Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

PI: Vijay K. Ramani

Department of Chemical and Biological Engineering

Illinois Institute of Technology

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Project ID #
FC085

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Overview

Timeline

- Project start date: Sept. 1st 2010*
- Project end date: Jan. 31st 2015
- Percent complete: 100%

Budget

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

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

*Official Start date per DOE. Actual start date Dec. 2010. Subcontract with Nissan North America Inc. in place effective February 2011.

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 m^2/g #
  - Low cost
- Electrochemical oxidation of carbon occurs during fuel cell operation

$$C + 2H_2O \longrightarrow CO_2 + 4H^+ + 4e^-; \quad U^\theta = 0.207 \text{ v vs. SHE} \quad *$$

- 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)

Relevance: Research Objectives and Related DOE Targets

- Research Objectives:
  - 1) Develop and optimize non-carbon mixed conducting materials with:
    - High corrosion resistance
    - High surface area (> 200 m^2/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).

Approach: Desired Properties

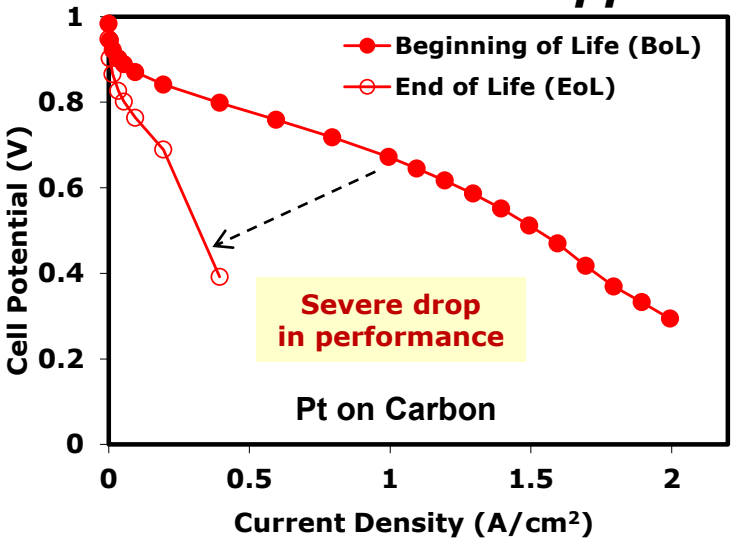
We are investigating mixed metal oxides functionalized with proton conducting groups that meet the following broad requirements:

- Surface area
  - > 100-300 m^2/g
  - Preferably higher, ~ 400-800 m^2/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 S/cm
- High Proton conductivity
  - > 100 mS/cm

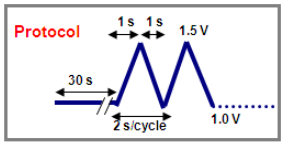
Approach: IIT-Nissan Pt/Non-carbon Research

Carbon supports have poor durability during fuel cell operation

■ Problem: Poor durability of Traditional Carbon Supports



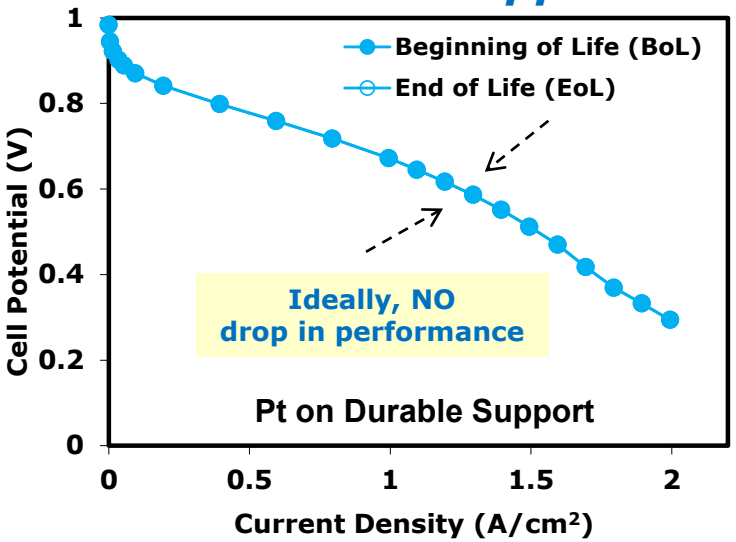
FCCJ (Japan)



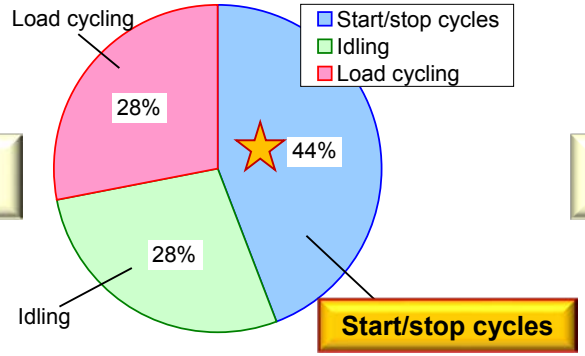
1000 cycles

Start-stop potential cycling protocol

■ Approach: Development of Non-carbon Supports

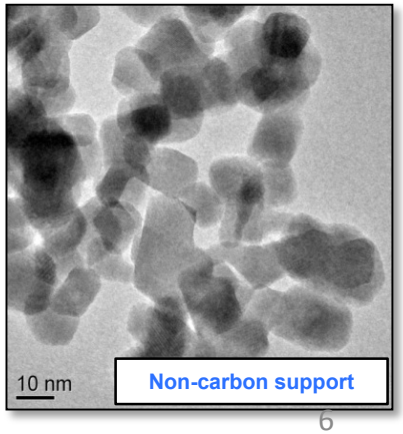


Nissan Study on Fuel Cell Degradation Modes



Shimoi et al, JSAE Spring Meeting (2009)

Example: TiO_2-RuO_2, SnO_2-$In2O_3$ metal oxides



Approach: Conceptual Outline

- **Start with a high surface area metal oxide support**
  - Functionalities can be added subsequently
  - Silica and Titania are model metal oxides used; 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 (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_3H-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** –
  - $Ru_xTi_{1-x}O_2$ 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.

C.-P. Lo *et. al.* ECS Transactions, 33(2010) 493
F. Takasaki, *et. al*., Journal of the Electrochemical Society. 158, B1270 (2011)
S. Trasatti, Electrochimica Acta, 36 (1991) 225
J.M. Fletcher, *et. al.* J. Chem. Soc. A 3 (1968) 653.

Approach: Milestones and GNG Criterion; Current Status

- Milestone 1 (End of Phase 1; Q1; 2012 [calender 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 m^2/g BET surface area [Current status > 250m^2/g]
    - Durability* in acidic electrolyte [C-S: durable]

* < 10% mass loss on cycling between:
- 1V and 1.5V at 0.5V/s
-0.95 V and 0.6V under load
- 1000 cycles

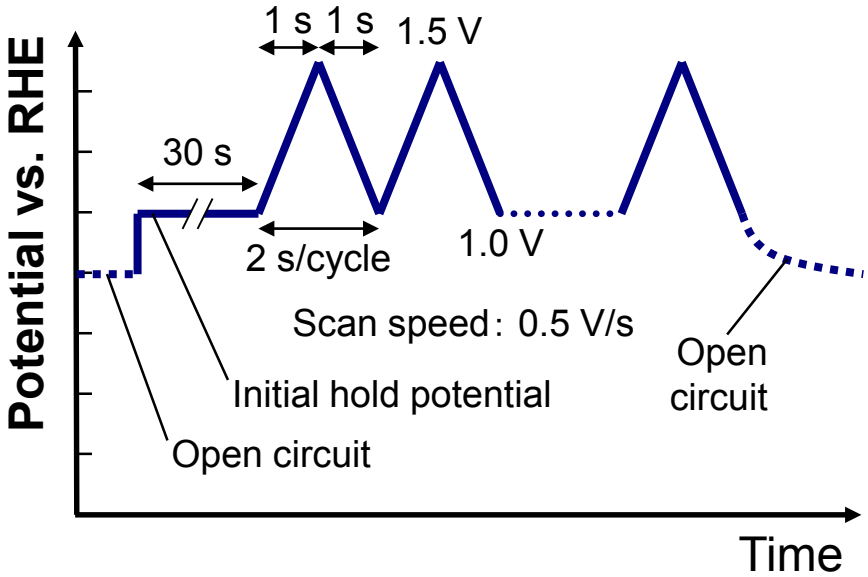
- Milestone 2 (End of Phase 2; Q3; 2013)
  - Synthesize a support that demonstrates at least:
    - 100 mS/cm proton conductivity [Current status > 120 mS/cm; stand-alone]
    - 5 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m^2/g BET surface area [Current status > 250m^2/g]
    - 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 cm^2 MEAs w/ optimal support formulation [Not required]
- GNG criterion (applied at end of Q1; 2012) – **PASSED in June 2012**

Approach: Milestones and GNG Criterion; Current Status

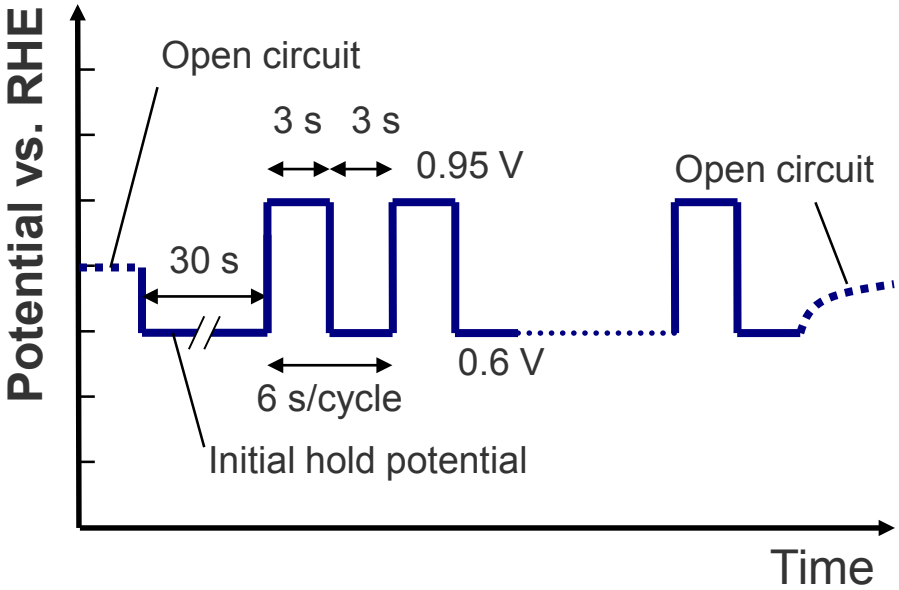
Milestone 1		RTO	RSO	RSO-sulfonated	Sulfated SnO_2	ITO
70 mS/cm proton conductivity		No	No	Yes	Yes	No
2 S/cm electron conductivity		Yes	Yes	Yes	No	No
50 m^2/g BET surface area		Yes	Yes	Yes	Yes	Yes
Durability in acidic electrolyte		Yes	Yes	No	N/A	Yes
Milestone 2						
100 mS/cm proton conductivity		No	No	No	Yes	No
5 S/cm electron conductivity		Yes	Yes	Yes	No	No
50 m^2/g BET surface area		Yes	Yes	Yes	Yes	Yes
Durability in acidic electrolyte		Yes	Yes	N/A	N/A	RDE: Yes MEA: No

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 m^2/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*"

Approach: Potential Cycling to Estimate Support and Electrocatalyst Durability



Support Durability—Support corrosion



Catalyst Durability– Pt Dissolution

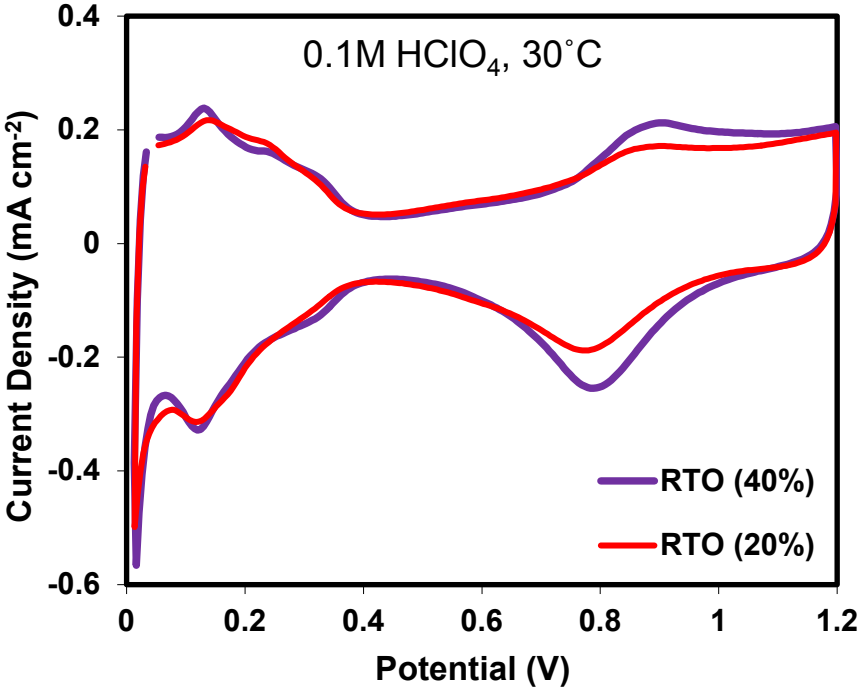
Electrolyte: 0.1 M $HClO_4$
Cycling rate – see Figure. Cycling Temperature: 60C at NTCNA, RT at IIT
CV sweep rate of 20 mV/S; Room Temperature CV

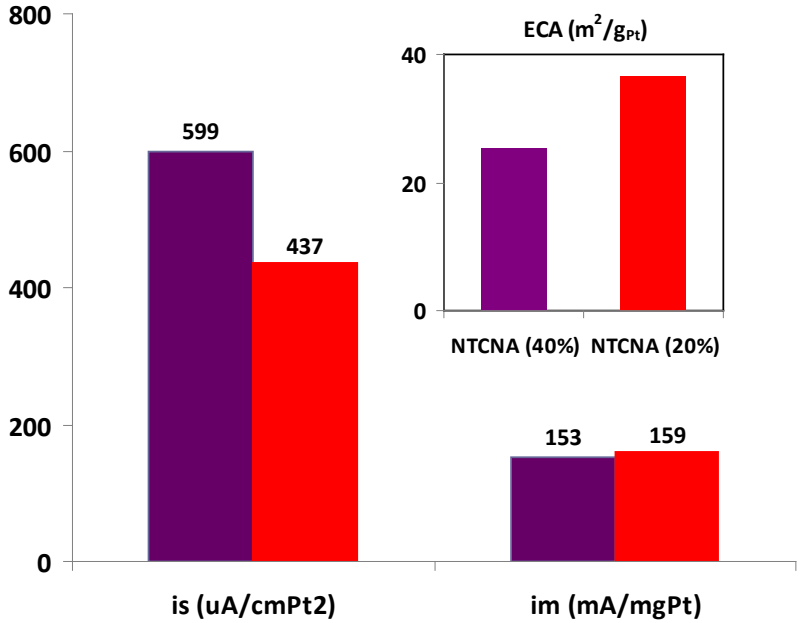
NISSAN R&D AMERICAS

Technical Accomplishments on Pt/RTO supports:
Summary of most significant results reported earlier

Technical Accomplishments (NTCNA): Pt/RTO Catalyst Synthesis and Evaluation in RDE

In RDE, both 40% and 20% Pt/RTO have comparable mass activities:
Potential to reduce cost by Pt reduction





- 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}).

Previous results demonstrating excellent ORR activity of Pt/RTO catalysts

MEA : Effect on iV performance Start/stop cycling

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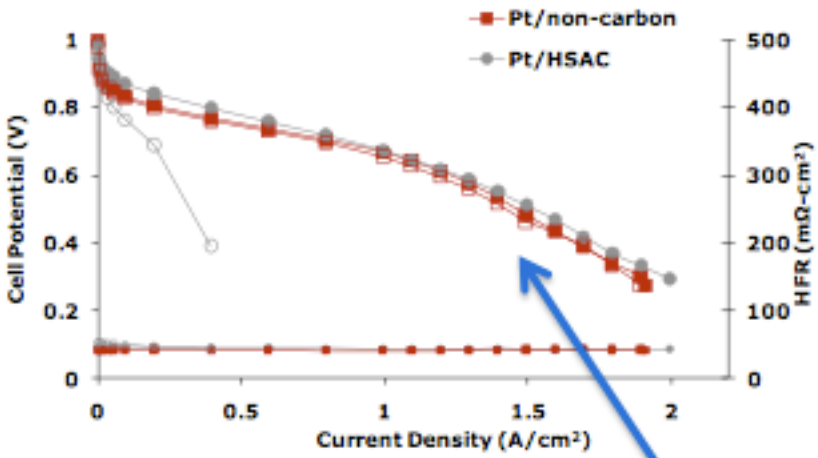
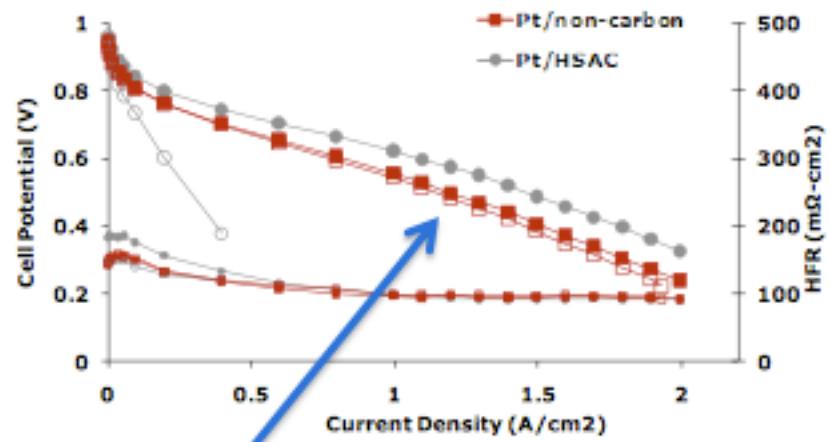
H_2/Air, 4/8 NLPM, 1 bar_g, 80 ° C,
Closed symbol: BoL
Open symbol: EoL

100% RH



40% RH



❖ **Minimal loss of performance BoL/EoL Start-stop cycling for Pt/non-carbon**

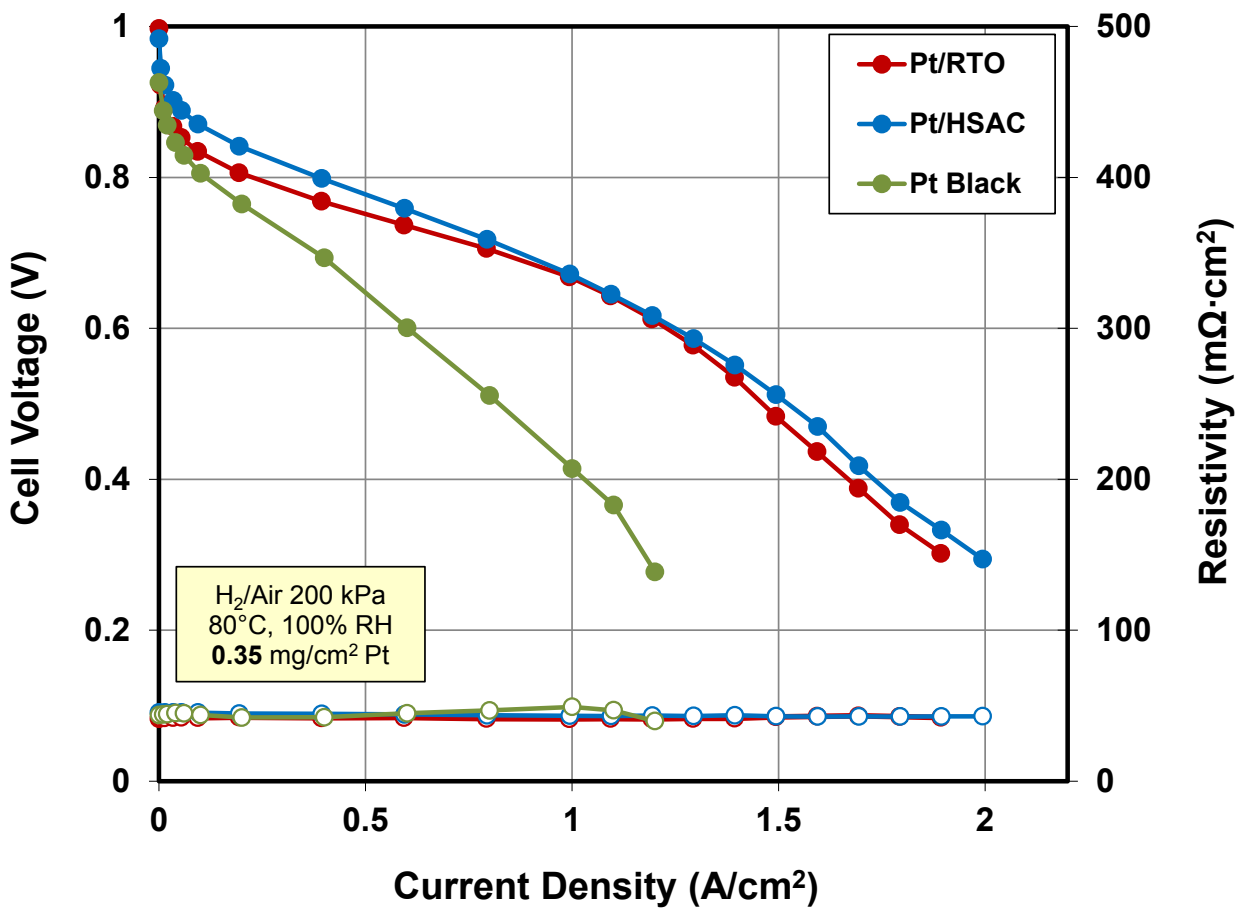
MEA Spec:
25cm², NRE211
Anode: 0.4 mg_{Pt}/cm^2 Pt/C
Cathode: 0.35 mg_{Pt}/cm^2

- ❑ 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/TiO_2-RuO_2) showed minimal loss in performance under start-stop cycling → Very stable support

Previous results demonstrating excellent performance and corrosion resistance of Pt/RTO catalysts

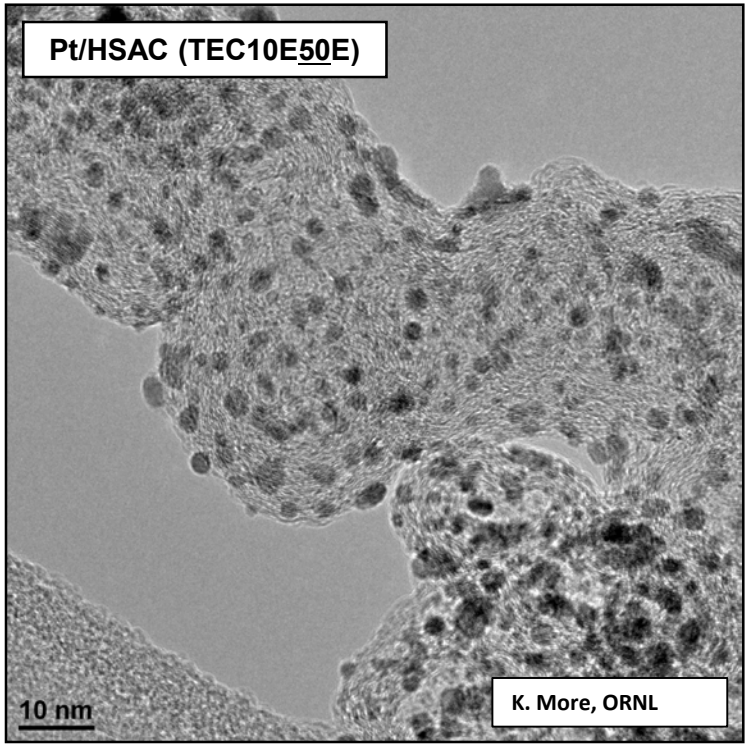
New results on Pt/RTO supports

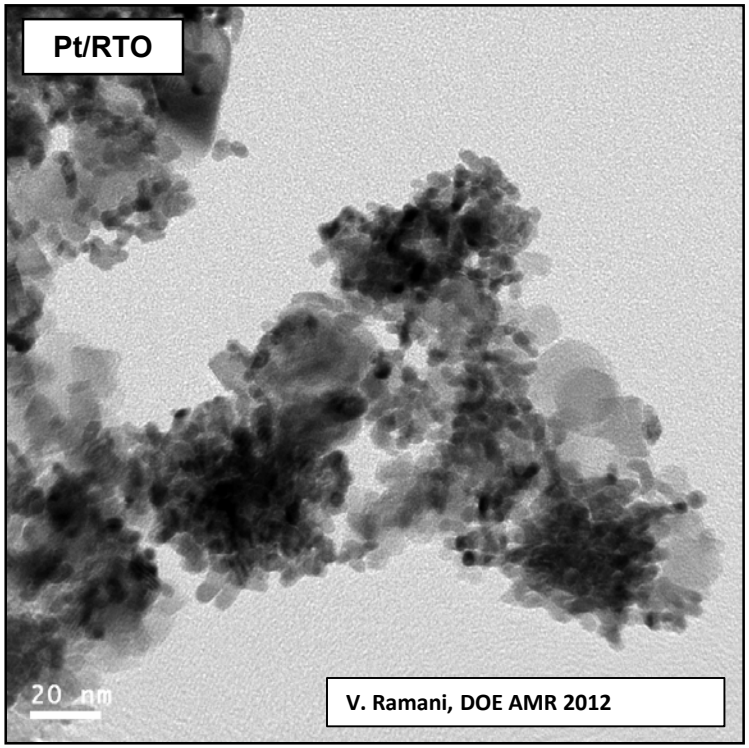
Technical Accomplishments (IIT-Nissan): **Pt/Non-carbon** Research; **H_2-Air** i-V Performance of **Pt Black** (unsupported)



- **Pt black (fuel cell grade) has significantly poorer iV performance compared to Pt/RTO and Pt/HSAC.**
- **In order to optimize the Pt/RTO <u>catalyst</u> and <u>catalyst layer,</u> we sought to obtain a better understanding of its microstructure and transport properties.**

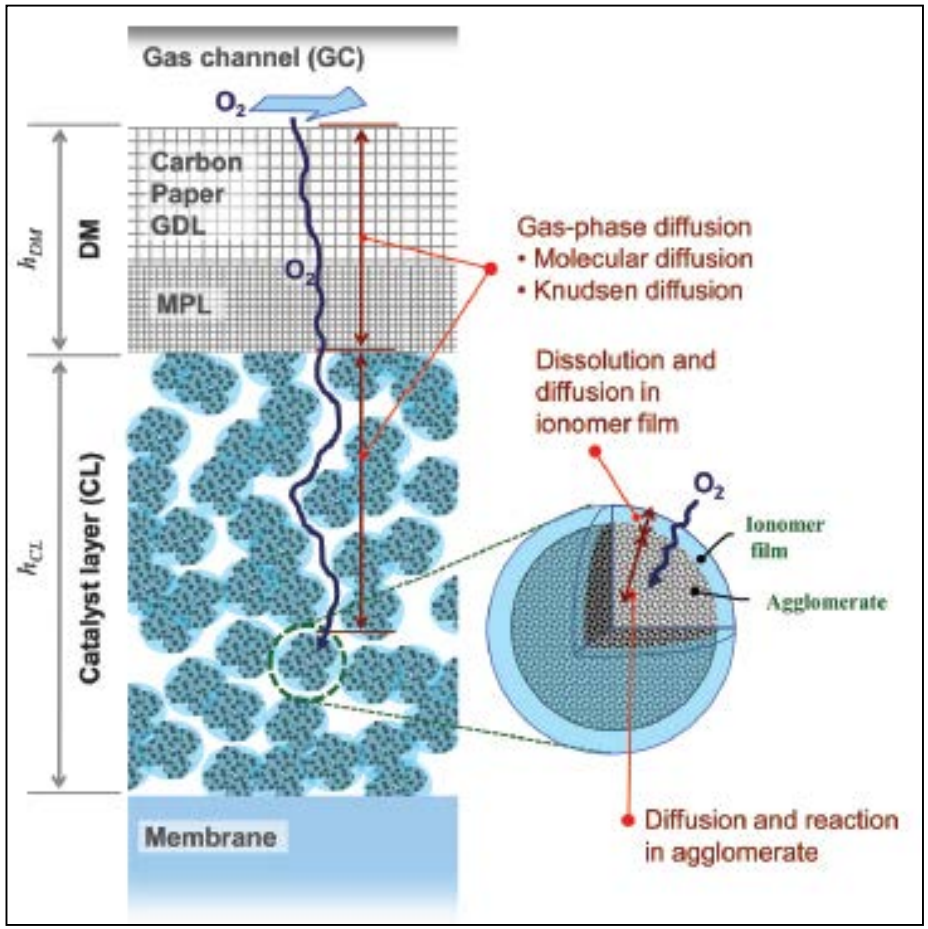
Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; TEM Images of Pt/HSAC and Pt/RTO Catalyst

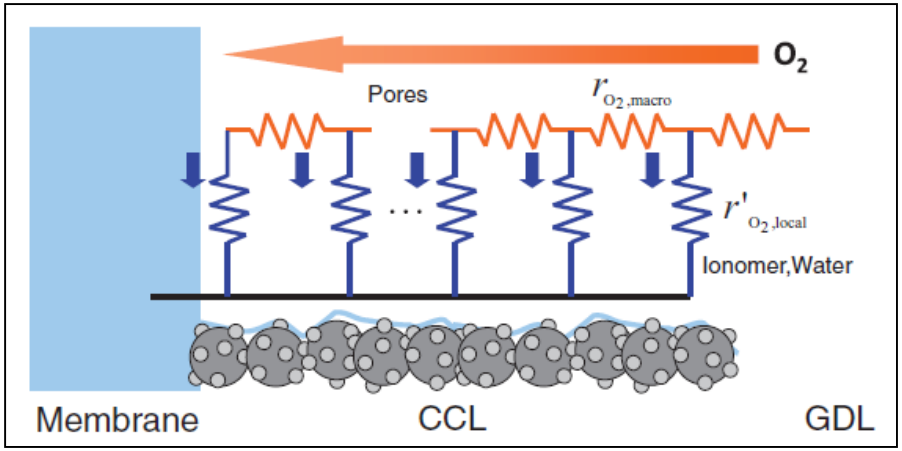


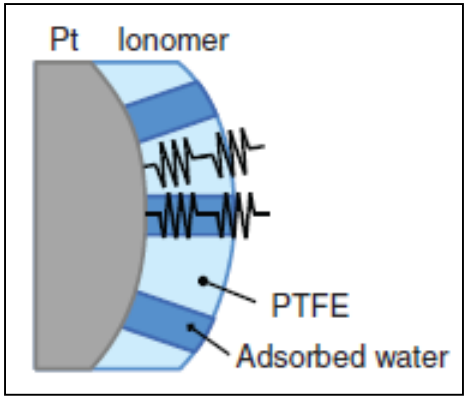


- **There are significant differences between the two catalysts, in terms of Pt particle size, Pt dispersion/agglomeration, Pt particle density, total surface area, etc.**
- **This suggests more optimization of electrode parameters is required. For example: Will species transport resistances differ in a Pt/RTO electrode?**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Analysis of O_2 Transport in the Catalyst Layer



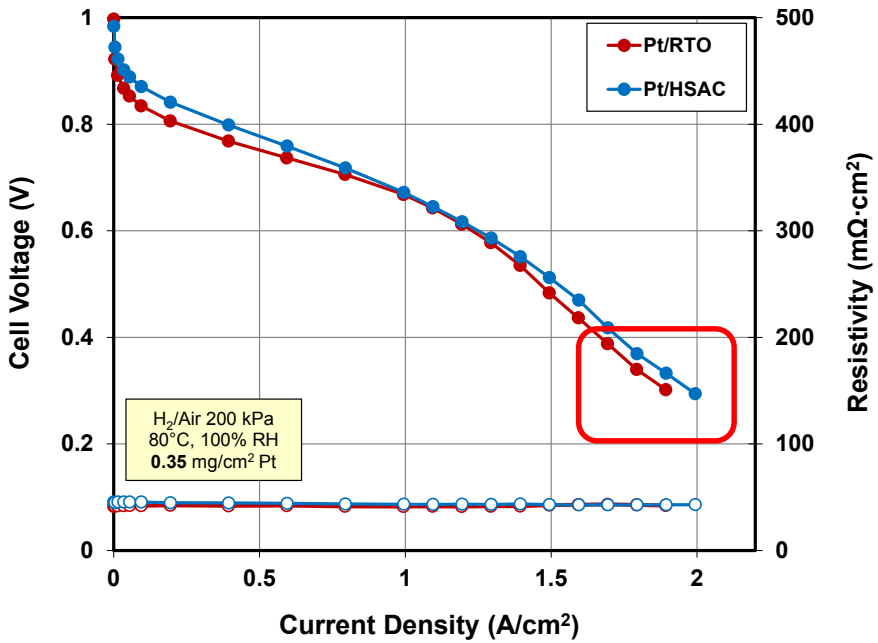


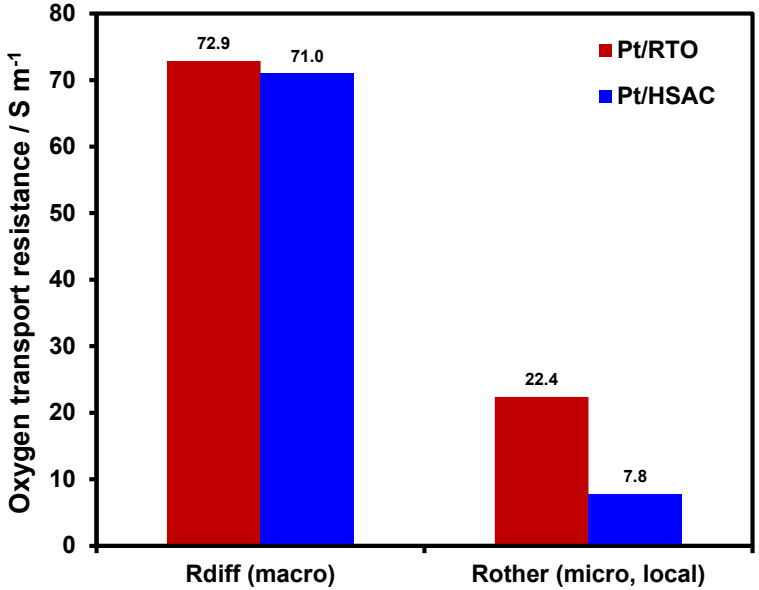


- **Limiting current measurements with dilute O_2 were performed in order to determine the O_2 gas transport resistance in the catalyst layer ($R_{O2,\ local}$).**

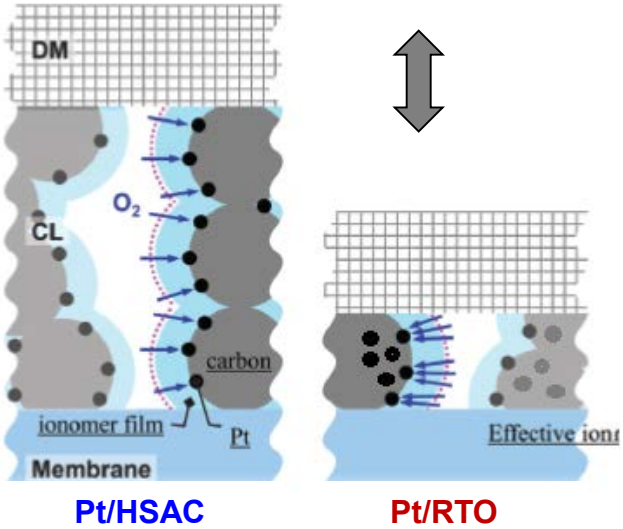
J. Electrochem. Soc., 158 (4) B416-B423 (2011) J. Electrochem. Soc., 160 (8) F779-F787 (2013)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; O_2 Transport Properties of Pt/RTO



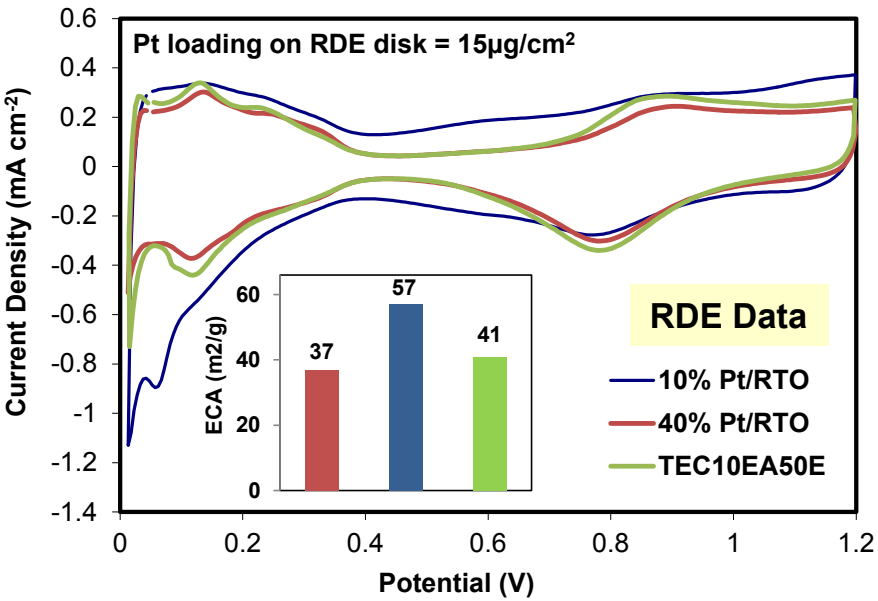


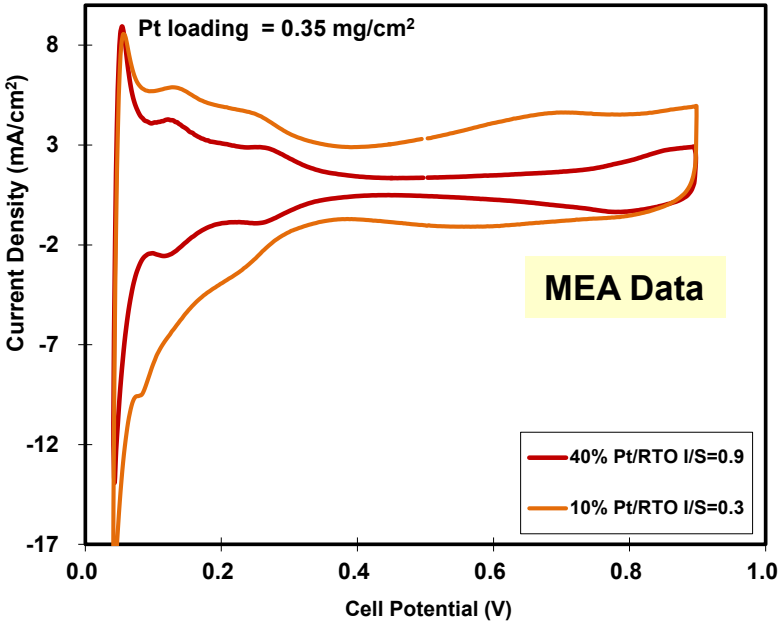
- **The O_2 gas transport resistance, R_{other}, for the Pt/RTO catalyst layer is higher than that for Pt/HSAC.**
- **This is consistent with the differences in the catalyst layer thickness, ionomer film thickness, Pt ECA, and effective ionomer area (ionomer covering Pt particles/agglomerates).**



[1] J. Electrochem. Soc., 160 (8) F779-F787 (2013)
[2] J. Electrochem. Soc., 158 (4) B416-B423 (2011)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Optimization of Ionomer Content for Pt/RTO CL



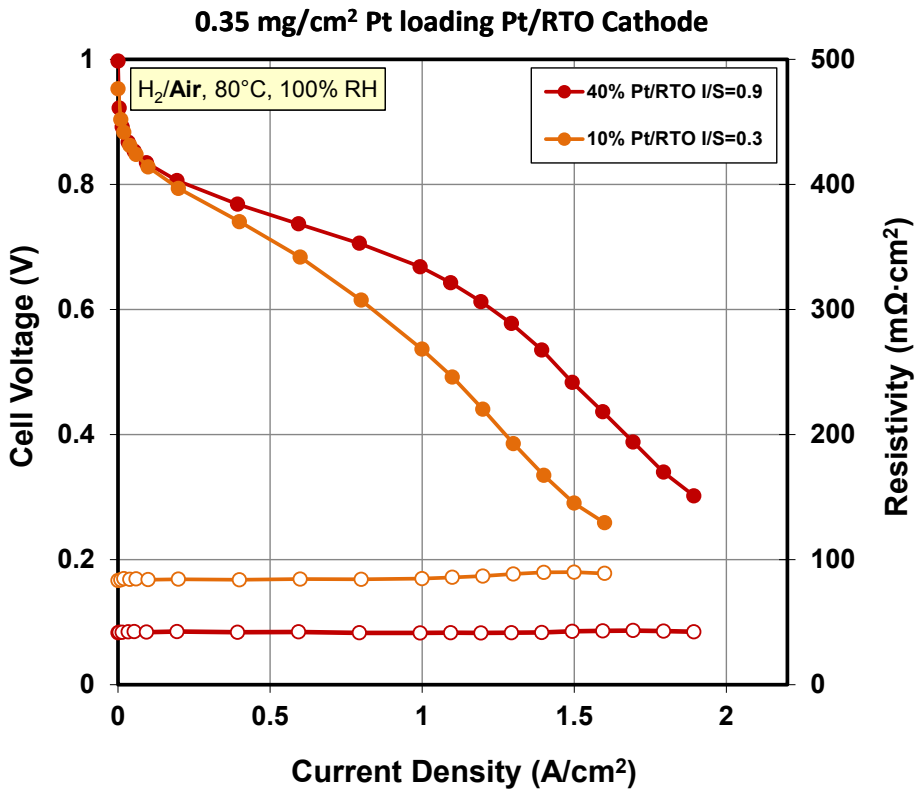


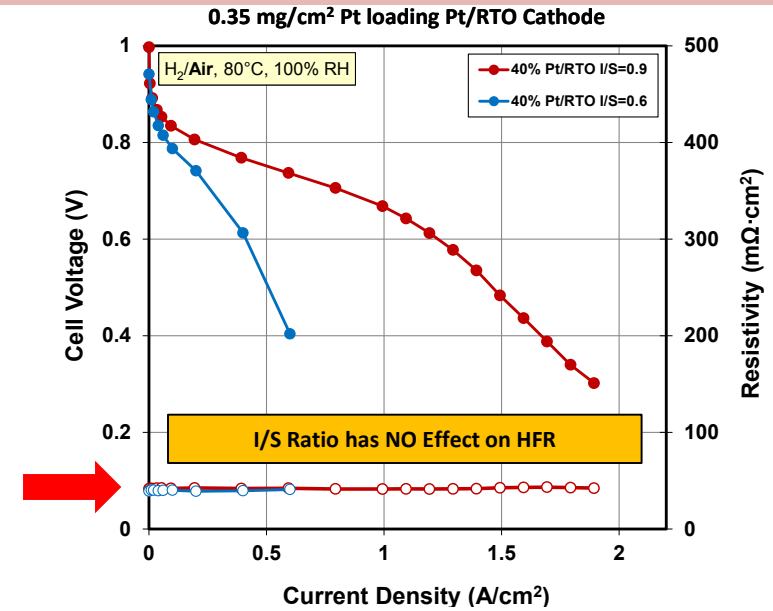
$$\sigma\ (\text{ionomer film thickness}) = \frac{V_{Nafion}}{A_{eff}} = \frac{V_{Nafion}}{(1-\gamma)A_{BET}\cdot 10^4\cdot m_{cat}}$$

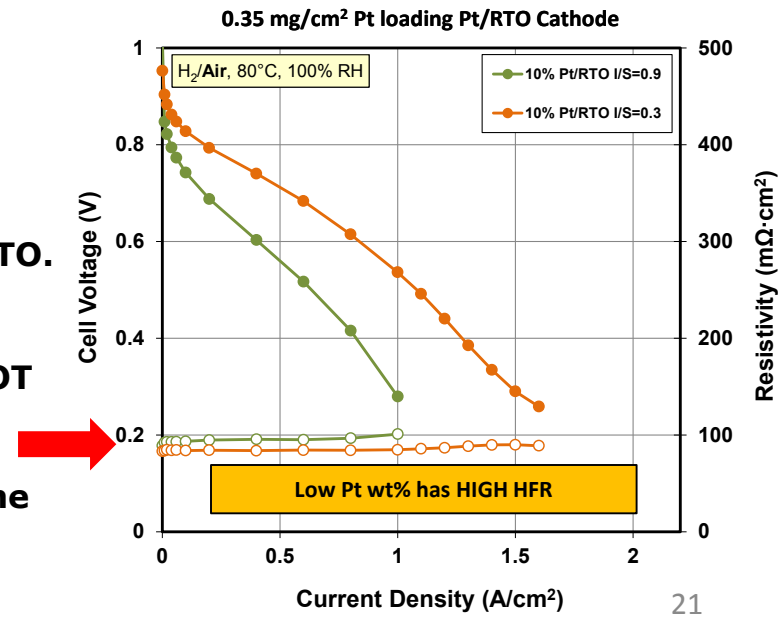
- **In order to match the estimated ionomer film thickness for 30% Pt/GKB electrode with I/S = 0.9, the target I/S mass ratio for a 10 wt% Pt/RTO would be 0.3.**
- **The ECA (from RDE & MEA) for the 10% Pt/RTO catalyst was higher than that of 40% Pt/RTO, indicating better Pt utilization.**

	30% Pt/GKB	10% Pt/RTO
σ_i (ionomer film thickness)	**3.3**	
BET Surface Area $(m^2/g)_{support}$	150	**39**
I/S mass ratio	0.9	**0.3**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; H_2-Air i-V Performance of 40% and 10% Pt/RTO (1)

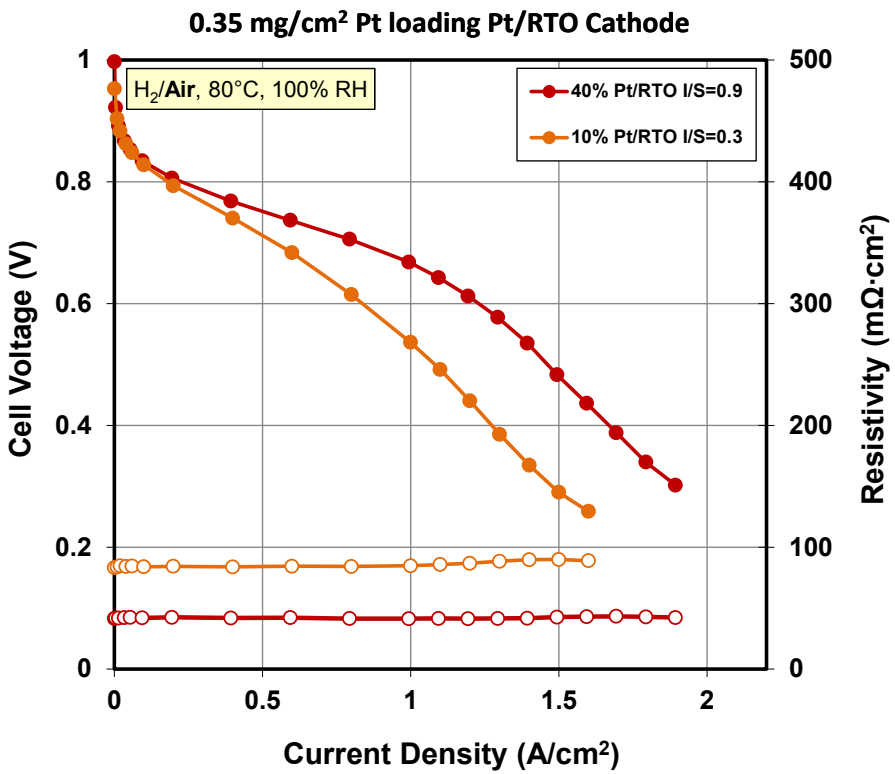




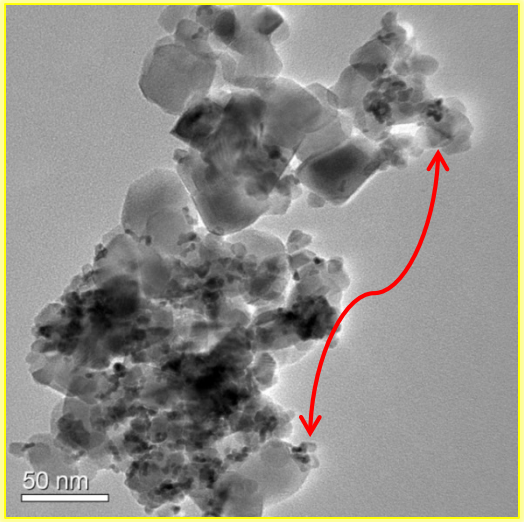


- **10% Pt/RTO showed lower performance than 40% Pt/RTO.**
- **The HFR for 10% Pt/RTO was ~2x that of 40% Pt/RTO.**
  - **Decreasing the I/S ratio or ionomer loading does NOT cause such a big increase in HFR, as shown.**
  - **It is thus likely that the HFR increase is caused by the decrease in Pt wt. % from 40% to 10%.**

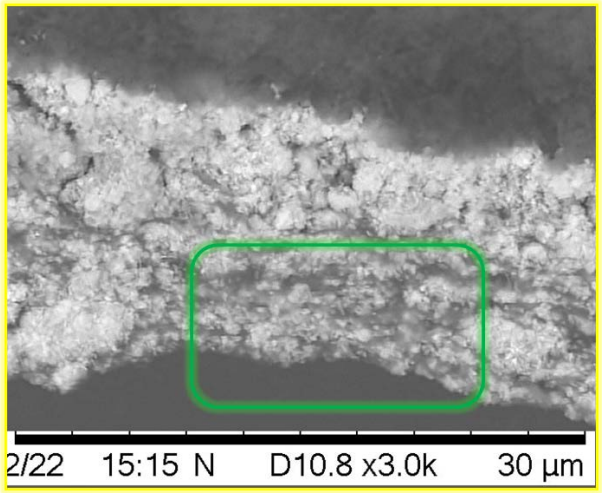
Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; H_2-Air i-V Performance of 40% and 10% Pt/RTO (2)



TEM of Catalyst

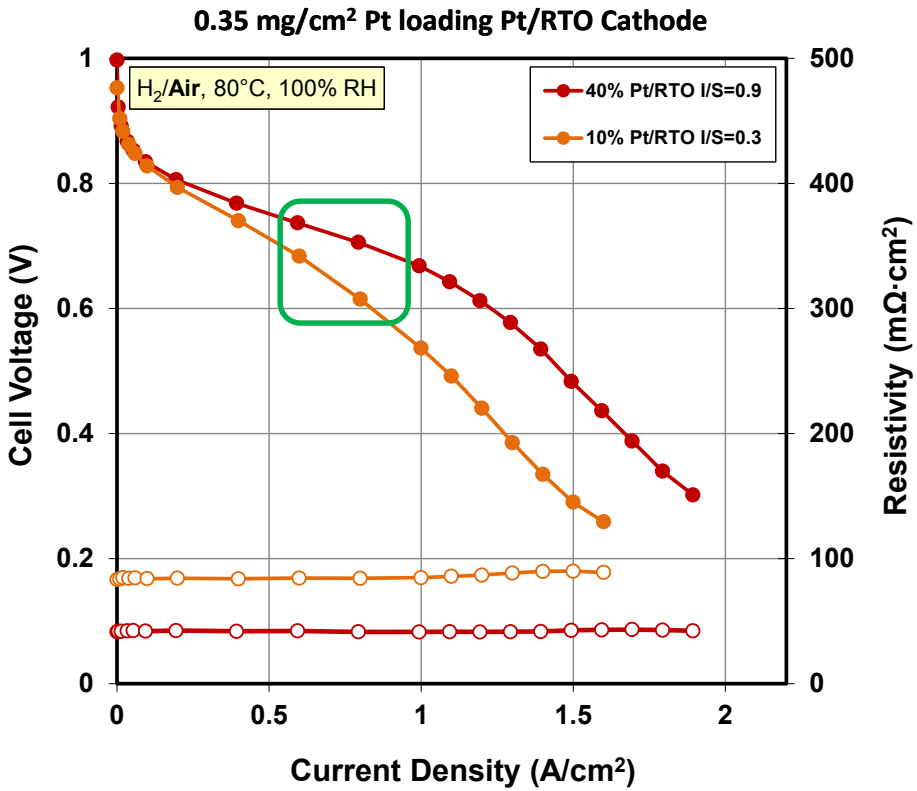


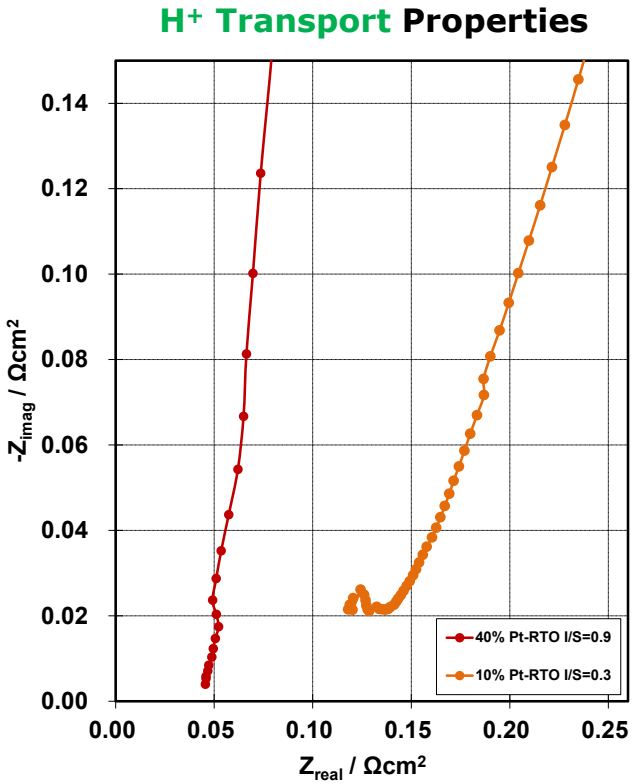
SEM of Catalyst Layer



- Decreasing the Pt wt. % down to 10% on RuO_2-TiO_2 may have decreased the electronic conductivity of the catalyst.
- If some fraction of Pt particles are anchored on the TiO_2 phase, they could become electronically isolated (hypothesis).
  - Catalyst powder electron conductivity is not measured yet but will be measured using 4 point probe conductivity meter soon.
- We have seen this effect before: (1) in Pt/ITO, (2) in Pt/SnO2, and (3) in some M-N-C, non-PGM catalyst formulations.

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; H^+ Transport Properties of 40% and 10% Pt/RTO





- The $R_{H+,cathode}$ for the 10% Pt/RTO cathode is not that much higher compared to the 40% Pt/RTO cathode.
- Taking into account the catalyst layer thickness and ionomer volume fraction, the calculated H^+ conductivity for both cathodes are comparable.

	40% Pt/RTO I/S = 0.9	10% Pt/RTO I/S = 0.3
HFR ($m\Omega \cdot cm^2$)	45	120
$R_{H+,cathode}$ ($m\Omega \cdot cm^2$)	**90**	**160**
$\sigma_{H+,cathode}$ (mS/cm)	**0.006**	**0.009**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Conclusions related with the microstructure and optimization of transport properties

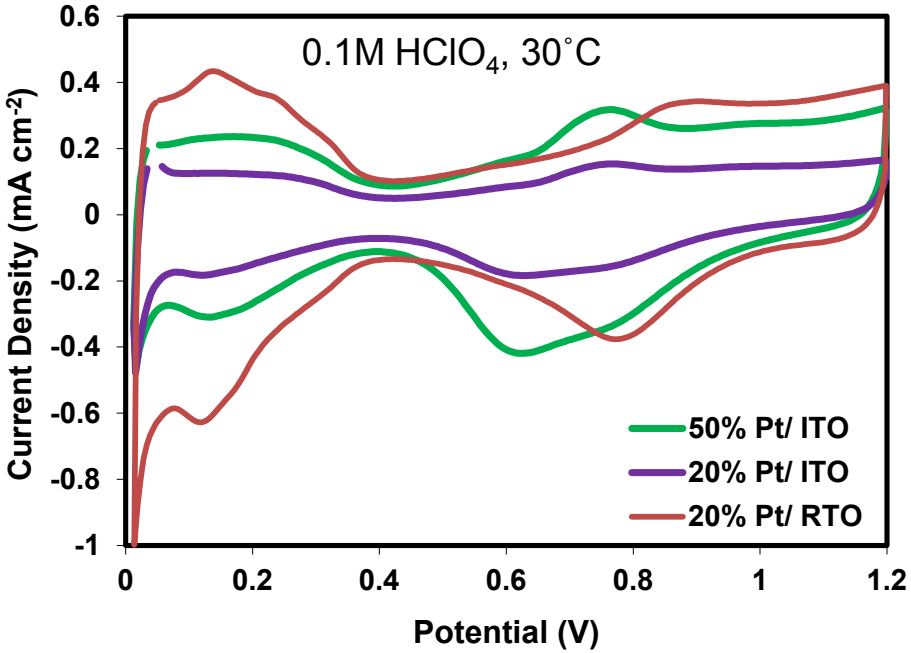
- **NTCNA sought to optimize the Pt/RTO catalyst and catalyst layer by:**
  1. **Calculating a more optimal Pt wt. % on RTO based primarily on the surface area of RTO.**
  2. **Estimating a more appropriate I/S weight ratio or ionomer loading based on ionomer volume fraction and ionomer film thickness calculations.**
- **NTCNA prepared a 10% Pt/RTO catalyst which showed better Pt particle dispersion (TEM analysis). The ECA & mass activity was higher than the 40% sample, indicating better Pt utilization.**
- **However, 10% Pt/RTO showed lower iV performance than 40% Pt/RTO in MEA testing, and its HFR was ~2x higher than the 40% sample.**
  - **the HFR increase is caused by the decrease in Pt wt. % from 40% to 10%, which may have decreased the *effective* electronic conductivity of the catalyst.**
  - **If some fraction of Pt particles are anchored on the TiO_2 phase (insulator), they could become electronically isolated, which leads to lower effective conductivity (hypothesis).**
- **Based on EIS analysis, the $R_{H+,cathode}$ for 10% Pt/RTO CL is not that much higher compared to the 40% Pt/RTO CL, and the calculated H^+ conductivity for both cathodes are even comparable.**
- **The optimal Pt wt. % may be in the ~20% range, and I/S ratio < 0.3 could still be effective.**
- **Better control of where to deposit Pt on mixed metal oxide supports (selective Pt deposition on RuO_2, for example) will be worth investigating in the future.**

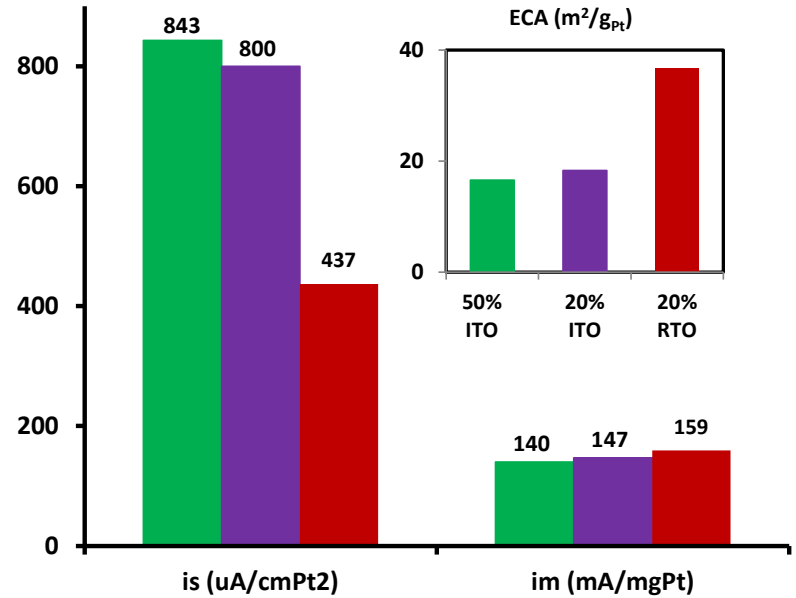
Technical Accomplishments on Pt/ITO supports:
Summary of most significant results reported earlier

Technical Accomplishments (NTCNA): Pt/ITO Catalyst Synthesis

RDE Evaluation (mg scale synthesis)

NTCNA Pt/ITO: similar mass activity as Pt/RTO



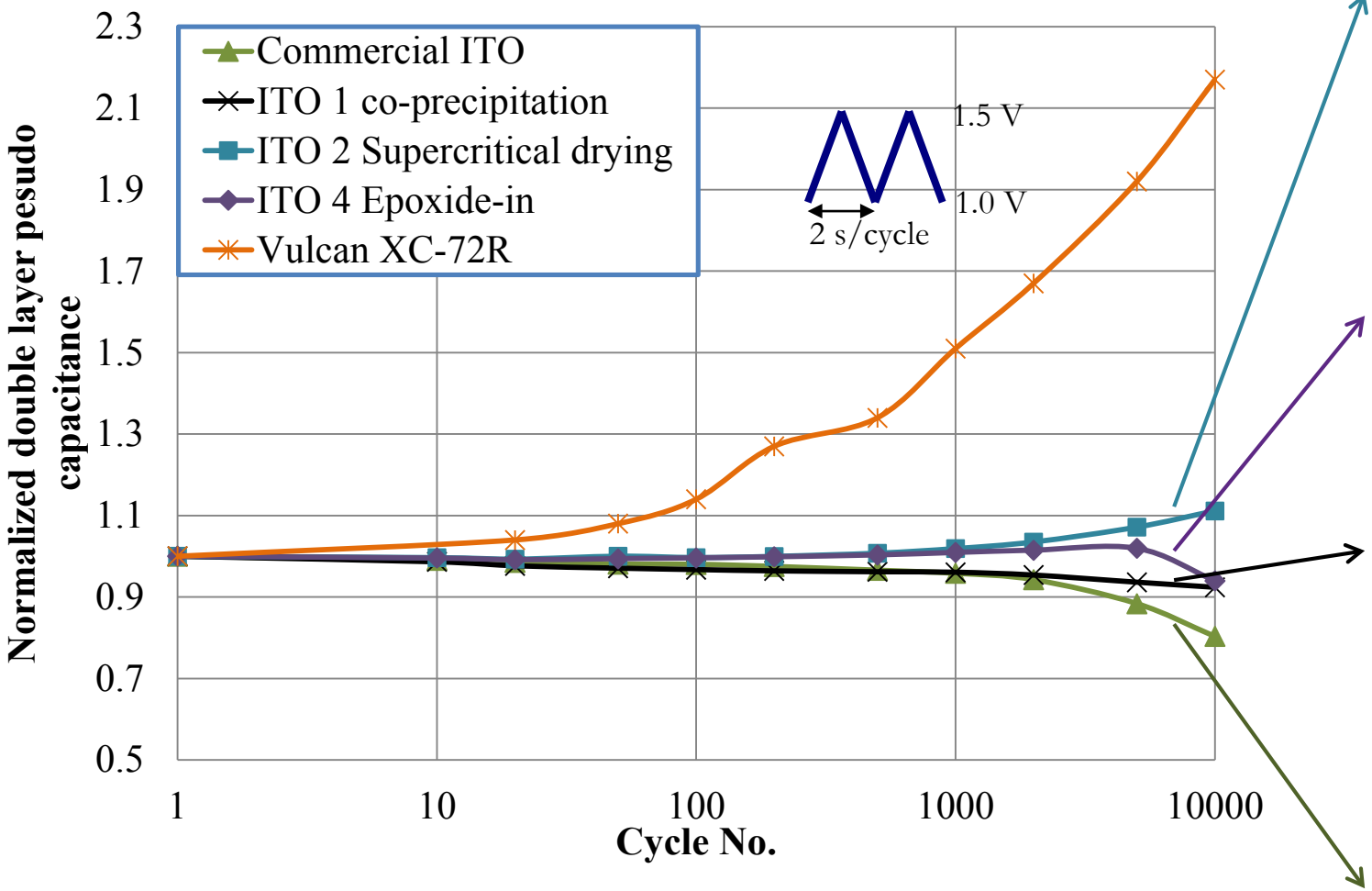


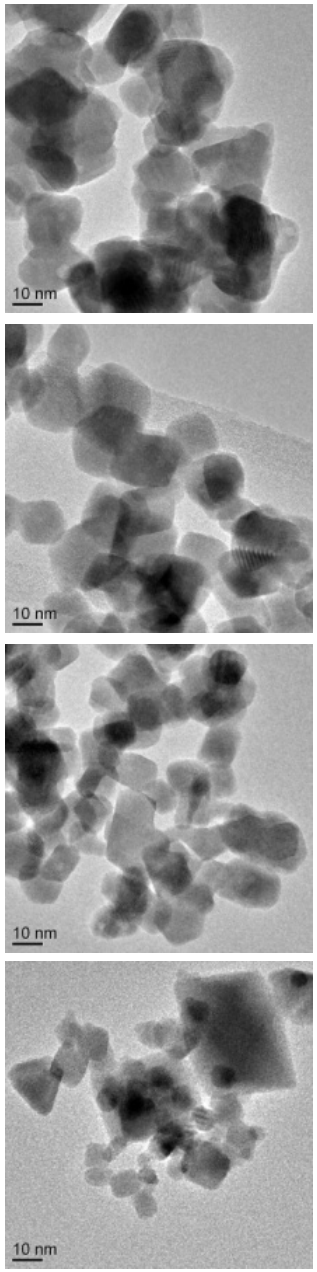
- The mass activity obtained for both 50% and 20% Pt/ITO is 140-150 mA/mg_{Pt}, comparable to Pt/RTO (in RDE).
- This value is comparable to the mass activity of a commercial sample, TEC10E50E-HT, (TKK Pt/Ketjen Black, heat-treated) at ~150 mA/mg_{Pt}).

Previous results from 2014 AMR presentation

Technical Accomplishments: Electrochemical Stability of ITO (Support Corrosion Protocol)

Electrolyte: 0.1 M $HClO_4$ under N_2 atmosphere;
CV sweep rate of 20 mV/S; Room temperature cycling

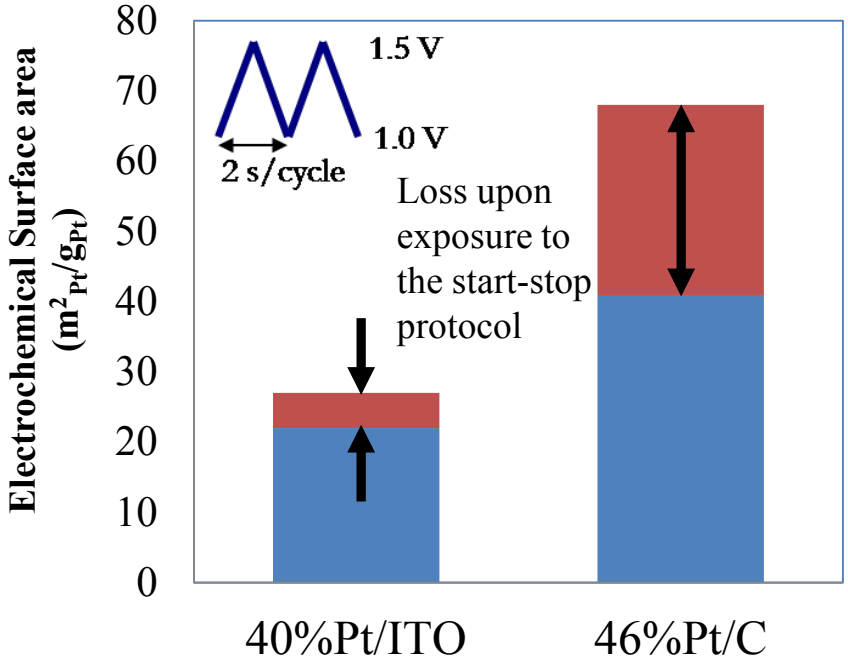




Previous results from 2014 AMR presentation

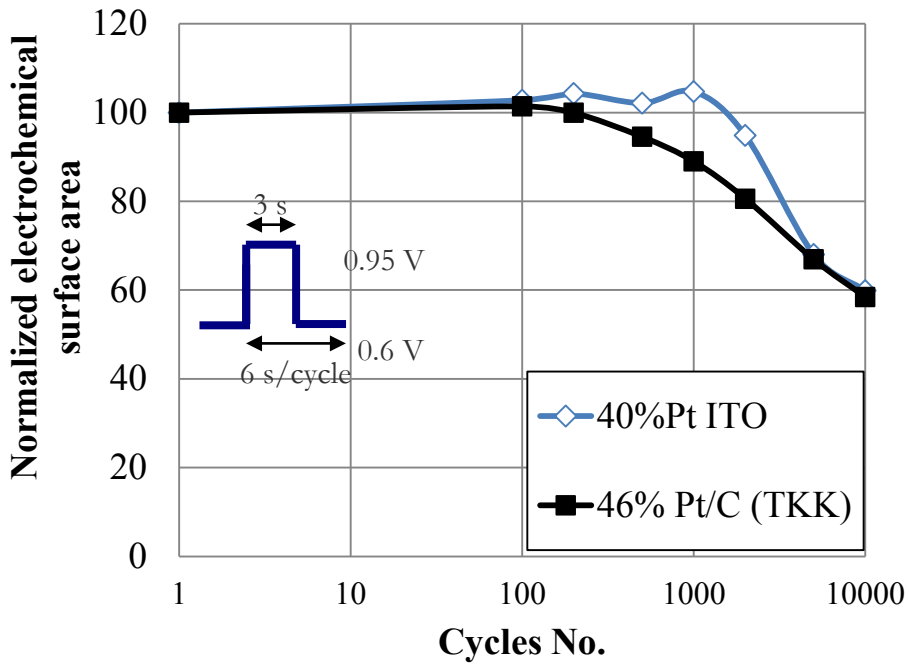
Technical Accomplishments: Stability of 40%Pt/ITO [ITO 1, protocol a)]

The Pt/ITO stability was evaluated from the change in ECSA .
0.1 M $HClO_4$ under N_2 atmosphere; room temperature
Start/Stop (left) and Load (right) Cycling Protocols



Support Durability—Support corrosion

The ECSA of 40% Pt/ITO decreased by 23% after 10,000 cycles.



Catalyst Durability– Pt Dissolution

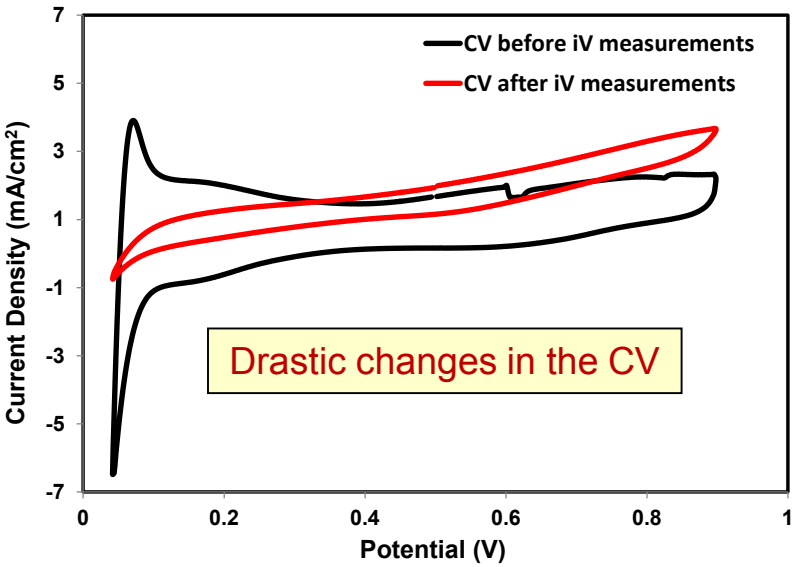
The ECSA of 40% Pt/ITO decreased by 40% after 10,000 cycles.

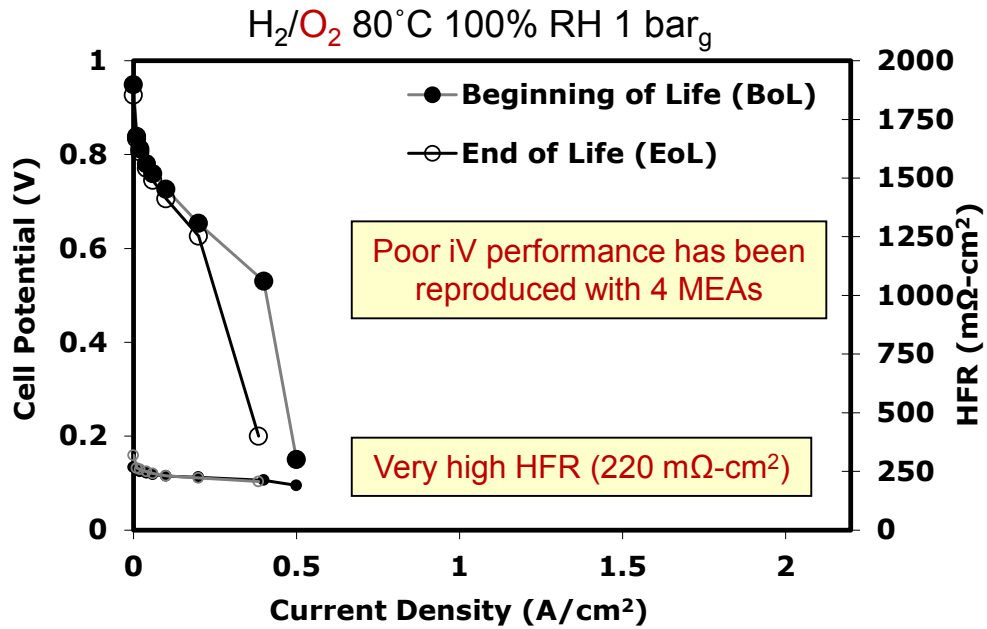
Previous results from 2014 AMR presentation

Technical Accomplishments (NTCNA): Pt/ITO Catalyst Testing

MEA Evaluation – iV Performance & Durability

Good RDE results seen for Pt/ITO could not be observed in MEA.





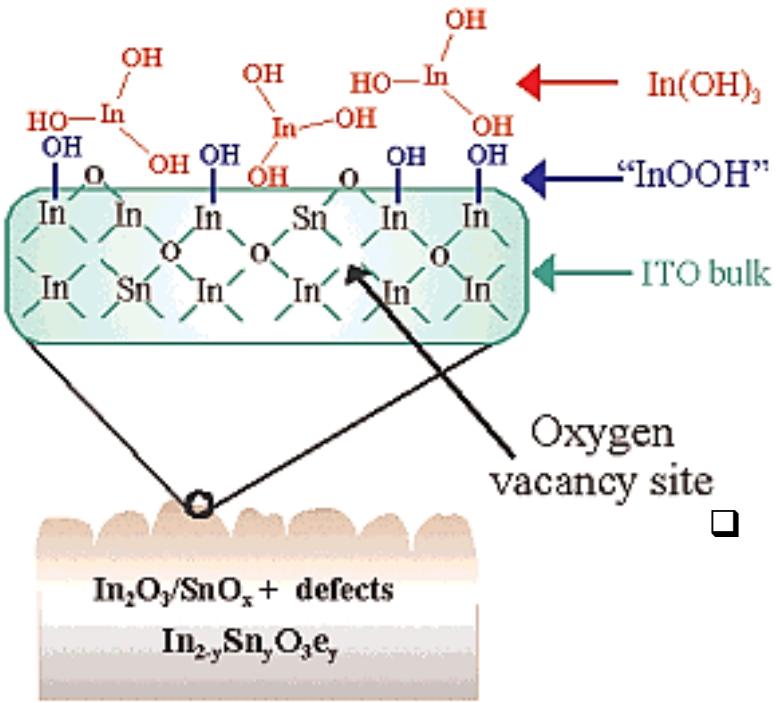
- Pt/ITO showed poor MEA performance even at a Pt loading of 0.35 mg/cm^2.
  - The high frequency resistance (HFR) was very high (220 mΩ-cm^2).
- Drastic changes in the CV profile (loss of H_{upd} features and resistive behavior) is observed, suggesting some changes in the chemical properties of the ITO support.
- 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.

Previous results from 2014 AMR presentation

Technical Accomplishments (NTCNA): Pt/ITO Catalyst Testing
Limitations of ITO in FC Operating Conditions

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.



$$In_2O_3 + 3H_2O \rightarrow 2In(OH)_3 \quad (1)$$

$$In_2O_3 + H_2O \rightarrow 2InOOH \quad (2)$$

- XPS[1] and electrochemical studies[2] suggest preferential hydrolysis of surface ITO.
- Degradation and structural deformation of ITO in fuel cell relevant potentials.[3]

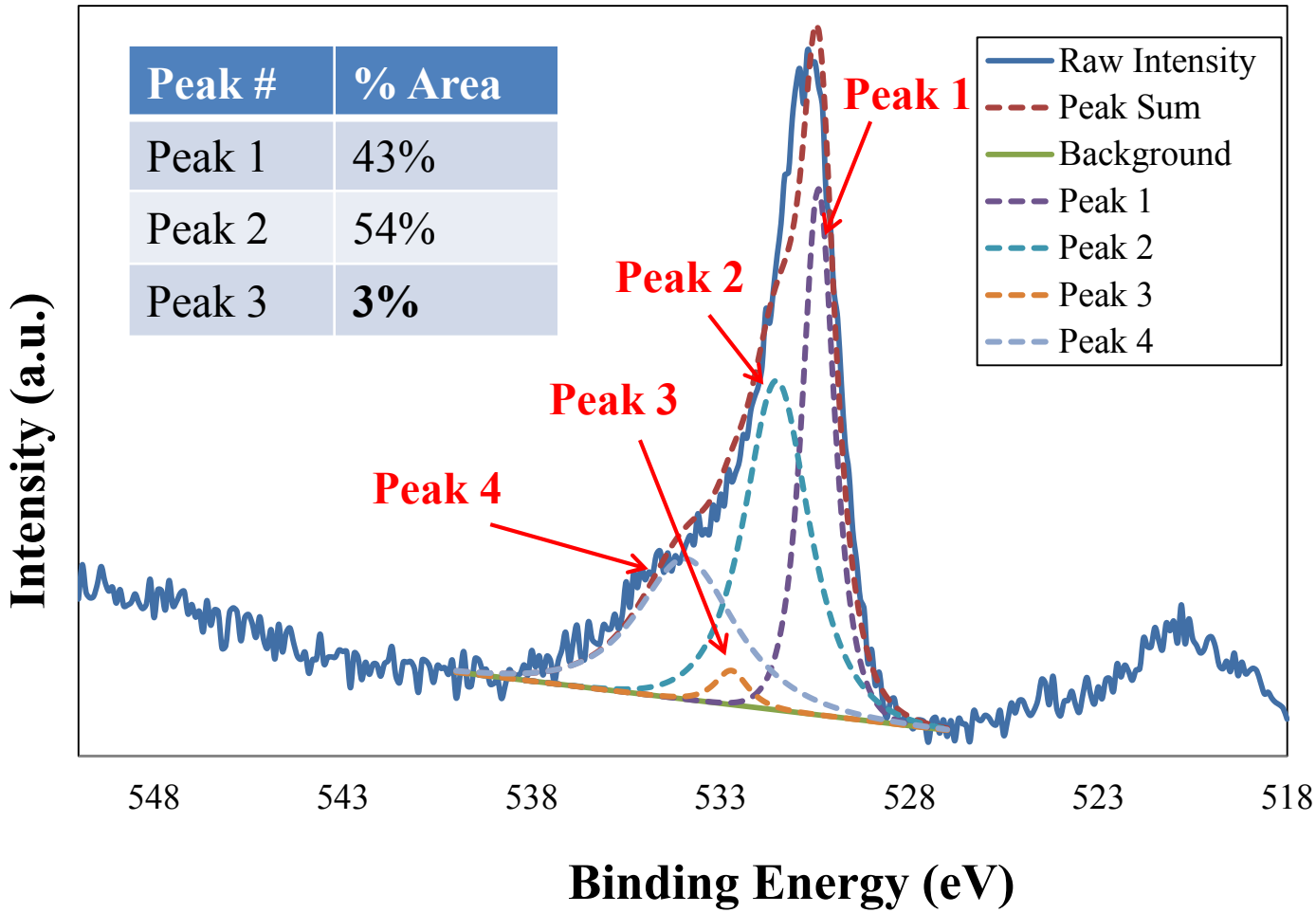
[1] Donley, Carrie, et al. *Langmuir* 18.2 (2002): 450-457
[2] Brumbach, Michael, et al. *Langmuir* 23.22 (2007): 11089-11099
[3] Liu, Ying, et. Al. Electrochimica Acta 115 (2004): 116-125

Previous results from 2014 AMR presentation

New technical Accomplishments (NTCNA): Pt/ITO Research;

XPS analysis of degradation modes of Pt/ITO during PEMFC operation

Technical Accomplishments. XPS results for O1s Before Fuel Cell Performance Test



Peak #	% Area
Peak 1	43%
Peak 2	54%
Peak 3	**3%**

Peak 1 (530 eV) was assigned to ITO-like oxygen (**oxide**)

Peak 2 (531 eV) was assigned to oxide that is adjacent to a oxygen deficiency site. Oxygen atoms adjacent to oxygen vacancies donate some of their electron density and hence shift slightly towards higher binding energies

Peak 3 (532 eV) was assigned to oxygen in the form of hydroxides or oxyhydroxides ($In(OH)_3$ & -OOH)

Peak 4 accounts for impurities (O-like) present in the sample

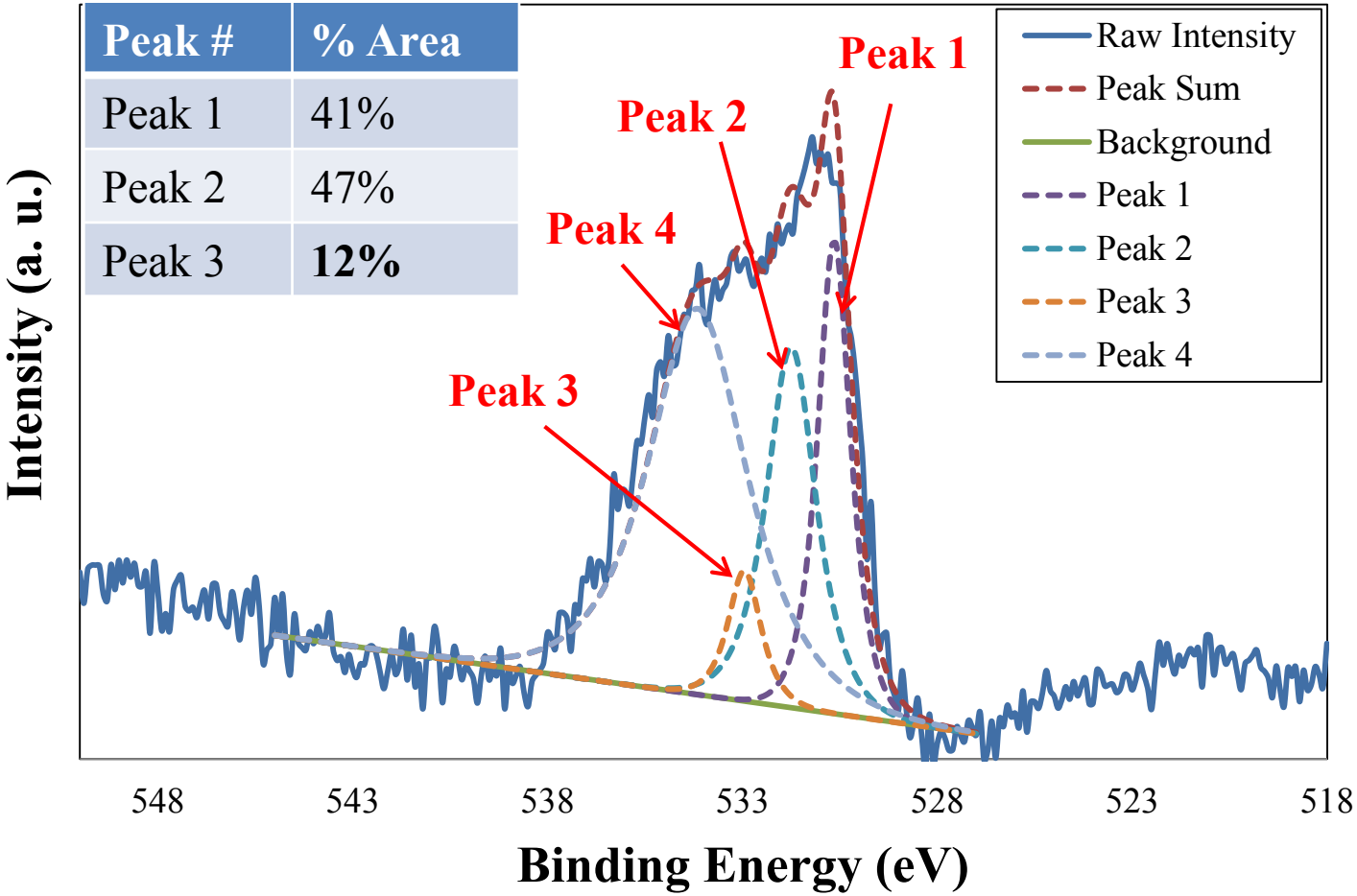
Before the fuel cell performance test, ITO contains less than 3% of hydroxides or oxyhydroxides.

Donley, C., et al., Langmuir, 18 (2001) 450-457.
Kim, H.-S., et al., Vacuum, 93 (2013) 7-12.

Peak fitting was done using XPS Peak Fit (Freeware). The Chinese University of Hong Kong

Technical Accomplishments. XPS results for O1s after Fuel Cell Performance Test: Anode

Peak #	% Area
Peak 1	41%
Peak 2	47%
Peak 3	**12%**



Peak 1 (530 eV) was assigned to oxides in the ITO.

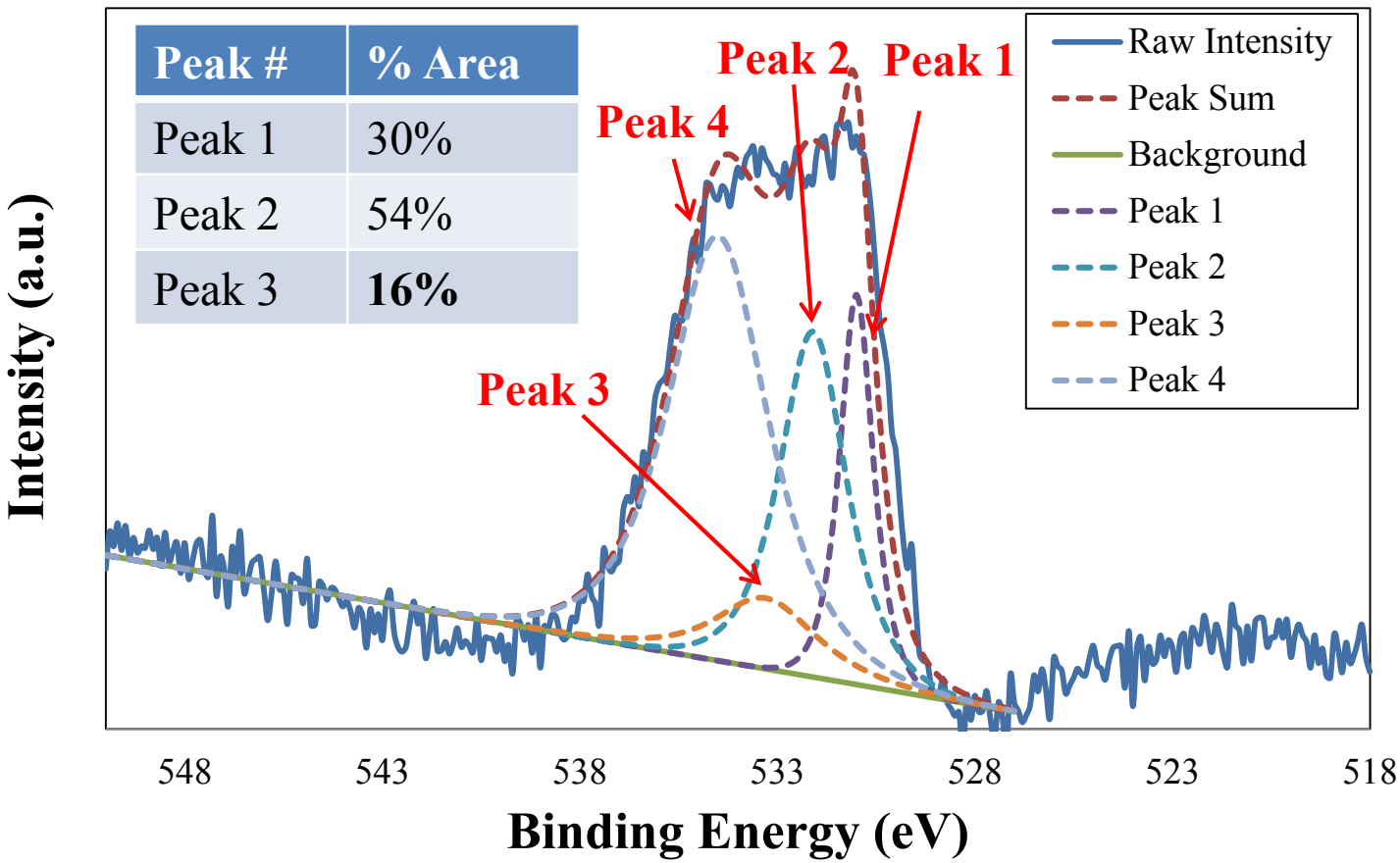
Peak 2 (531 eV) was assigned to oxide atoms adjacent to oxygen vacancies.

Peak 3 (532 eV) was assigned to oxygen in the form of hydroxide and oxyhydroxide.

Peak 4 accounts for impurities, and was included to improve the overall fitting.

After the fuel cell performance test, the surface concentration of hydroxide and oxyhydroxide in ITO increased to approx 12% (initially was around 3%)

Technical Accomplishments. XPS results for O1s after Fuel Cell Performance Test: Cathode



Peak #	% Area
Peak 1	30%
Peak 2	54%
Peak 3	**16%**

Peak 1 (530 eV) was assigned to oxides in the ITO.

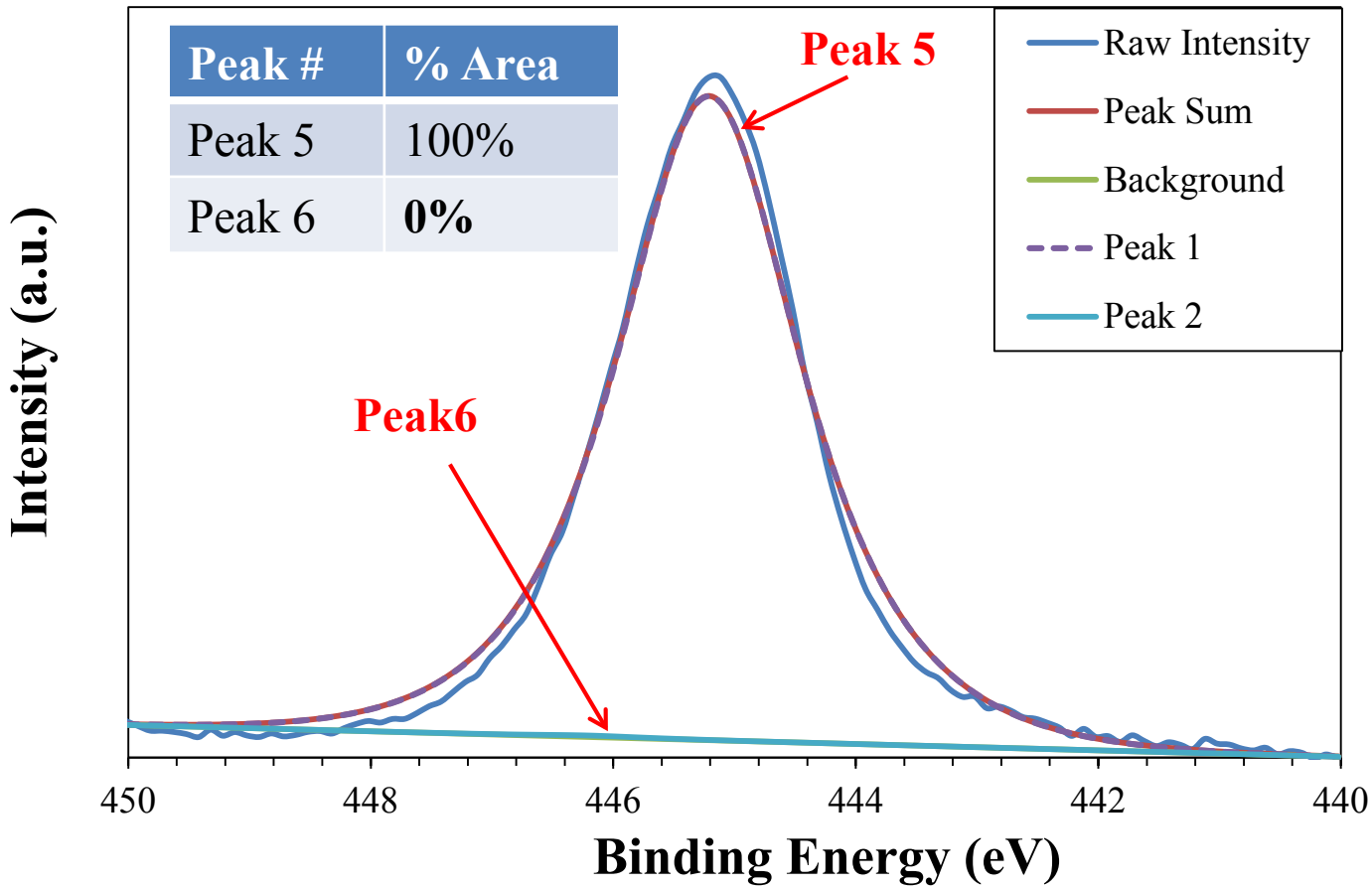
Peak 2 (531 eV) was assigned to oxide atoms adjacent to oxygen vacancies.

Peak 3 (532 eV) was assigned to oxygen in the form of hydroxide and oxyhydroxide.

Peak 4 accounts for impurities, and was included to improve the overall fitting.

After the fuel cell performance test, the surface concentration of hydroxide and oxyhydroxide in ITO increased to approx 16%. This concentration was higher than in the anode side (12%)

Technical Accomplishments. XPS results for $In3d_{5/2}$ Before Fuel Cell Performance Test



Peak #	% Area
Peak 5	100%
Peak 6	**0%**

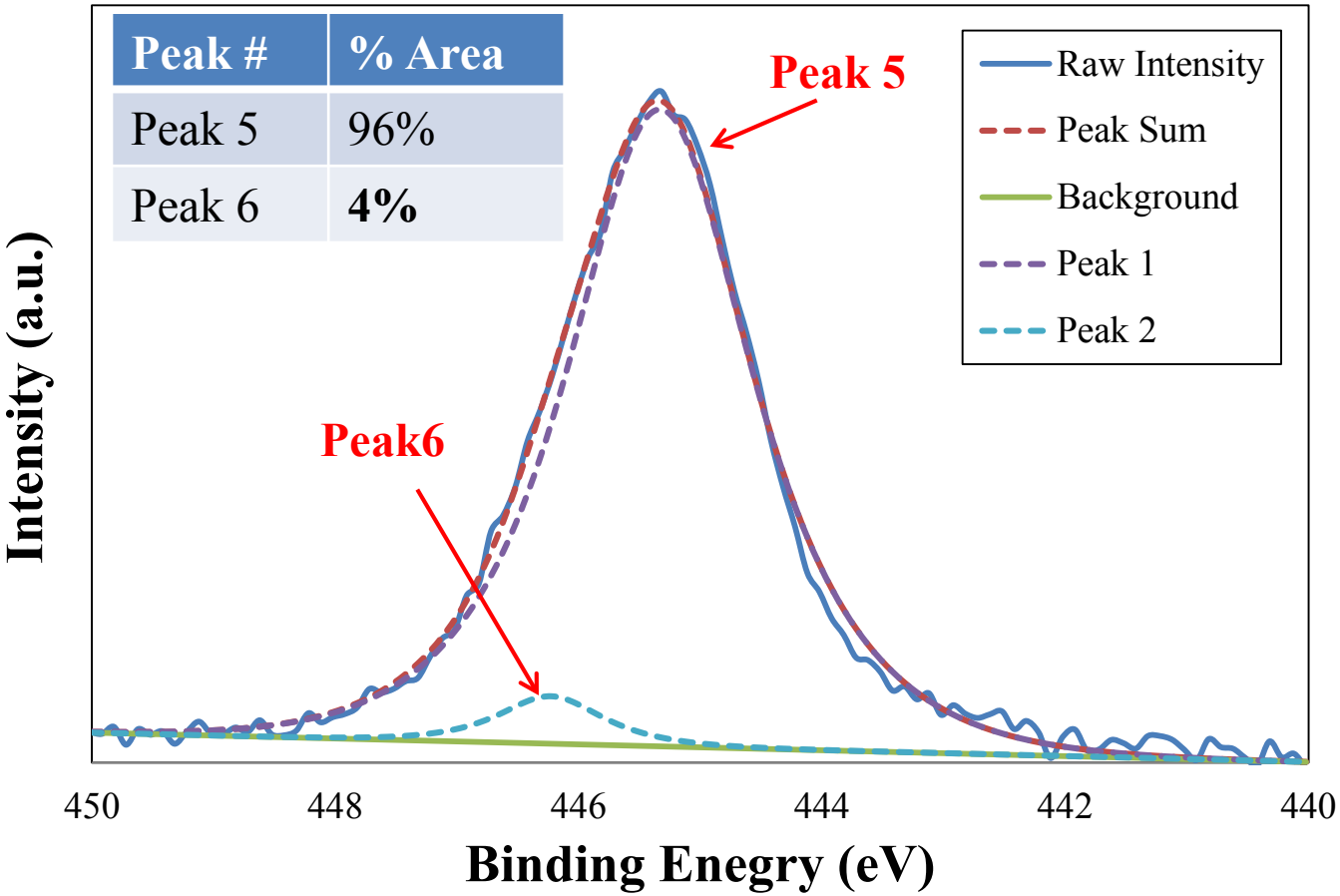
Peak 5 (445 eV) was assigned to **In^{3+} in the oxide** (ITO).

Peak 6 (446 eV) was assigned to In3+ adjacent to hydroxides and oxyhydroxides.

References used in the assignments:
Donley, C., et al., Langmuir, 18 (2001) 450-457.
Kim, H.-S., et al., Vacuum, 93 (2013) 7-12

Before the fuel cell performance test, In^{3+} was only in the form of oxides (ITO). The concentration of hydroxide and oxy-hydroxides was neglectible.

Technical Accomplishments. XPS results for $In3d_{5/2}$ After Fuel Cell Performance Test: Anode



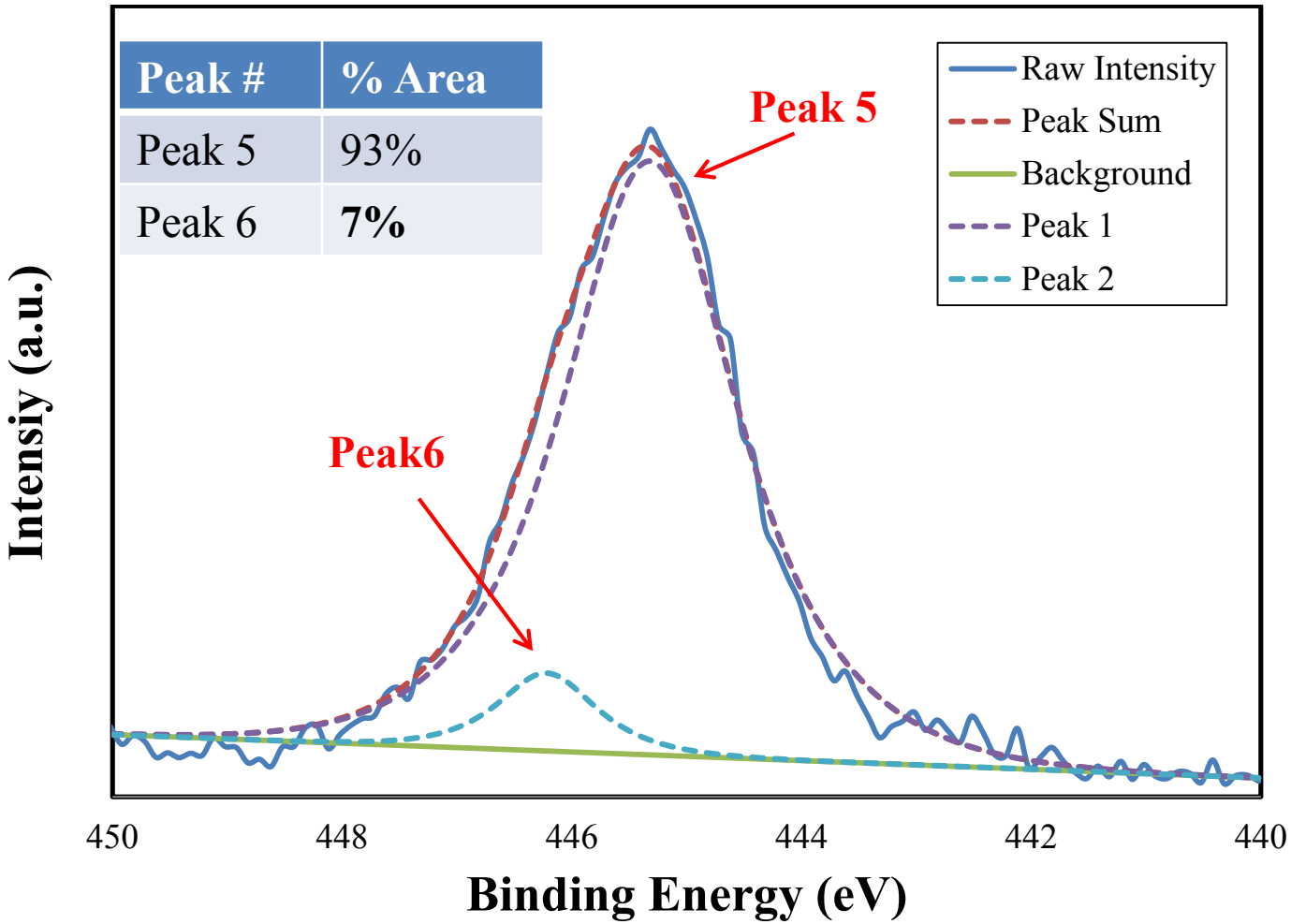
Peak #	% Area
Peak 5	96%
Peak 6	**4%**

Peak 5 (445 eV) was assigned to **In^{3+} in the oxide** (ITO).

Peak 6 (446 eV) was assigned to In^{3+} adjacent to **hydroxides** and oxyhydroxides.

After the fuel cell performance test, we detected the formation of small amounts of hydroxide and oxy-hydroxides in the anode catalyst. The concentration (4%) is lower than the calculated from O1s curve fitting probably because the Peak 4 (impurities) affects the fitting. A hydroxide content of 4% is a more accurate estimate.

Technical Accomplishments. XPS results for $In3d_{5/2}$ After Fuel Cell Performance Test: Cathode



Peak #	% Area
Peak 5	93%
Peak 6	**7%**

Peak 5 (445 eV) was assigned to **In^{3+} in the oxide** (ITO).

Peak 6 (446 eV) was assigned to In^{3+} adjacent to **hydroxides** and oxyhydroxides.

After the fuel cell performance test, the concentration of hydroxides in the ITO cathode electrocatalyst was estimated at 7%

In closing: the XPS analysis conclusively confirms that hydroxide formation will inhibit the performance of the ITO support. ITO is therefore unsuitable for use as a support in the MEA.

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 m^2/g
    (50 m^2/g overall target)
  - High durability upon aggressive potential cycling (including in MEAs)
    (NTCNA protocol, performed at IIT and at NTCNA)
  - High performance – RDE experiments
- A number of non-RuO_2 supports have been evaluated and found to be stable
- Optimization of Pt/RTO (on down-selected support)
- New stable class of non-carbon supports (ITO – lowering / eliminating Ru). Great RDE results but not translated to MEA. ITO degrades under MEA conditions, shown by XPS
- In collaboration with Nissan North America Inc., extensive benchmarking of state-of-the-art electrocatalysts and electrocatalyst supports has been performed.
- Cost model suggests no significant cost disadvantages

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 of > 10 S/cm (5 S/cm overall target)
- BET surface areas of > 250 m^2/g (50 m^2/g overall target)
- Excellent support durability upon aggressive potential cycling + good MEA performance and durability

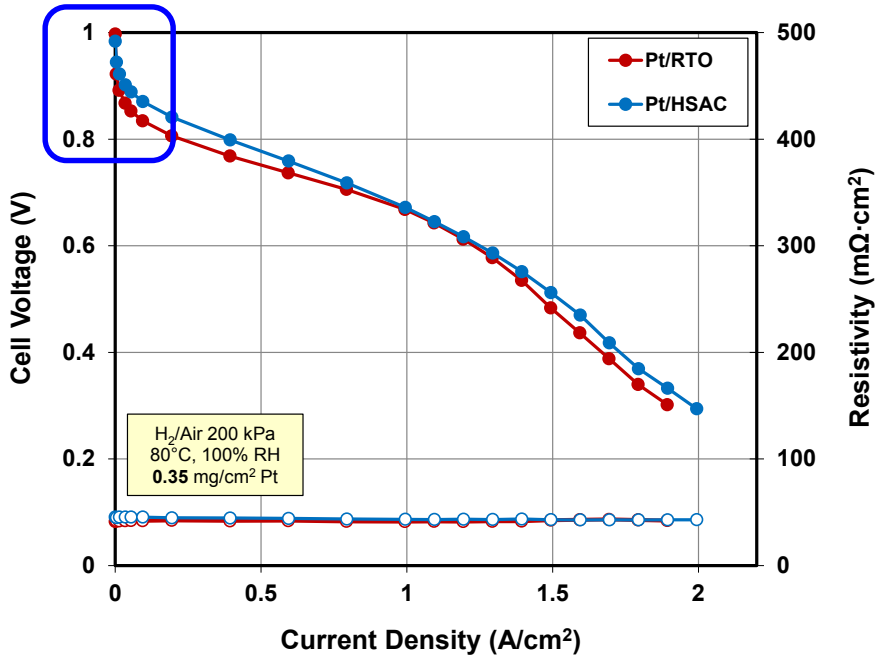
Collaborations: With Nissan, North America Inc. on benchmarking, durability testing, MEAs manufacture etc.

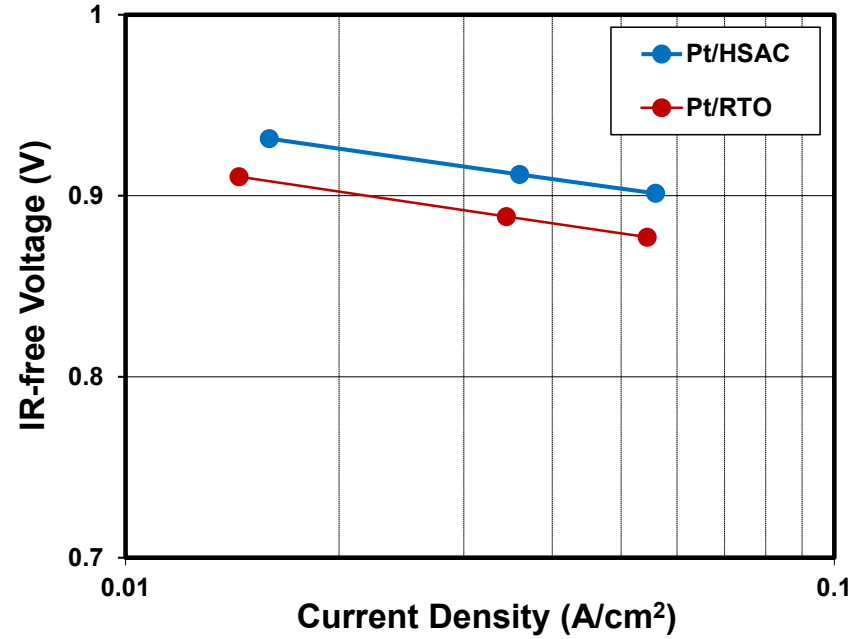
Supplementary Slides

Acronyms Used in the Presentation

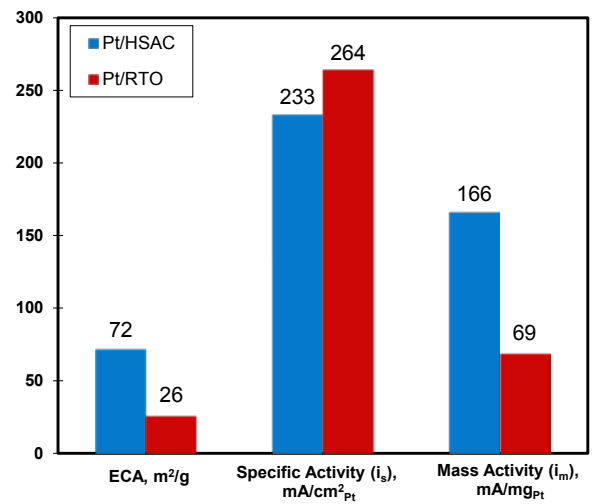
ITO	Indium tin oxide
NHE	Normal hydrogen electrode
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
CV	Cyclic voltammetry
ORR	Oxygen reduction reaction
ECSA	Electrochemical surface area

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Kinetic Properties of Pt/RTO CL

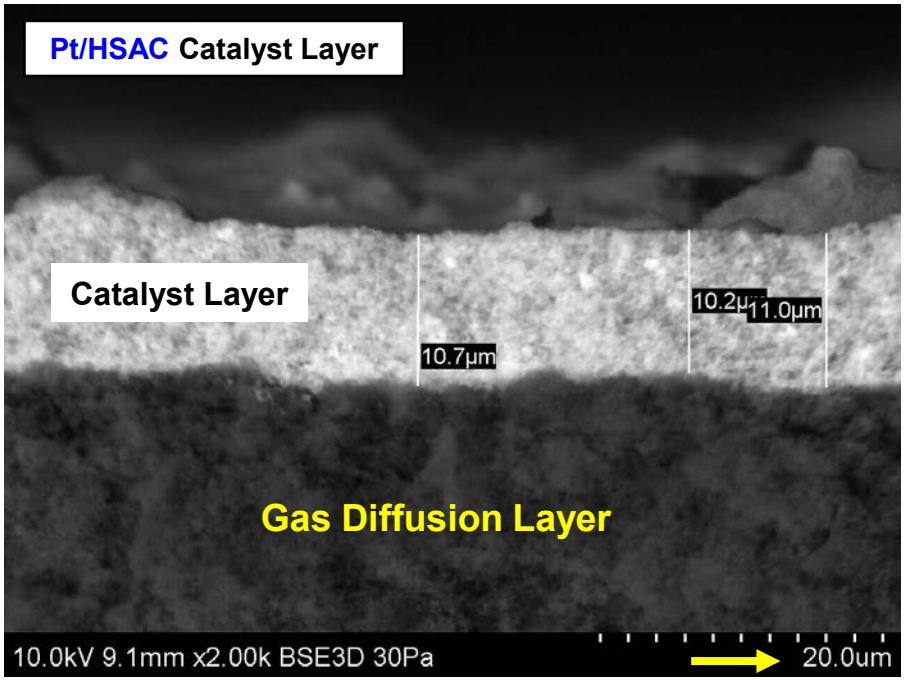


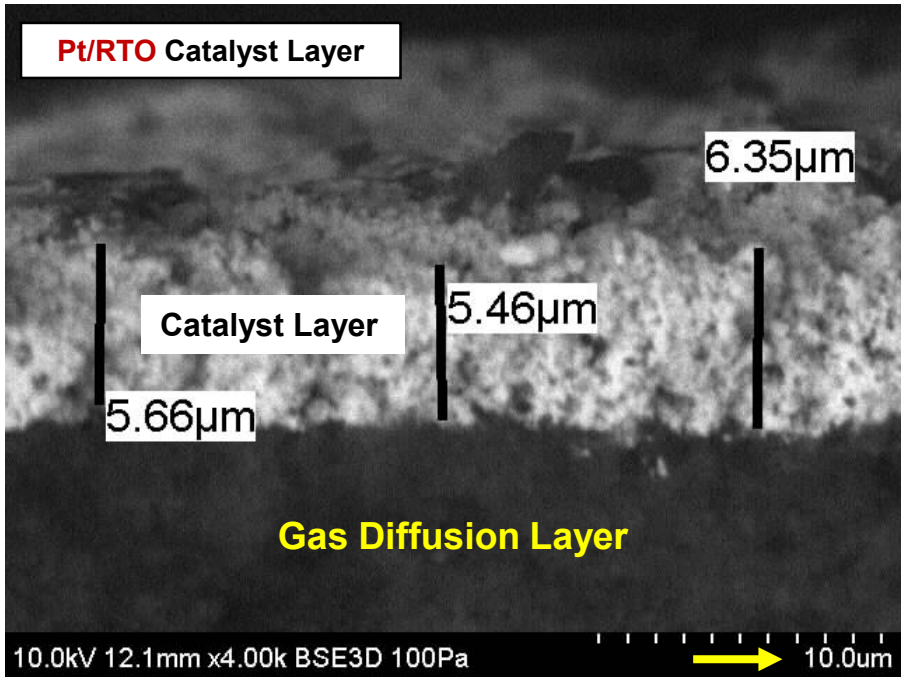


- **Some kinetic losses are observed for Pt/RTO, due to its larger Pt particle size and unoptimized particle dispersion, consistent with the TEM micrographs.**
- **Even though the mass activity of Pt/RTO is lower than Pt/HSAC, its overall iV performance especially at higher current densities is comparable to Pt/HSAC.**



Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; SEM Images of Pt/HSAC and Pt/RTO Catalyst Layer





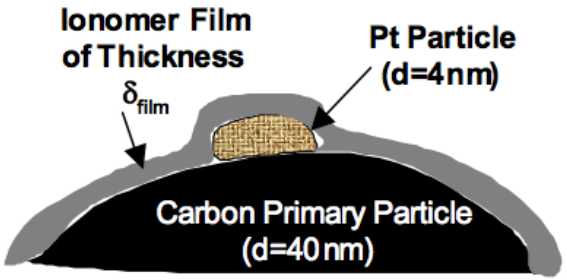
	Pt/HSAC	Pt/RTO
CL thickness (µm)	11	**5.5**
I/C mass ratio	0.9	0.9
BET Surface Area (m^2/g)	313	**39**
ε_i (ionomer volume fraction)	0.21	**0.66**

$$\varepsilon_i \equiv \frac{V_{I,wet}}{V_{cath}} = \left(\frac{I}{C}\right)\frac{10}{f_t d_{I,dry}}\left(1 + \frac{M_w d_{I,dry}\lambda}{d_w EW}\right)^*$$

- **RTO is denser than carbon and has significantly lower surface area.**
- **The Pt/RTO CL is much thinner than Pt/HSAC.**
- **The ionomer volume fraction (ε_i) is much higher in Pt/RTO.**

*J. Elecrochem. Soc. 156 (8) B970-B980 (2009)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Analysis of the Pt/RTO Catalyst Layer



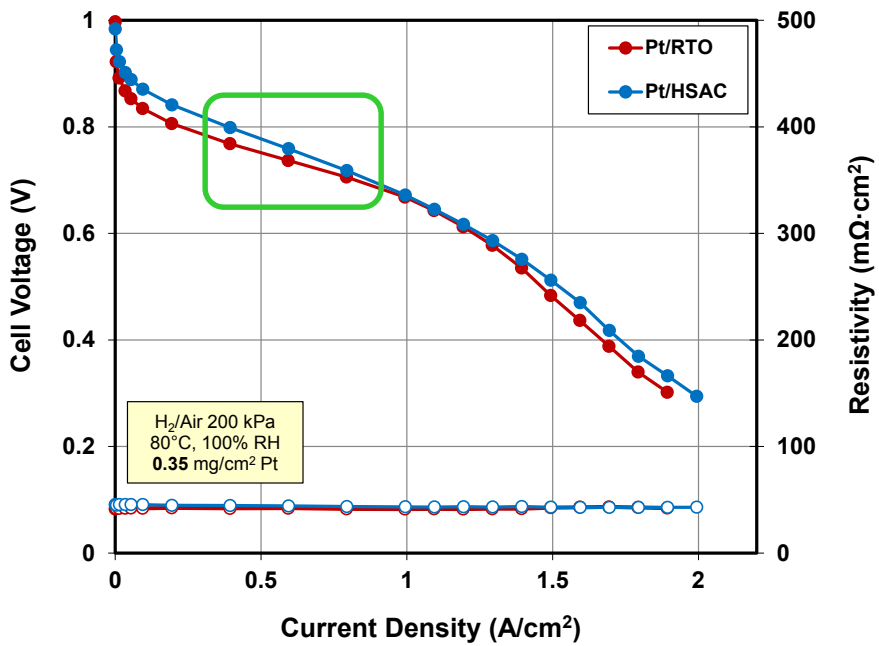
$$\sigma\ (\text{ionomer film thickness}) = \frac{V_{Nafion}}{A_{eff}} = \frac{V_{Nafion}}{(1-\gamma)A_{BET} \cdot 10^4 \cdot m_{cat}}$$

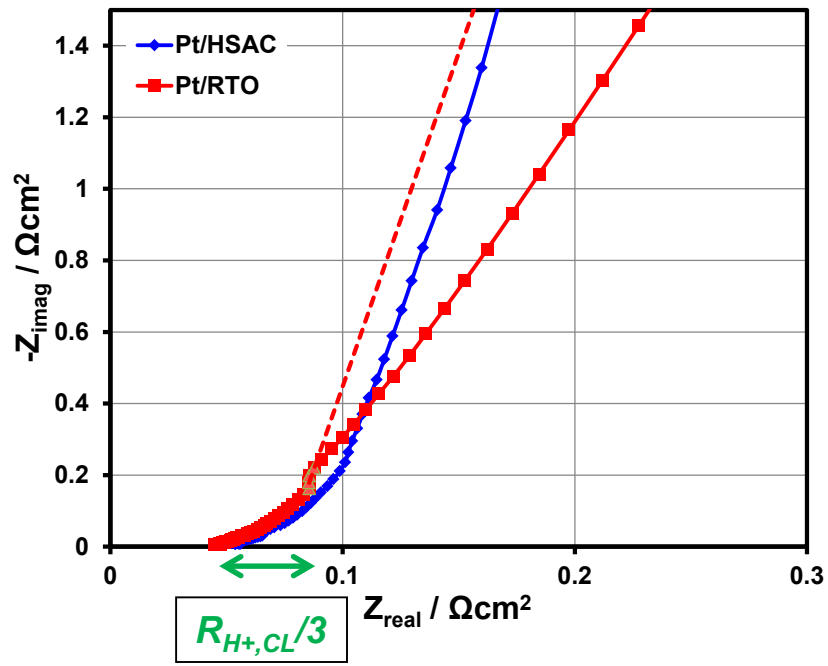
	Pt/HSAC	Pt/RTO
I/C mass ratio	0.9	0.9
BET Surface Area (m^2/g)	313	39
ε_i (ionomer volume fraction)	0.21	0.66
σ_i (ionomer film thickness)	**1.2**	**7.2**

- **The thickness (σ) of the ionomer mixed with the catalyst can be estimated by dividing the volume of Nafion® by the effective catalyst surface area (A_{eff}), the area over which Nafion® could spread.**
- **A_{eff} ≈ BET surface area for non-microporous supports such as RTO.**
- **The ionomer film thickness will be significantly higher for Pt/RTO due to its low surface area.**

Ignaszak, Gyenge (2009) and Gasteiger, Mathias (2003)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; H^+ Transport Properties of Pt/RTO CL

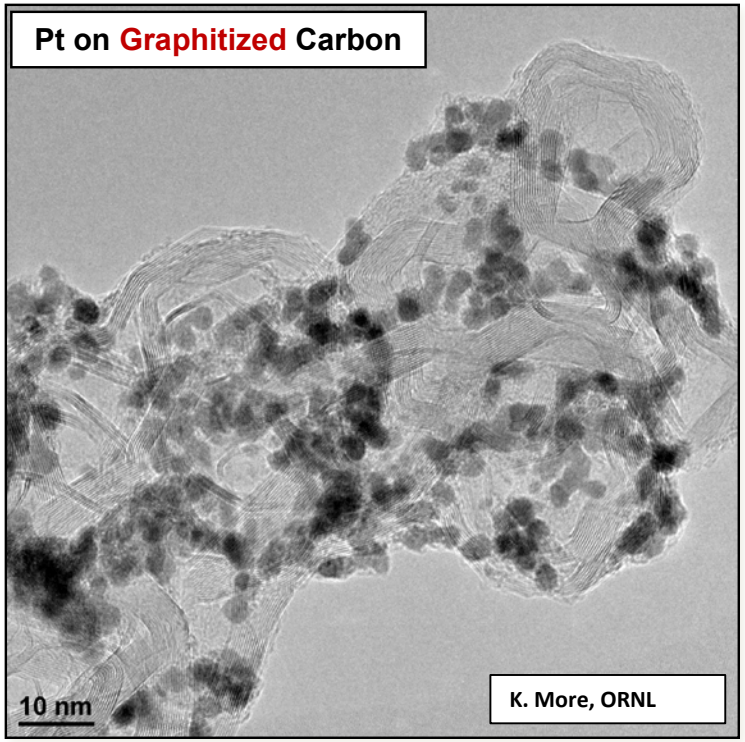


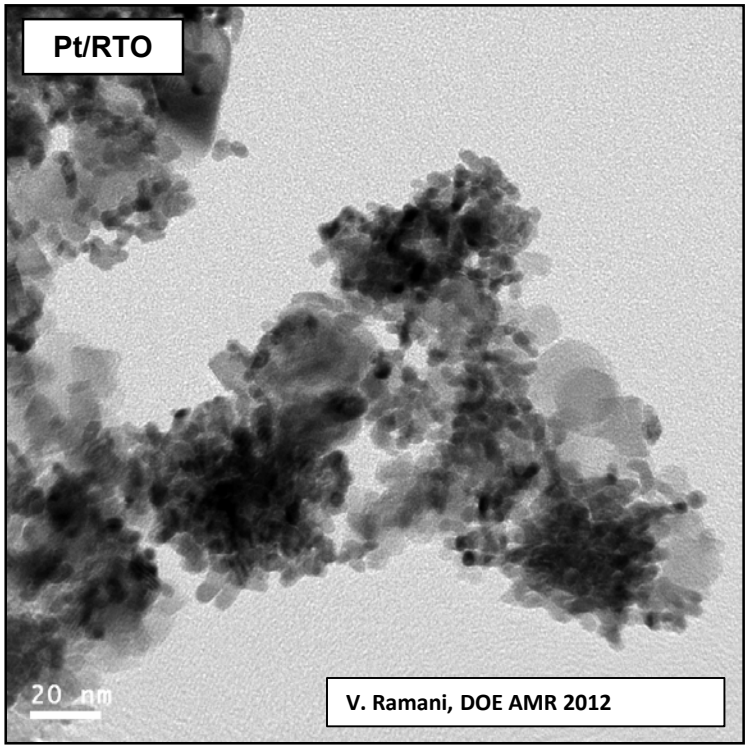


- **Even though, the estimated ionomer film thickness and ionomer volume fraction are very different, the ohmic losses between the 2 MEAs are comparable.**
- **Questions arise on the proton conductivity of Nafion® thin films vs. bulk Nafion® and how this affects catalyst layer H^+ transport.**

	Pt/HSAC	Pt/RTO
σ_i (ionomer film thickness)	**1.2**	**7.2**
$R_{membrane}$ (mΩ·cm²)	49	45
$R_{H+,cathode}$ (mΩ·cm²)	**150**	**90**
$\sigma_{H+,\ cathode}$ **(mS/cm)**	**0.007**	**0.006**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; TEM Images of Pt/GKB and Pt/RTO Catalyst





- **Pt/Graphitized Ketjen Black (GKB) would be a good comparison for Pt/RTO since both GKB & RTO have low surface areas and low microporosity (almost no pores < 2nm)**
- **An improved Pt/RTO catalyst may result if it had comparable Pt particle density as Pt/GKB.**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Optimization of Pt Loading on Low Surface Area RTO

- **30% Pt/GKB would be a good comparison for Pt/RTO since both GKB & RTO have low surface areas and low microporosity (almost no pores < 2nm).**
- **The target wt% of Pt for Pt/RTO should be 10%, in order to match the Pt particle density of 30% Pt/GKB.**

From TEM measurements, the average diameter of Pt particles in 30% Pt/GKB is **5 nm**, therefore the volume of 1 Pt particle would be:

$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi(2.5\times10^{-9}m)^3 = 6.54\times10^{-26}\ m^3\ \text{Pt}$$

The surface area of 1 Pt particle would be:

$$4\pi r^2 = 4\pi(2.5\times10^{-9}\text{m})^2 = 7.85\times10^{-17}\ \text{m}^2\ \text{Pt}$$

The mass ratio of Pt to carbon is:

$$\frac{0.3\text{g Pt}}{0.7\text{g Carbon}} = 0.43\ \frac{\text{g Pt}}{\text{g C}}$$

The density of Pt is **21.45 g/cm³** so the volume of Pt per gram C is:

$$\frac{0.43\ \text{g Pt}}{\text{g C}}\times\frac{1\ \text{cm}^3\ \text{Pt}}{21.45\ \text{g Pt}}\times\frac{1\ \text{m}^3\ \text{Pt}}{100^3\ \text{cm}^3\ \text{Pt}} = 2.0\times10^{-8}\ \frac{\text{m}^3\ \text{Pt}}{\text{g C}}$$

The number of Pt particles per gram of carbon would be:

$$2\times10^{-8}\ \frac{\text{m}^3\ \text{Pt}}{\text{g C}}\times\frac{1\ \text{Pt particle}}{6.54\times10^{-26}\ \text{m}^3\text{Pt}} = 3.0\times10^{17}\ \frac{\text{Pt particles}}{\text{g C}}$$

The surface area of graphitized Ketjen Black (GKB) is **150 m²/g** so the number of Pt particles per m² C is:

$$3.0\times10^{17}\ \frac{\text{Pt particles}}{\text{g C}}\times\frac{1\ \text{g C}}{150\ \text{m}^2\ \text{C}} = 2.0\times10^{15}\ \frac{\text{Pt particles}}{\text{m}^2\ \text{C}}$$

Therefore, the 'roughness factor' or the ratio surface area of Pt/surface area of C is:

$$2.0\times10^{15}\ \frac{\text{Pt particles}}{\text{m}^2\ \text{C}}\times\frac{7.85\times10^{-17}\ \text{m}^2\ \text{Pt}}{1\ \text{Pt particle}} = \boxed{0.16\ \frac{\text{m}^2\ \text{Pt}}{\text{m}^2\ \text{C}}}$$

This 'roughness factor' obtained for Pt/GKB will have to be matched using the RTO support. Similar calculations were performed for the RTO support (**39 m²/g** surface area).

The number of Pt particles per gram of RTO is:

$$2.0\times10^{15}\ \frac{\text{Pt particles}}{\text{m}^2\ \text{RTO}}\times\frac{39\ \text{m}^2\ \text{RTO}}{1\ \text{g RTO}} = 8.0\times10^{16}\ \frac{\text{Pt particles}}{\text{g RTO}}$$

The volume of Pt per gram of RTO would be:

$$8.0\times10^{16}\ \frac{\text{Pt particles}}{\text{g RTO}}\times\frac{6.54\times10^{-26}\ \text{m}^3\text{Pt}}{1\ \text{Pt particle}} = 5.2\times10^{-9}\ \frac{\text{m}^3\ \text{Pt}}{\text{g RTO}}$$

Since the density of Pt is **21.45 g/cm³**, the necessary mass ratio of Pt to RTO is:

$$5.2\times10^{-9}\ \frac{\text{m}^3\ \text{Pt}}{\text{g RTO}}\times\frac{21.45\ \text{g Pt}}{1\ \text{cm}^3\ \text{Pt}}\times\frac{100^3\ \text{cm}^3\ \text{Pt}}{1\ \text{m}^3\ \text{Pt}} = 0.11\ \frac{\text{g Pt}}{\text{g RTO}}$$

Therefore, the target Pt wt.% for Pt/RTO where RTO has a surface area of **39 m²/g** should be:

$$\frac{0.11\text{g Pt}}{1.11\ \text{g Pt/RTO}} = 10\%\ \text{Pt}$$

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Analysis of the Pt/RTO Catalyst Layer

Estimation of Ionomer Volume Fraction

	50% Pt/HSAC	40% Pt/RTO
CL thickness (μm)	11	**5.5**
I/C mass ratio	0.9	
BET Surface Area (m^2/g)	313	**39**
ε_i (ionomer volume fraction)	0.2	**0.7**

Estimation of Ionomer Film Thickness

	50% Pt/HSAC	40% Pt/RTO
I/C mass ratio	0.9	
BET Surface Area (m^2/g)	313	39
ε_i (ionomer volume fraction)	0.2	0.7
σ_i (estimated ionomer film thickness)	**1.2**	**7.2**

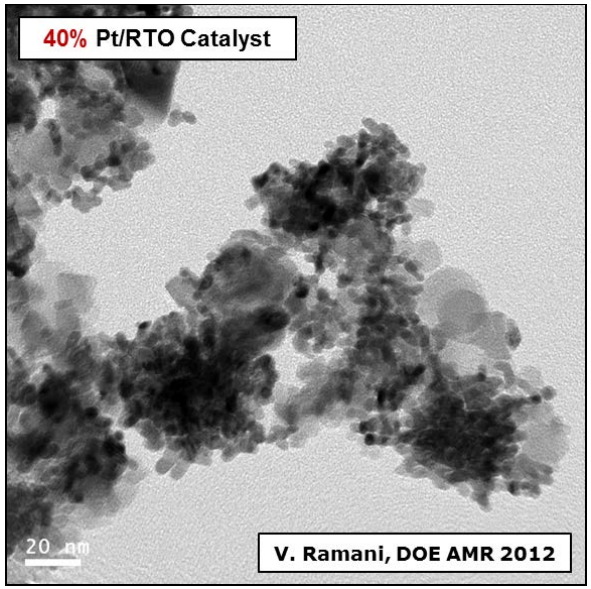
$$\varepsilon_i \equiv \frac{V_{\mathrm{I,wet}}}{V_{\mathrm{cath}}} = \left(\frac{I}{C}\right)\frac{10}{f_t d_{\mathrm{I,dry}}}\left(1 + \frac{M_w d_{\mathrm{I,dry}} \lambda}{d_w \mathrm{EW}}\right)$$

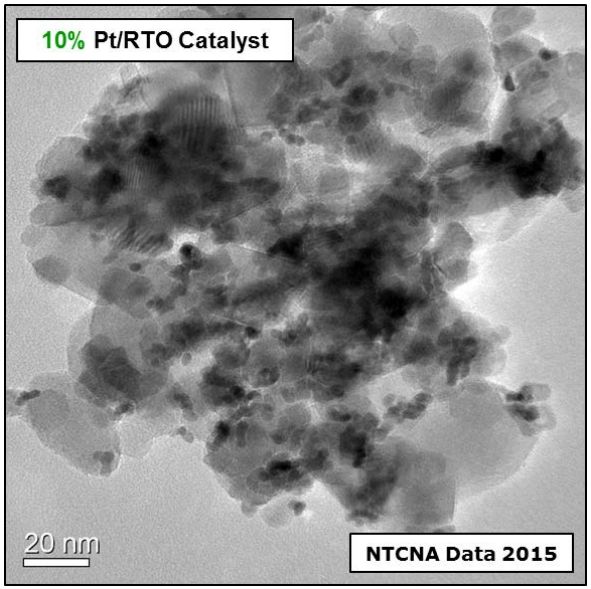
$$\sigma\ (\text{ionomer film thickness}) = \frac{V_{\mathrm{Nafion}}}{A_{\mathrm{eff}}} = \frac{V_{\mathrm{Nafion}}}{(1-\gamma)A_{\mathrm{BET}} \cdot 10^4 \cdot m_{\mathrm{cat}}}$$

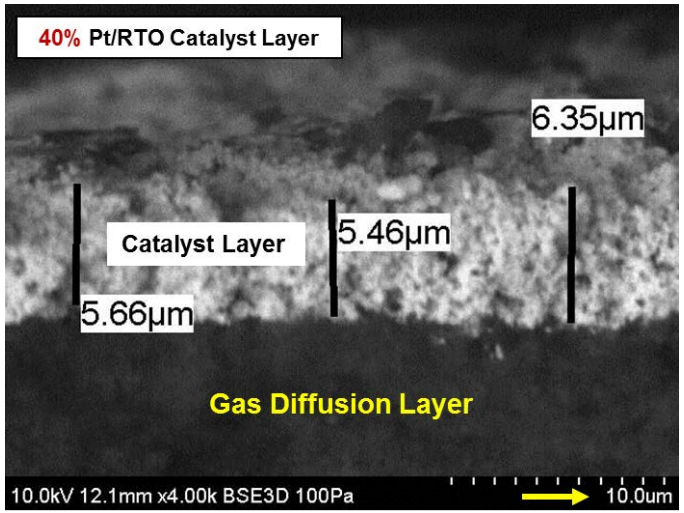
- **RTO is denser than carbon and has lower surface area, so the Pt/RTO CL is much thinner than Pt/HSAC. For the same I/S wt. ratio, the ionomer volume fraction (ε_i) would be higher for Pt/RTO.**
- **The thickness (σ) of the ionomer mixed with the catalyst can be estimated by dividing the volume of Nafion® by the effective catalyst surface area (A_{eff}), the area over which Nafion® could spread.**
- **Since $A_{eff} \approx$ BET surface area for non-microporous supports such as RTO, the ionomer film thickness will be significantly higher for Pt/RTO due to its low surface area.**

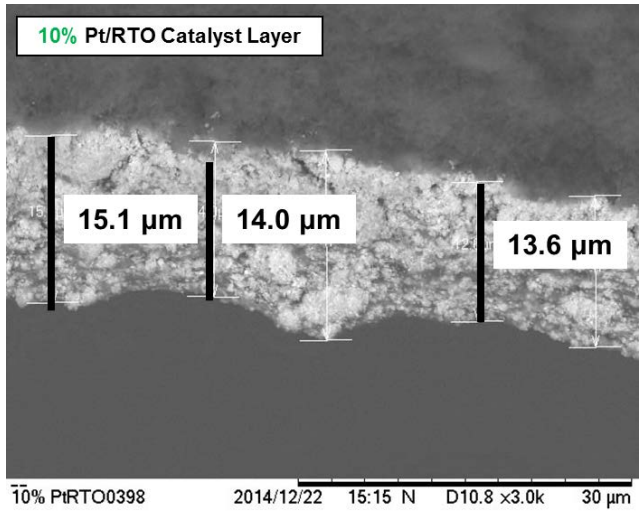
*J. Elecrochem. Soc. 156 (8) B970-B980 (2009)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; TEM & SEM Images of 40% and 10% Pt/RTO









- **For a 0.35 mg/cm^2 Pt loading cathode, the resulting catalyst layer thickness using 10% Pt/RTO is ~ 15 microns.**

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Analysis of the Pt/RTO Catalyst Layer

Estimation of Ionomer Volume Fraction

	40% Pt/RTO I/S = 0.9	10% Pt/RTO I/S = 0.3
Measured CL thickness (μm)	**5.5**	14.5
Measured BET Surface Area (m^2/g)	**40**	
ε_i (calculated ionomer volume fraction)	**0.7**	**0.1**

$$\varepsilon_i \equiv \frac{V_{I,wet}}{V_{cath}} = \left(\frac{I}{C}\right)\frac{10}{f_t d_{I,dry}}\left(1 + \frac{M_w d_{I,dry}\lambda}{d_w EW}\right)$$

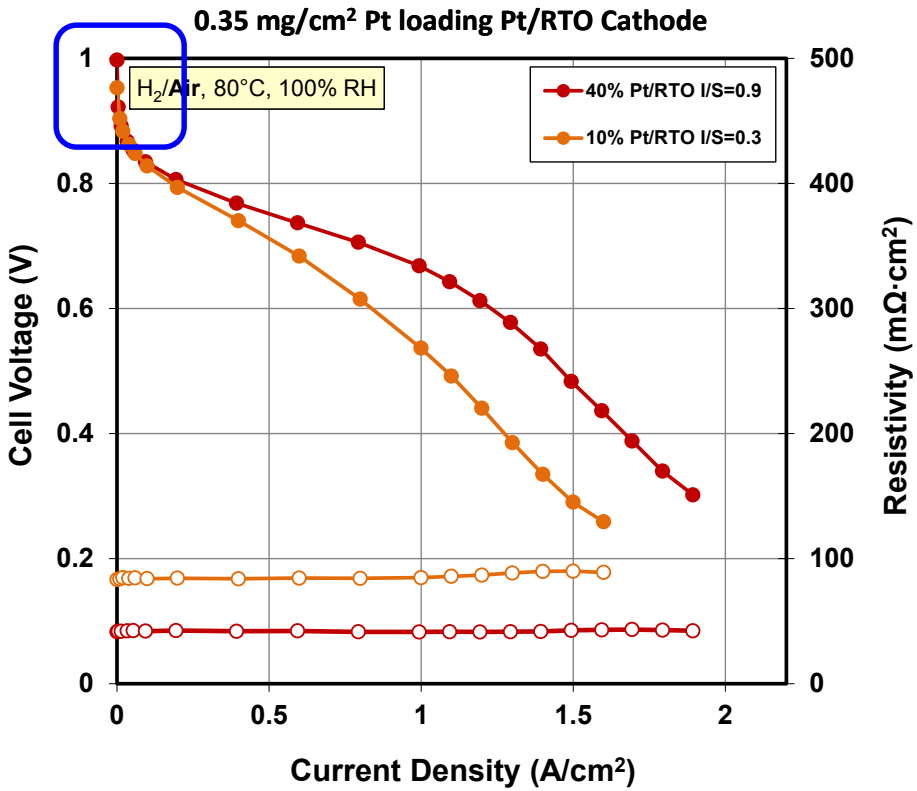
Estimation of Ionomer Film Thickness

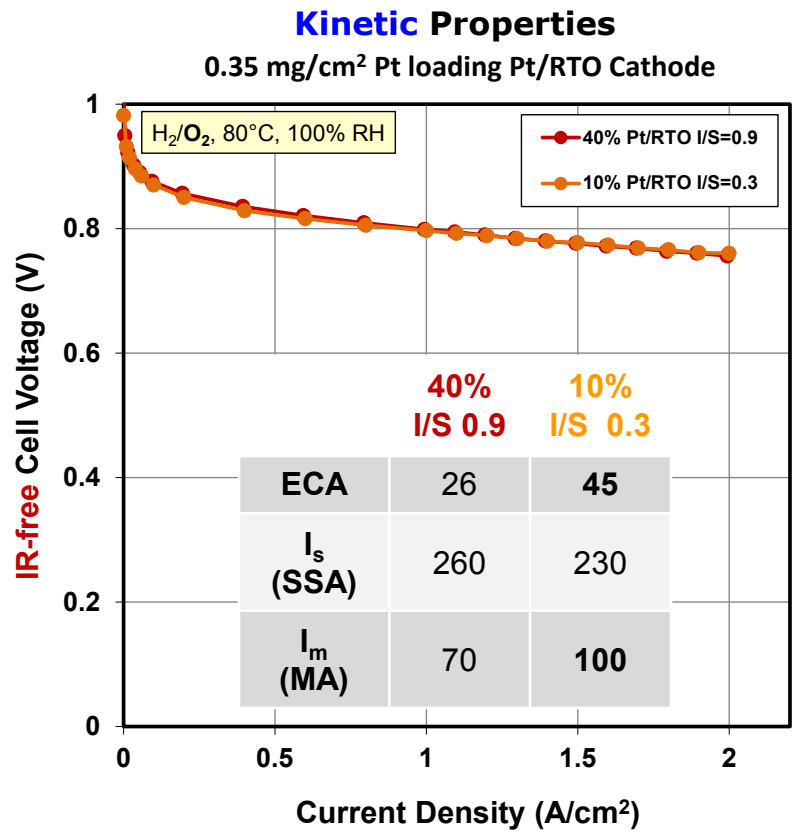
	40% Pt/RTO I/S = 0.9	10% Pt/RTO I/S = 0.3
ε_i (calculated volume fraction)	0.7	0.1
σ_i (calculated ionomer film thickness)	**7.2**	**3.1**

- **The thickness (σ) of the ionomer mixed with the catalyst can be estimated by dividing the volume of Nafion® by the effective catalyst surface area (A_{eff}), the area over which Nafion® could spread.**
- **The calculated ionomer volume fraction for the 10% Pt/RTO is 0.1 and the estimated ionomer film thickness is 3.1, values which are now more comparable to typical Pt on low surface area carbon (Pt/LSAC) cathodes.**

*J. Elecrochem. Soc. 156 (8) B970-B980 (2009)
J. Phys. Chem. C, 2009 113 (1)

Technical Accomplishments (IIT-Nissan): Pt/Non-carbon Research; Kinetic Properties of 40% and 10% Pt/RTO



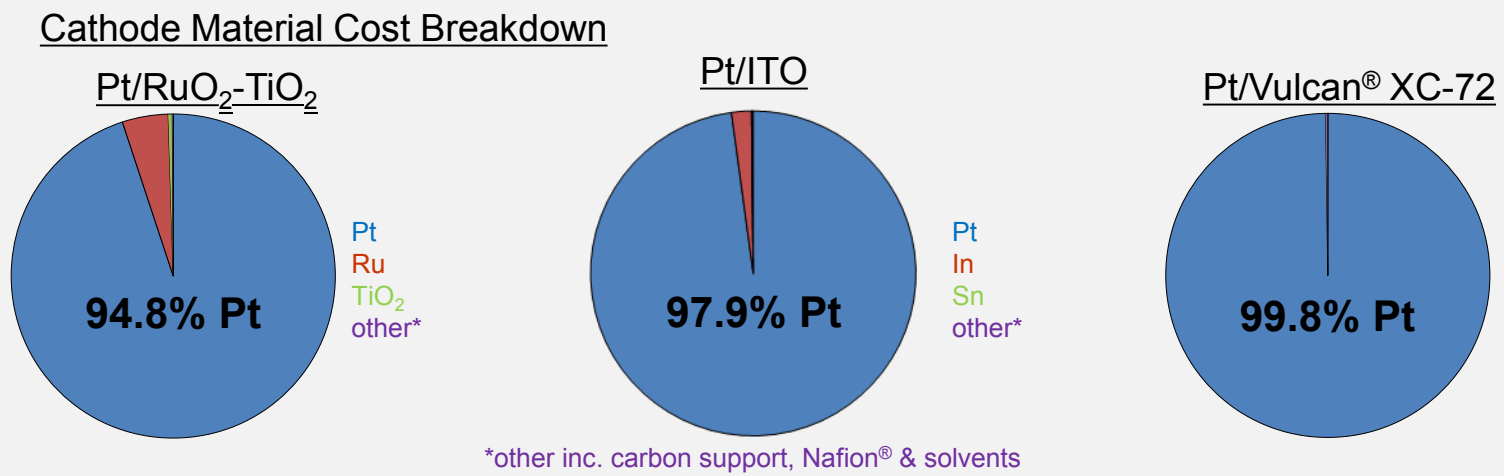


	40% I/S 0.9	10% I/S 0.3
ECA	26	**45**
I_s (SSA)	260	230
I_m (MA)	70	**100**

- **The 10% Pt/RTO MEA has lower iV performance due to ohmic losses (poor electronic conductivity).**
- **The HFR-corrected H_2-O_2 iV performance is identical for both MEAs, and higher ECA and mass activities are obtained with 10% Pt/RTO.**

Technical Accomplishments. Cost Model for Pt/RuO_2-TiO_2 & Pt/ITO

- **Material costs for production of Pt/RuO_2-TiO_2 and Pt/ITO electrodes as compared to Pt/Vulcan® XC-72**
  - **Vulcan® XC-72 data from 2008 FC System Cost Estimation from the DOE† (latest to include Pt/C cost)**
- **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

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

Previous results from 2014 AMR presentation

Technical Accomplishments: 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

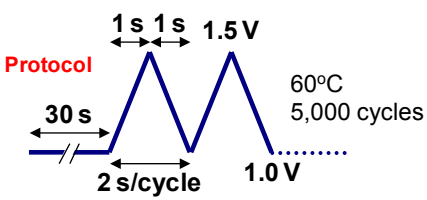
- **With durability considered, how do the two catalysts compare?**

A Durability Factor can be calculated for each catalyst

- **Durability Factor**

$$= \frac{\text{Mass Activity retention of Catalyst}}{\text{Mass Activity retention of Pt/non-Carbon}}$$

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



	Pt/RuO_2-TiO_2	Pt/ITO	Pt/Vulcan® XC-72
Mass Activity retention (loss)	86%	86*	59%
Durability Factor	1	1*	**0.69**

- Based on this protocol, Vulcan® XC-72 is only 69% as durable as the RuO_2-TiO_2 and ITO supports

	Pt/RuO_2-TiO_2	Pt/ITO	Pt/Vulcan® XC-72
Cathode Pt loading (mg_{Pt}/cm^2)	**0.35**	**0.35**	**0.18**
Rated Power (mW/cm^2)	650	650*	715
Pt (i.e. total Pt in electrode)	$1,718.45	$1,718.45	$1,203.42
Metal 1	$90.31 (Ru=$83.02)	$34.68 (In=$34.61)	$ -
other	$3.00 (est.)	$3.00 (est.)	$2.64
Total Material Cost ($)	$1,811.76	$1756.14	$1,206.06
Total Material Cost ($/$kW_{net}$)	$22.65	$21.95	$15.08
Durability Factor	1	1	0.69
Total Material Cost ($/$kW_{net}$) w/ durability	**$22.65**	**$21.95**	**$21.85**

- 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

Previous results from 2014 AMR presentation