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Zero Emission

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: Dec. 31st 2013
- Percent complete: ~ 65%

Budget

- Total project funding
  - DOE share: $ 1,476,230
  - Contractor share: $ 415,775
- Total DOE funding to date $1,036,900

Barriers

- Barriers addressed:
  - Fuel cell component durability to be improved
- Targets addressed
  - < 40% ECA Loss tested per GM protocol
  - < 30mV electrocatalyst support loss after 100 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.

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
  - Under fuel starvation conditions
  - 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 100 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 100 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.

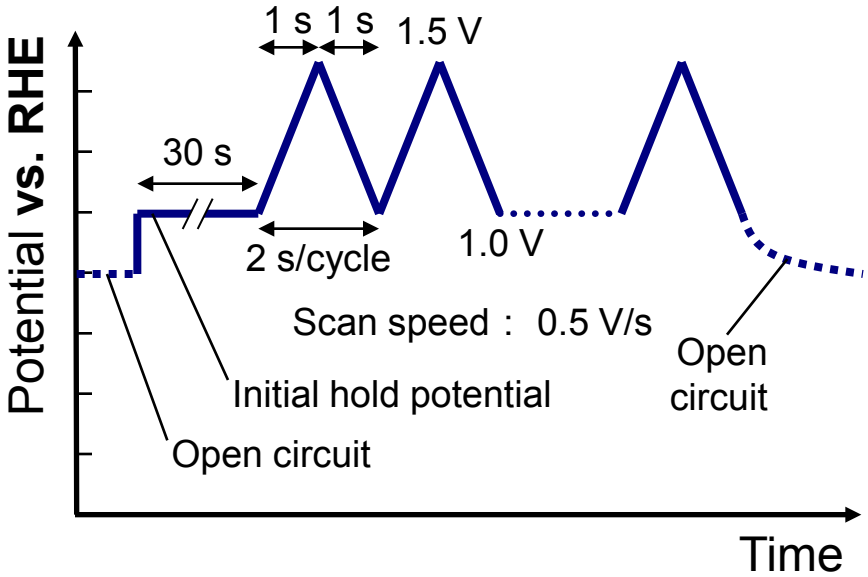
Approach: Milestones and GNG Criterion; Current Status

- 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]

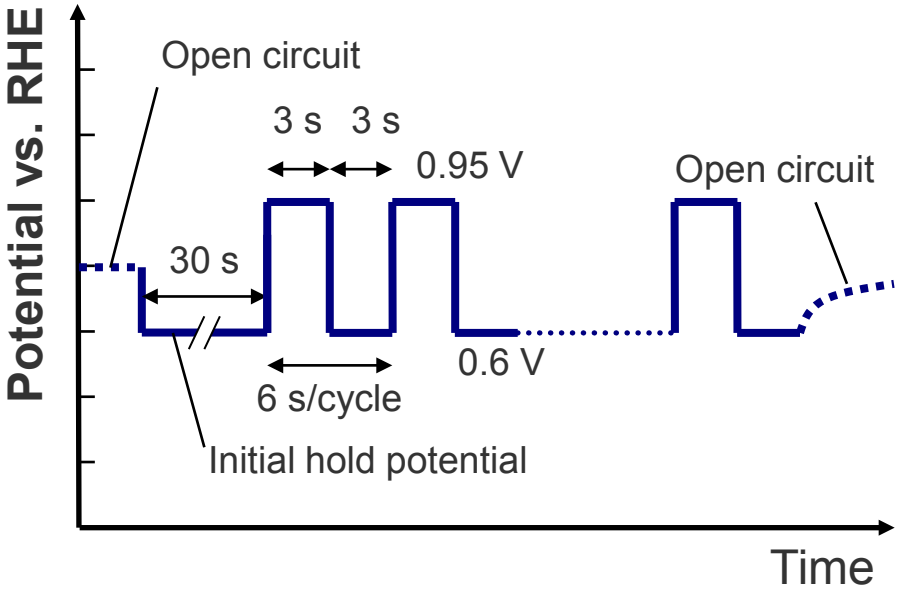
* < 10% mass loss on cycling between:
- 1V and 1.5V at 0.5V/s
-0.95 V and 0.6V under load
- 1000 cycles

- 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, further tests ongoing]
  - Prepare and evaluate high-performance Pt-catalyzed supports [C-S: ongoing]
  - Identify optimal ionomer loading in electrode [Current Status: in progress]
  - Prepare 6 100 cm^2 MEAs w/ optimal support formulation [Not yet started]
- GNG criterion (applied at end of Q1; 2012) – **PASSED in June 2012**

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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MEA : Catalyst Durability
Load Cycling

Technical Accomplishments

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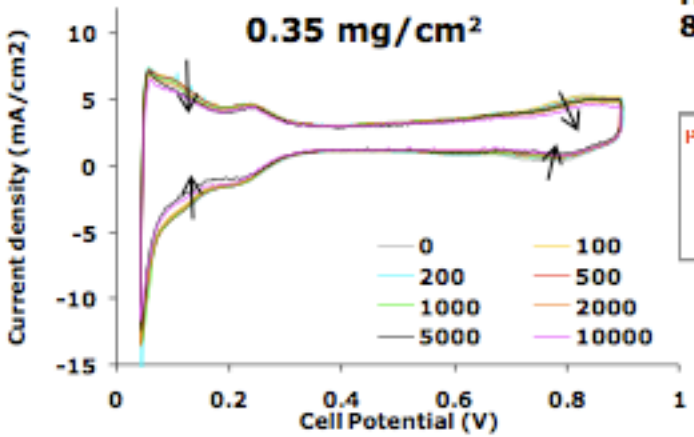
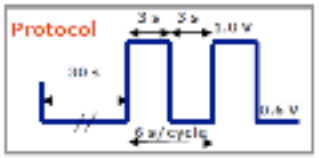
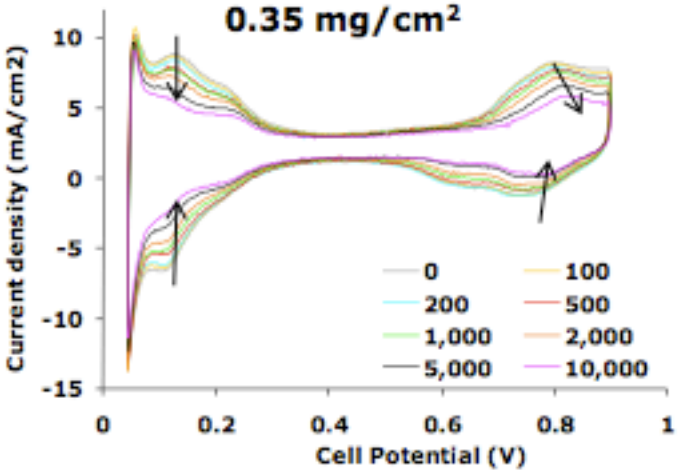
Pt/non-carbon support



H_2/N_2, 0.5/0.5 LPM, 80 ° C, 100% RH

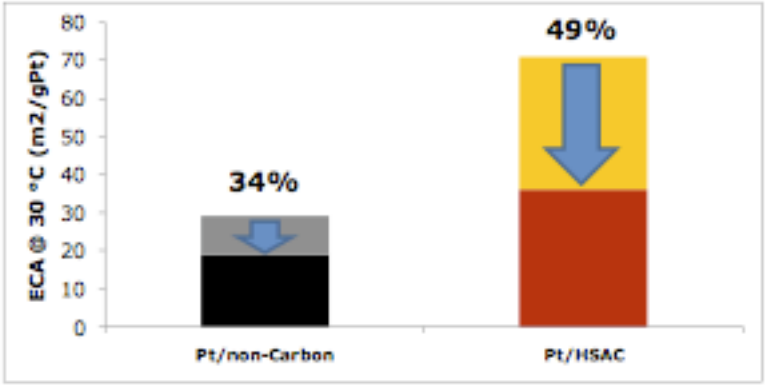


Pt/HSAC support



40% Pt/RuO_2-TiO_2

MEA Spec:
25cm², NRE211
Anode: 0.4 mg_{Pt}/cm^2 Pt/C
Cathode: 0.35 mg_{Pt}/cm^2
Pt/TiO_2-RuO_2



50 % Pt/HSAC

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

- Better catalyst durability for non-carbon support catalyst than carbon supported catalyst observed in MEA
  - CV shapes are not clearly defined in MEA (vs. RDE) for non-carbon support catalyst, hence lead to discrepancy in ECA measurements

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MEA : Effect on iV performance Start/stop cycling

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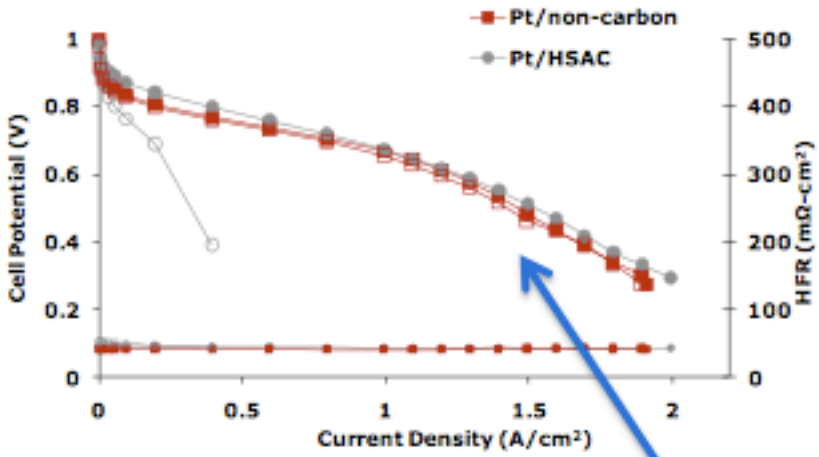
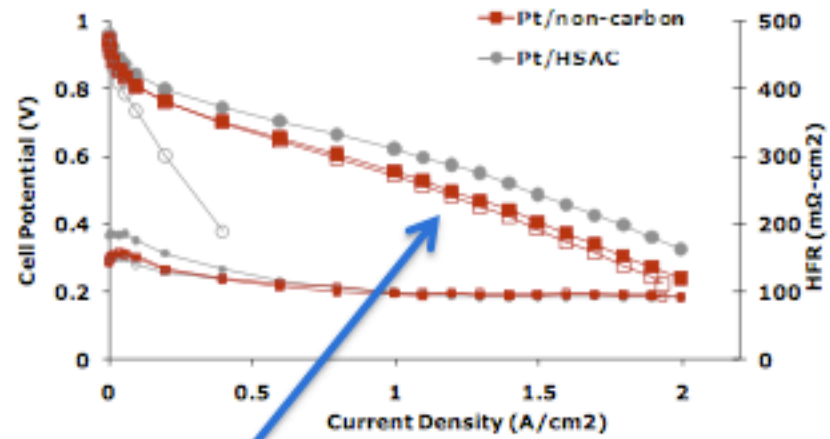
H_2/Air, 4/8 NLPM, 1 bar_g, 80 ° C,
Closed symbol: BoL
Open symbol: EoL

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

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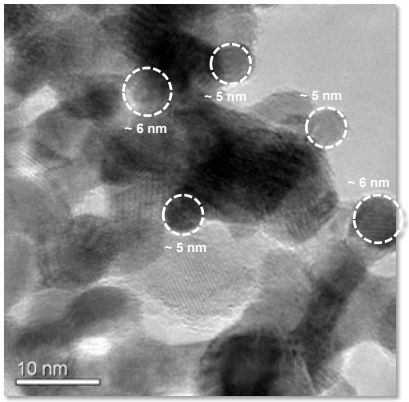
Technical Accomplishments

Pt/RuO_2-TiO_2 Catalyst Synthesis @ NTCNA

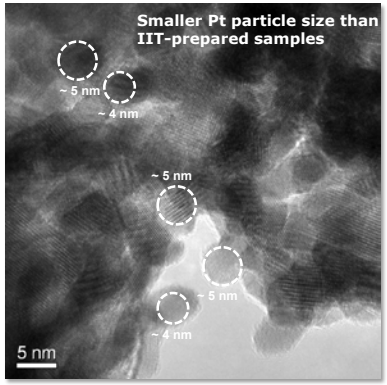
- The support RuO_2-TiO_2 was catalyzed using microwave assisted catalyst synthesis process

Objectives and Challenges

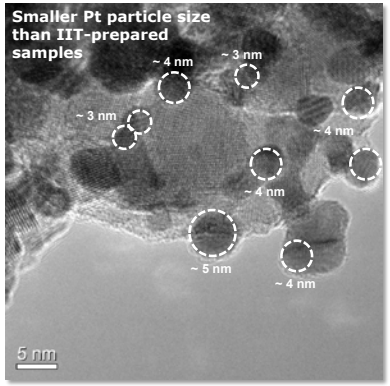
- Decrease Pt particle size to ~ 4 nm to improve catalyst performance. The goal is to have good particle size distribution and dispersion on the RTO support.
- Challenges in depositing ~ 4 nm Pt nanoparticles on RuO_2-TiO_2 (or metal oxides in general):
  - RuO_2-TiO_2 support has low surface area, unlike Ketjen Black or other HSAC.
  - It has a low number of functional groups or anchoring sites for Pt deposition.
  - We cannot go to high pH during synthesis since the support is unstable at high pH and may dissolve. High pH, however, helps in making ~4 nm Pt particles.



Catalyst synthesized at IIT



Catalyst synthesized at NTCNA (Approach 1) Modified IIT procedure



Catalyst synthesized at NTCNA (Approach 2) Microwave assisted synthesis

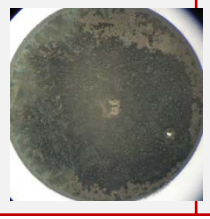
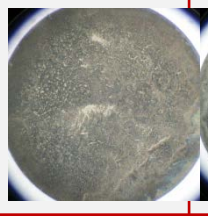
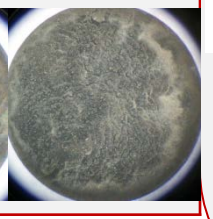
Microwave synthesis

- TEM analysis showed that the catalyst synthesized at NTCNA using approach 1 has a slightly better dispersion and slightly smaller particle size (4-5 nm) than the IIT-prepared sample.
- Our preliminary results using approach 2, microwave-assisted synthesis with yet-unoptimized conditions, show smaller particle size (3-5 nm) than IIT-prepared sample (reported previously)

Pt/RuO_2-TiO_2 Catalyst Synthesis @ NTCNA

Results –Electrochemical Evaluation

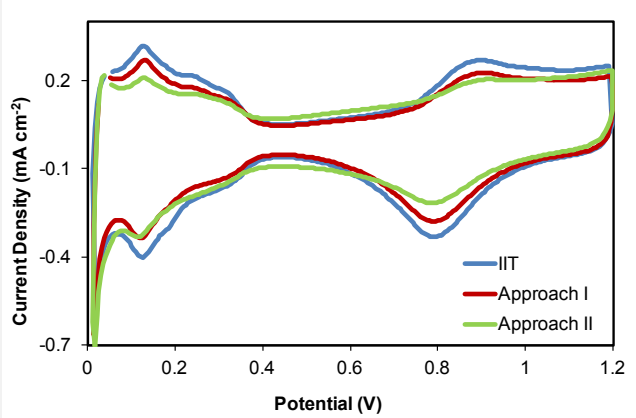
- The catalysts synthesized at NTCNA (Approach 1 and 2) have smaller particle size but lower activity than the IIT-prepared samples.
  - NTCNA approach 1 showed higher limiting current, which might be due to better Pt dispersion on the support which facilitates O_2 diffusion.
- Optimization of synthesis conditions (Approach 2) will continue in order to improve the activity.

Sample	IIT	Approach 1	Approach 2
Pt loading (%)	40	47*	37*
Pt particle size (nm)	5-9	4-5	3-4
Disk image			

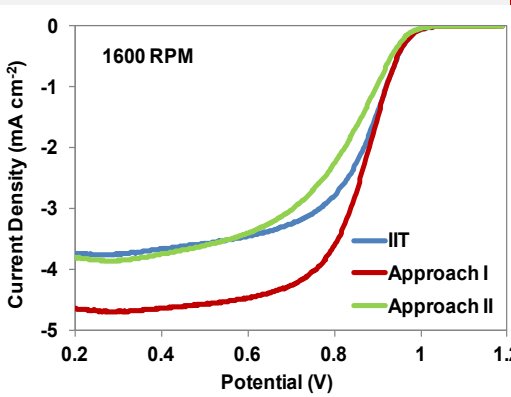
*actual % loading, based on ICP analysis

Activity Characterization

CV@50 mV/s



iV@10 mV/s



Sample	ECA (m^2/g_{Pt})	I_s (uA/cm_{Pt}^2)	I_m (mA/mg_{Pt})
IIT	32.7	575	188.6
Approach 1	24.8	648	161
Approach 2	24.5	491	121

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.

Technical Accomplishments: XRD of ITO

Crystallite sizes were estimated using the Scherrer equation.

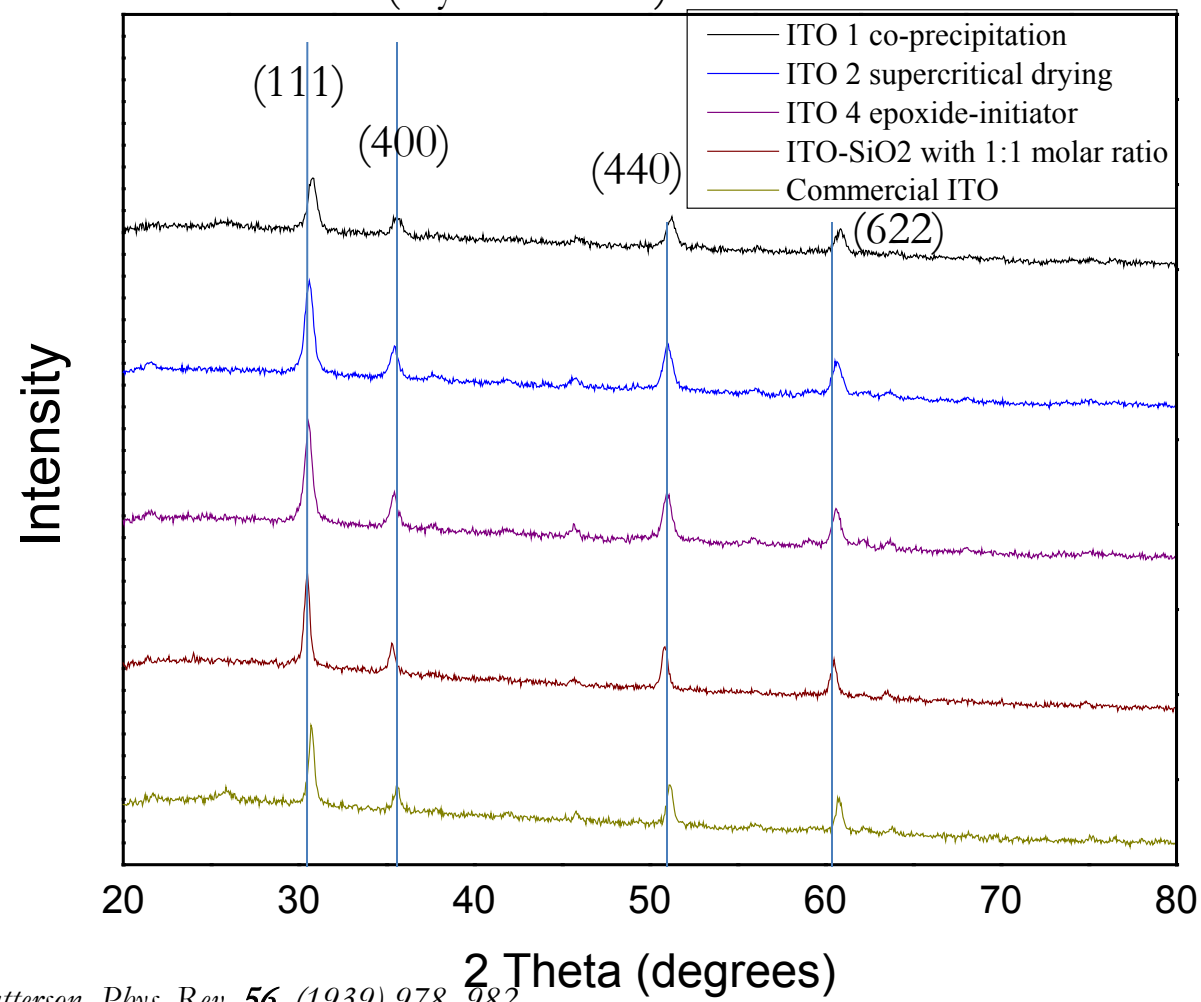
K(shape factor)=0.94; λ (x-ray wavelength)=1.54Å;

β(the line broadening at half the maximum intensity in radians);

Θ(Bragg angle)

τ(crystallite size)

$$\tau = K^* \lambda / \beta \cos \Theta$$

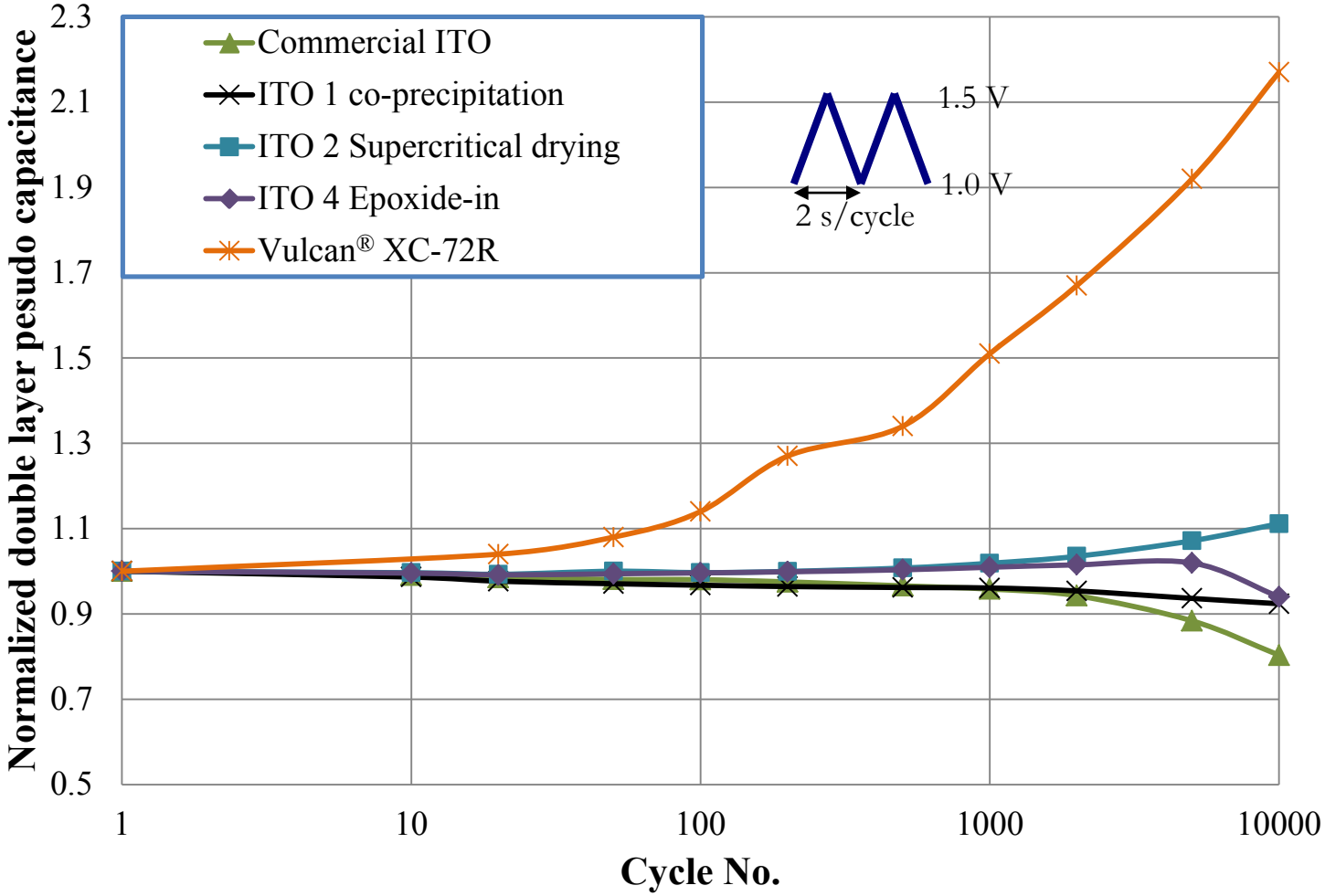


	ITO crystallite sizes(nm)
ITO 1	17.3
ITO 2	16.8
ITO 4	19.2
ITO –SiO_2	18.2
Commercial ITO	24.5

A, Patterson, Phys. Rev. ***56*** *(1939) 978–982*

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



Technical Accomplishments: Change in Double Layer Pseudo-Capacitance

Loss of double layer pseudo capacitance	Commercial ITO	ITO 1 co-precipitation	ITO 2 supercritical drying	ITO 4 epoxide initiator	Vulcan XC- 72 R
1000 cycles	4%	4%	2%	1%	51%
2000 cycles	6%	5%	4%	2%	67%
5000 cycles	12%	6%	7%	2%	92%
10000 cycles	20%	8%	11%	6%	217%

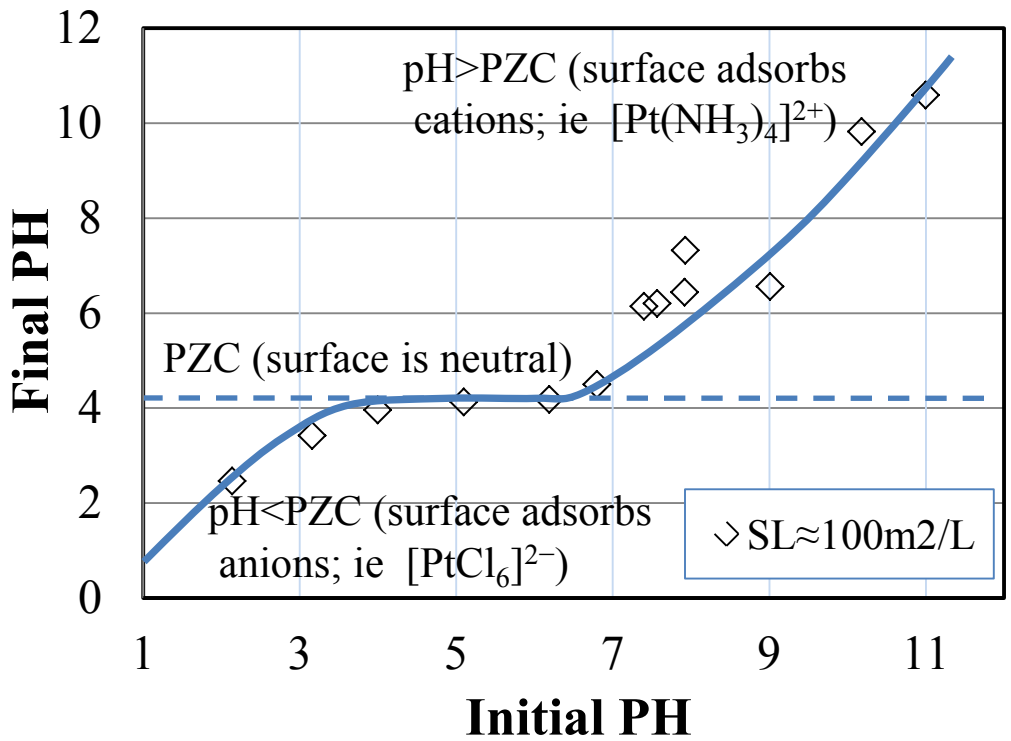
ITO materials synthesized at IIT showed better stability than the commercial ITO.

The ITO obtained from epoxide-initiated method showed the best stability.

Approach: Point of Zero Charge (PZC) Determination for ITO (Surface Loading: 100m^2/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.



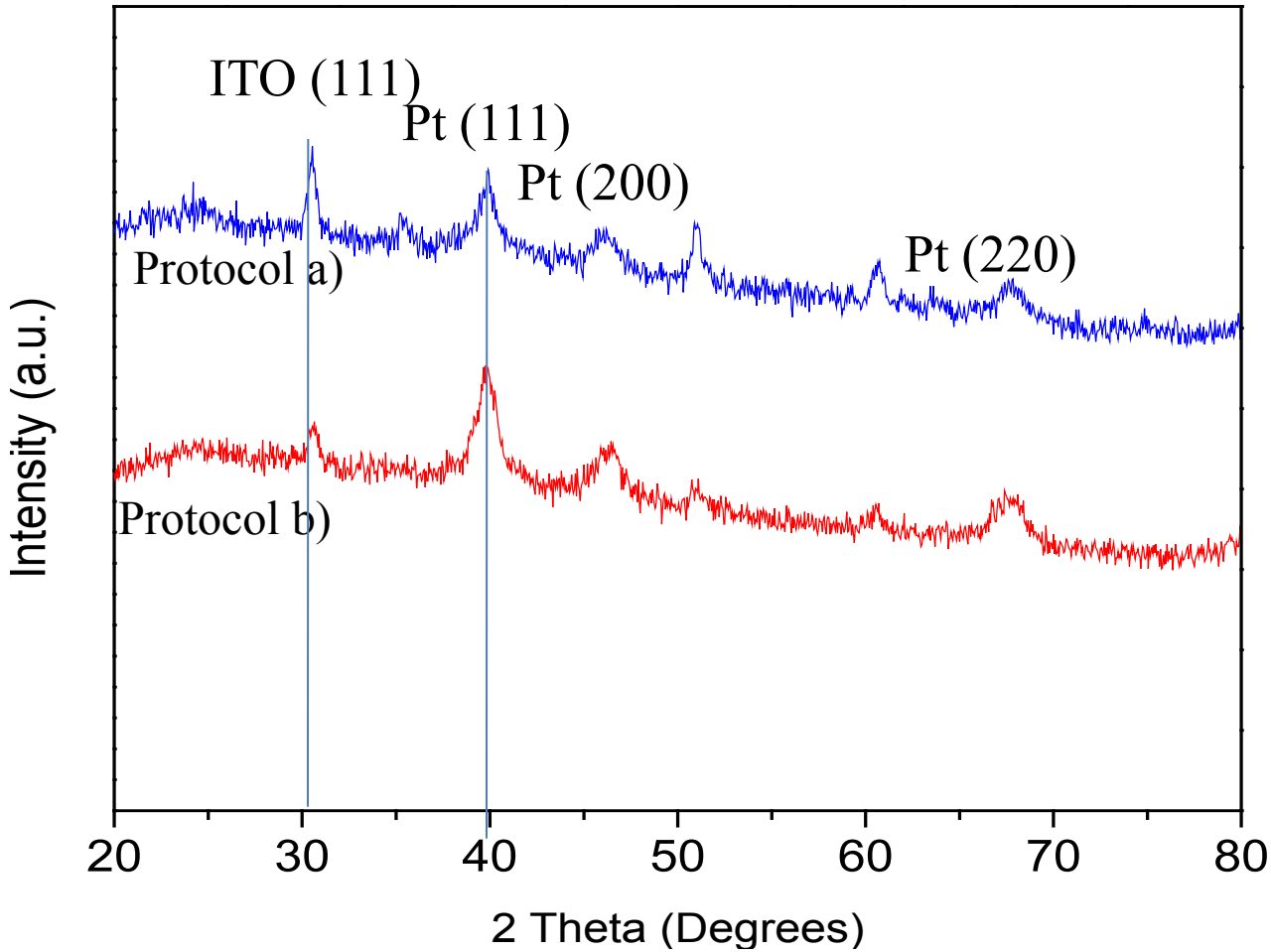
The PZC value of the ITO was ~ 4. Plateau was small but if the surface loading was higher, then the plateau would be broader.

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

We used H_2PtCl_6 as the precursor when using the "SEA method"

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

Technical Accomplishments: XRD of Pt/ITO



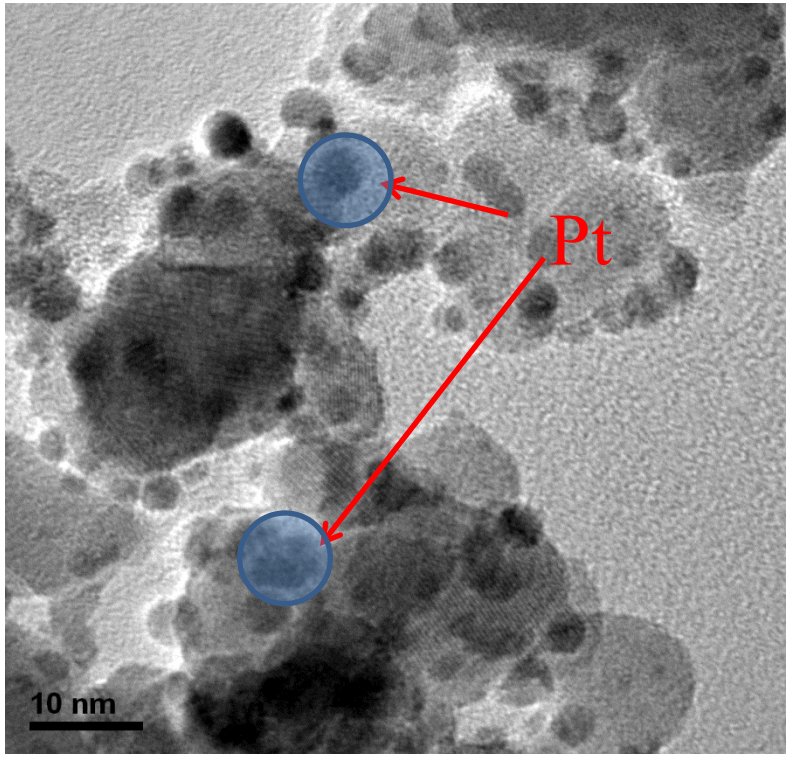
	ECSA (m^2/gPt)
Protocol (a)	20
Protocol (b)	10

ECSA:Electrochemical surface area

Supports with higher BET surface area resulted in well-dispersed Pt particles with smaller crystallite size.

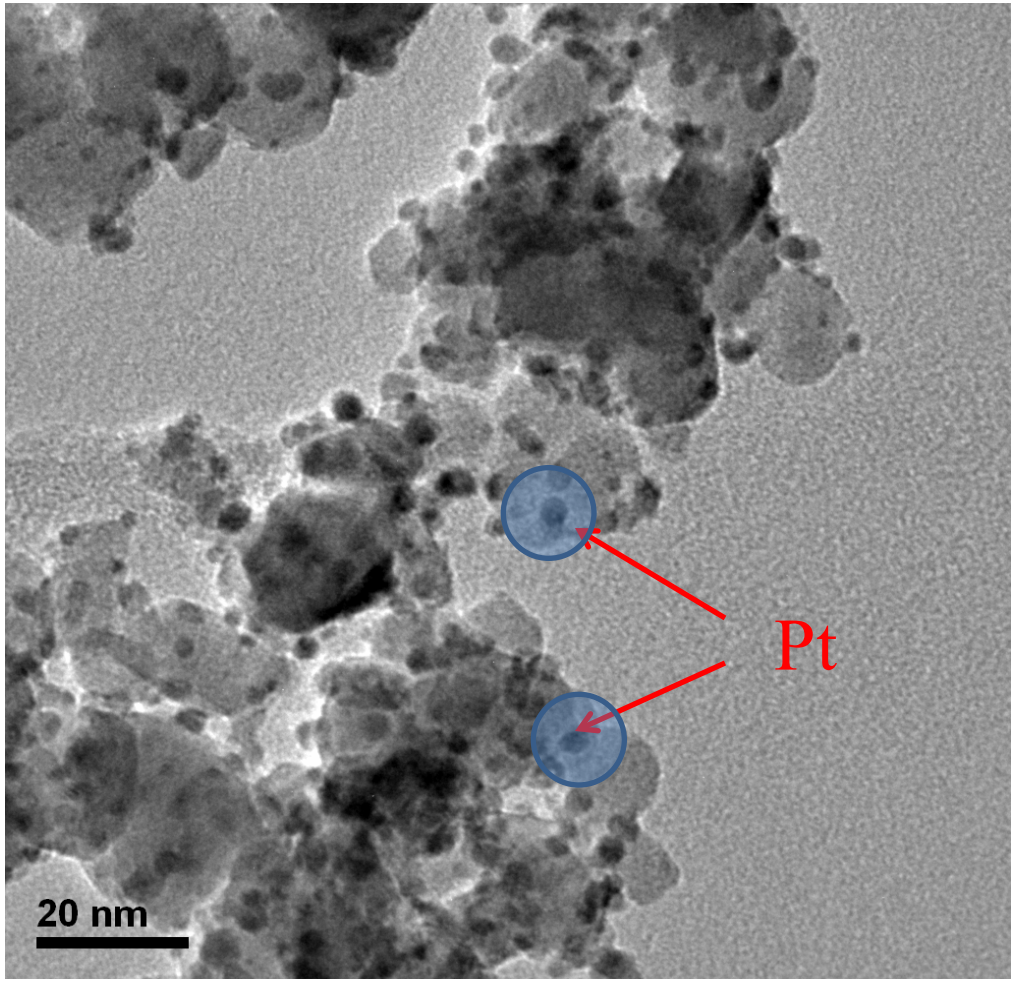
A, Patterson, *Phys. Rev.* **56** (1939) 978–982

Technical Accomplishments: TEM of Pt/ITO



Pt particle size: 3~5 nm

BET surface area ITO
: 45±3 m^2/g



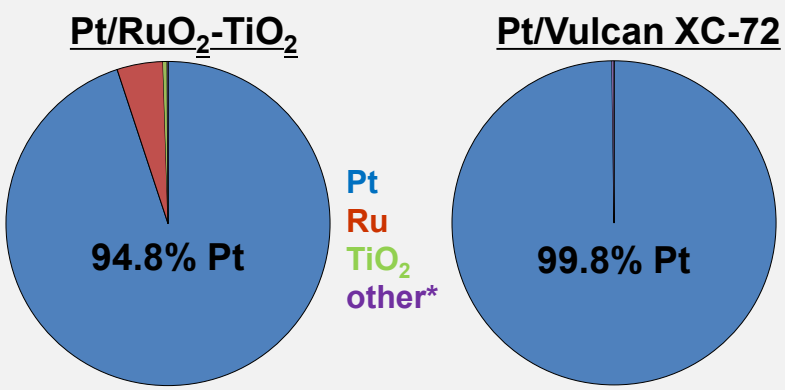
40P wt% Pt/ITO obtained from Protocol (a)

Preliminary Cost Model

Pt/RuO_2-TiO_2

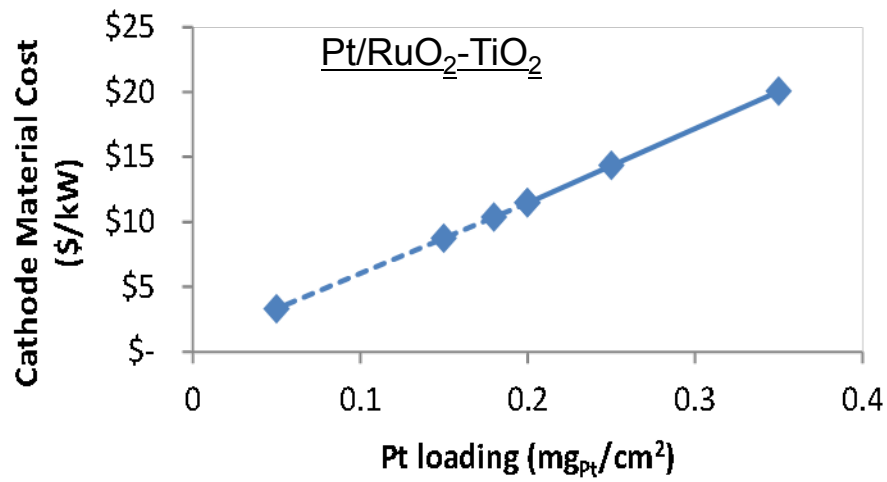
- Material costs for production of Pt/RuO2-TiO2 electrodes as compared to Pt/Vulcan XC-72
  - Vulcan XC-72 data from 2008 FC System Cost Estimation from the DOE† (latest to include Pt/C cost)
- Assumptions :
  - With the exception of the Cathode, the rest of the MEA is identical (Anode, membrane, GDL, 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
- The only differences in these systems comes down to material cost of the Cathode (Pt/RuO_2-TiO_2 vs. Pt/Vulcan XC-72)

Cathode Material Cost Breakdown



*other inc. carbon support, Nafion® & solvents

- The RuO_2-TiO_2 support is more expensive, but the total material cost is still dominated by Pt
  - Pt still accounts for ~95% of the cathode material cost



- Cathode material cost is dominated by Pt
  - A reduction in Pt loading will allow for a significant reduction of cathode material cost
- Cathode material cost is virtually proportional to Pt loading

†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/RuO_2-TiO_2

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* =

Mass Activity retention of Catalyst / Mass Activity retention of Pt/ RuO↓2 − TiO↓2

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

Based on this protocol, Vulcan XC-72 is only <u>69%</u> as durable as the RuO_2-TiO_2 support

	Pt/RuO_2-TiO_2	Pt/Vulcan XC-72
Cathode Pt loading (mg_{Pt}/cm^2)	**0.35**	**0.18**
Rated Power (mW/cm^2)	650	715
Pt	$1,718.45	$1,203.42
Ru	$83.02	$ -
TiO_2	$7.29	$ -
other	$3.00 (est.)	$2.64
Total Material Cost ($)	$1,811.76	$1,206.06
Total Material Cost ($/$kW_{net}$)	$22.65	$15.08
Durability Factor	1	0.69
Total Material Cost ($/$kW_{net}$) w/ durability	**$22.65**	**$21.85**

- **In FC Systems with equal lifetimes, one utilizing Pt/RuO_2-TiO_2 costs only <u>4% more</u> than one with Pt/Vulcan XC-72.**
  - **<u>This is with almost double the Pt loading. Significant potential to reduce cost with reduced Pt loading</u>**

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.
- In collaboration with Nissan North America Inc., extensive benchmarking of state-of-the-art electrocatalysts and electrocatalyst supports has been performed.
- Cost Model is under preparation. Initial 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.
  - Discussions are ongoing to house an IIT researcher (student) at Nissan North America Inc. for 1-2 weeks; with a reciprocal visit to IIT
  - 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 13:**
  - **Incorporate best electron conducting formulation into sulfonic acid functionalized supports and quantify mixed-conductivity (Task 1/2)**
  - **Complete work on ITO supports (Task 1 and 2)**
  - **Work in conjunction with Nissan North America Inc. to synthesize and test catalysts with lower Pt particle sizes (Task 2)**
  - **Optimize introduction of platinum nanoparticles onto durable mixed-conducting supports; continue to evaluate specific and mass activities (RDE and MEA), and stability under cycling (Task 1,3)**
  - **Finish cost model; commence large scale MEA fabrication (Task 3,5)**
- **Future directions in Phase 2**
  - **Continue work on incorporating Pt nanoparticles onto durable supports using standard and supercritical impregnation methods (Task 1,3)**
  - **Substantially complete work leading to ionomer reduction in the electrode through sub-scale MEA studies (Task 3)**
  - **Begin large scale MEA fabrication and testing and complete cost analysis on downselected supports (Task 4, 5)**

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 100 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 FY13 and beyond

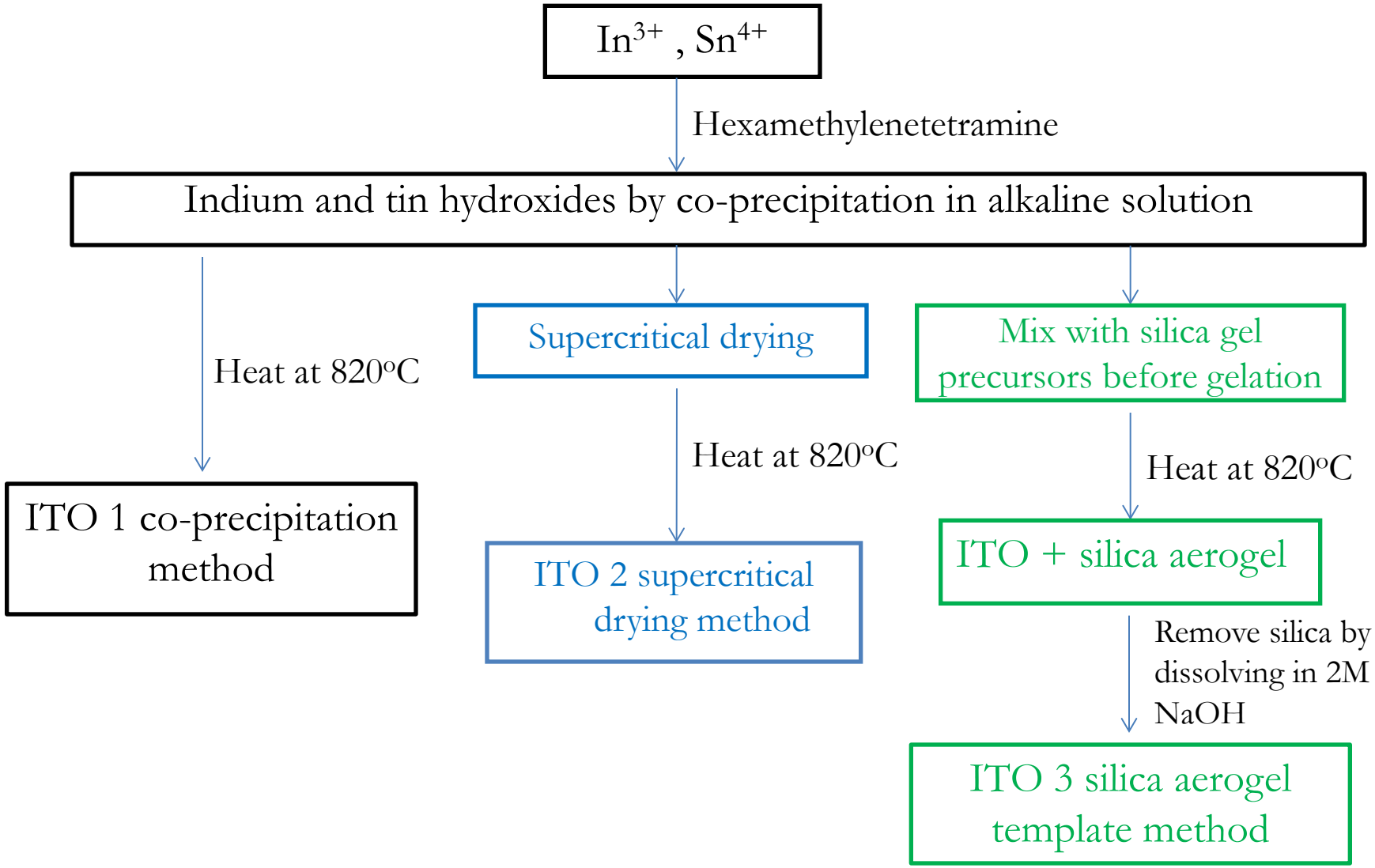
- Study and quantify mixed-conductivity in synthesized supports (Task 1,2)
- Work in conjunction with Nissan North America Inc. to complete durability testing and synthesize catalysts with lower Pt particle size (Task 2)
- Introduce platinum nanoparticles onto ITO and onto durable mixed-conducting supports; evaluate specific and mass activities, and stability under cycling using RDE and MEA studies (Task 1,3)
- Complete ionomer reduction studies, initiate scale up of MEAs and comlete formulation of cost model for downselected formulations (Tasks 3-5).

Supplementary Slides

Acronyms Used in Presentation

ITO	Indium tin oxide
RTO	RuO_2-TiO_2
SRO	SiO_2-RuO_2
SEA	Strong electrostatic adsorption
PZC	Point of zero charge
NHE	Normal hydrogen electrode
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
CV	Cyclic voltammetry
ECSA	Electrochemical surface area

Approach: Strategies to Synthesis Indium Tin Oxide (ITO)



Z.Ding, C. An, et al. J. of Nanomaterials, Volume 2010, Article ID 543601

H.C. Lu,et al. "Synthesis and characterization of crystalline sol-gel derived ITO nano-powders by supercritical C02 drying," 3rd IEEE International Conference, 2008

Approach: Strategies to Synthesize Indium Tin Oxide (ITO)

Synthesis of ITO precursor in the aerogel form (using propylene oxide to condense the hydroxides)

Dissolve $InCl_3$ and $SnCl_4$ in ethanol/water solution (3/1 vol)

↓ Add propylene oxide

Indium and tin hydroxides alcogel

↓ Supercritical drying

Indium hydroxide and tin hydroxide aerogel

↓ Heat at 820°C

ITO 4 epoxide inititator method

Precipitation of ITO precursor inside the porous structure of silica aerogel.

↓

Dissolve $In(acac)_3$ and $[SnCl_2](acac)_2$, in acetone. Add silica aerogel to the solution

↓ Supercritical drying

$In(acac)_3$, $[SnCl_2](acac)_2$ in the pore of the silica aerogel

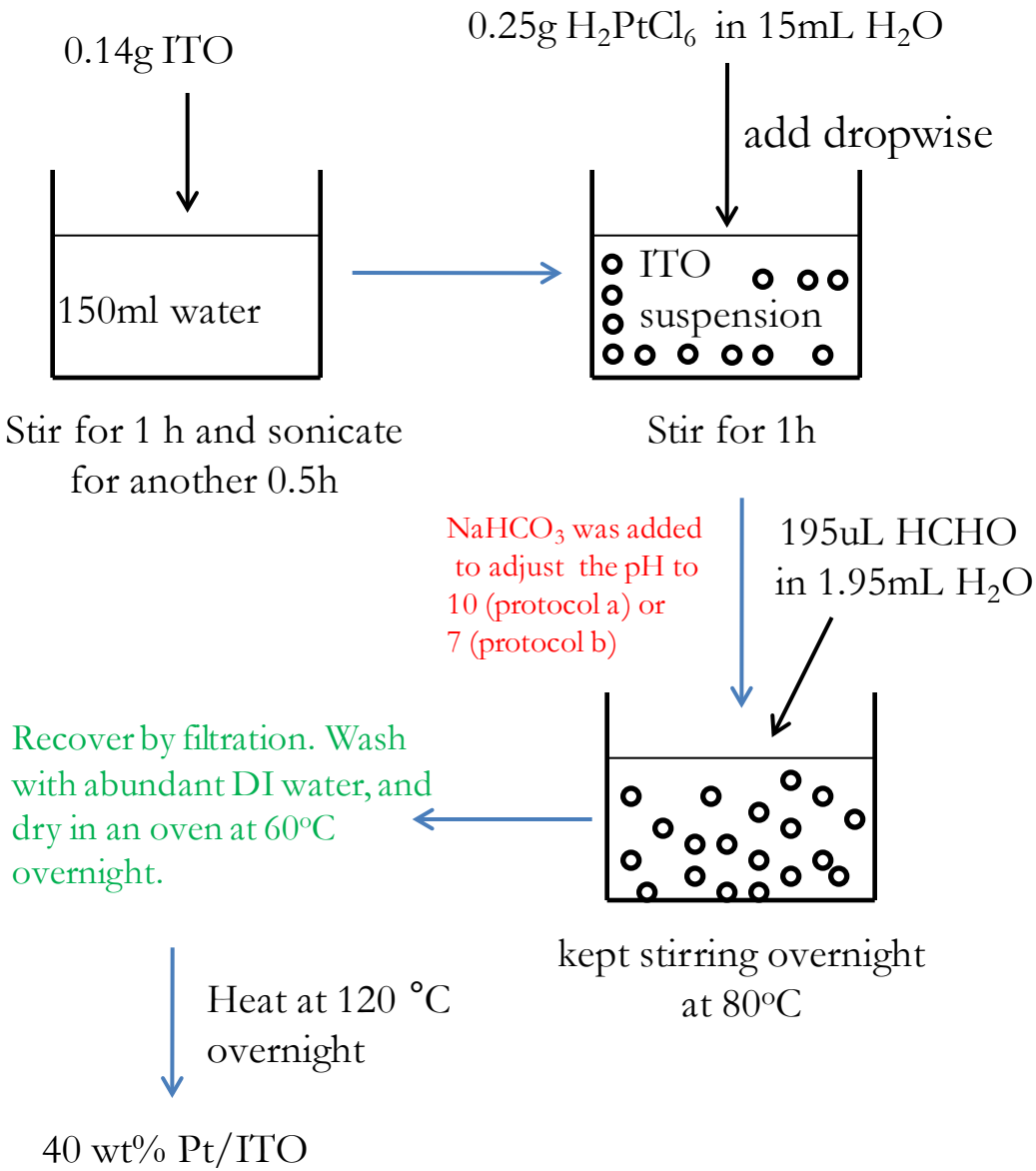
↓ Heat at 820°C

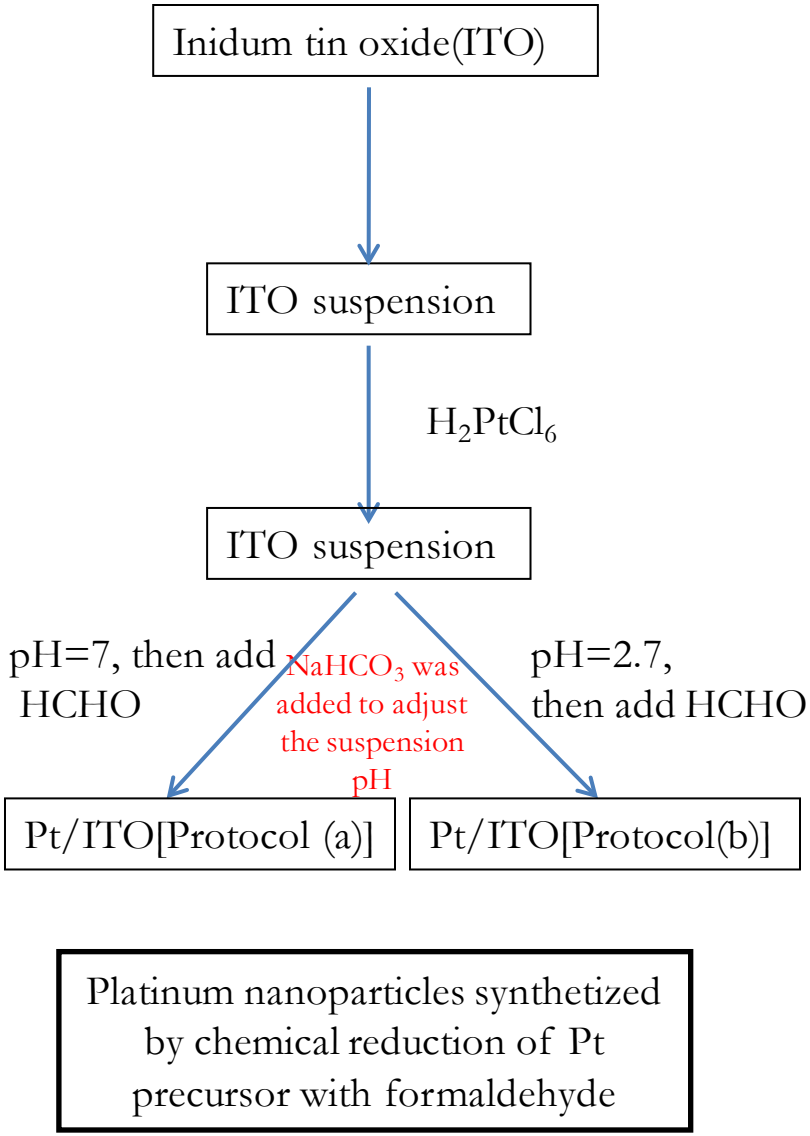
ITO-SiO_2 (1:1 molar ratio)

Work in progress

T. F. Baumann, S. O. Kucheyev, A. E. Gash, J. H. Satcher Jr., Adv. Mater. 2005, 17, 1546-1548

Approach: Platinum nanoparticles synthesis by chemical reduction of Pt precursor with formaldehyde [protocol (a) and (b)]





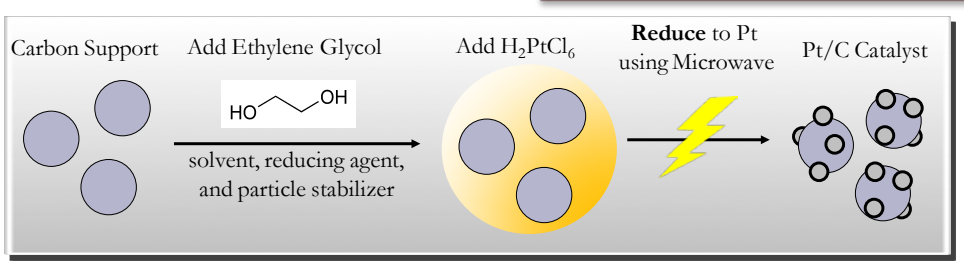
Pt/RuO_2-TiO_2 Catalyst Synthesis @ NTCNA

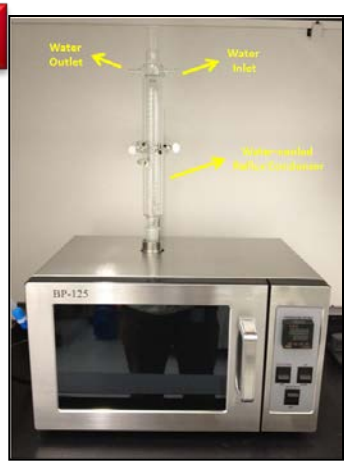
Experimental

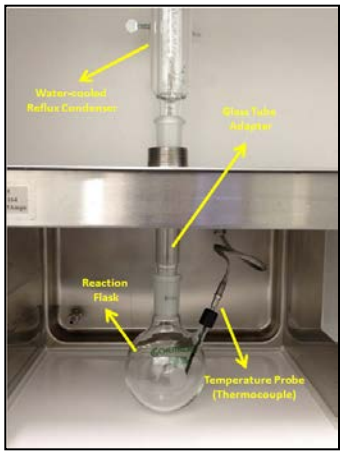
- IIT used water as the solvent and formic acid as the reducing agent in their synthesis of Pt nanoparticles from a chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) precursor.
- NTCNA used two preliminary approaches in decreasing the Pt particle size:

	Approach 1 (Modified IIT Procedure)	Approach 2 (NTCNA IR –microwave assisted synthesis)
Details	**Replaced water with ethylene glycol** (EG) as the solvent. Upon heating, EG forms ethylene glycolate ions which act as stabilizers that prevent particle agglomeration	Microwave-assisted synthesis using ethylene glycol (EG) as solvent, mild reducing agent, and particle stabilizer.
Advantage	The use of formic acid reducing agent may facilitate more complete reduction of H_2PtCl_6 to Pt. Formic acid is a stronger reducing agent than ethylene glycol (EG).	A faster method. Microwave heating should also produce nanoparticles with a narrower size distribution compared to conventional heating (hotplate).

Approach 2







Microwave-Reflux Catalyst Synthesis System and diagram of typical process involved in the synthesis.

Pt/RuO_2-TiO_2 Catalyst Synthesis @ NTCNA

Approach 1

(Modified IIT Procedure)
(slow conventional (hot plate) heating)

RTO in 2M formic acid EG solution

sonicated for 1 hour

↓ Heated to 80˚C with stirring for 1 hour

H_2PtCl_6 precursor dissolved in pH 11 EG solution was added

↓ Kept heated at 80˚C with stirring for 1 hour

Mixture was cooled, filtered, and washed several times with hot water

↓

Powder was dried in vacuum oven at 120˚C overnight

Approach 2

(NTCNA Procedure)
(fast microwave heating)

RTO dispersed in EG

sonicated for 1 hour

↓

H_2PtCl_6 precursor was added

↓ pH was adjusted to pH = 10 using 1M NaOH

Microwaved for 15 minutes at 180˚C at a ramp rate of 10 ˚C/min

↓ pH was adjusted to pH = 3 using 1M HCl

Mixture was cooled, filtered, and washed several times with hot water

↓

Powder was dried in vacuum oven at 120˚C overnight