 <sup>-5</sup>

<sup>a</sup>annealed at 820°C

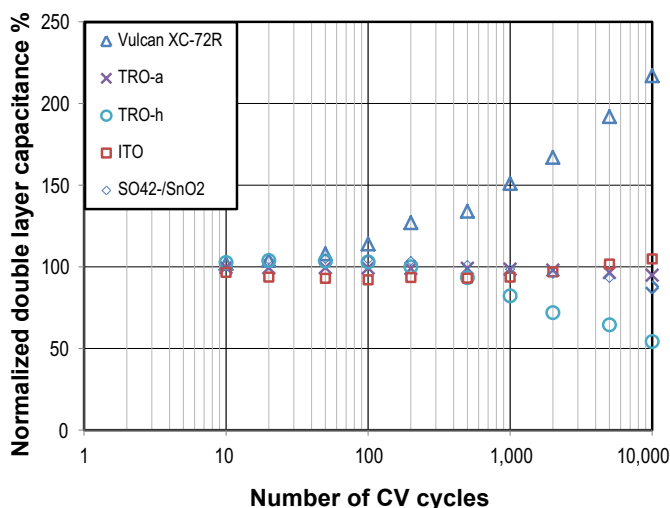
## RDE Characterization

The stability data obtained using the TRO-a, TRO-h, ITO, and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> and XC-72R carbon samples upon performing the start-stop stability protocol in RDE are shown in Figure 1. All non-carbon supports exhibited excellent stability in contrast to carbon. Carbon showed a 220% change in capacitance after 10,000 cycles due to the hydroquinone–quinone (HQ–Q) redox couple of carbon. TRO-h showed less stability, where Ru is mixed III/IV valent and therefore Ru<sup>III</sup> can be further oxidized to Ru<sup>IV</sup> during the potential cycling.

The various TRO powders were then catalyzed by depositing platinum nanoparticles by an impregnation-reduction method to yield Pt/TRO electrocatalysts. The Pt/TRO-a electrocatalysts possessed a mass activity of 220 mA/mg<sub>Pt</sub> and a specific activity of 580 μA/cm<sub>Pt</sub><sup>2</sup> for the oxygen reduction reaction.

## MEA Characterization of Pt/TRO-a

In situ durability of TRO-a MEAs was evaluated using NTCNA's accelerated start-stop and load cycling test protocols. Change in ECA and cell potential at 1 A/cm<sup>2</sup> were employed as parameters to study the effect of the durability tests on TRO-a MEAs.

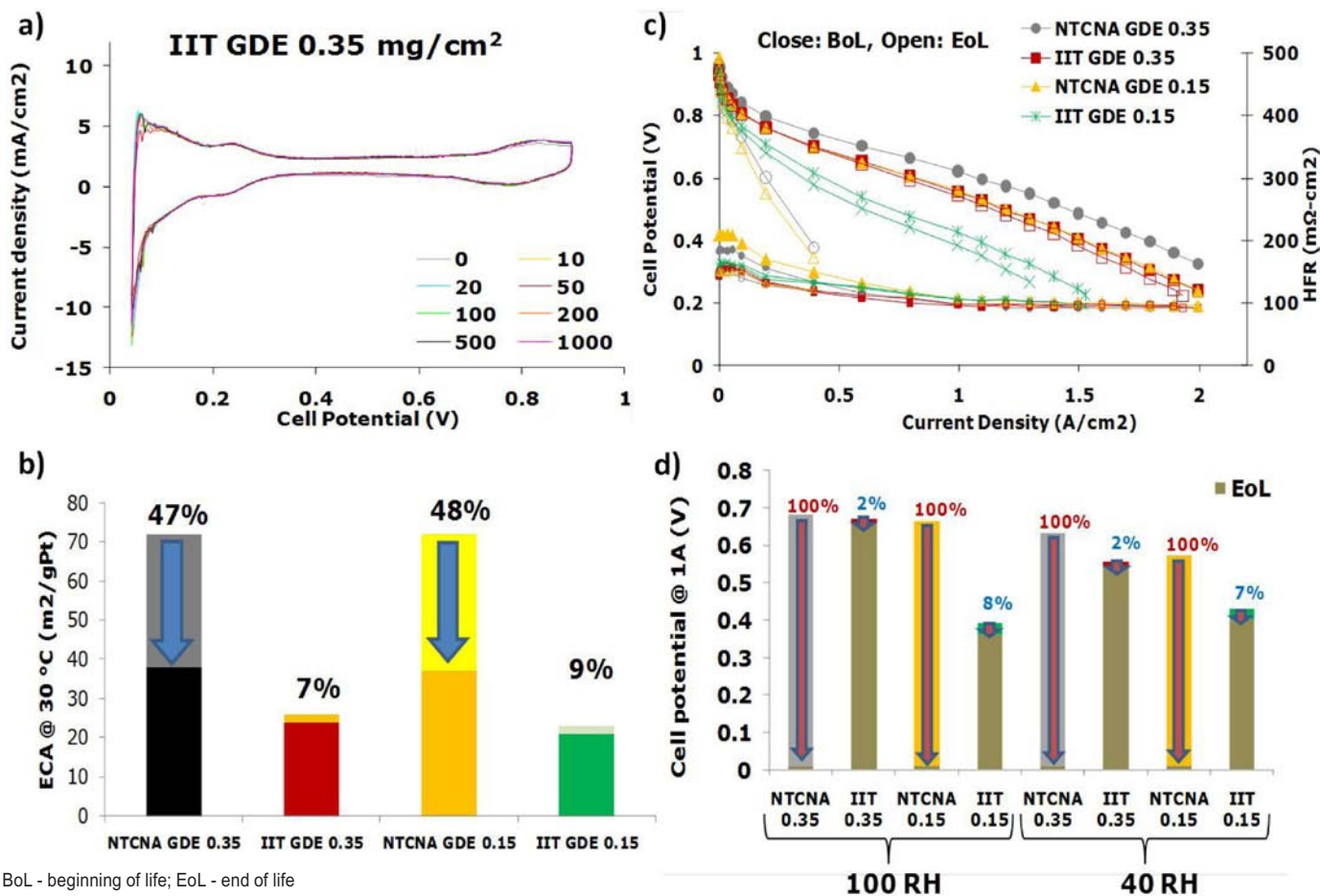


**FIGURE 1.** Change of double layer capacitance of catalyst supports as a function of cycling numbers. The cycling experiments were conducted in a  $N_2$  saturated 0.1M  $HClO_4$  solution at room temperature.

### Effect of Start-Stop Cycling

The  $RuO_2$ - $TiO_2$  support showed excellent support durability compared to high surface area carbon (HSAC). Minimal change in cyclic voltammetry (CV) pattern for  $0.35\text{ mg}_{Pt}/\text{cm}^2$  TRO-a MEA (IIT MEA) was observed after 1,000 cycles as shown in Figure 2(a). Similar results were also observed for  $0.15\text{ mg}_{Pt}/\text{cm}^2$  loaded MEA. Change in ECSA due to start-stop cycling at the beginning and at the end is shown in Figure 2(b). This study proves the excellent stability of  $RuO_2$ - $TiO_2$  support ( $\sim 7\sim 9\%$  ECSA change) over conventional carbon support ( $\sim 47\sim 48\%$  ECSA change) under this accelerated stress test.

Effect of this stability test on current-voltage (iV) performance is shown in Figure 2(c) under 40% relative humidity (RH) condition. Similar measurements were also performed under 100% RH condition. As shown, minimal loss in performance was observed for the Pt/TRO support (IIT MEA) compared to Pt/carbon support (NTCNA gas diffusion electrode) that showed substantial loss in performance due to support loss, loss in electronic conductivity and flooding. Similar behavior is also evident



BoL - beginning of life; EoL - end of life

**FIGURE 2.** In situ durability of TRO-a MEAs was evaluated using NTCNA accelerated start-stop cycling protocol. Change in a) CV b) ECSA as a function of cycle number c) iV performance under  $H_2$ /Air,  $80^\circ C$ , 40% RH and d) loss in cell potential at  $1\text{ A}/\text{cm}^2$  under both 100 and 40% RH.

in the results of cell potential loss at 1 A/cm<sup>2</sup> as shown in Figure 2 (d). Under both RH conditions, the carbon supported catalyst demonstrated significant loss in activity, while the TRO supported catalyst showed minimal loss in performance, exhibiting its superior stability.

### Effect of Load Cycling

Catalyst stability under load cycling was tested using Nissan’s accelerated protocol test. Less ECSA loss than Pt/HSAC catalyst was observed for TRO catalyst as an effect of this durability test as shown in Figure 3(a) for 0.35 mg<sub>Pt</sub>/cm<sup>2</sup> loading. Similar loss in iV performance was

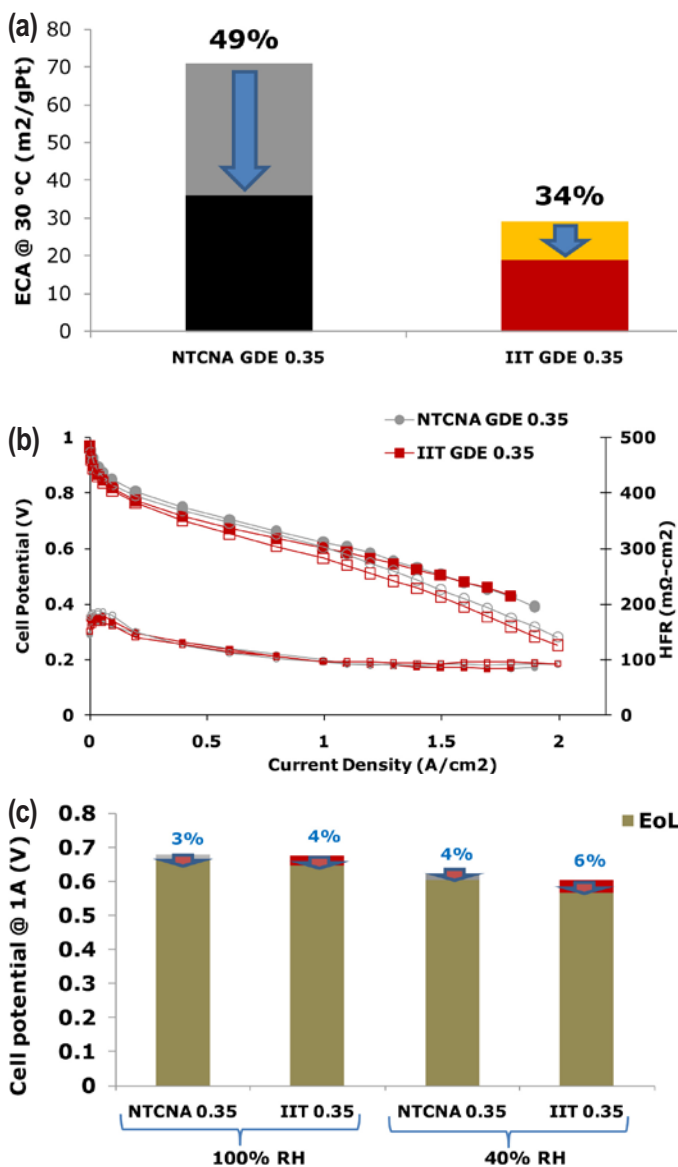
observed for both the catalyst as shown in Figure 3(b). Cell potential at 1 A/cm<sup>2</sup> is compared in Figure 3(c) shows similar loss for both the carbon and non-carbon supported catalyst under this durability test. This was consistent with expectation as the load cycling protocol tests electrocatalyst durability and not support durability.

### Sulfonic Acid Functionalized Silica Aerogel

In FY 2011, sulfonic acid functionalized silica with high proton conductivity was prepared. However, it was not thermally stable and decomposed around 100°C. In FY 2012, a different synthesis procedure for preparing functionalized silica was employed to improve stability and proton conductivity. The properties of the functionalized silica aerogels are summarized in Table 2. Even though the ion exchange capacity (IEC) of the functionalized silica aerogels increased from 1.4 to 2.1 mmol/g, very small change was observed in the ionic conductivities of the silica with extent of functionalization (33, 50 and 67 mol%). This was because that the increase of IEC and carrier groups was offset by the concomitant decrease of internal surface, leading to a constant value for ionic conductivity. The conductivity at each extent of sulfonation was measured three times at four temperatures (60, 80, 100 and 120°C) and four RHs (25, 50, 75 and 100%). The conductivity variations between the samples with different extents of functionalization were within the measured experimental error at all conditions; the values obtained are shown in Figure 4.

### Conclusions and Future Directions

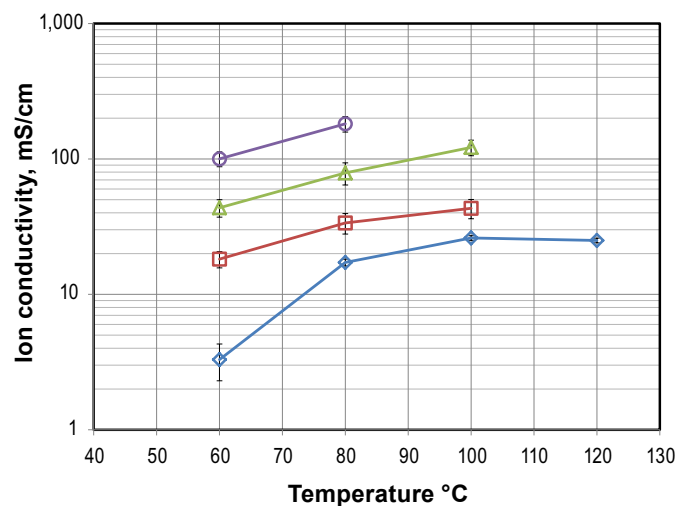
- Non-carbon supports including RuO<sub>2</sub>-TiO<sub>2</sub> (hydrous and anhydrous), ITO, and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> were synthesized and had higher stability over baseline Vulcan carbon.
- The performance of MEA with Pt/RTO-a was comparable with a commercial Pt/C MEA.
- The MEA with Pt/RTO-a demonstrated superior stability in comparison to carbon catalyst supports under start-stop cycling test.
- The MEA with Pt/RTO-a showed similar Pt dissolution stability to that with Pt on HSAC under load cycling test.



**FIGURE 3.** In situ durability of TRO-a MEAs was evaluated using NTCNA accelerated load cycling protocol. Change in a) ECSA as a function of cycle number c) iV performance under H<sub>2</sub>/Air, 80°C, 40% RH and d) loss in cell potential at 1 A/cm<sup>2</sup> under both 100 and 40% RH.

**TABLE 2.** Properties of the Functionalized Silica Aerogels

Functionalization degree, %	Ion exchange capacity, mmol/g	BET surface area, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Average pore diameter, nm
0	0	944±63	2.4	10.1
33	1.4	499±8	1.0	8.4
50	1.7	233±2	0.6	9.6
67	2.1	116±3	0.2	8.3



**FIGURE 4.** Proton conductivity of sulfonic acid functionalized silica aerogel at various temperatures at (●) 25% RH, (○) 50% RH, (▼) 75% RH and (△) 100% RH.

- Several samples of sulfonic acid functionalized silica aerogel with high thermal stability have been prepared and demonstrate excellent proton conductivity.
- In phase two, the initial focus will be on enhancing mass activity of the catalysts prepared with RTO supports as well as to incorporate proton conducting functionalities onto the support. Studies on ITO and sulfonated tin oxide supports will continue.

## References

1. Landsman, D.A., Luczak, F.J., In Handbook of Fuel Cells Fundamentals, Technology, and Applications; Vielstich, W., Gasteiger, H.A., Lamm, A., Eds.; John Wiley and Sons Ltd.: West Sussex, England, 2003; Vol. 4.