ILLINOIS INSTITUTE OF TECHNOLOGY

NISSAN R&D AMERICAS

Zero Emission

Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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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: ~ 85%

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%

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. 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 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: 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

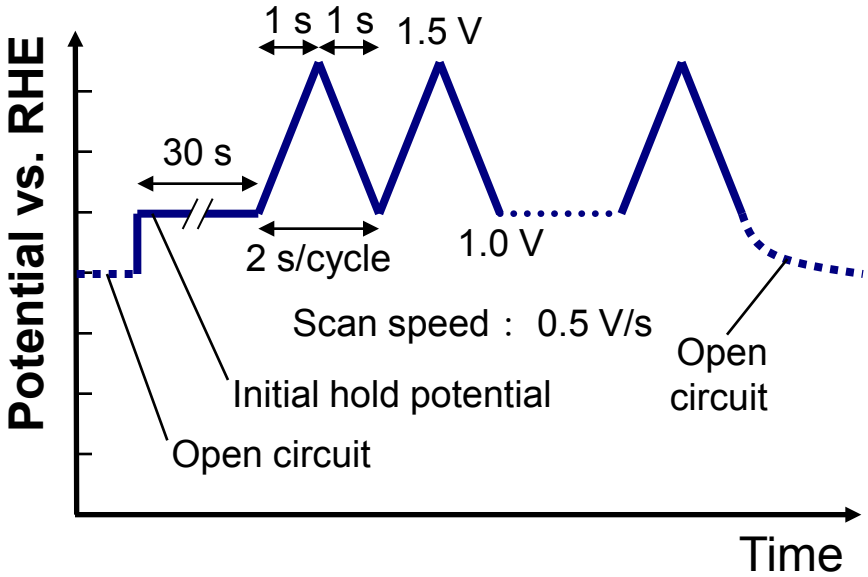
- Milestone 2 (End of Phase 2; Q3; 2013)
  - Synthesize a support that demonstrates at least:
    - 100 mS/cm proton conductivity [Current status > 120 mS/cm; stand-alone]
    - 5 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m^2/g BET surface area [Current status > 250m^2/g]
    - 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 [Under negotiation]
- GNG criterion (applied at end of Q1; 2012) – **PASSED in June 2012**

Approach: Milestones and GNG Criterion; Current Status

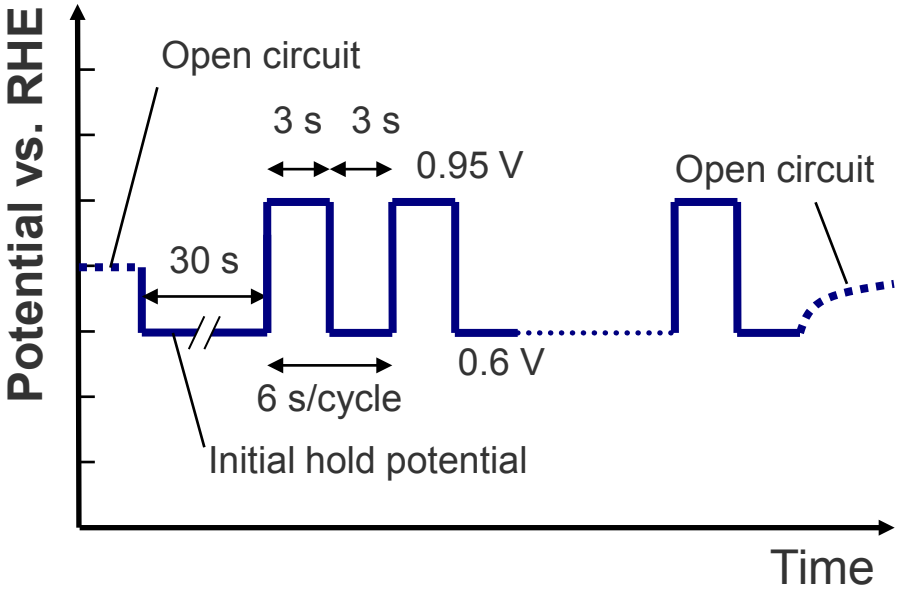
Milestone 1		RTO	RSO	RSO-sulfonated	Sulfated SnO_2	ITO
70 mS/cm proton conductivity		No	No	Yes	Yes	No
2 S/cm electron conductivity		Yes	Yes	Yes	No	No
50 m^2/g BET surface area		Yes	Yes	Yes	Yes	Yes
Durability in acidic electrolyte		Yes	Yes	No	N/A	Yes
Milestone 2						
100 mS/cm proton conductivity		No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

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

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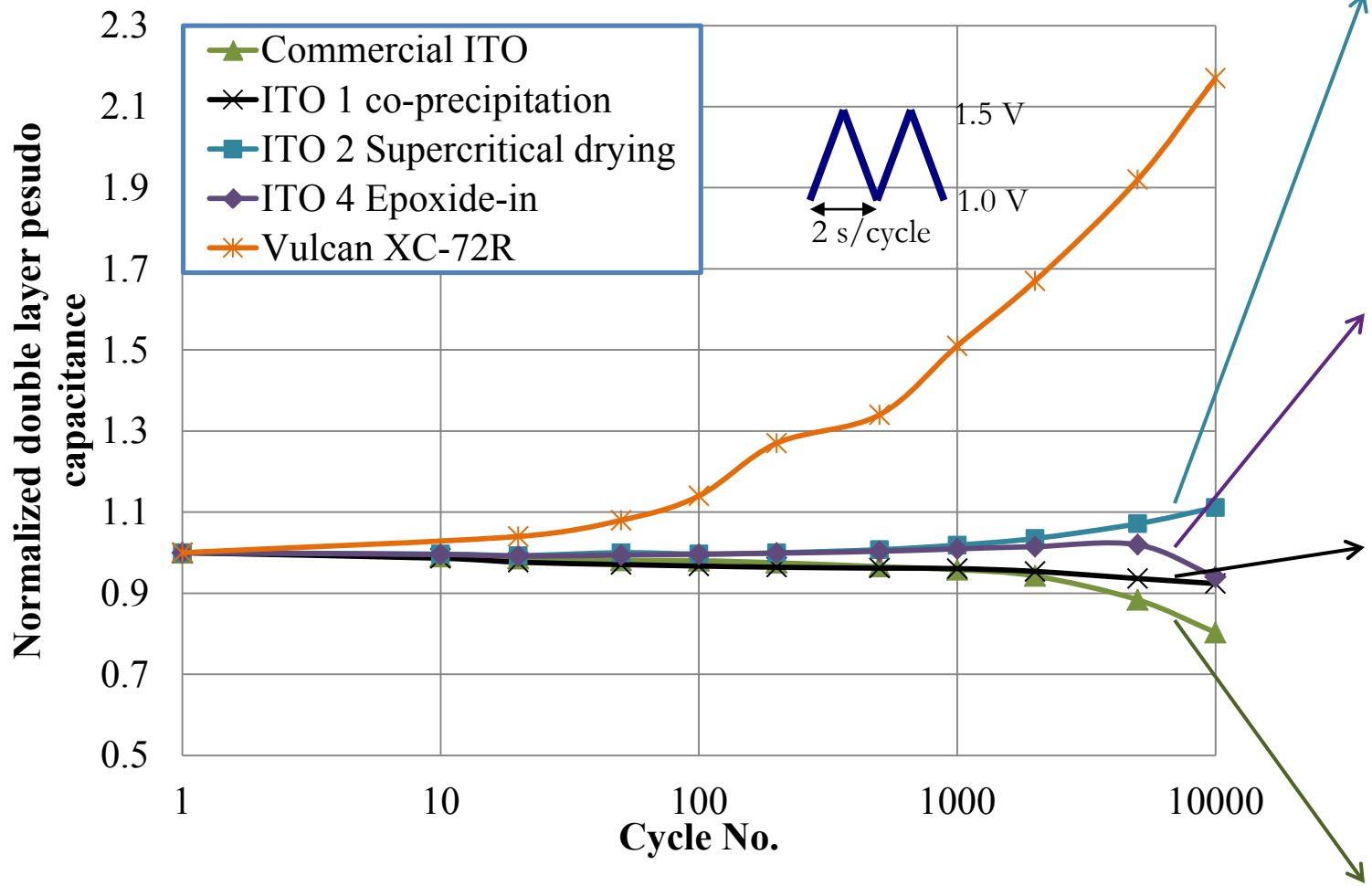
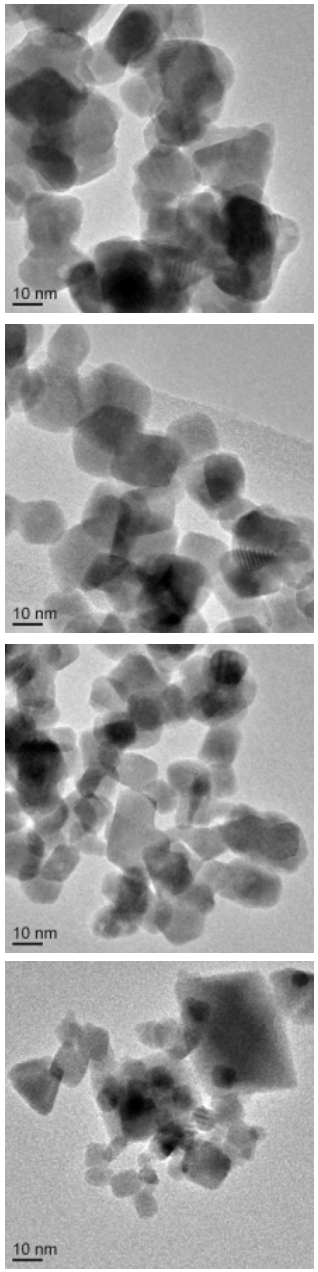
Technical Accomplishments: Electrochemical Stability of ITO (Support Corrosion Protocol)

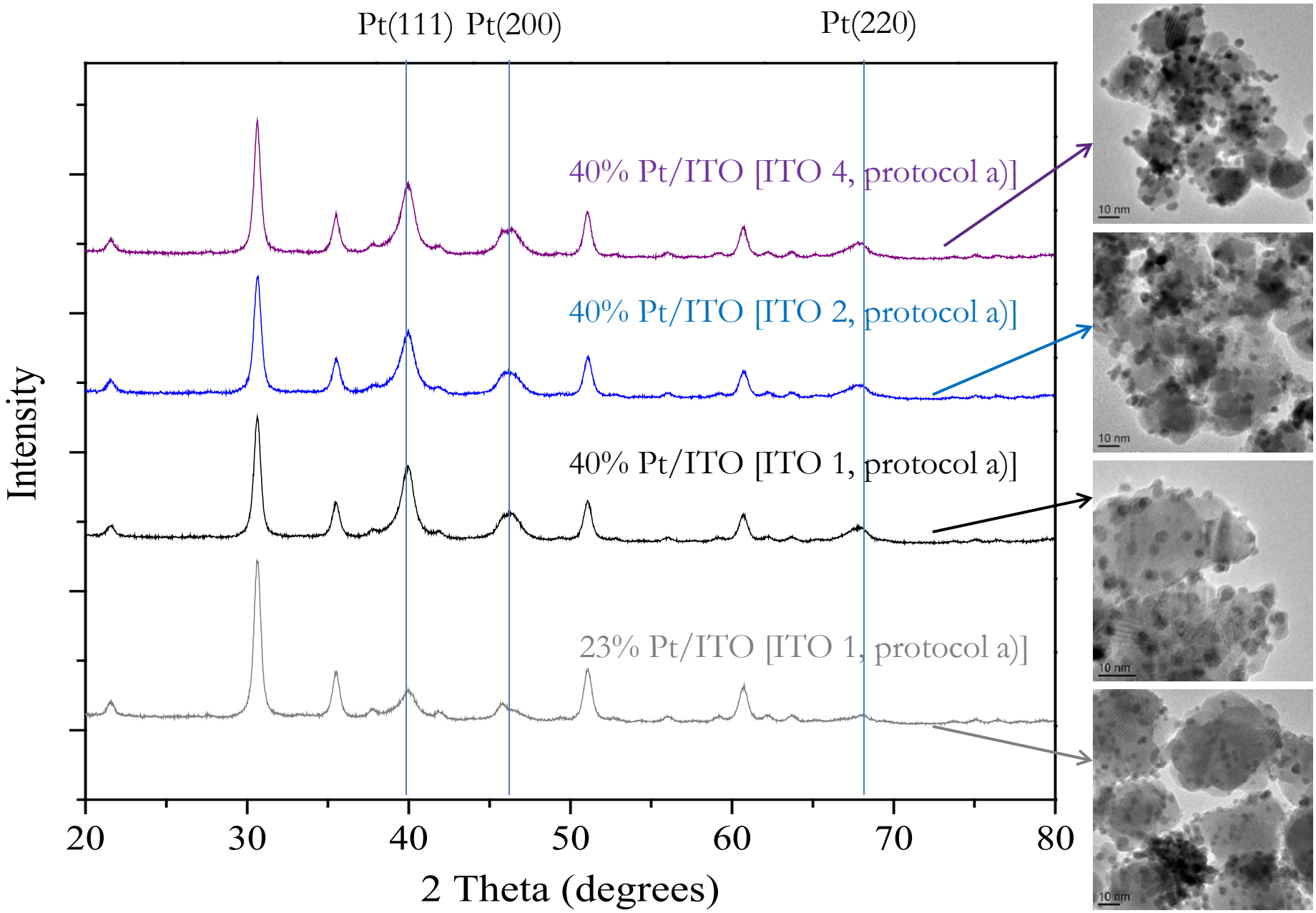
Electrolyte: 0.1 M $HClO_4$ under N_2 atmosphere;
CV sweep rate of 20 mV/S; Room temperature cycling



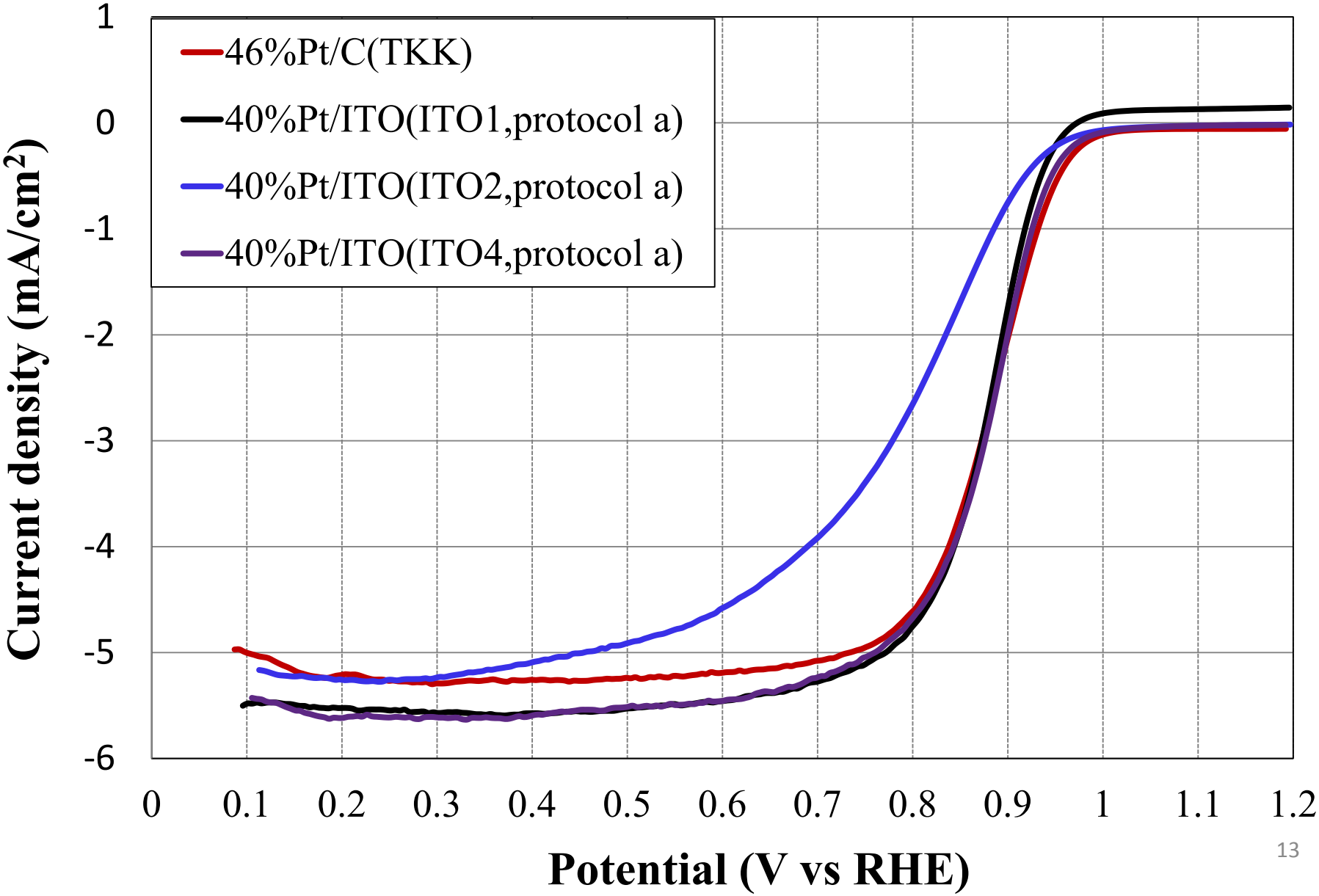


Cyclic voltammograms of commercial ITO sample before, during, and after 10,000 cycles in 0.1 M $HClO_4$ under the start-stop cycling test.

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



Technical Accomplishments: ORR Activity for 40% Pt/ITO [Platinum Nanoparticles Synthesized by Chemical Reduction of Chloroplatinic Acid with Formaldehyde]



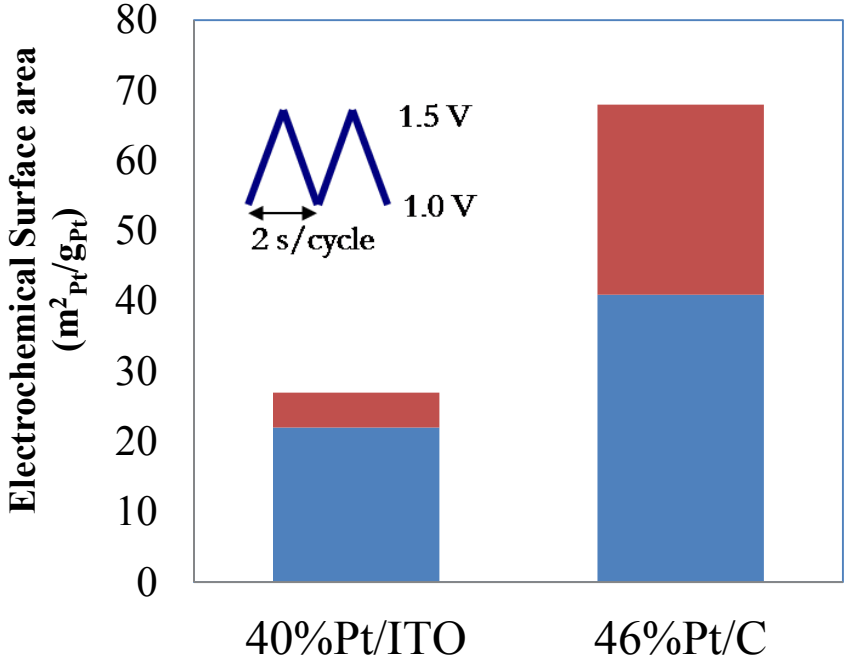
Technical Accomplishments: ECSA, Mass Activity and Area-specific Activity for Pt/ITO

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

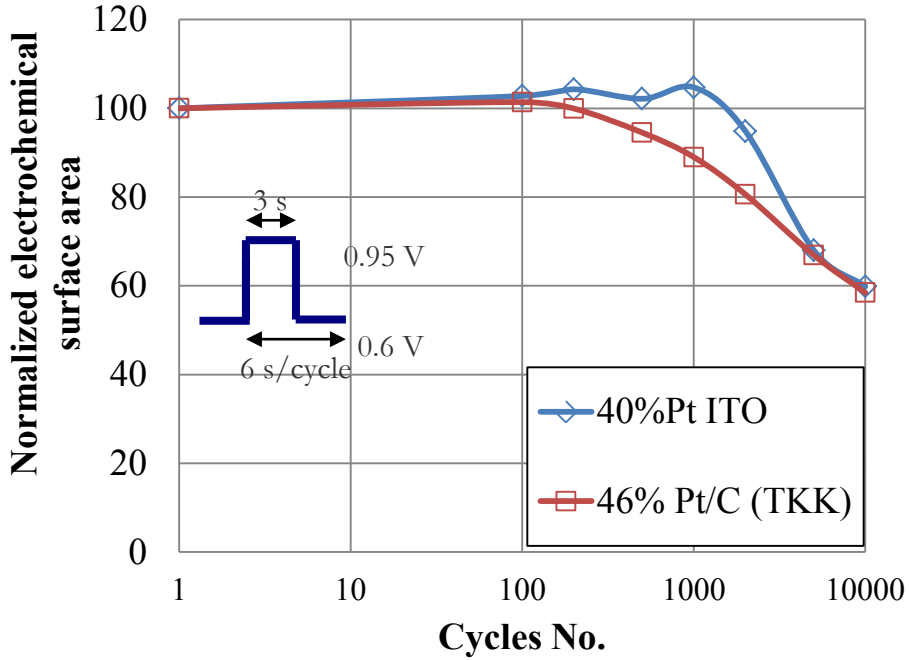
- The 40%Pt/ITO sample obtained by epoxide-initiated method showed the highest ECSA value among all 40%Pt/ITO. However, in general, ECA was low. Pt Agglomeration.
- Mass activity was in general, low, but varied with extent of agglomeration in sample.
- Pointed to need for new Pt deposition method..

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 and Load Cycling Protocols



Support Durability—Support corrosion



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

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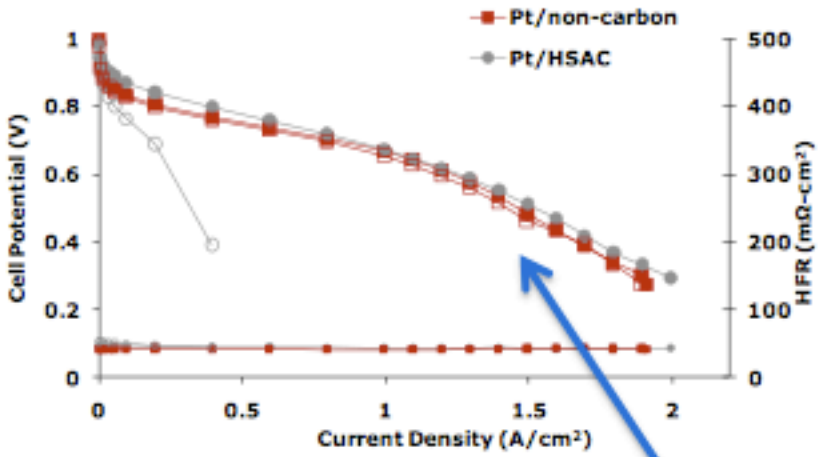
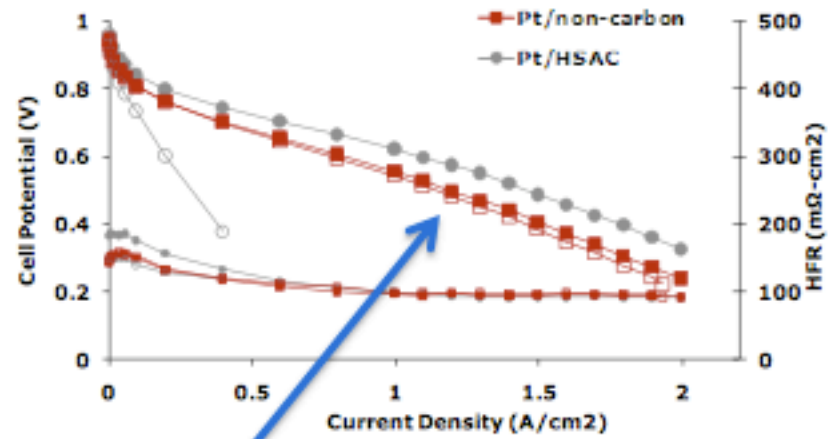
H_2/Air, 4/8 NLPM, 1 bar_g, 80 ° C,
Closed symbol: BoL
Open symbol: EoL

100% RH



40% RH



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

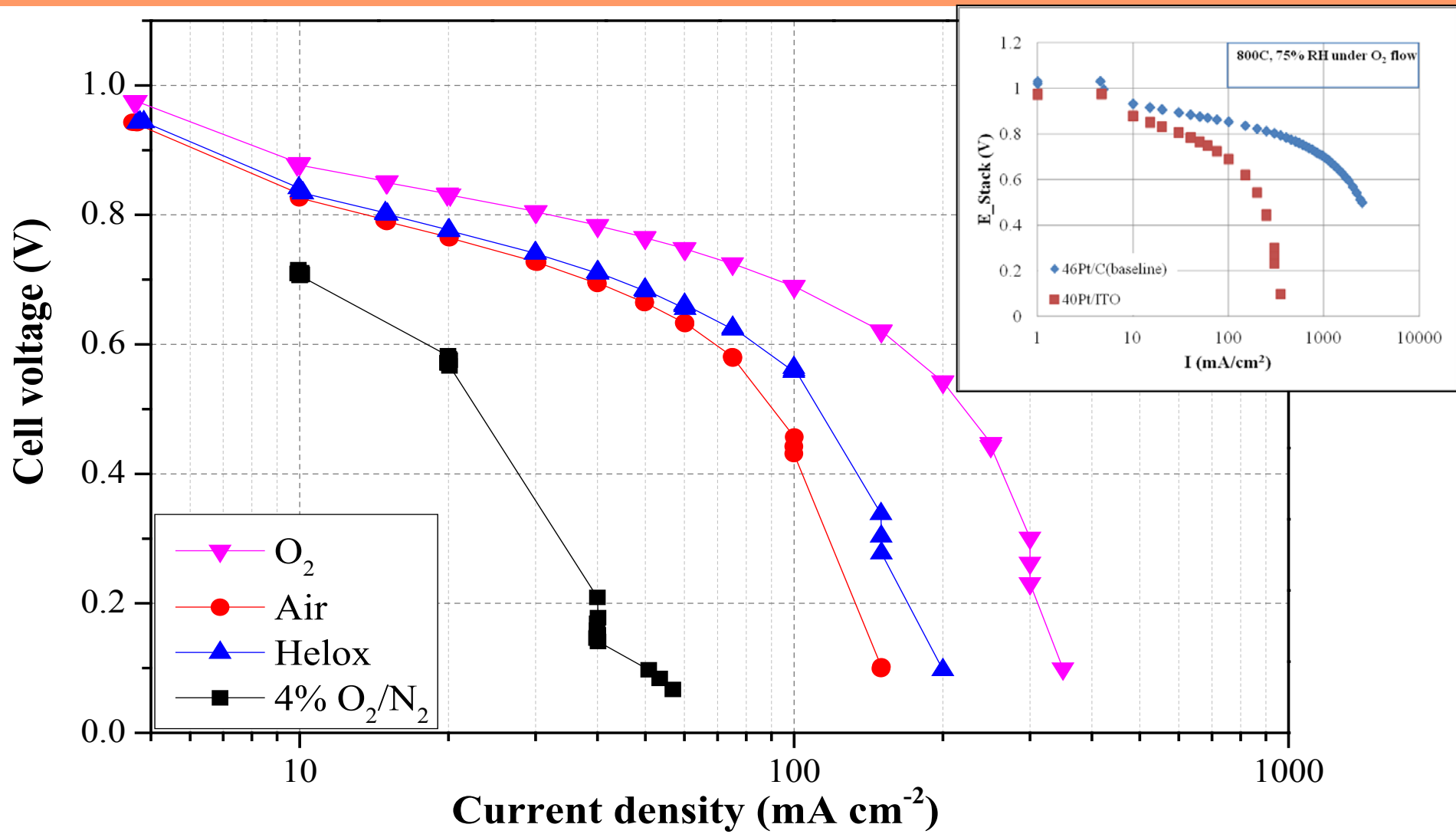
MEA Spec:
25cm², NRE211
Anode: 0.4 mg_{Pt}/cm^2 Pt/C
Cathode: 0.35 mg_{Pt}/cm^2

- ❑ **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**

Zero Emis

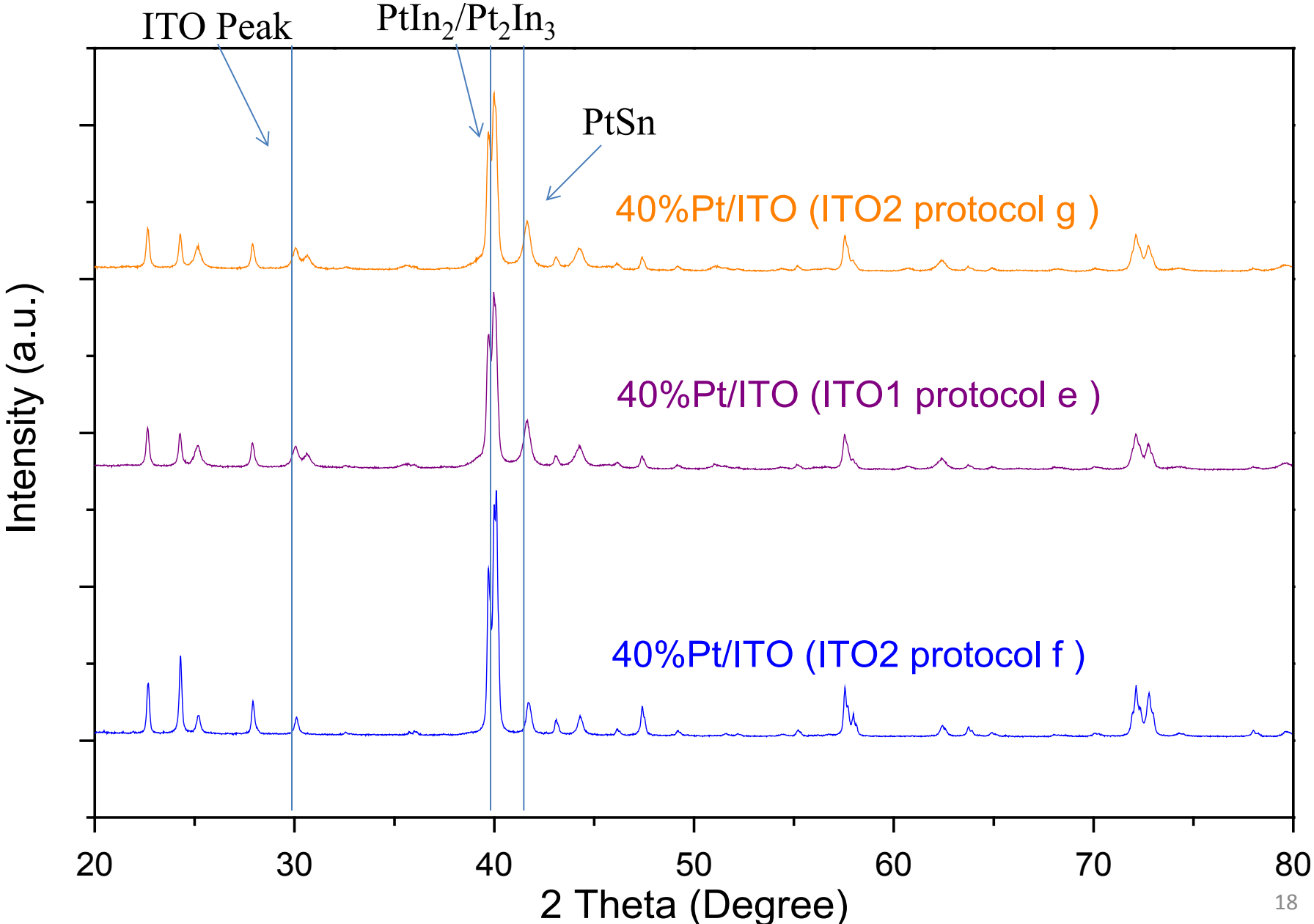
Previous Results (from 2013 AMR presentation demonstrating excellent performance and corrosion resistance of Pt/RTO catalysts

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

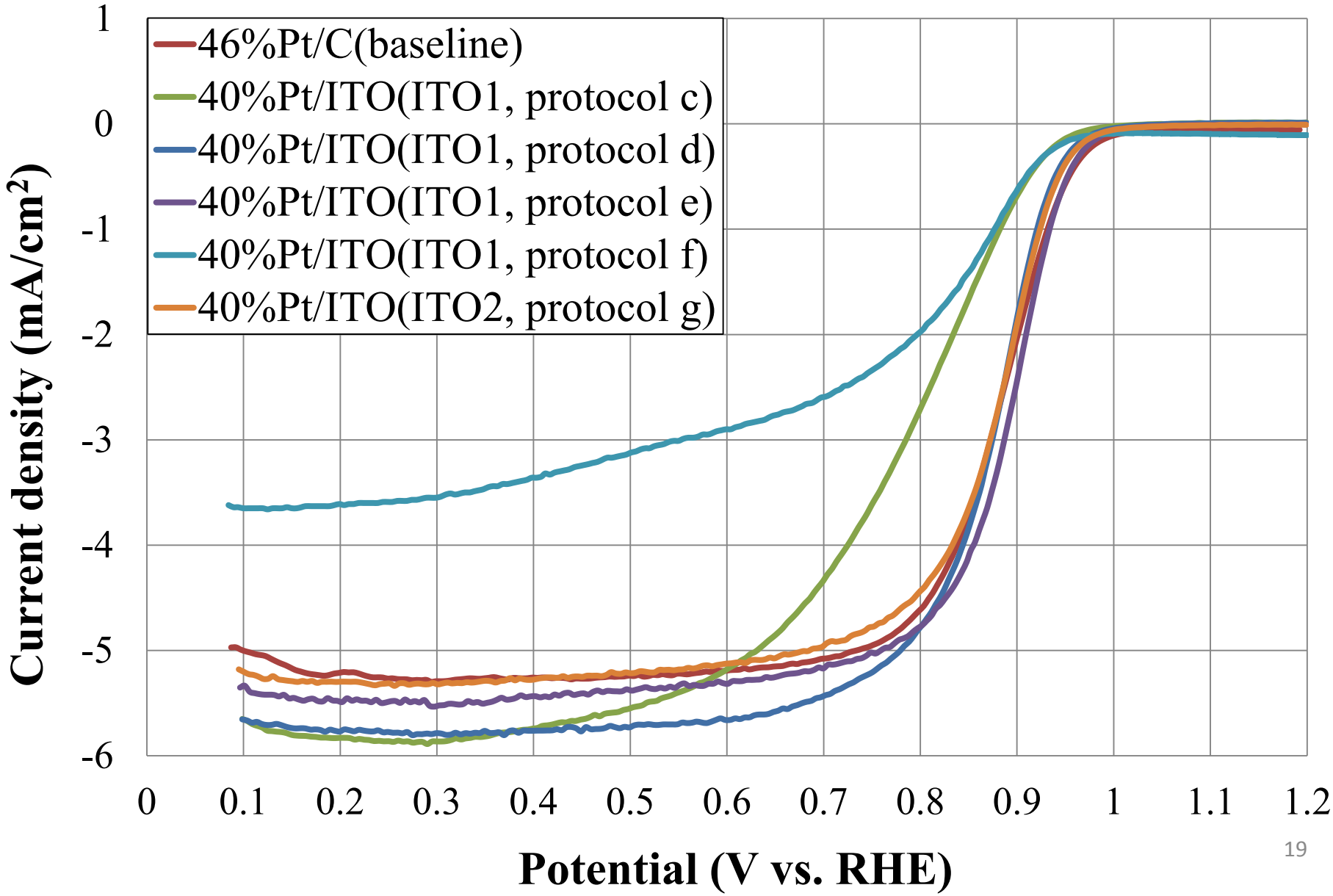


- The electrodes were prepared with 0.4 mg Pt/cm^2 and 30wt% Nafion® binder.
- Much lower performance than observed with Pt/RTO – also seen at NTCNA

Technical Accomplishments: XRD of 40%Pt/ITO [Platinum Nanoparticles Synthesis by Chemical Reduction of tetraammineplatinum(II) Chloride Hydrate as Precusor]



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



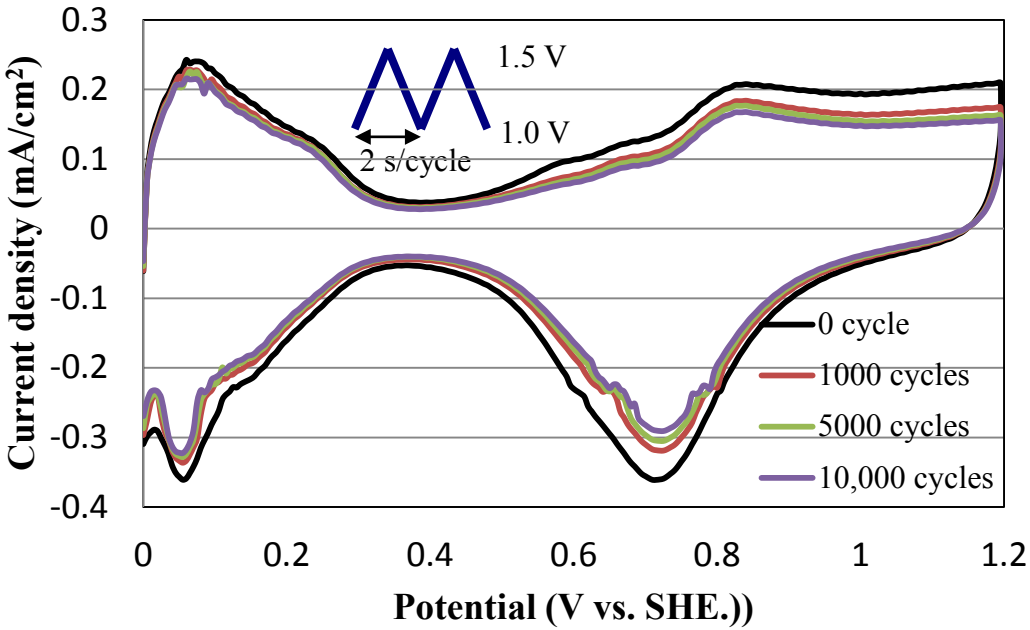
Technical Accomplishments: ECSA, Mass Activity and Area-specific Activity for 40% Pt/ITO

Synthesis method	40%Pt/ITO [ITO1, protocol c)]	40%Pt/ITO [ITO1, protocol d)]	40%Pt/ITO [ITO1, protocol e)]	40%Pt/ITO [ITO1, protocol f)]	40%Pt/ITO [ITO2, protocol g)]	46%Pt/C (baseline)
i_L, (mA/cm^2)	5.8±0.1	5.8±0.2	5.5±0.1	3.6±0.5	5.3±0.2	5.6±0.1
Pt loading ($\mu g/cm^2$)	44.6±2	44.6±2	44.6±2	44.6±2	44.6±2	17.3±1
i_m (mA/mg Pt)	18±4	62±2	98±5	21±3	67±5	190±5
ECSA (m^2/gPt)	19±1	24±2	21±2	-----	24±2	81±4
i_s ($\mu A/cm^2$ Pt)	93±2	236±10	445.5±12	-----	279±10	224±10

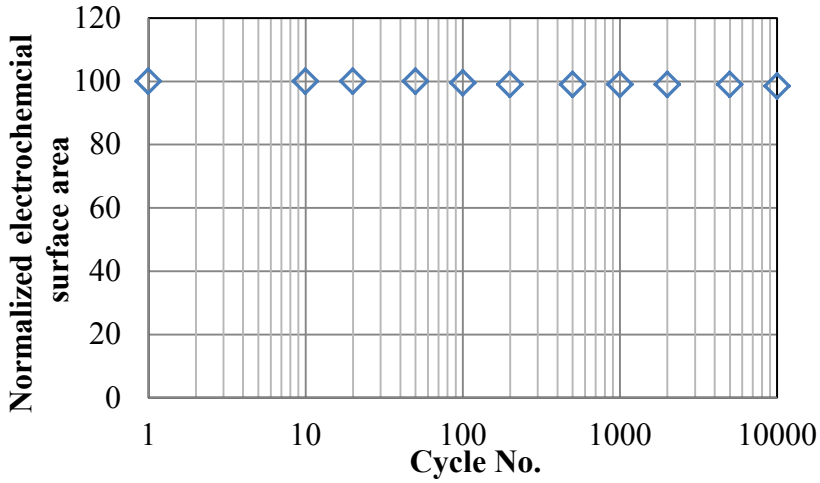
- The 40%Pt/ITO sample obtained by protocol e (cationic precursor, reduced in hydrogen) had the highest mass and specific activities.
- Possibly due to more uniform reduction of precursor.
- However, mass activity value was sill only about 50% of that of the Pt/C benchmark.

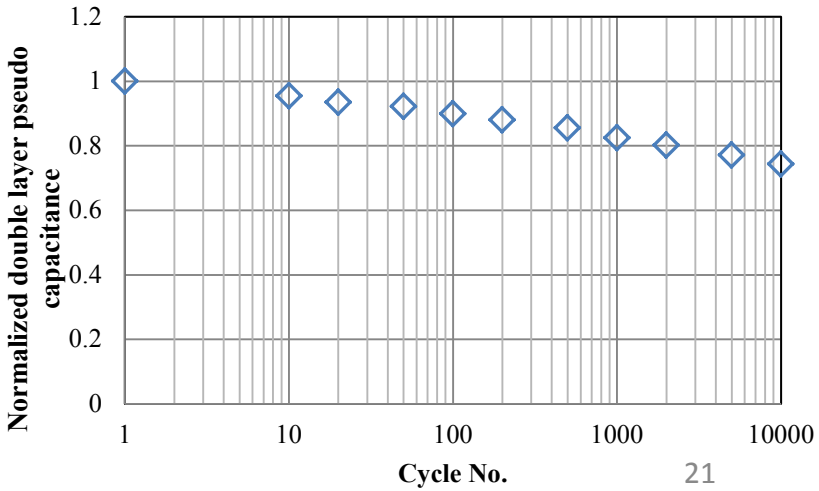
Technical Accomplishments: Support Corrosion Test for 40% Pt/ITO [ITO 2, protocol g)][Pt was reduced from $Pt(NH_3)_2Cl_2$ using $NaBH_4$]

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.



Support Durability—Support corrosion

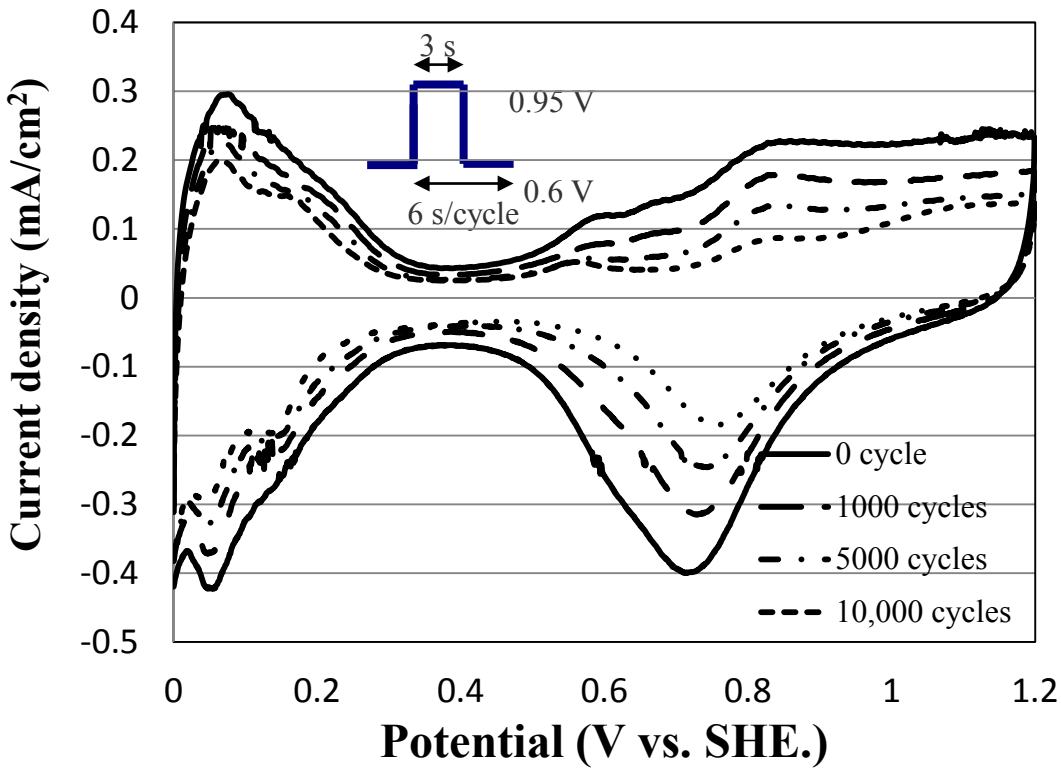


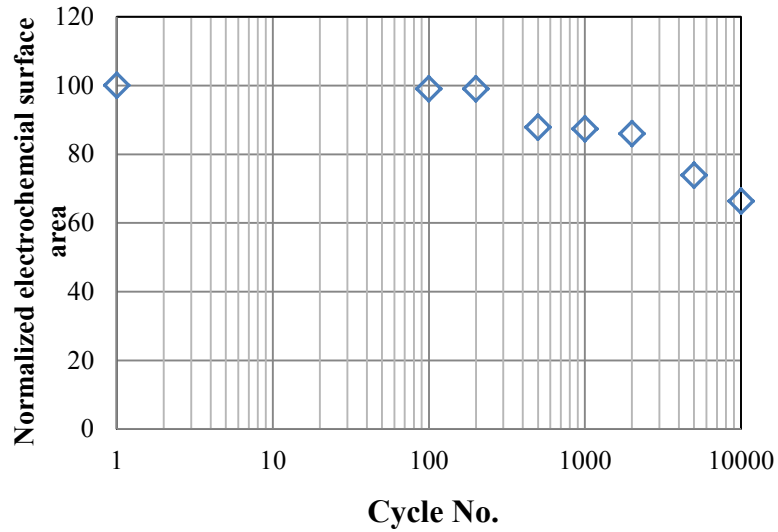


The ECSA decreased by less than 2% and the double layer pseudo capacitance decreased by 26% after 10,000 cycles.

Technical Accomplishments: Platinum Dissolution Test for 40% Pt/ITO [ITO 2, protocol g)]Pt was reduced from $Pt(NH_3)_2Cl_2$ 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





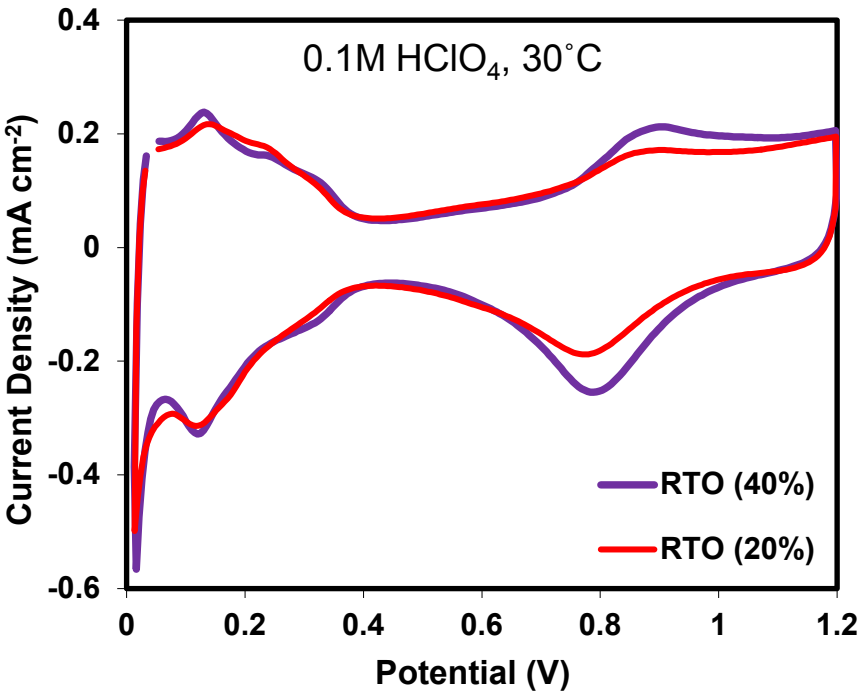
The ECSA of 40% Pt/ITO decreased by 34% after 10,000 cycles.

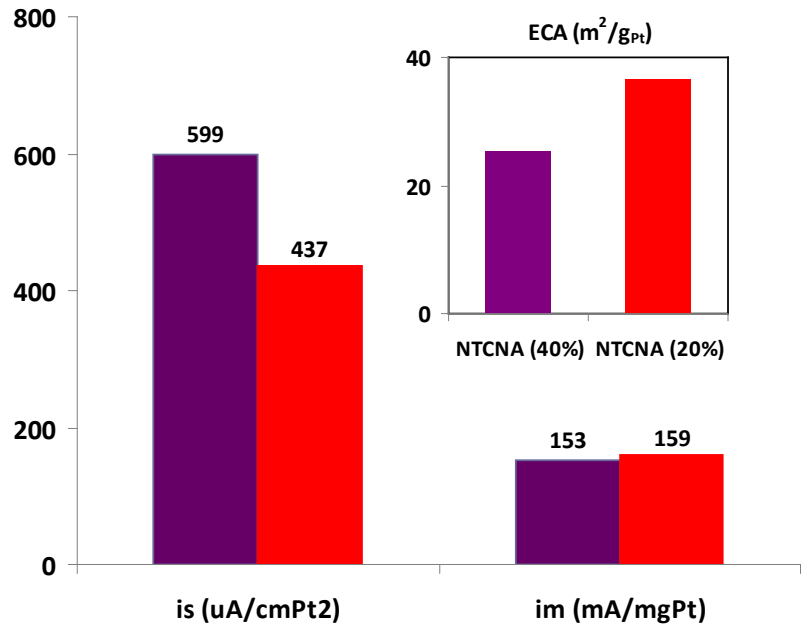
Catalyst Durability– Pt Dissolution

NTCNA Pt/RTO Catalyst Synthesis

Evaluation of Pt/RTO in RDE: 40% vs. 20% Pt

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



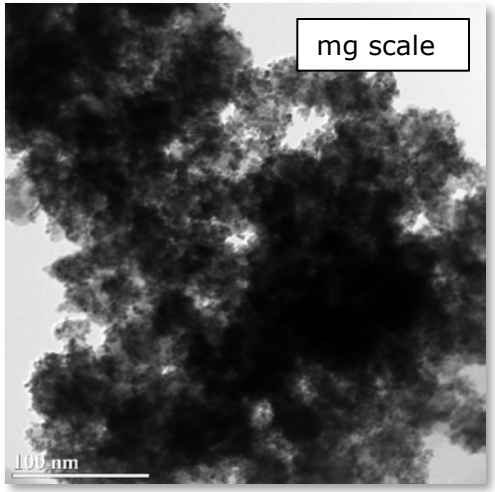


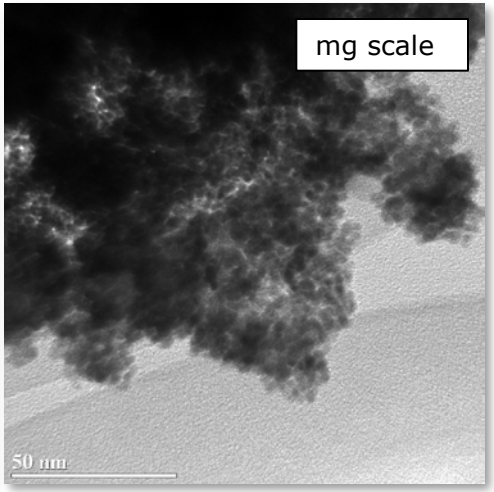
- The ECA increased when the Pt loading was decreased from 40% to 20%, but the mass activity (i_m) remained within 150-160 mA/mg_{Pt}.
- This value is comparable to the mass activity of a commercial sample, TEC10E50E-HT, (TKK Pt/Ketjen Black, heat-treated) at ~150 mA/mg_{Pt}).

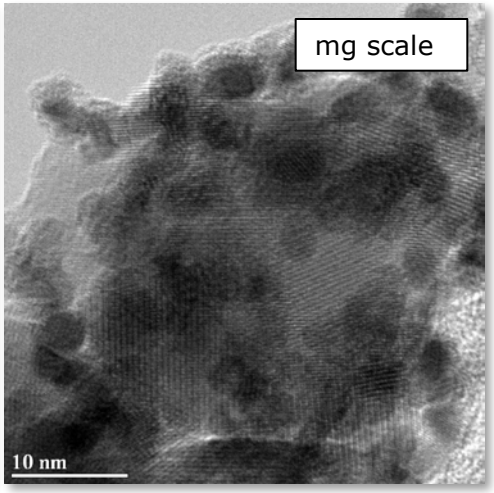
NTCNA Pt/ITO Catalyst Synthesis

mg scale vs. gram scale synthesis – TEM Images

Reproducible syntheses - good dispersion and similar Pt particle size

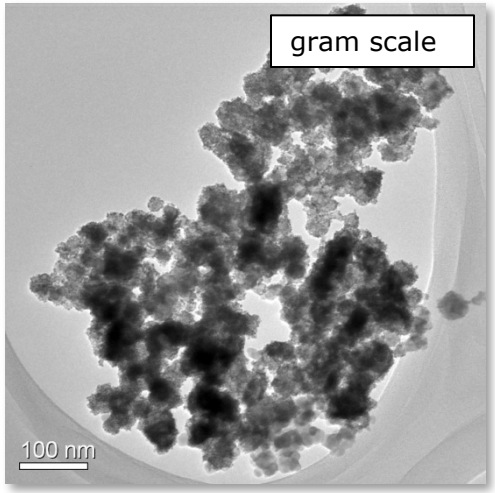


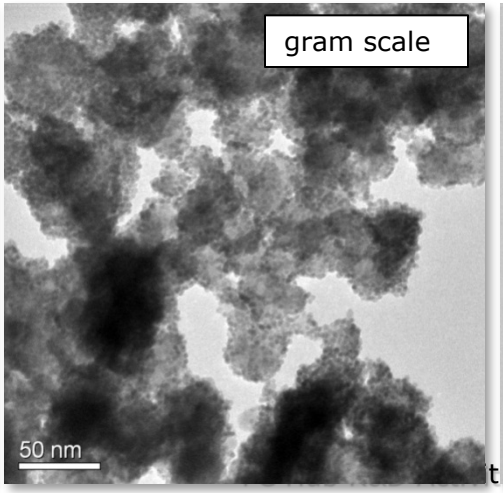


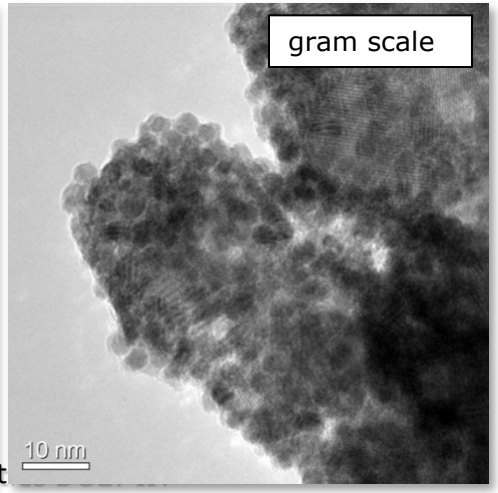


mg scale synthesis

- 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.





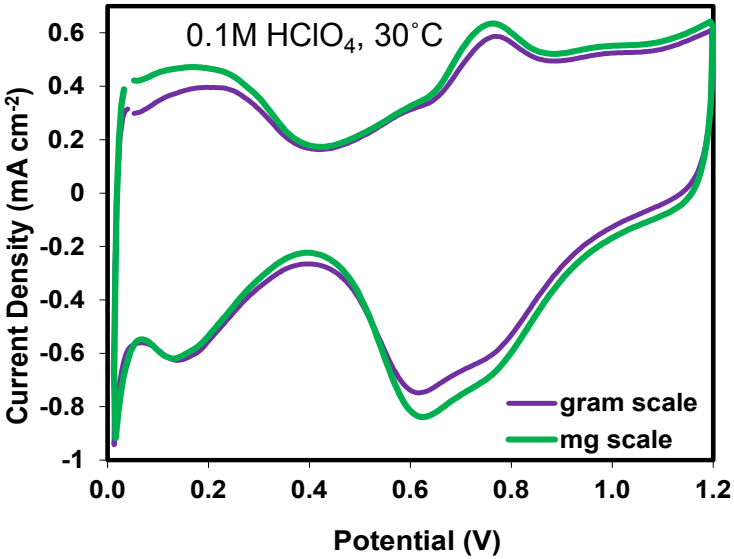


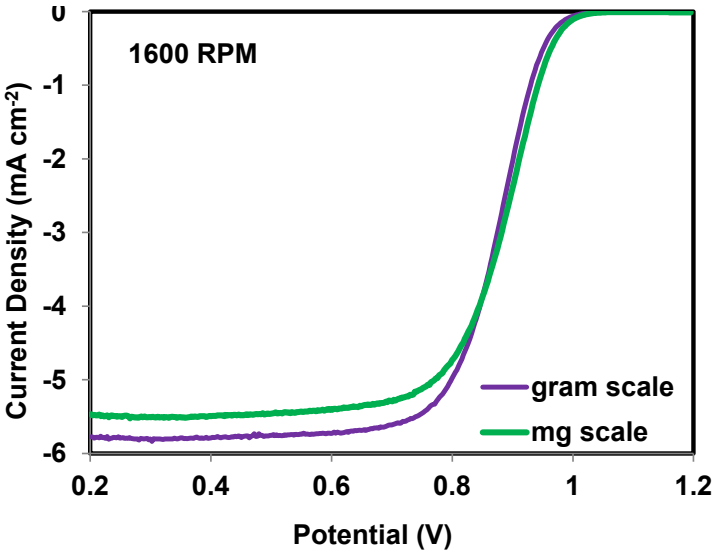
gram scale synthesis

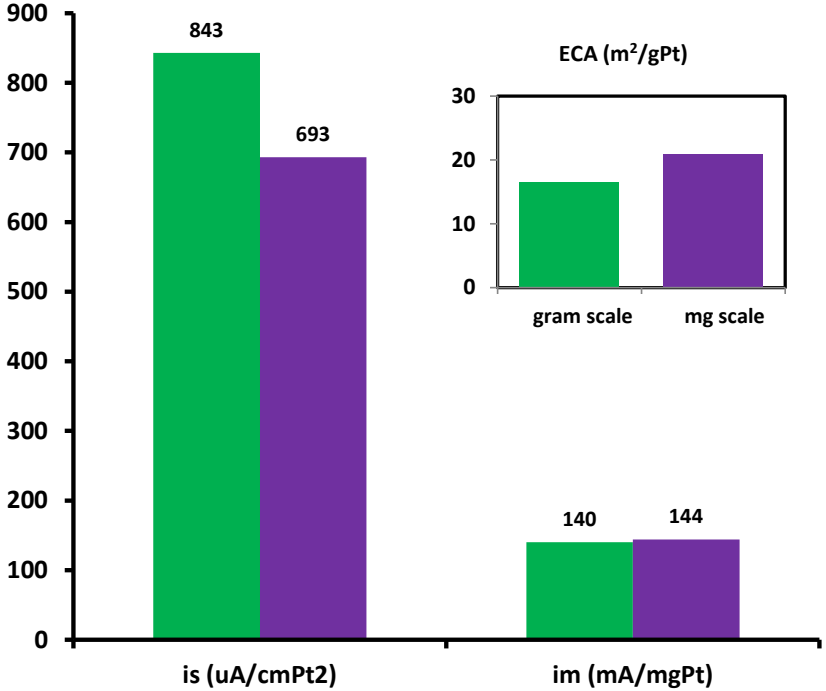
NTCNA Pt/ITO Catalyst Synthesis

mg scale vs. gram scale synthesis – RDE Results

Verification of reproducibility between mg and gram scale syntheses





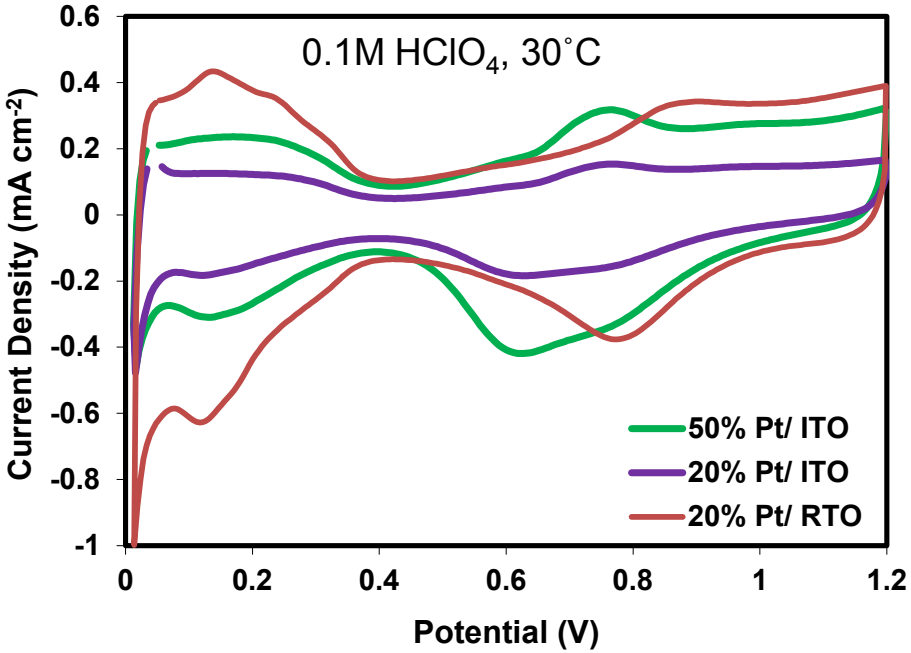


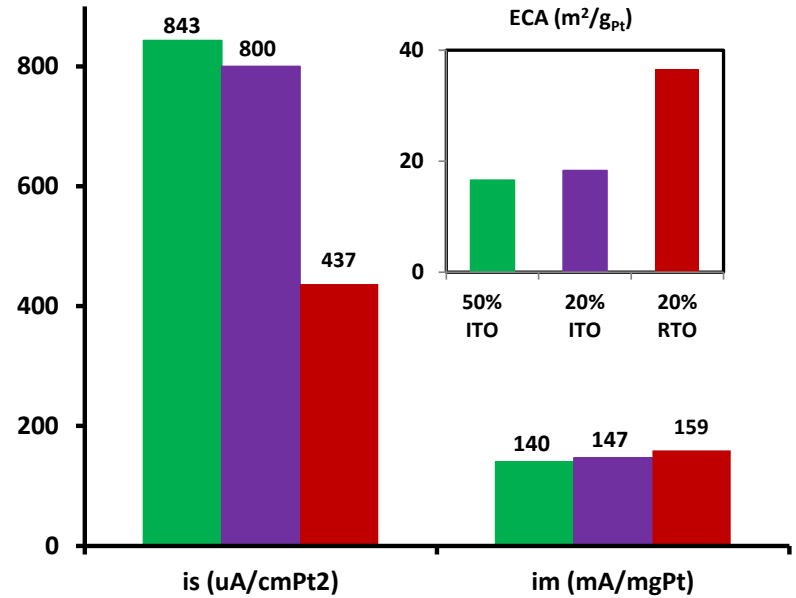
- Nearly overlapping CV and ORR LSV profiles for mg and gram scale syntheses.
- The mass activity obtained in RDE is consistently around 150 mA/mg_{Pt}.

NTCNA Pt/ITO Catalyst Synthesis

RDE Evaluation (mg scale synthesis)

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



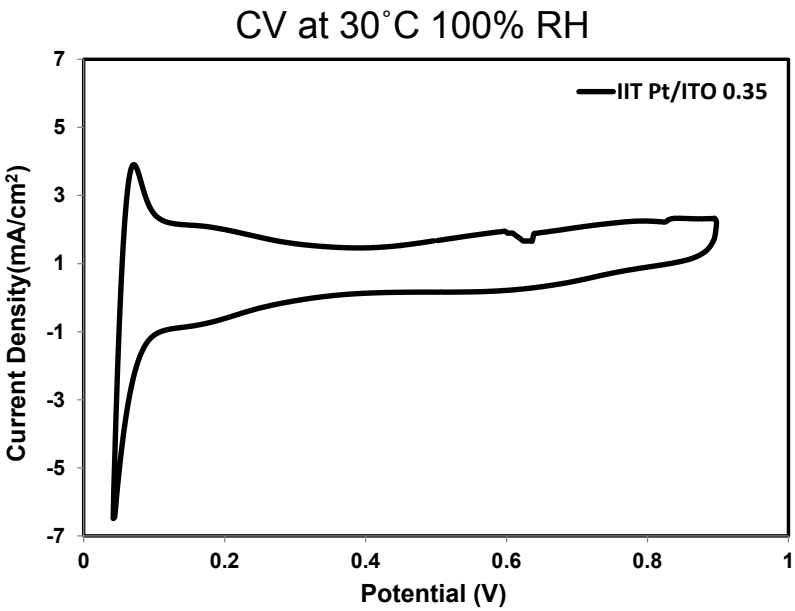


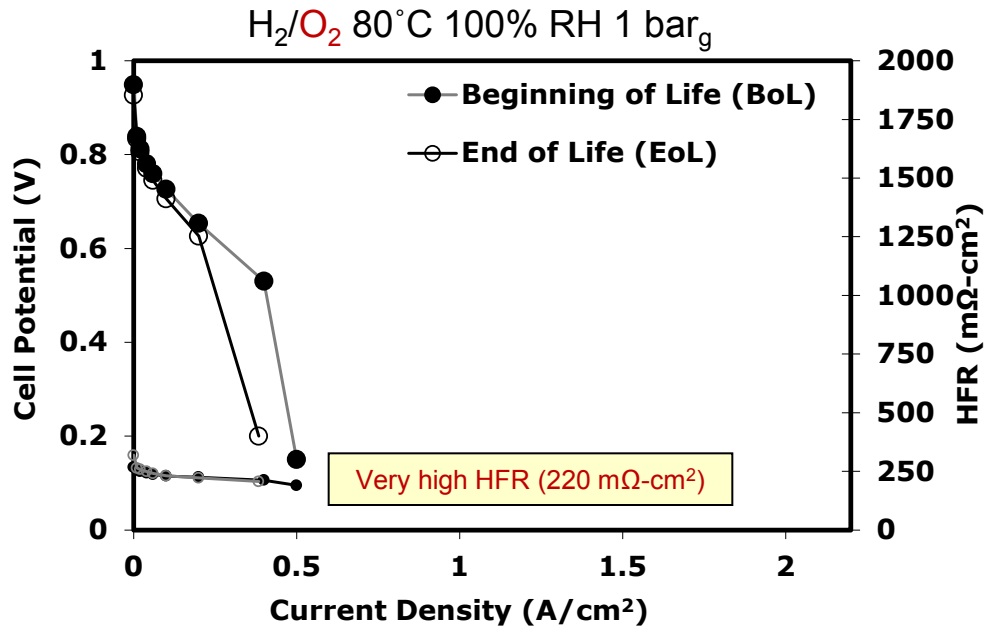
- The mass activity obtained for both 50% and 20% Pt/ITO is 140-150 mA/mg_{Pt}, comparable to Pt/RTO (in RDE).
- This value is comparable to the mass activity of a commercial sample, TEC10E50E-HT, (TKK Pt/Ketjen Black, heat-treated) at ~150 mA/mg_{Pt}).

NTCNA Pt/ITO Catalyst Testing

MEA Evaluation – iV Performance & Durability

Pt/ITO showed poor performance in MEA testing





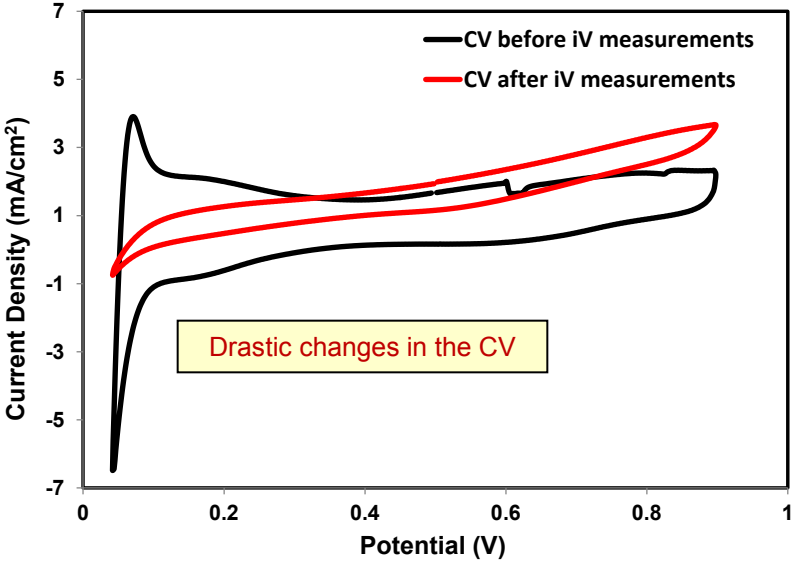
- Pt/ITO showed poor MEA performance even at a Pt loading of 0.35 mg/cm^2.
  - The high frequency resistance (HFR) was very high (220 mΩ-cm^2).
- The start-stop cycling durability of the ITO support may be satisfactory, as shown by the small change in the iV curve after 1000 potential cycles from 1.0 to 1.5V.

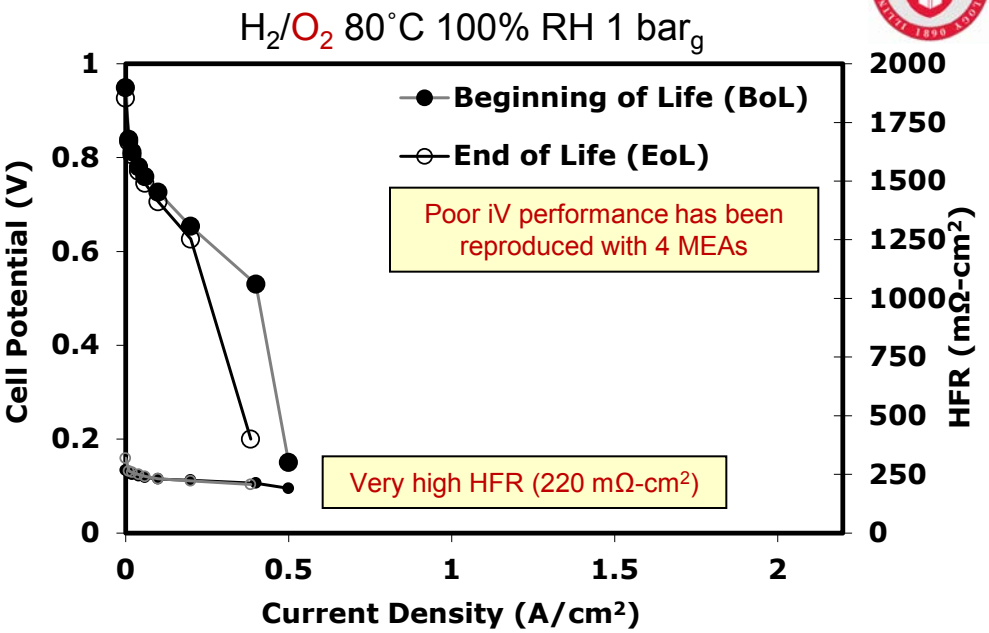
Good RDE results seen for Pt/ITO could not be observed in MEA.

NTCNA Pt/ITO Catalyst Testing

MEA Evaluation – iV Performance & Durability

Pt/ITO showed poor performance in MEA testing





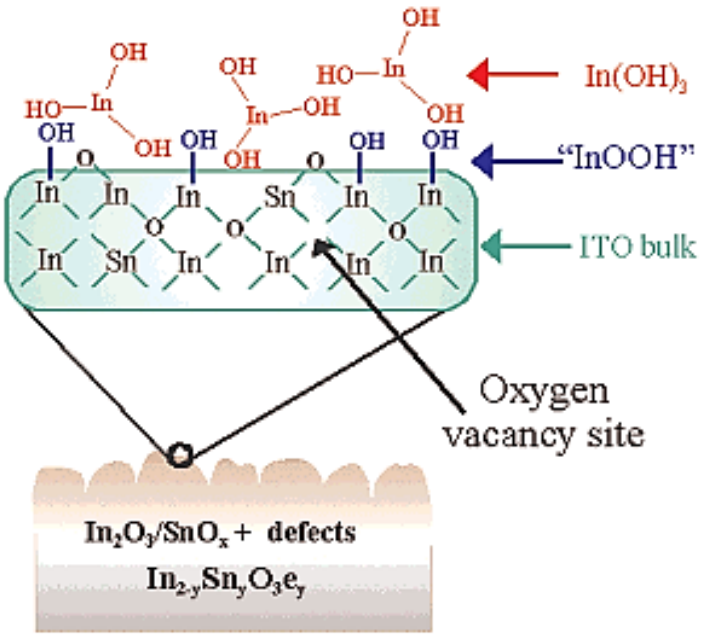
- Pt/ITO showed poor MEA performance even at a Pt loading of 0.35 mg/cm^2.
  - The high frequency resistance (HFR) was very high (220 mΩ-cm^2).
- Drastic changes in the CV profile (loss of H_{upd} features and resistive behavior) is observed, suggesting some changes in the chemical properties of the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

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.



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

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

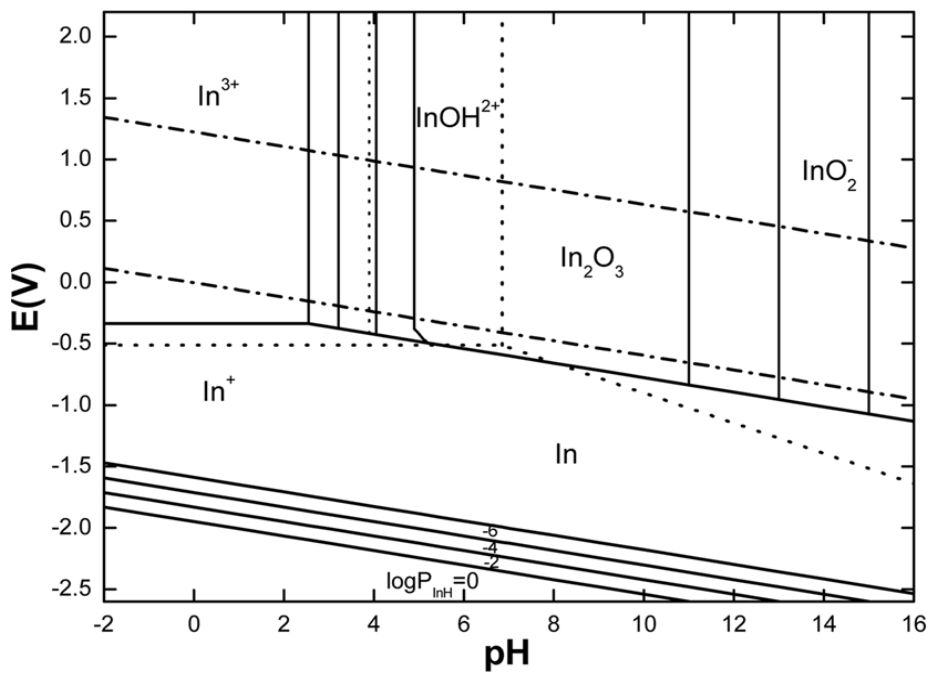
- XPS[1] and electrochemical studies[2] suggest preferential hydrolysis of surface ITO.
- Degradation and structural deformation of ITO in fuel cell relevant potentials.[3]

[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

NTCNA Pt/ITO Catalyst Testing

Limitations of ITO in FC Operating Conditions

- The hydroxide formation is consistent with the Pourbaix diagram for indium, which shows that In^{3+} is the favored species at low pH and between 0-1.5 V vs RHE.



- The solubility of these $In(OH)_3$ 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.

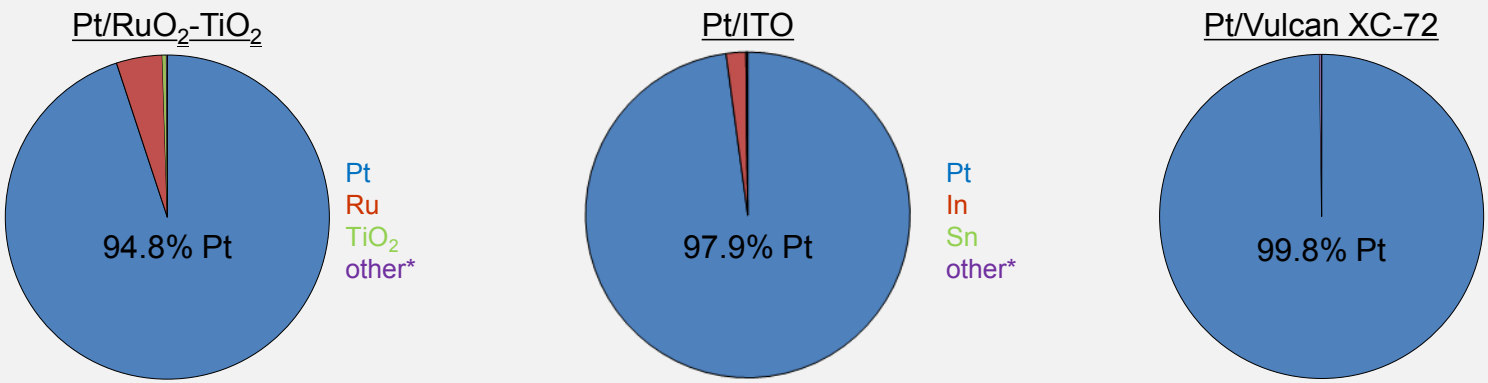
[4] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd English ed., Houston, Tex.: Natl Assn of Corrosion, 439 (1974).

Preliminary Cost Model

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)**

Cathode Material Cost Breakdown



*other inc. carbon support, Nafion® & solvents

- 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*

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

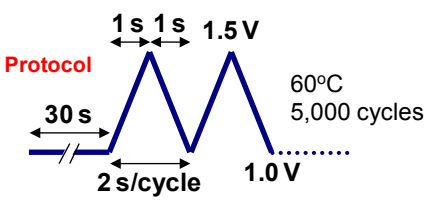
- **With durability considered, how do the two catalysts compare?**

A Durability Factor can be calculated for each catalyst

- **Durability Factor**

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

- **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

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)
  - Moderate to high performance – efforts ongoing to reduce Pt particle size
- A number of non-RuO_2 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 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.

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

Acronyms Used in Presentation

ITO	Indium tin oxide
SEA	Strong electrostatic adsorption
PZC	Point of zero charge
NHE	Normal hydrogen electrode
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
CV	Cyclic voltammetry
ORR	Oxygen reduction reaction
ECSA	Electrochemical surface area

Acronyms Used in Presentation

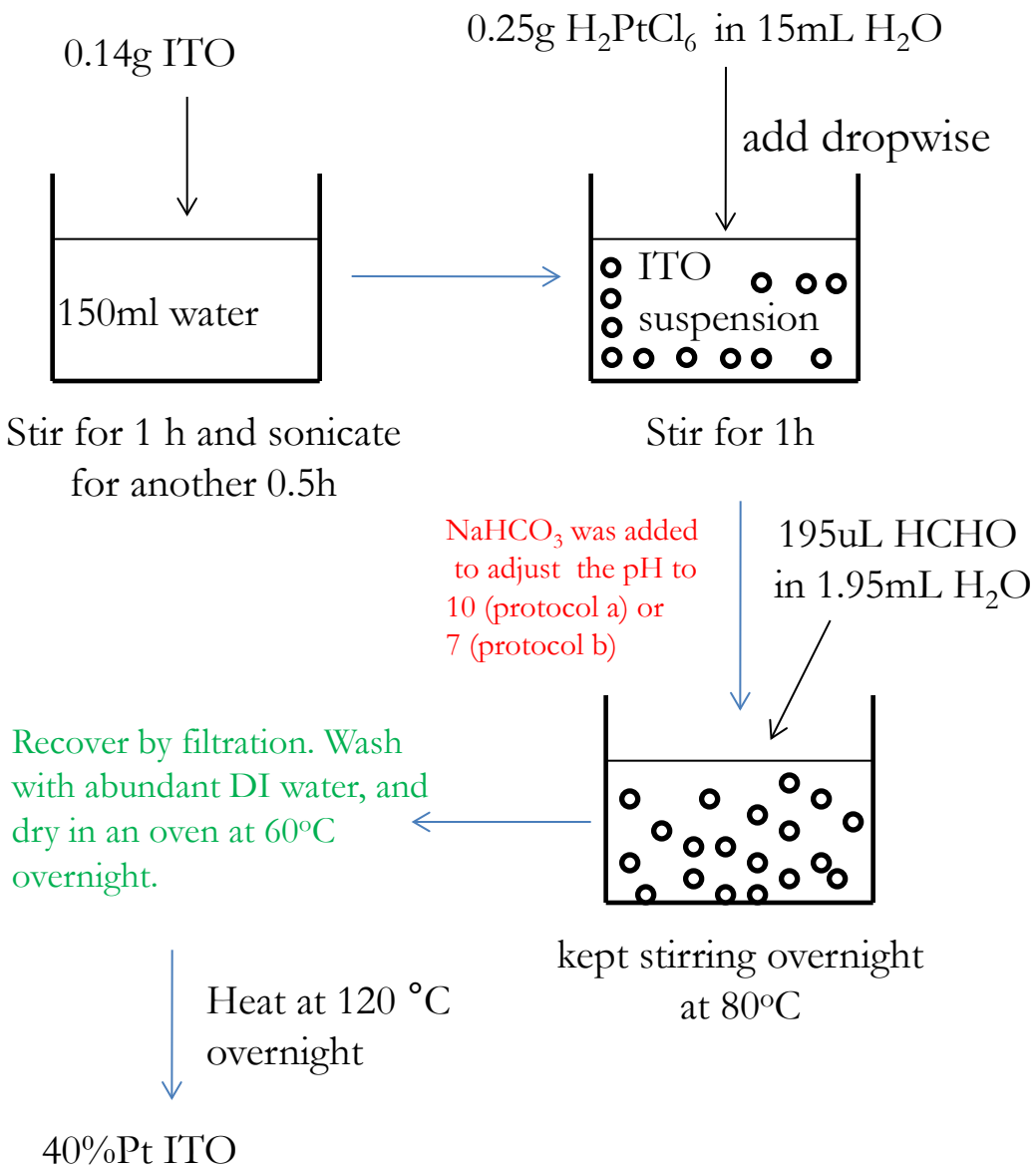
ITO 1	ITO synthesized using co-precipitation method
ITO 2	ITO synthesized using silica aerogel template method
ITO 3	ITO synthesized using supercritical CO2 drying method
ITO 4	ITO synthesized using epoxide initiator method
Protocol a)	Pt nanoparticles reduced from chloroplatinic acid by using formaldehyde as the reducing agent at pH=7
Protocol b)	Pt nanoparticles reduced from chloroplatinic acid by using formaldehyde as the reducing agent at pH=2.7
Protocol c)	Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as the reducing agent at pH=8-9
Protocol d)	Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as the reducing agent at pH=10-11
Protocol e)	Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using 4% hydrogen (nitrogen balanced) as reducing agent at 250°C.
Protocol f)	Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using 4% hydrogen (nitrogen banlaced) as reducing agent at 300°C.
Protocol g)	Pt nanoparticles reduced from tetraammineplatinum(II) chloride hydrate by using sodium borohydride as reducing agent.

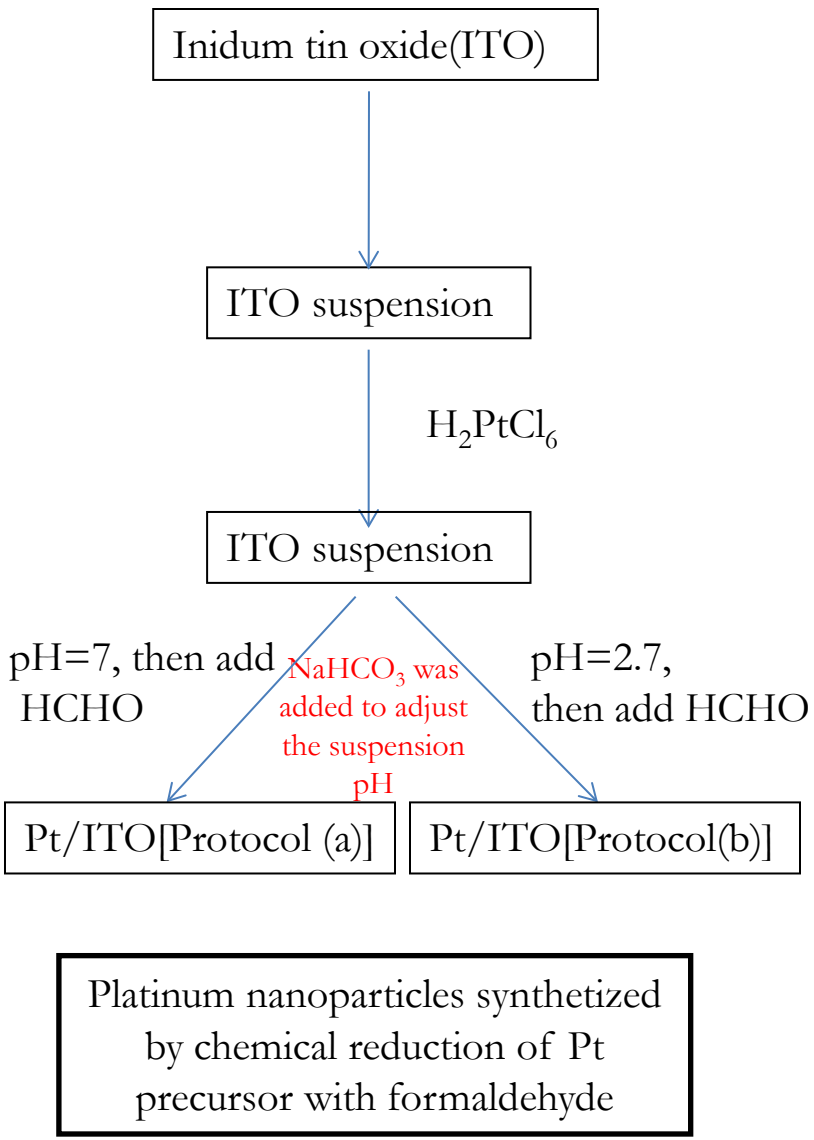
Technical Accomplishments: Characterization of ITO

	Commercial ITO	ITO 1 coprecipitation	ITO 2 supercritical drying	ITO 4 epoxide initiator	ITO 3 silica aerogel template
ITO hydroxide precursor surface area (m^2/g)	Not available	124± 2	224± 2	275± 5	224± 2
ITO BET surface area (m^2/g)	30± 2	45± 2	72± 2	41±1(820°C) 47±1(600°C) 84±1(450°C)	130± 10
Conductivity (S/cm)	0.6-0.7	1.3± 0.1	1.2±0.1	1.9±0.1(820°C) 1.2±0.1(600°C) 0.31± 0.01(450°C)	$\sim 10^{-6}$

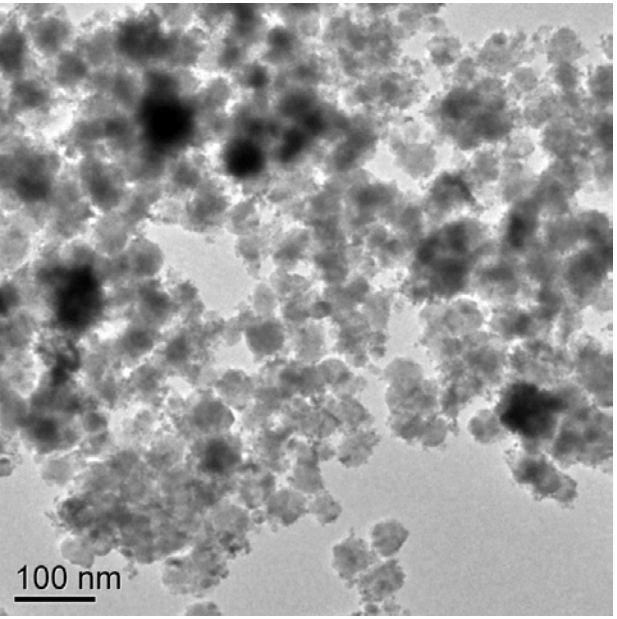
The ITO obtained by epoxide-initiated method showed the best conductivity.
The ITO obtained using silica aerogel template method showed the best BET surface area, however the conductivity was very low.

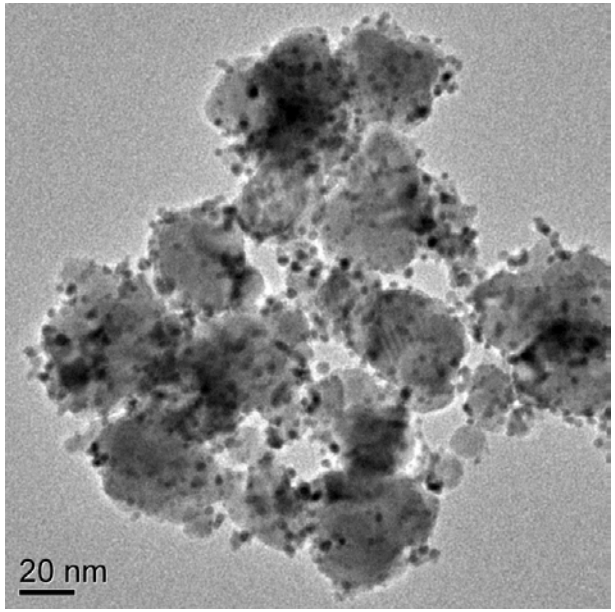
Approach: Platinum Nanoparticles Synthesis by Chemical Reduction of Pt Precursor with Formaldehyde [protocol (a) and (b)]

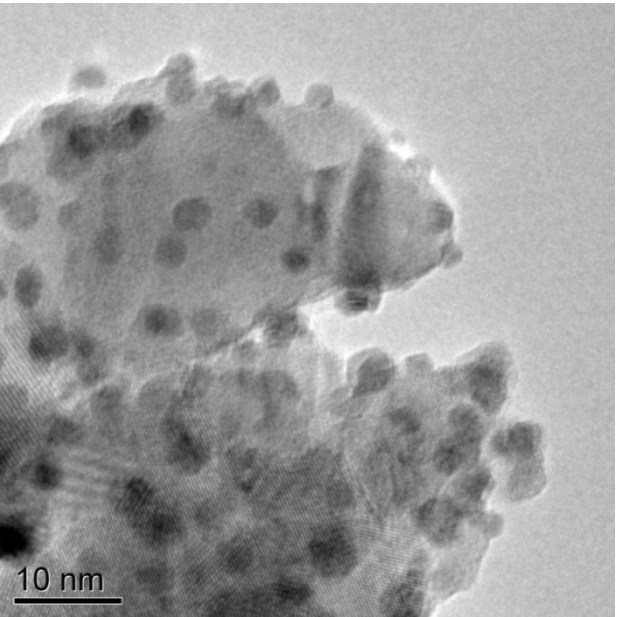


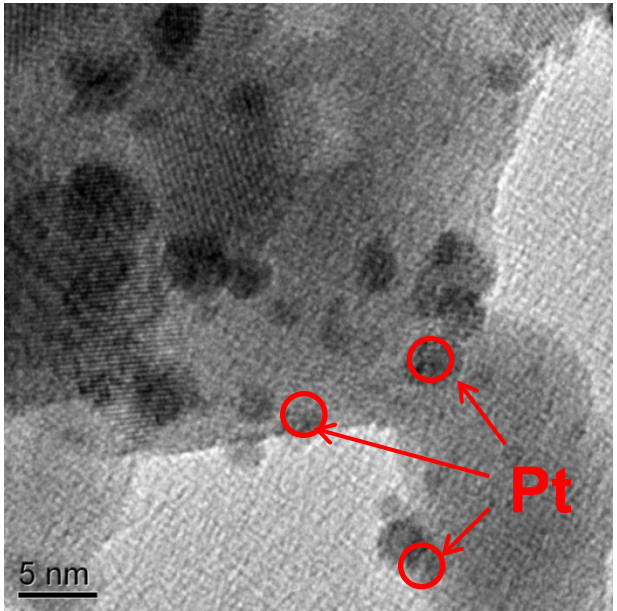


Technical Accomplishments: TEM of 40%Pt/ITO [ITO 1 co-precipitation, protocol a) was used to deposit Pt]









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.

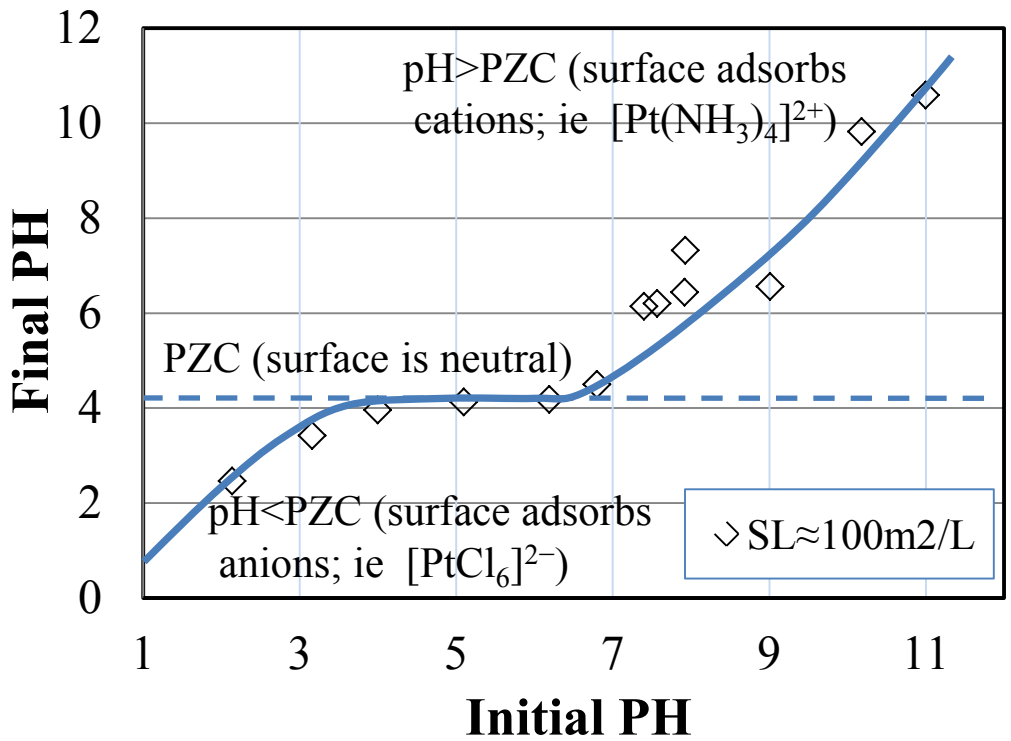
Some of the small Pt NPs agglomerated and formed large Pt clusters.

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.



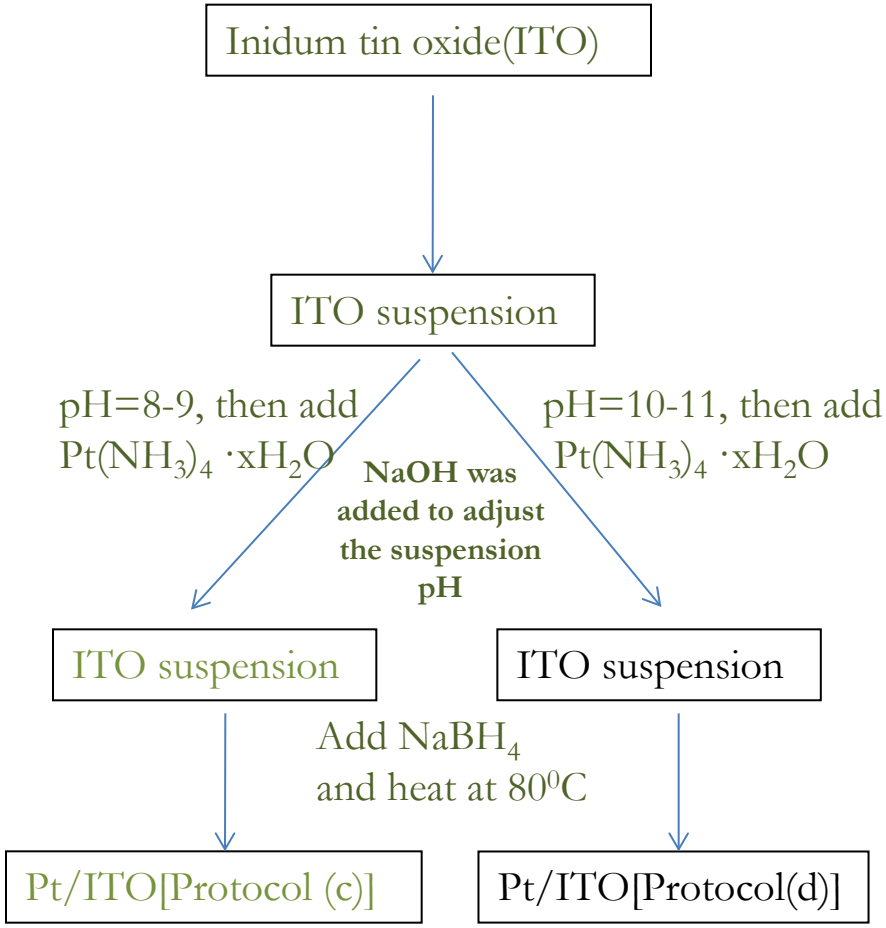
The PZC value of the ITO was ~4. Plateau was small but if the surface loading was higher, then the plateau would be broader.

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

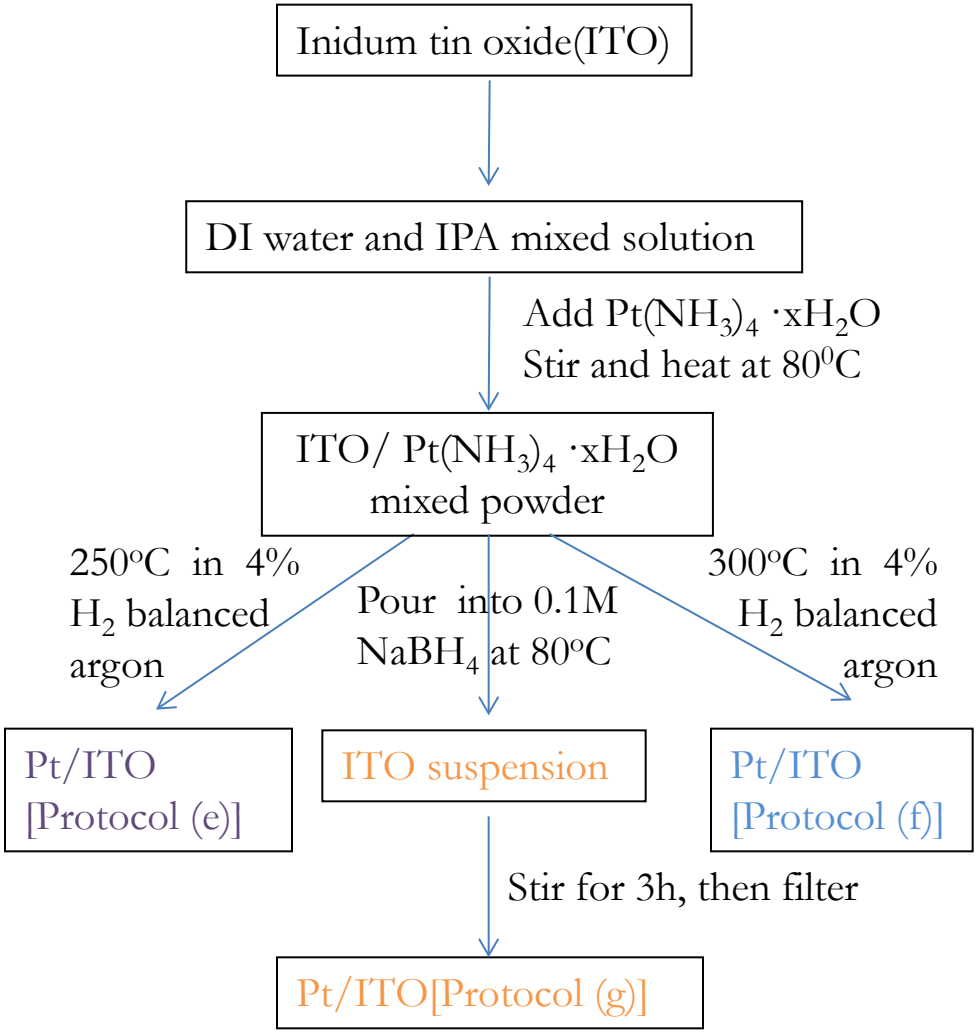
We used $Pt(NH_3)_4$-xH_2O as the precursor when using the "SEA method"

S. Lambert et al, J. of Catalysis, 261 (2009), 23

Approach: Platinum Nanoparticles Synthesis by Chemical Reduction of tetraammineplatinum(II) chloride hydrate



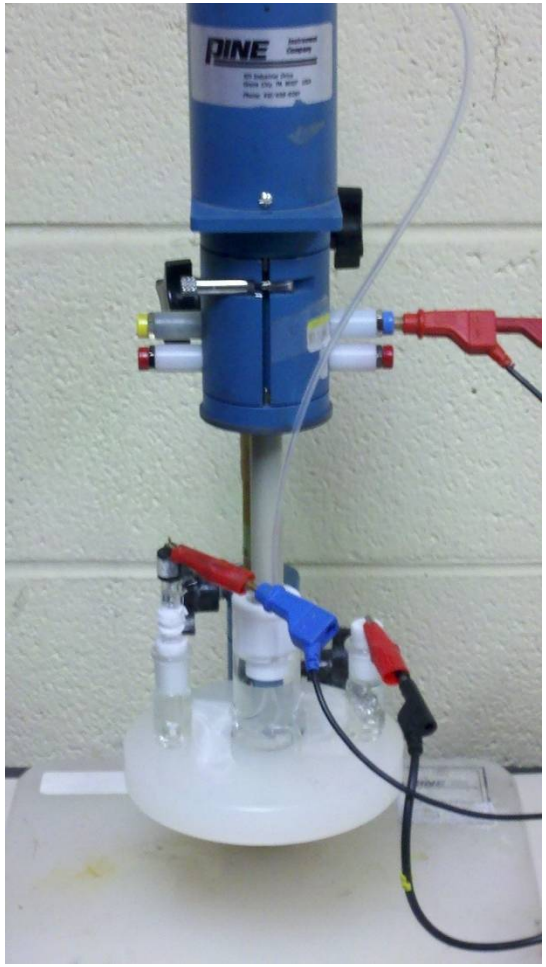
Platinum nanoparticles synthetized by chemical reduction of Pt precursor by sodium borohydride



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 carbo coated with catalyst support
  - Counter Electrode : Pt foil
  - Reference Electrode : Saturated Calomel Electrode (SCE)
  - Electrolyte : N_2 saturated 0.1M $HClO_4$
- Support loading on W.E.: 200 $\mu g/cm^2_{geo}$
- Pt loading: 44.6$\mu g/cm^2_{geo}$
- Potential cycling protocol
  - See following slides



NTCNA Pt/ITO Catalyst Synthesis

Catalyst Synthesis Procedure – mg and gram scale

(Ethylene Glycol + Formic Acid)
(dry impregnation)

H_2PtCl_6 precursor dissolved in ACETONE was added to ITO

sonicated

To ensure better precursor-support interaction

Heated at ~50˚C to evaporate ACETONE

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