Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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Project ID # FC085

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
- Project start date: Sept. 1st 2010*
- Project end date: Jan. 31st 2015
- Percent complete: ~ 85%

Barriers
- Barriers addressed:
  - Fuel cell component durability to be improved
- Targets addressed
  - < 40% ECA Loss tested per GM protocol
  - < 30mV electrocatalyst support loss after 400 hrs at 1.2 mV; tested per GM protocol
  - Targets taken from Table 3.14.12, Multi-Year RDD plan

Partners
- Nissan North America Inc.
- Project lead: Illinois Institute of Technology

Budget
- Total funding assigned/spent to date: $ 1,317,900**
- Total project funding
  - DOE share: $ 1,476,230
  - Cost share: $ 415,775
  - Cost share percentage: 20%

*Official Start date per DOE. Actual start date Dec. 2010. Subcontact with Nissan North America Inc. in place effective February 2011. ** Pending NTCNA invoices to be paid for costs incurred
Relevance: Impact of Carbon Corrosion on PEFCs

• Carbon is mainly used as an electrocatalyst support due to its:
  – High electrical conductivity
  – High BET surface area: 200 - 300 m²/g
  – Low cost

• Electrochemical oxidation of carbon occurs during fuel cell operation

\[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-; \quad U^0 = 0.207 \text{ v vs. SHE} \]

• Carbon corrosion is accelerated:
  – During start/stop operation (cathode carbon corrosion)
  – Under fuel starvation conditions (anode carbon corrosion)
  – At high temperature and low humidity

• Kinetic and ohmic losses result due to:
  – Pt sintering
  – Loss of contact between Pt and C

• Mass transport losses occur due to
  – Formation of hydrophilic groups=> flooding

• To avoid corrosion issues, need a new, non-carbon support material
  – Primary focus of this project

* N. Takeuchi; T.F. Fuller, J. Electrochemical Society, 155 (7) B770-B775 (2008)
• **Research Objectives:**
  – 1) Develop and optimize non-carbon mixed conducting materials with:
    – High corrosion resistance
    – High surface area (> 200 m²/g)  **Focus of Project Phase 1**
    – High proton (≥ 100 mS/cm) and electron (> 5 S/cm) conductivity
  – 2) Concomitantly facilitate the lowering of ionomer loading in the electrode
    – Enhanced performance and durability  **Main Focus of Project Phase 2**
    – By virtue of surface proton conductivity of the electrocatalyst support
    – Reduce Ruthenium content in support
    – Cost model

• **Relevance to DOE Targets:**
  – Addresses the issue of electrocatalyst and support stability, both of which are important in the context of fuel cell durability
  – The development of stable, non-carbon supports will help address technical targets for:
    – Operational lifetime (5000 hrs under cyclic operation),
    – ECA loss (< 40% per GM protocol) and
    – Electrocatalyst support loss (< 30 mV after 400 hrs at 1.2 V, per GM protocol).
We are investigating mixed metal oxides functionalized with proton conducting groups that meet the following broad requirements:

- **Surface area**
  - $> 100-300 \text{ m}^2/\text{g}$
  - Preferably higher, $\sim 400-800 \text{ m}^2/\text{g}$
- **Porosity**
  - Minimal micro-porosity
  - Meso and macro porosity preferred, 10-100 nm pore size
- **Stable in acidic media**
  - Low solubility at pH 1
- **Corrosion resistant**
  - Upon standard test protocols provided by NTCNA, described later.
- **High Electronic conductivity**
  - $> 5-10 \text{ S/cm}$
- **High Proton conductivity**
  - $> 100 \text{ mS/cm}$
• Start with a high surface area metal oxide support
  – Functionalities can be added subsequently
  – Silica and Titania are model metal oxides used; \( \text{SnO}_2 \) and ITO are also explored

• Functionalize sequentially to introduce proton/electron conductivity
  – Ruthenium oxide used as model electron conducting functionality (Pt can also be used)
  – Sulfonic acid groups introduced to provide proton conductivity (\( \text{SO}_4^{2-} \) can also be used)
  – Platinum will be deposited on durable supports that meet milestones [next slide]
  – Materials will be benchmarked against state-of-the-art carbon and Pt/C catalysts

• Project sub-divided into 5 Tasks (T1-5)
  – IIT: materials synthesis and characterization + ionomer reduction studies (T 1 , 3 and 5)
    • Synthesis and characterization of MMO supports (catalyzed and uncatalyzed)
    • Preliminary durability testing and catalytic activity measurements
    • Ionomer reduction studies in sub-scale MEAs
    • Provide materials and optimal electrode formulations to Nissan North America Inc.
  – Nissan North America Inc.: durability/performance testing + cost model (T 2, 4 and 5)
    • Accelerated test protocols on materials provided by IIT (Start-Stop + Load Cycling)
    • Fabrication / testing of sub-scale and 50 cm\(^2\) MEAs
    • Development of cost model.
Approach: Systems Studied and Rationale

Five catalyst-support systems have been investigated:

- **RuO$_2$-SiO$_2$**: RuO$_2$ deposited on high surface area SiO$_2$.
- **RuO$_2$-SO$_3$H-SiO$_2$**: RuO$_2$ deposited on sulfonic acid functionalized SiO$_2$, conducts electrons and protons.
- **RuO$_2$-TiO$_2$**: Hydrous or anhydrous RuO$_2$ deposited on commercial TiO$_2$ (P25).
- **SO$_4^{2-}$/SnO$_2$**: Sulfated tin oxide nanoparticles (preliminary; lower cost).
- **ITO**: Indium tin oxide nanoparticles (preliminary; lower cost).

**High stability** –
- Ru$_x$Ti$_{1-x}$O$_2$ has been shown to have high stability in our previous work.
- SiO$_2$ and SnO$_2$ are known to be chemically inert in acidic media.

**High surface area** –
- High surface area of SiO$_2$ can be prepared with surfactant method or supercritical drying technique.

**High conductivity** –
- Pure RuO$_2$ and ITO film have high electrical conductivity around 400 and 1000 S/cm, respectively.
- Hydrous RuO$_2$ is a mixed conducting material.
- SO$_4^{2-}$/SnO$_2$ is a proton conducting material.

Approach: Milestones and GNG Criterion; Current Status

• Milestone 1 (End of Phase 1; Q1; 2012 [calendar year])
  – Synthesize a support that demonstrates at least:
    • 70 mS/cm proton conductivity [Current status ~ >120 mS/cm; stand-alone]
    • 2 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    • 50 m²/g BET surface area [Current status > 250 m²/g]
    • Durability* in acidic electrolyte [C-S: durable]

• Milestone 2 (End of Phase 2; Q3; 2013)
  – Synthesize a support that demonstrates at least:
    • 100 mS/cm proton conductivity [Current status > 120 mS/cm; stand-alone]
    • 5 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    • 50 m²/g BET surface area [Current status > 250 m²/g]
    • Durability* in acidic electrolyte [Current status – durable, in RDE and MEA]
  – Prepare and evaluate high-performance Pt-catalyzed supports [C-S: demonstrated with RTO]
  – Identify optimal ionomer loading in electrode [Current Status: done for RTO]
  – Prepare 6 100 cm² MEAs w/ optimal support formulation [Under negotiation]

• GNG criterion (applied at end of Q1; 2012) – PASSED in June 2012

* < 10% mass loss on cycling between:
  - 1V and 1.5V at 0.5 V/s
  - -0.95 V and 0.6 V under load
  - 1000 cycles
**GNG Criterion Statement:** “At the end of Phase I, IIT and Nissan North America Inc. will have prepared or showed significant progress towards preparing a support material with a surface area of 50 m²/g; an electron conductivity of 2 S/cm, a proton conductivity of 0.07S/cm and durability in acidic electrolyte of 1000 cycles per the defined accelerated test protocols*”

<table>
<thead>
<tr>
<th>Milestone 1</th>
<th>RTO</th>
<th>RSO</th>
<th>RSO-sulfonated</th>
<th>Sulfated SnO₂</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 mS/cm proton conductivity</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>2 S/cm electron conductivity</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>50 m²/g BET surface area</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Durability in acidic electrolyte</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>N/A</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Milestone 2</th>
<th>RTO</th>
<th>RSO</th>
<th>RSO-sulfonated</th>
<th>Sulfated SnO₂</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mS/cm proton conductivity</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>5 S/cm electron conductivity</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>50 m²/g BET surface area</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Durability in acidic electrolyte</td>
<td>Yes</td>
<td>Yes</td>
<td>N/A</td>
<td>N/A</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Approach: Potential Cycling to Estimate Support and Electrocatalyst Durability

Electrolyte: 0.1 M HClO₄

Cycling rate – see Figure. Cycling Temperature: 60°C at NTCNA, RT at IIT

CV sweep rate of 20 mV/S; Room Temperature CV
Technical Accomplishments: Electrochemical Stability of ITO (Support Corrosion Protocol)

Electrolyte: 0.1 M HClO₄ under N₂ atmosphere; CV sweep rate of 20 mV/S; Room temperature cycling

Normalized double layer pseudo capacitance

- Commercial ITO
- ITO 1 co-precipitation
- ITO 2 Supercritical drying
- ITO 4 Epoxide-in
- Vulcan XC-72R

Cyclic voltammograms of commercial ITO sample before, during, and after 10,000 cycles in 0.1 M HClO₄ under the start-stop cycling test.
Technical Accomplishments: XRD and TEM of 40% Pt/ITO

Technical Accomplishments: XRD and TEM of 40% Pt/ITO

- 40% Pt/ITO [ITO 4, protocol a)]
- 40% Pt/ITO [ITO 2, protocol a)]
- 40% Pt/ITO [ITO 1, protocol a)]
- 23% Pt/ITO [ITO 1, protocol a)]
Technical Accomplishments: ORR Activity for 40% Pt/ITO
[Platinum Nanoparticles Synthesized by Chemical Reduction of Chloroplatinic Acid with Formaldehyde]

![Graph showing ORR activity for different samples.](attachment:graph.png)
Technical Accomplishments: ECSA, Mass Activity and Area-specific Activity for Pt/ITO

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>40% Pt/ITO (ITO 1 co-precipitation)</th>
<th>23%Pt/ITO (ITO 1 co-precipitation)</th>
<th>40% Pt/ITO (ITO 4 epoxide initiator)</th>
<th>40% Pt/ITO (ITO 2 supercritical drying)</th>
<th>46%Pt/C (baseline)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_L$, (mA/cm$^2$)</td>
<td>5.7 ± 0.1</td>
<td>5.3 ± 0.2</td>
<td>5.6 ± 0.1</td>
<td>5.3 ± 0.2</td>
<td>5.6 ± 0.1</td>
</tr>
<tr>
<td>Pt loading (µg/cm$^2$)</td>
<td>44.6 ± 2</td>
<td>44.6 ± 2</td>
<td>44.6 ± 2</td>
<td>44.6 ± 2</td>
<td>17.3 ± 1</td>
</tr>
<tr>
<td>$i_m$ (mA/mg Pt)</td>
<td>56 ± 4</td>
<td>27 ± 3</td>
<td>65 ± 3</td>
<td>20 ± 2</td>
<td>190 ± 5</td>
</tr>
<tr>
<td>ECSA (m$^2$ Pt/g Pt)</td>
<td>22 ± 2</td>
<td>26 ± 1</td>
<td>24 ± 1</td>
<td>24 ± 2</td>
<td>81 ± 4</td>
</tr>
<tr>
<td>$i_s$ (µA/cm$^2$ Pt)</td>
<td>257 ± 3</td>
<td>98 ± 4</td>
<td>270 ± 2</td>
<td>83 ± 4</td>
<td>224 ± 10</td>
</tr>
</tbody>
</table>

- The 40%Pt/ITO sample obtained by epoxide-initiated method showed the highest ECSA value among all 40%Pt/ITO. However, in general, ECA was low. Pt Agglomeration.
- Mass activity was in general, low, but varied with extent of agglomeration in sample.
- Pointed to need for new Pt deposition method.
The Pt/ITO stability was evaluated from the change in ECSA. 0.1 M HClO₄ under N₂ atmosphere; room temperature
Start/Stop and Load Cycling Protocols

The ECSA of 40% Pt/ITO decreased by 40% after 10,000 cycles.

Catalyst Durability—Pt Dissolution
The ECSA of 40% Pt/ITO decreased by 40% after 10,000 cycles.
MEA: Effect on iV performance
Start/stop cycling

H₂/Air, 4/8 NLPM, 1 bar, 80 °C,
Closed symbol: BoL
Open symbol: EoL

100% RH

40% RH

Mineral loss of performance BoL/EoL Start-stop cycling for Pt/non-carbon

MEA Spec:
25 cm², NRE211
Anode: 0.4 mgPt/cm² Pt/C
Cathode: 0.35 mgPt/cm²

Under both 100% and 40% RH conditions, significant effect of start-stop cycling observed for Pt/HSAC
- Due to carbon corrosion (loss of support), Change in hydrophobicity etc.

This Pt/non-carbon (40% Pt/TiO₂-RuO₂) showed minimal loss in performance under start-stop cycling → Very stable support

Previous Results (from 2013 AMR presentation demonstrating excellent performance and corrosion resistance of Pt/RTO catalysts
Technical Accomplishments: Fuel Cell Performance at 80°C for an MEA with 40%Pt/ITO Catalyst[ITO 1, protocol a) at Cathode and 46%Pt/C(Tanaka) at Anode. Atmospheric Pressure. 75%RH

- The electrodes were prepared with 0.4 mg Pt/cm² and 30wt% Nafion® binder.
- Much lower performance than observed with Pt/RTO – also seen at NTCNA
Technical Accomplishments: XRD of 40%Pt/ITO
[Platinum Nanoparticles Synthesis by Chemical Reduction of tetraammineplatinum(II) Chloride Hydrate as Precusor]

Intensity (a.u.)

2 Theta (Degree)

ITO Peak PtIn₂/Pt₂In₃

40%Pt/ITO (ITO2 protocol g)

40%Pt/ITO (ITO1 protocol e)

40%Pt/ITO (ITO2 protocol f)

PtSn
Technical Accomplishments: ORR Activity for 40% Pt/ITO
[Platinum Nanoparticles Synthesis by Chemical Reduction of Tetraammineplatinum(II) Chloride Hydrate as Precusor]

![Graph showing ORR Activity for 40% Pt/ITO](image-url)
### Technical Accomplishments: ECSA, Mass Activity and Area-specific Activity for 40% Pt/ITO

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>40%Pt/ITO [ITO1, protocol c)]</th>
<th>40%Pt/ITO [ITO1, protocol d)]</th>
<th>40%Pt/ITO [ITO1, protocol e)]</th>
<th>40%Pt/ITO [ITO1, protocol f)]</th>
<th>40%Pt/ITO [ITO2, protocol g)]</th>
<th>46%Pt/C (baseline)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_L$ (mA/cm²)</td>
<td>5.8 ± 0.1</td>
<td>5.8 ± 0.2</td>
<td>5.5 ± 0.1</td>
<td>3.6 ± 0.5</td>
<td>5.3 ± 0.2</td>
<td>5.6 ± 0.1</td>
</tr>
<tr>
<td>Pt loading (µg/cm²)</td>
<td>44.6±2</td>
<td>44.6±2</td>
<td>44.6±2</td>
<td>44.6±2</td>
<td>44.6±2</td>
<td>17.3±1</td>
</tr>
<tr>
<td>$i_m$ (mA/mg Pt)</td>
<td>18±4</td>
<td>62±2</td>
<td>98±5</td>
<td>21±3</td>
<td>67±5</td>
<td>190±5</td>
</tr>
<tr>
<td>ECSA (m²/gPt)</td>
<td>19±1</td>
<td>24±2</td>
<td>21±2</td>
<td>-----</td>
<td>24±2</td>
<td>81±4</td>
</tr>
<tr>
<td>$i_s$ (µA/cm² Pt)</td>
<td>93±2</td>
<td>236±10</td>
<td>445.5±12</td>
<td>-----</td>
<td>279±10</td>
<td>224±10</td>
</tr>
</tbody>
</table>

- The 40%Pt/ITO sample obtained by protocol e (cationic precursor, reduced in hydrogen) had the highest mass and specific activities.
- Possibly due to more uniform reduction of precursor.
- However, mass activity value was still only about 50% of that of the Pt/C benchmark.
Technical Accomplishments: Support Corrosion Test for 40% Pt/ITO
[ITO 2, protocol g)] [Pt was reduced from Pt(NH$_3$)$_2$Cl$_2$ using NaBH$_4$]

The Pt/ITO stability was evaluated from the change in ECSA. Scan rate of 500 mV/s with cycles up to 10,000 in a nitrogen purged 0.1 M HClO$_4$ electrolyte at room temperature. Support durability test criteria was used.

The ECSA decreased by less than 2% and the double layer pseudo capacitance decreased by 26% after 10,000 cycles.
Technical Accomplishments: Platinum Dissolution Test for 40% Pt/ITO
[ITO 2, protocol g)]Pt was reduced from Pt(NH$_3$)$_2$Cl$_2$ using NaBH$_4$]

The Pt/ITO stability was evaluated from the change in ECSA. 0.1 M HClO$_4$ under N$_2$ atmosphere; sweep rate of 20 mV/S; room temperature. Catalyst durability test criteria was used.

The ECSA of 40% Pt/ITO decreased by 34% after 10,000 cycles.

Catalyst Durability—Pt Dissolution
The ECA increased when the Pt loading was decreased from 40% to 20%, but the mass activity ($i_m$) remained within 150-160 mA/mg$_{Pt}$.

This value is comparable to the mass activity of a commercial sample, TEC10E50E-HT, (TKK Pt/Ketjen Black, heat-treated) at ~150 mA/mg$_{Pt}$.

In RDE, both 40% and 20% Pt/RTO have comparable mass activities: **Potential to reduce cost by Pt reduction**
Both milligram scale and gram scale synthesis of Pt/ITO at Nissan produced catalysts with good Pt dispersion; comparable Pt particle sizes of ~ 3 - 4 nm.
Nearly overlapping CV and ORR LSV profiles for mg and gram scale syntheses.

The mass activity obtained in RDE is consistently around 150 mA/mgPt.
The mass activity obtained for both 50% and 20% Pt/ITO is 140-150 mA/mg_{Pt}, comparable to Pt/RTO (in RDE).

This value is comparable to the mass activity of a commercial sample, TEC10E50E-HT, (TKK Pt/Ketjen Black, heat-treated) at ~150 mA/mg_{Pt}).
- Pt/ITO showed poor MEA performance even at a Pt loading of 0.35 mg/cm².
- The high frequency resistance (HFR) was very high (220 mΩ-cm²).
- The start-stop cycling durability of the ITO support may be satisfactory, as shown by the small change in the iV curve after 1000 potential cycles from 1.0 to 1.5V.

Good RDE results seen for Pt/ITO could not be observed in MEA.
Pt/ITO showed poor performance in MEA testing

- Pt/ITO showed poor MEA performance even at a Pt loading of 0.35 mg/cm².
  - The high frequency resistance (HFR) was very high (220 mΩ-cm²).
  - Drastic changes in the CV profile (loss of $H_{upd}$ features and resistive behavior) is observed, suggesting some changes in the chemical properties of the ITO support.

$$\begin{align*}
\text{H}_2/\text{O}_2 & \quad 80^\circ \text{C} \quad 100\% \text{ RH} \quad 1 \text{ bar}_g \\
\end{align*}$$
Hydroxylated species form on the ITO surface at fuel cell operating conditions

- Hydroxide and oxy-hydroxide species form on the surface of ITO due to (1) hydrolysis and (2) incomplete hydrolysis reactions.

- XPS\textsuperscript{[1]} and electrochemical studies\textsuperscript{[2]} suggest preferential hydrolysis of surface ITO.

- Degradation and structural deformation of ITO in fuel cell relevant potentials\textsuperscript{[3]}

The solubility of these \( \text{In(OH)}_3 \) and the other hydroxylated species is quite low\(^4\), hence they remain adsorbed on the ITO surface and forms a passivating layer. This explains the increase in ohmic resistance during operation in RDE and MEA.

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Material costs for production of Pt/RuO$_2$-TiO$_2$ and Pt/ITO electrodes as compared to Pt/Vulcan® XC-72

Assumptions:
- With the exception of the Cathode, the rest of the MEA is identical (Anode, membrane, GDL, etc.)
- Rated Power is at 80°C 100%RH to make use of performance data from Nissan testing
- All cells in the stack are operating identically
- Processing costs (cathode ink manufacturing, catalyst application) are equal
- Pt/ITO performance and durability can be improved to match Pt/RuO$_2$-TiO$_2$

The only differences in these systems comes down to material cost of the Cathode (Pt/RuO$_2$-TiO$_2$ vs. Pt ITO vs. Pt/Vulcan XC-72)

The RuO$_2$-TiO$_2$ and ITO supports are more expensive than the carbon support, but the total material cost is still dominated by the Platinum
- Pt still accounts for ~95% and ~98% of the cathode material cost in Pt/RuO$_2$-TiO$_2$ and Pt/ITO cathodes respectively

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*Cother inc. carbon support, Nafion® & solvents

†James, B.D.; Mass Production Cost Estimation for Direct H$^2$ PEM Fuel Cell Systems for Automotive Applications: 2008 Update
Preliminary Cost Model

**Durability Considerations for Cost - Pt/non-carbon**

The major advantage to using a non-carbon cathode support is its resistance to degradation during Start-Stop cycling.

- **With durability considered, how do the two catalysts compare?**

**A Durability Factor can be calculated for each catalyst**

- **Durability Factor**
  \[ \text{Durability Factor} \ = \ \frac{\text{Mass Activity retention of Catalyst}}{\text{Mass Activity retention of Pt/non-Carbon}} \]

- **Nissan’s ex-situ Start/Stop Cycling protocol is used**

<table>
<thead>
<tr>
<th>Protocol</th>
<th>1s</th>
<th>1s</th>
<th>1.5 V</th>
<th>60°C</th>
<th>5,000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 s</td>
<td>2 s/cycle</td>
<td>1.0 V</td>
<td></td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt/RuO$_2$-TiO$_2$</th>
<th>Pt/ITO</th>
<th>Pt/Vulcan XC-72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Activity retention (loss)</td>
<td>86%</td>
<td>86*</td>
<td>59%</td>
</tr>
<tr>
<td>Durability Factor</td>
<td>1</td>
<td>1*</td>
<td>0.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pt/RuO$_2$-TiO$_2$</th>
<th>Pt/ITO</th>
<th>Pt/Vulcan XC-72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode Pt loading (mgPt/cm$^2$)</td>
<td>0.35</td>
<td>0.35</td>
<td>0.18</td>
</tr>
<tr>
<td>Rated Power (mW/cm$^2$)</td>
<td>650</td>
<td>650*</td>
<td>715</td>
</tr>
<tr>
<td>Pt (i.e. total Pt in electrode)</td>
<td>$1,718.45</td>
<td>$1,718.45</td>
<td>$1,203.42</td>
</tr>
<tr>
<td>Metal 1</td>
<td>$90.31 (Ru=$83.02)</td>
<td>$34.68 (In=$34.61)</td>
<td>$ -</td>
</tr>
<tr>
<td>Total Material Cost ($)</td>
<td>$1,811.76</td>
<td>$1,756.14</td>
<td>$1,206.06</td>
</tr>
<tr>
<td>Total Material Cost ($/kW$_{net}$)</td>
<td>$22.65</td>
<td>$21.95</td>
<td>$15.08</td>
</tr>
</tbody>
</table>

- In FC Systems with equal lifetimes, one utilizing Pt/RuO$_2$-TiO$_2$ or Pt/ITO costs only 4% more or 0.5% than one with Pt/Vulcan XC-72, respectively.
- This is with almost double the Pt loading. Significant potential to reduce cost with reduced Pt loading.

*Pt/ITO performance and durability assumed to match Pt/RuO$_2$-TiO$_2$*
Summary of Technical Accomplishments

• Proton and electron conducting metal oxides (SRO; RTO; ITO) have been synthesized in support of project objectives with
  - Stand-alone proton conductivities > 100 mS/cm
    (100 mS/cm overall target)
  - Stand-alone electron conductivities of > 10 S/cm
    (5 S/cm overall target)
  - BET surface areas of > 250 m²/g
    (50 m²/g overall target)
  - High durability upon aggressive potential cycling (including in MEAs)
    (NTCNA protocol, performed at IIT and at NTCNA)
  - Moderate to high performance – efforts ongoing to reduce Pt particle size

• A number of non-RuO₂ supports have been evaluated and found to be stable

• New stable class of non-carbon supports (ITO – lowering / eliminating Ru)
  still under study. Great RDE results but not translated to MEA yet.

• In collaboration with Nissan North America Inc., extensive benchmarking of
  state-of-the-art electrocatalysts and electrocatalyst supports has been
  performed.

• Initial cost model suggests no significant cost disadvantages
Summary of Collaboration with NTCNA

- Nissan North America Inc. is a key project partner from industry
  - Dr. Kev Adjemian / Dr. Nilesh Dale are PIs from Nissan North America Inc.
  - Focus on providing an industry perspective performing benchmarking, durability testing, and large scale MEA fabrication and testing
  - Regular visits between the 2 teams (3-4 per year)
  - Opportunities for IIT students to visit NTCNA.
  - NTCNA has housed an IIT researcher (student) at Nissan North America Inc. for 1-2 weeks; with a reciprocal visit to IIT planned.
  - Nissan North America Inc. has provided outstanding support on:
    - Benchmarking of baseline materials
    - Characterization and testing of catalyst supports + reduction of Pt particle size + MEA testing including durability testing under stringent protocols
    - Prioritizing the types of tests that have most relevance
    - Manufacture and testing of MEAs
    - Providing industry perspective.
  - Slides within presentation and under supplementary slides discuss in detail Nissan North America Inc.’s outstanding contributions to this project.
Proposed Future Work

Future directions in FY 14:

- Complete work on ITO supports *(Task 1 and 2)*
- Specifically: Work to understand disparity between RDE and MEA results while using ITO – we have suggested possible reasons in this presentation and will work to examine these hypotheses.
- XPS studies are already underway.

- Finish cost model; commence large scale MEA fabrication *(Task 3, 5)*
- Complete work leading to ionomer reduction in the electrode through sub-scale MEA studies for ITO-based MEAs - this would also serve to improve ITO MEA performance *(Task 3)*
- Begin large scale MEA fabrication and testing and complete cost analysis on downselected supports *(Task 4, 5)* *(As of now, this support will be RTO).*
Summary

Relevance: Proposed work will lead to non-carbon supports with high durability and will address support loss/ECA targets
- < 40% ECA Loss tested per NTCNA protocol
- < 30mV electrocatalyst support loss after 400 hrs at 1.2 mV; tested per GM protocol; NTCNA has own protocol

Approach:
- Sequentially functionalize high surface area silica to introduce proton/electron conductivity
  - Ruthenium oxide used as model electron conducting functionality (ITO, SnO2 are options)
  - Sulfonic acid groups introduced to provide proton conductivity (sulfate groups are an option)
  - Platinum will be deposited on durable supports that meet milestones
  - Materials will be benchmarked against state-of-the-art carbon and Pt/C catalysts

Accomplishments/Progress
Proton/electron conducting metal oxides have been synthesized with
- Stand-alone proton conductivities > 100 mS/cm (100 mS/cm overall target)
- Stand-alone electron conductivities > 10 S/cm (5 S/cm overall target)
- BET surface areas of > 250 m²/g (50 m²/g overall target)
- Excellent support durability upon aggressive potential cycling + good MEA performance and durability

Collaborations: With Nissan, North America Inc. on benchmarking, durability testing, MEAs manufacture etc.

Proposed work for FY14 and beyond
• Work in conjunction with Nissan North America Inc. to complete durability testing and synthesize catalysts with lower Pt particle size (Task 2)
• Introduce platinum nanoparticles onto ITO and onto durable mixed-conducting supports; evaluate specific and mass activities, and stability under cycling using MEA studies (Task 1,3)
• Complete ionomer reduction studies, initiate scale up of MEAs and complete formulation of cost model for downselected formulations (Tasks 3-5).
Supplementary Slides
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>SEA</td>
<td>Strong electrostatic adsorption</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of zero charge</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>ECSA</td>
<td>Electrochemical surface area</td>
</tr>
<tr>
<td>Acronyms Used in Presentation</td>
<td></td>
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<tr>
<td>--------------------------------</td>
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<tr>
<td><strong>ITO 1</strong></td>
<td>ITO synthesized using co-precipitation method</td>
</tr>
<tr>
<td><strong>ITO 2</strong></td>
<td>ITO synthesized using silica aerogel template method</td>
</tr>
<tr>
<td><strong>ITO 3</strong></td>
<td>ITO synthesized using supercritical CO2 drying method</td>
</tr>
<tr>
<td><strong>ITO 4</strong></td>
<td>ITO synthesized using epoxide initiator method</td>
</tr>
<tr>
<td><strong>Protocol a)</strong></td>
<td>Pt nanoparticles reduced from chloroplatinic acid by using formaldehyde as the reducing agent at pH=7</td>
</tr>
<tr>
<td><strong>Protocol b)</strong></td>
<td>Pt nanoparticles reduced from chloroplatinic acid by using formaldehyde as the reducing agent at pH=2.7</td>
</tr>
<tr>
<td><strong>Protocol c)</strong></td>
<td>Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as the reducing agent at pH=8-9</td>
</tr>
<tr>
<td><strong>Protocol d)</strong></td>
<td>Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as the reducing agent at pH=10-11</td>
</tr>
<tr>
<td><strong>Protocol e)</strong></td>
<td>Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using 4% hydrogen (nitrogen balanced) as reducing agent at 250°C.</td>
</tr>
<tr>
<td><strong>Protocol f)</strong></td>
<td>Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using 4% hydrogen (nitrogen balanced) as reducing agent at 300°C.</td>
</tr>
<tr>
<td><strong>Protocol g)</strong></td>
<td>Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as reducing agent.</td>
</tr>
</tbody>
</table>
## Technical Accomplishments: Characterization of ITO

<table>
<thead>
<tr>
<th>ITO hydroxide precursor surface area (m²/g)</th>
<th>Commercial ITO</th>
<th>ITO 1 coprecipitation</th>
<th>ITO 2 supercritical drying</th>
<th>ITO 4 epoxide initiator</th>
<th>ITO 3 silica aerogel template</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO BET surface area (m²/g)</td>
<td>30± 2</td>
<td>45± 2</td>
<td>72± 2</td>
<td>41±1(820°C)</td>
<td>130± 10</td>
</tr>
<tr>
<td>Conductivity (S/cm)</td>
<td>0.6-0.7</td>
<td>1.3± 0.1</td>
<td>1.2±0.1</td>
<td>1.9±0.1(820°C)</td>
<td>~10⁻⁶</td>
</tr>
</tbody>
</table>

The ITO obtained by epoxide-initiated method showed the best conductivity. The ITO obtained using silica aerogel template method showed the best BET surface area, however the conductivity was very low.
**Approach: Platinum Nanoparticles Synthesis by Chemical Reduction of Pt Precursor with Formaldehyde [protocol (a) and (b)]**

0.14g ITO

150ml water

0.25g H$_2$PtCl$_6$ in 15mL H$_2$O

ITO suspension

Stir for 1h

add dropwise

NaHCO$_3$ was added to adjust the pH to 10 (protocol a) or 7 (protocol b)

195uL HCHO in 1.95mL H$_2$O

kept stirring overnight

Heat at 120 °C overnight

Pt/ITO[Protocol (a)]

Pt/ITO[Protocol (b)]

Platinum nanoparticles synthetized by chemical reduction of Pt precursor with formaldehyde
Technical Accomplishments: TEM of 40%Pt/ITO [ITO 1 co-precipitation, protocol a) was used to deposit Pt]

- Weak reducing agent HCHO helped to form small Pt nanoparticles (3-5nm).
- Some of the small Pt NPs anchored in the ITO support, which maintained the original small nanoparticle size.
- Some of the small Pt NPs agglomerated and formed large Pt clusters.

Hence: Bimodal size distribution seen (not good for mass activity)
Approach: Point of Zero Charge (PZC) Determination for ITO (Surface Loading: 100m²/L)

- Solid was soaked in water solutions of various starting pHs (NaOH and HCl used to adjust the pH)
- Solid stirred for 2 hours
- Final pH was measured
- PZC is the plateau in plot of final pH vs initial pH

“Strong electrostatic adsorption” (SEA) method was used.

The PZC value of the ITO was ~ 4. Plateau was small but if the surface loading was higher, then the plateau would be broader.

To use the SEA method to deposit the Pt nanoparticles, the pH value of the solution should be adjusted to pH<4.

We used Pt(NH₃)₄-xH₂O as the precursor when using the “SEA method”

*S. Lambert et al, J. of Catalysis, 261 (2009), 23*
Platinum nanoparticles synthetized by chemical reduction of Pt precursor by sodium borohydride

Platinum nanoparticles synthetized by using improved incipient wetness method
Approach: Potential Cycling to Estimate Support Stability

• Three Electrode Cell with Rotating Disk Electrode
  – Working Electrode: Glassy carbon coated with catalyst support
  – Counter Electrode: Pt foil
  – Reference Electrode: Saturated Calomel Electrode (SCE)
  – Electrolyte: N\textsubscript{2} saturated 0.1M HClO\textsubscript{4}

• Support loading on W.E.: 200 µg/cm\textsuperscript{2}\textsubscript{geo}

• Pt loading: 44.6µg/cm\textsuperscript{2}\textsubscript{geo}

• Potential cycling protocol
  – See following slides
H$_2$PtCl$_6$ precursor dissolved in ACETONE was added to ITO. Heated at ~50°C to evaporate ACETONE (Ethylene Glycol + Formic Acid) (dry impregnation).

To ensure better precursor-support interaction, dry paste was dispersed in pH 9-10 EG solution. Heated to 80°C, Formic Acid (2M total) was added dropwise. Kept heated at 80°C for 2 hours, mixture was cooled, filtered, and washed several times with hot water. Powder was dried in vacuum oven at 100°C for 2 hours and left overnight.