

# Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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Project ID #  
**FC085**

# Overview

## Timeline

- Project start date: Sept. 1<sup>st</sup> 2010\*
- Project end date: Aug. 31<sup>st</sup> 2013
- Percent complete: ~ 45%

## Budget

- Total project funding
  - DOE share: \$ 1,476,230
  - Costshare: \$ 415,775
- FY11 Funding: \$ 387K
- Planned FY12 funding: \$300K

## 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

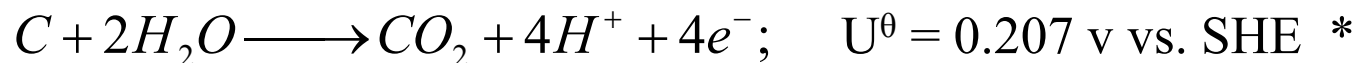
## Partners

- 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<sup>2</sup>/g #
  - Low cost
- Electrochemical oxidation of carbon occurs during fuel cell operation



- 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 ( $> 200 \text{ m}^2/\text{g}$ ) **Focus of Project Phase 1**
  - High proton ( $\geq 100 \text{ mS/cm}$ ) and electron ( $> 5 \text{ S/cm}$ ) 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

- Relevance:

- 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 ( $< 30 \text{ mV}$  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
  - $> 100\text{-}300 \text{ m}^2/\text{g}$
  - Preferably higher,  $\sim 400\text{-}800 \text{ m}^2/\text{g}$
- Porosity
  - Minimal micro -porosity
  - Meso and macro porosity preferred, 10 -100 nm pore size
- Stable in acidic media
  - Low solubility at pH 1
- Corrosion resistant
  - Upon standard test protocols provided by NTCNA, described later.
- High Electronic conductivity
  - $> 5\text{-}10 \text{ S/cm}$
- High Proton conductivity
  - $> 100 \text{ mS/cm}$

# 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<sub>2</sub> 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<sub>4</sub><sup>2-</sup> 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 Mixed Metal Oxide (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<sup>2</sup> MEAs
    - Development of cost model.

# Approach: Systems Studied and Rationale

Five catalyst-support systems have been investigated:

- **RuO<sub>2</sub>-SiO<sub>2</sub>**: RuO<sub>2</sub> deposited on high surface area SiO<sub>2</sub> (RSO or SRO))
- **RuO<sub>2</sub>-SO<sub>3</sub>H-SiO<sub>2</sub>**: RuO<sub>2</sub> deposited on sulfonic acid functionalized SiO<sub>2</sub>, conducts electrons and protons
- **RuO<sub>2</sub>-TiO<sub>2</sub>**: Hydrous or anhydrous RuO<sub>2</sub> deposited on commercial TiO<sub>2</sub> (P25) (RTO or TRO)
- **SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>**: Sulfated tin oxide nanoparticles (preliminary; lower cost)
- **ITO**: Indium tin oxide nanoparticles (preliminary; lower cost)

- **High stability** –
  - Ru<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> has been shown to have high stability in our previous work.
  - SiO<sub>2</sub> and SnO<sub>2</sub> are known to be chemically inert in acidic media.
- **High surface area** –
  - High surface area of SiO<sub>2</sub> can be prepared with surfactant method or supercritical drying technique.
- **High conductivity** –
  - Pure RuO<sub>2</sub> and ITO film have high electrical conductivity around 400 and 1000 S/cm, respectively.
  - Hydrous RuO<sub>2</sub> is a mixed conducting material.
  - SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> 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

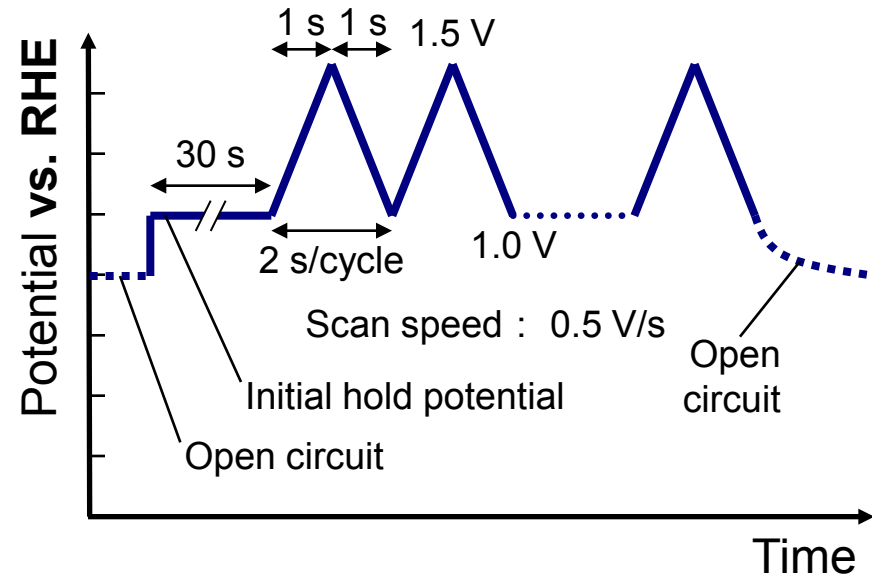
- Milestone 1 (End of Phase 1; Q1; 2012 [calendar year])
  - Synthesize a support that demonstrates at least:
    - 70 mS/cm proton conductivity [Current status ~ >120 mS/cm; stand-alone]
    - 2 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m<sup>2</sup>/g BET surface area [Current status > 250m<sup>2</sup>/g]
    - Durability\* in acidic electrolyte [C-S: durable; ongoing]
- 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<sup>2</sup>/g BET surface area [Current status > 250m<sup>2</sup>/g]
    - Durability\* in acidic electrolyte [Current status – durable, further tests ongoing]
  - Prepare and evaluate Pt-catalyzed supports [Current Status: ongoing]
  - Identify optimal ionomer loading in electrode [Current Status: Not yet started]
  - Prepare 6 100 cm<sup>2</sup> MEAs w/ optimal support formulation [Not yet started]
- GNG criterion (applied at end of Q1; 2012)

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

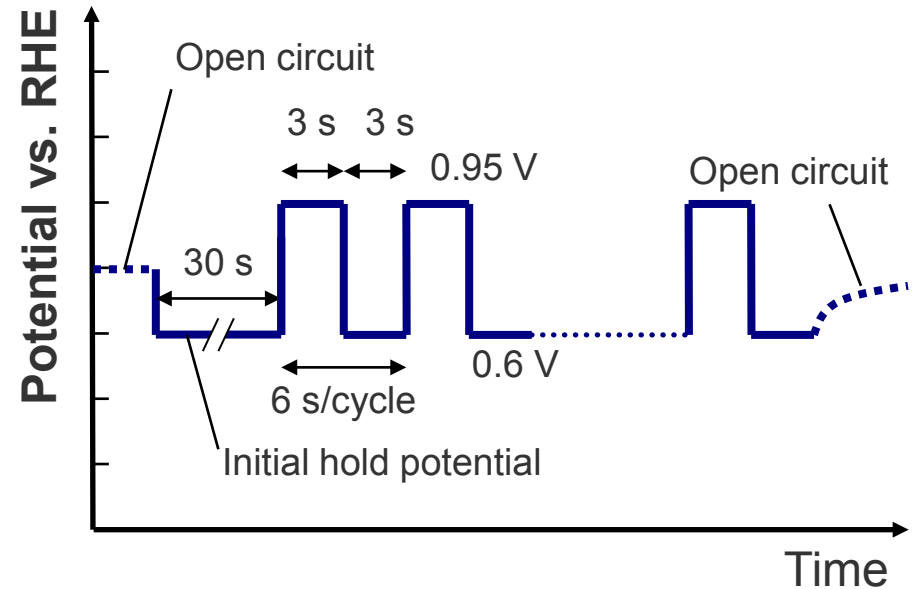
“At the end of Phase I, IIT and Nissan North America Inc. will have prepared or showed significant progress towards preparing a support material with a surface area of 50 m<sup>2</sup>/g; an electron conductivity of 2 S/cm, a proton conductivity of 0.07S/cm and durability in acidic electrolyte of 1000 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<sub>4</sub>

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

# Technical Accomplishments: XRD of RuO<sub>2</sub>- SiO<sub>2</sub>

Crystallite sizes were estimated using the Scherrer equation.

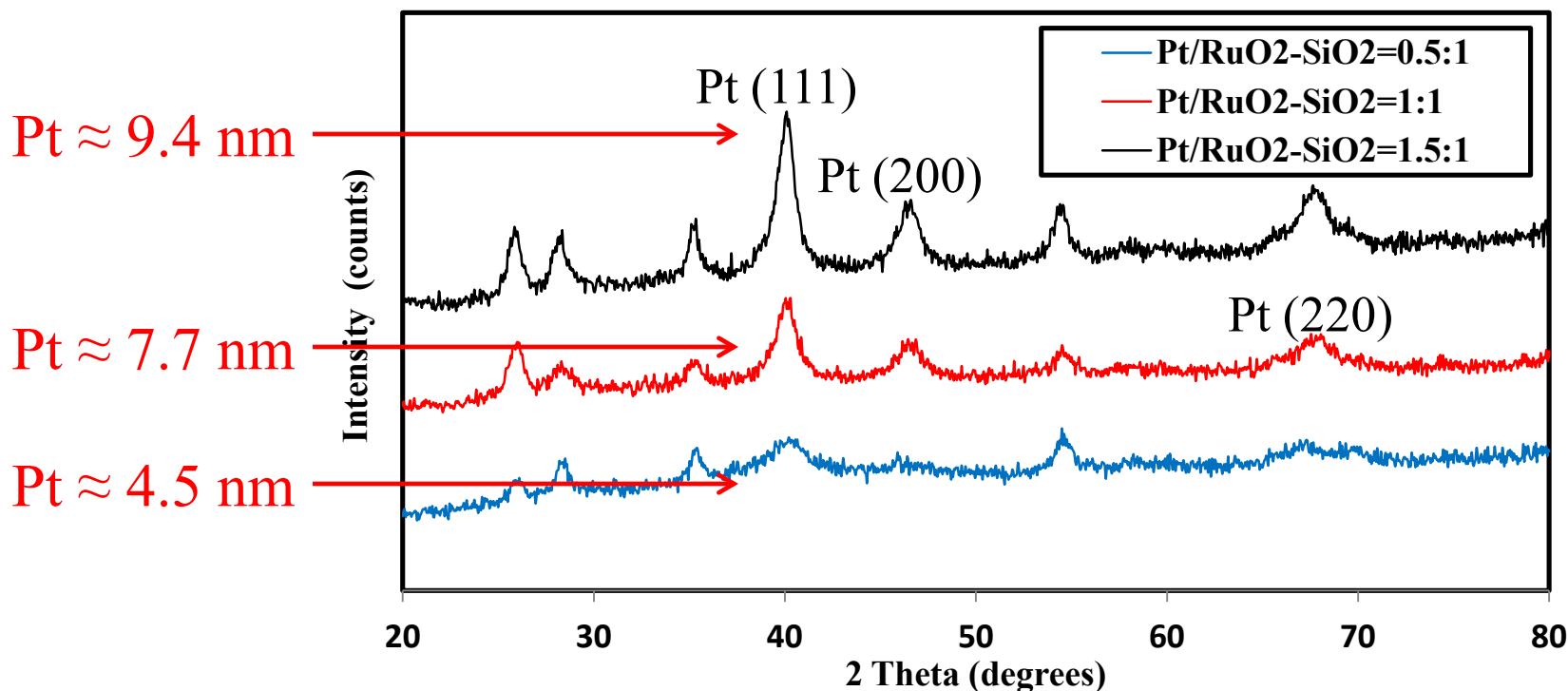
$K$ (shape factor)=0.94;  $\lambda$  (x-ray wavelength)=1.54Å;

$\beta$ (the line broadening at half the maximum intensity in radians)=0.01571;

$\Theta$ (Bragg angle)=40.1°;

$\tau$ (crystallite size)=  $0.94 * 1.54 / 0.01571 / \cos(40.1 / 2 / 360 * 2 * \pi) = 93.96 \text{ \AA}$

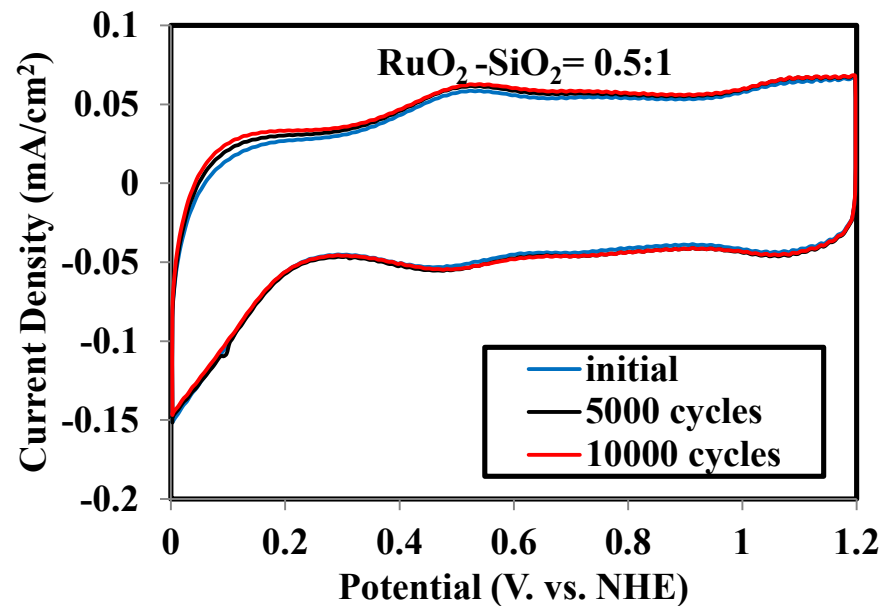
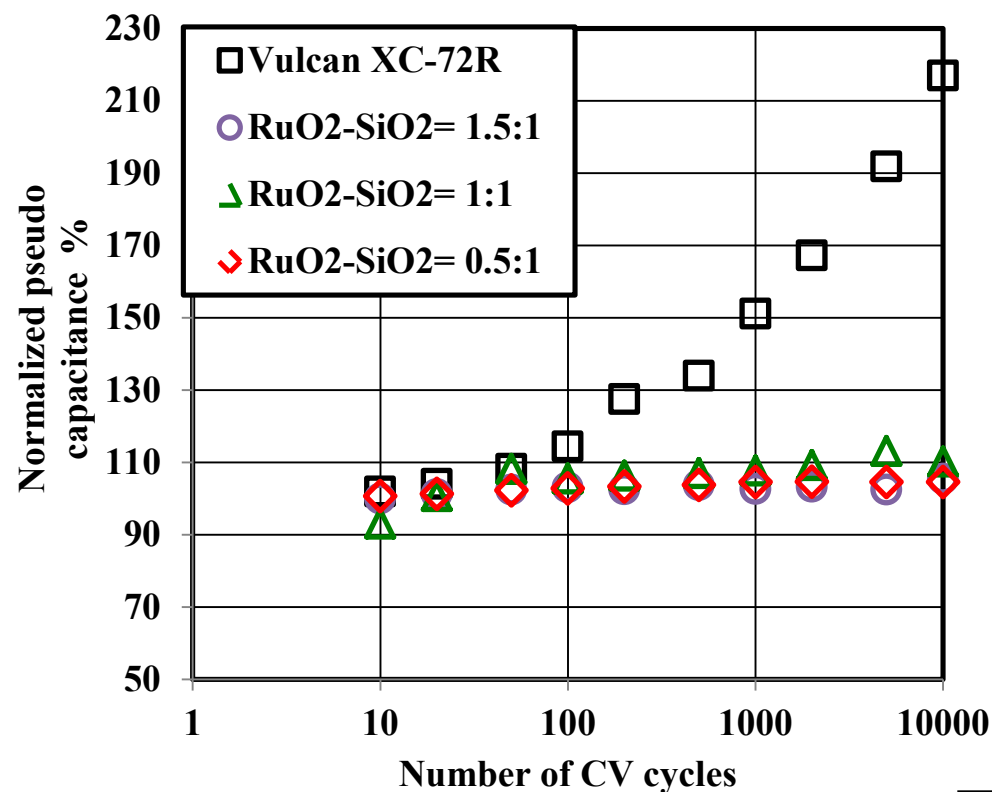
$$\tau = K * \lambda / \beta \cos \Theta$$



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

# Technical Accomplishments: Electrochemical Stability of RuO<sub>2</sub>-SiO<sub>2</sub>

Electrolyte: 0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere;  
CV sweep rate of 20 mV/S; Room temperature cycling and CV

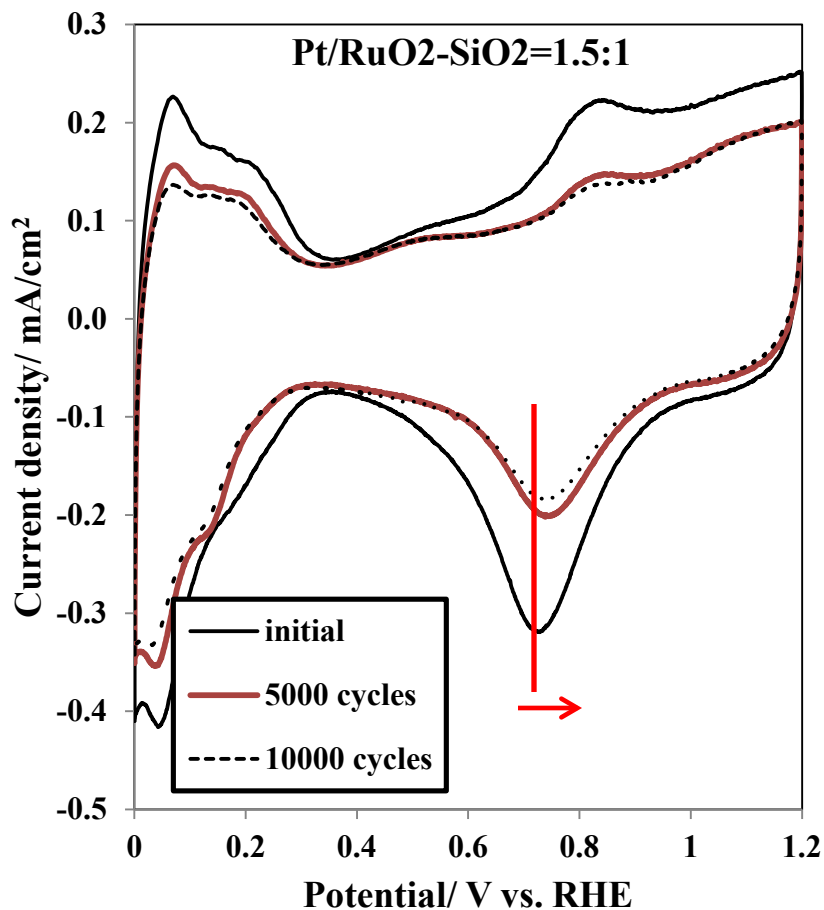


All RuO<sub>2</sub>-SiO<sub>2</sub> supports exhibited higher stability than Vulcan carbon.

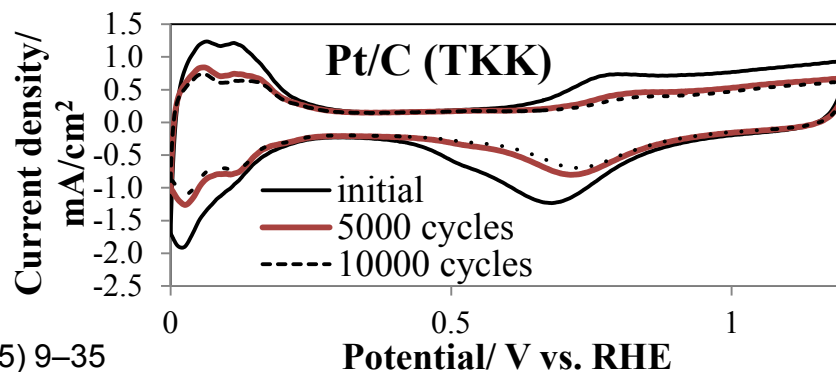
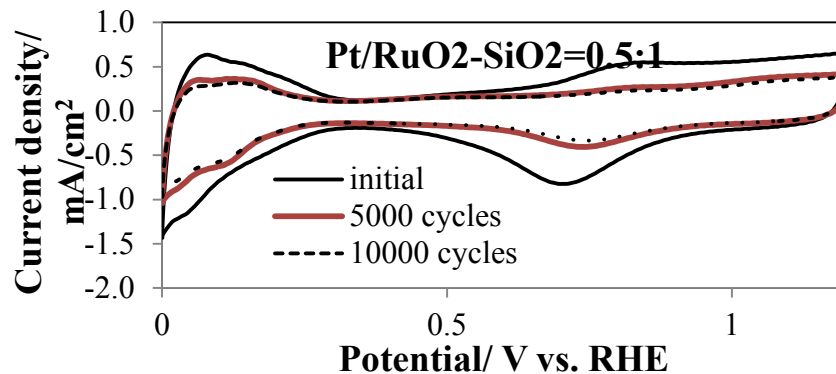
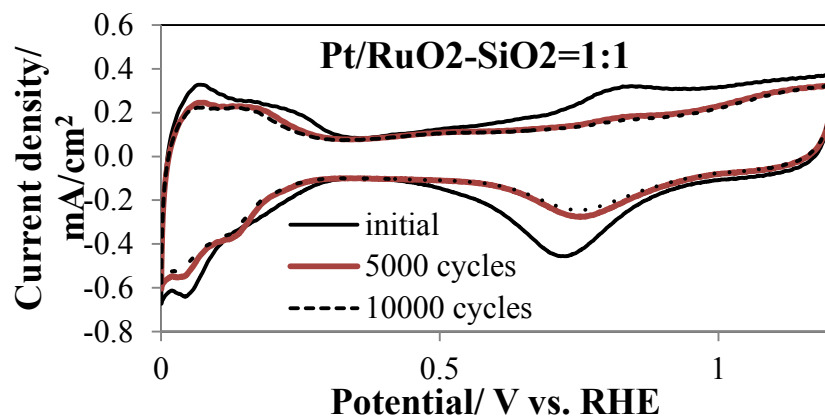
Ru(II)→Ru(III) between 0.244V and 0.444V vs. NHE  
Ru(III)→Ru(IV) between 0.444V and 1.044V vs. NHE  
Ru(IV)→Ru(VI) between 1.044V and 1.444V vs. NHE

# Technical Accomplishments: Stability of Pt/SRO Electrocatalysts

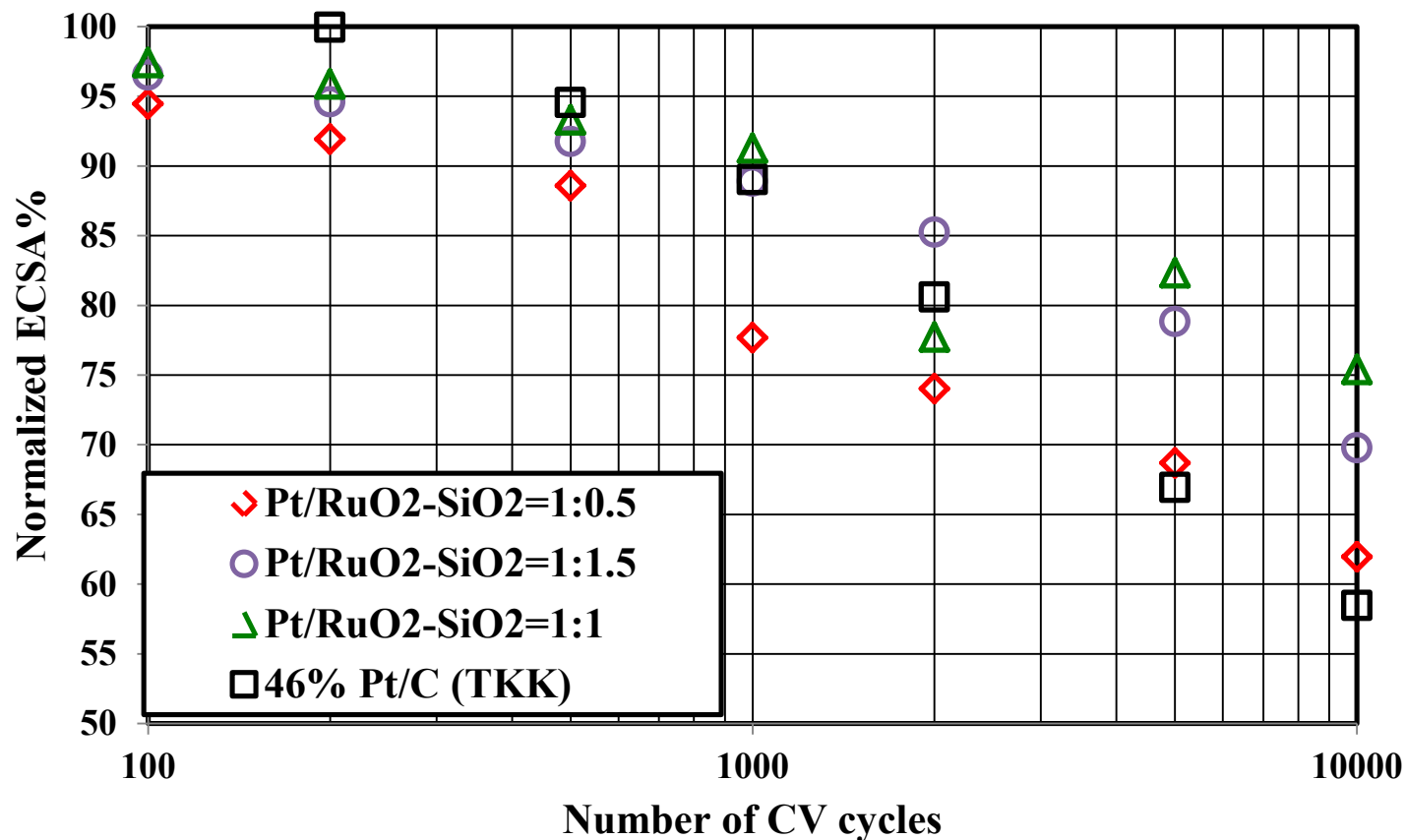
0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; sweep rate of 20 mV/S; room temperature



The positive shift of this peak suggests that Pt particle size increased.



# Technical Accomplishments: Stability of Pt/SRO Electrocatalysts



- All Pt/RuO<sub>2</sub>-SiO<sub>2</sub> supports exhibited higher stability than Pt/C.
- Pt particles with larger crystallite size showed better stability: lower surface free energy.

Pt Crystallite sizes:

Pt/SiO<sub>2</sub>-RuO<sub>2</sub> = 1: 0.5 → 4.5nm

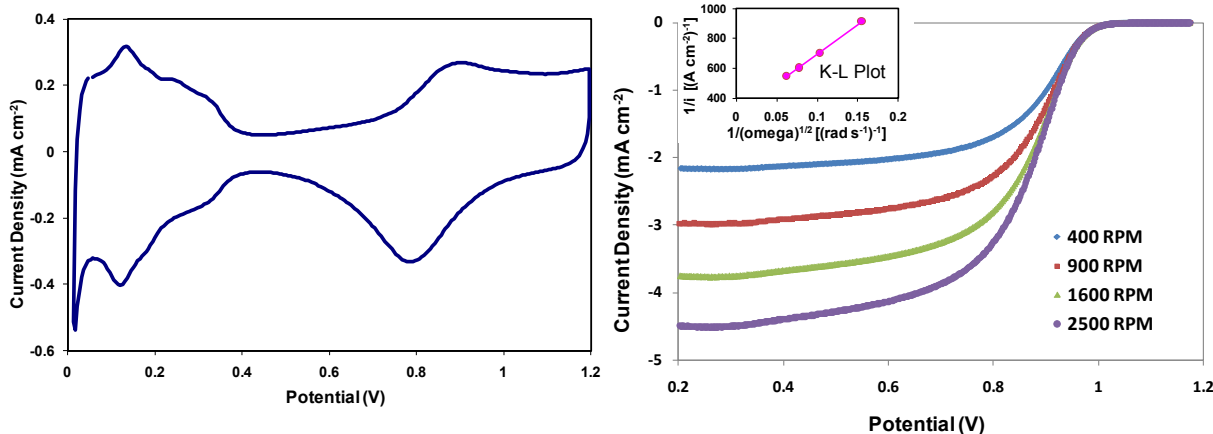
Pt/SiO<sub>2</sub>-RuO<sub>2</sub> = 1: 1 → 7.7nm

Pt/SiO<sub>2</sub>-RuO<sub>2</sub> = 1: 1.5 → 9.4nm

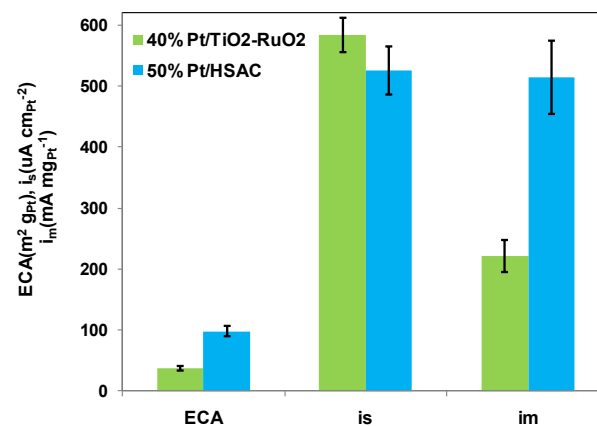
## ORR Activity-RDE

- The ORR activity of the catalyst was evaluated in RDE with optimized ink formulation (I:S=0.58).
  - The results were compared with TTK baseline catalyst TEC10E50E (50% Pt/HSAC).

Example of CV and iV of 40%Pt/TiO<sub>2</sub>-RuO<sub>2</sub>



Activity Benchmarking with Pt/C



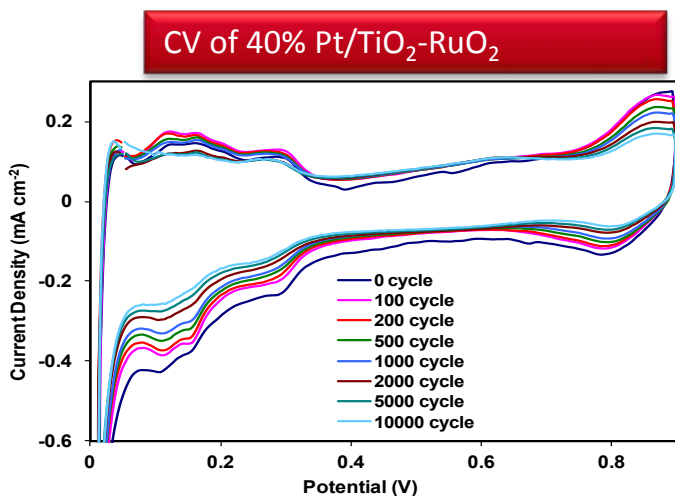
- The catalyst showed the similar H<sub>2</sub> adsorption and desorption characteristic as TEC10E50E
  - ECA was ~ 38 m<sup>2</sup>/g<sub>Pt</sub> (40% of TEC10E50E)
  - Resulted in higher specific activity than TEC10E50E due to lower ECA
- ORR mass specific activity was around 220 mA/mg<sub>Pt</sub> (40% of TEC10E50E)
  - Low mass activity may be due to the larger Pt particle sizes (6-9 nm) than expected ~3 nm

# Technical Accomplishments: Stability of Pt/SRO Electrocatalysts

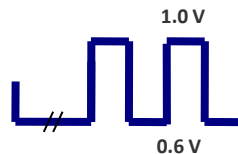


## Catalyst Load-cycling Durability-RDE

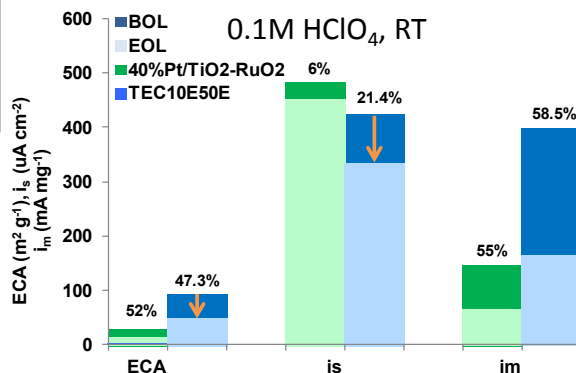
- The Pt stability of the catalyst was tested under Nissan load cycling protocol.
  - The results were compared with TTK baseline catalyst TEC10E50E (50% Pt/HSAC).



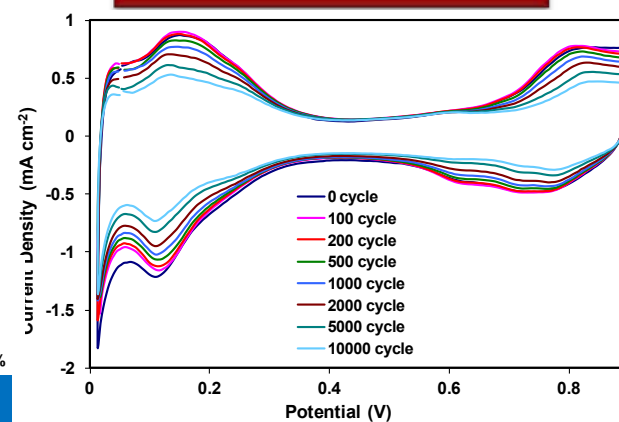
0.1M HClO<sub>4</sub>, N<sub>2</sub> saturated, 60°C



0.1M HClO<sub>4</sub>, RT



CV of 50% Pt/HSAC



- 40% Pt/TiO<sub>2</sub>-RuO<sub>2</sub> showed similar Pt dissolution stability as TEC10E50E
  - ECA loss was ~ 52% (~47% for TEC10E50E)
  - Mass specific activity loss was ~55% (58% for TEC10E50E)

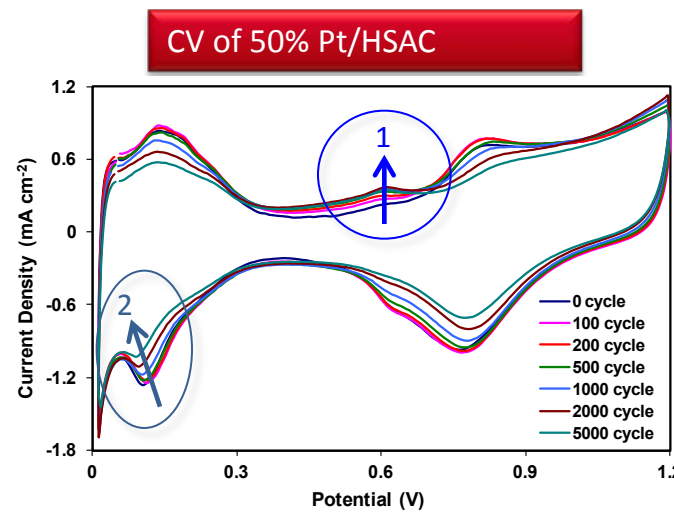
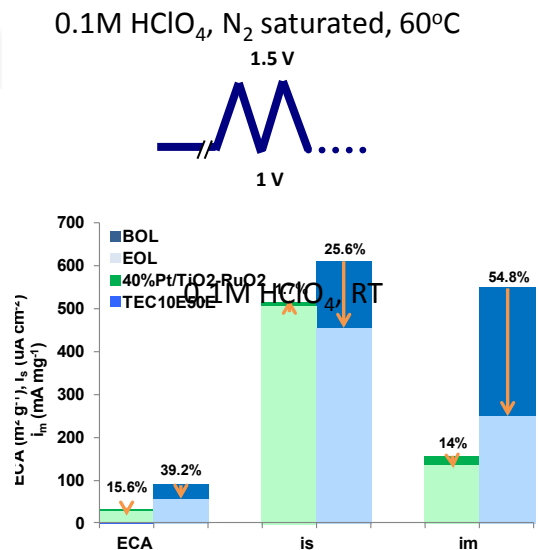
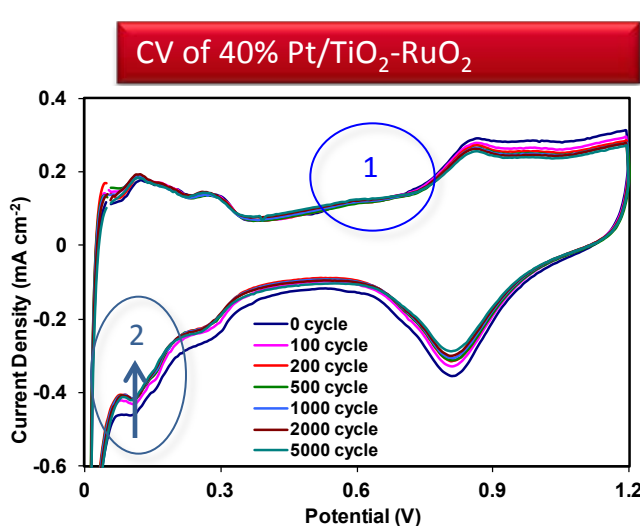


# Technical Accomplishments: Stability of Pt/SRO Electrocatalysts

## Catalyst Start-stop Durability-RDE



- The support stability of the catalyst was tested under Nissan start-stop cycling.
  - The results were compared with TKK baseline catalyst TEC10E50E (50% Pt/HSAC).



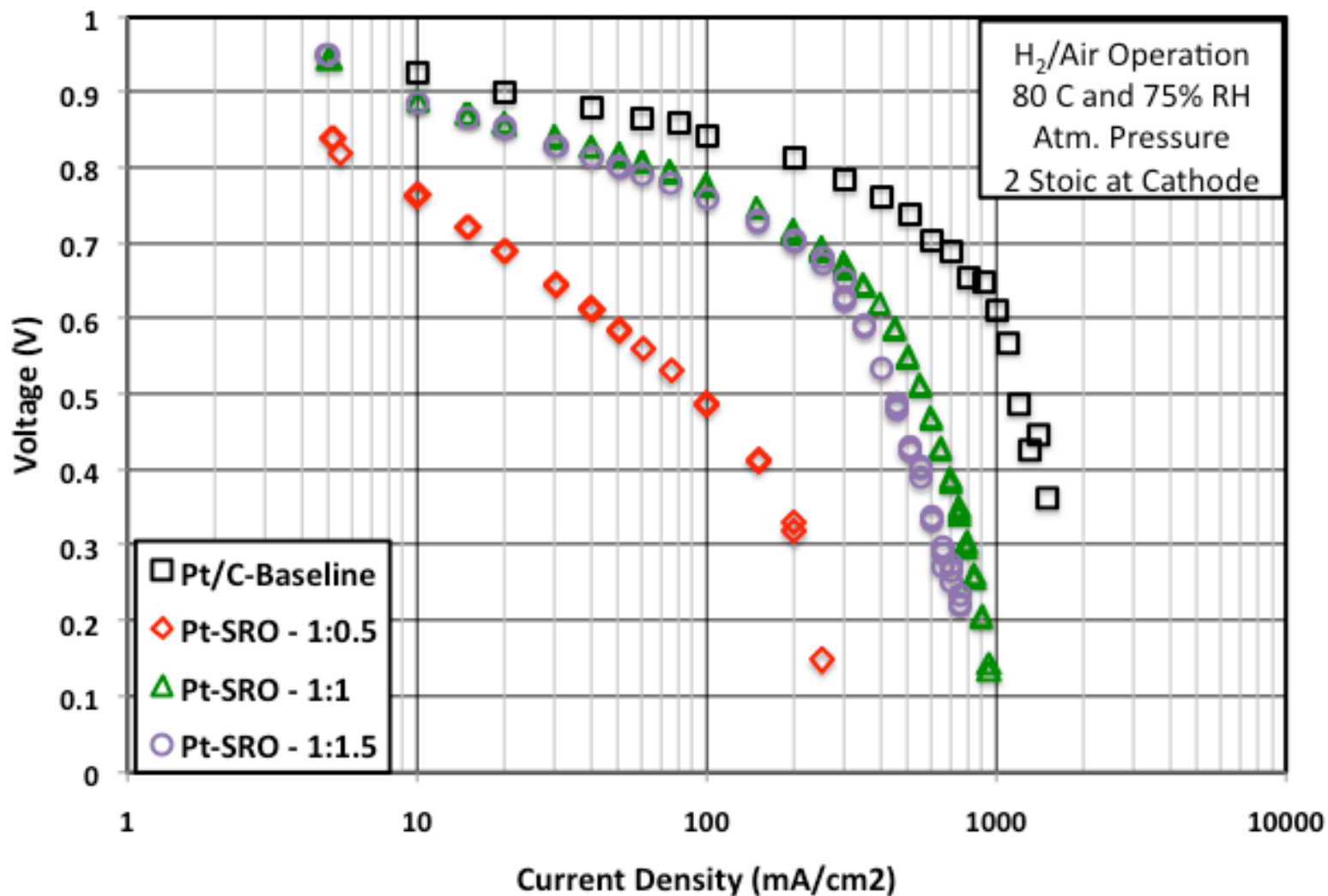
- The TiO<sub>2</sub>-RuO<sub>2</sub> support showed much improved stability in start-stop cycling compared to HSAC support TEC10E50E.
  - ECA loss was ~ 16% (~40% for TEC10E50E)
  - Mass specific activity loss was ~14% (55% for TEC10E50E)
- 1. TiO<sub>2</sub>-RuO<sub>2</sub> did not show any sign of surface oxides as observed for TEC10E50E.
- 2. H<sub>2</sub> adsorption peak potential did not shift like TEC10E50E, which confirms its stability during potential cycling.





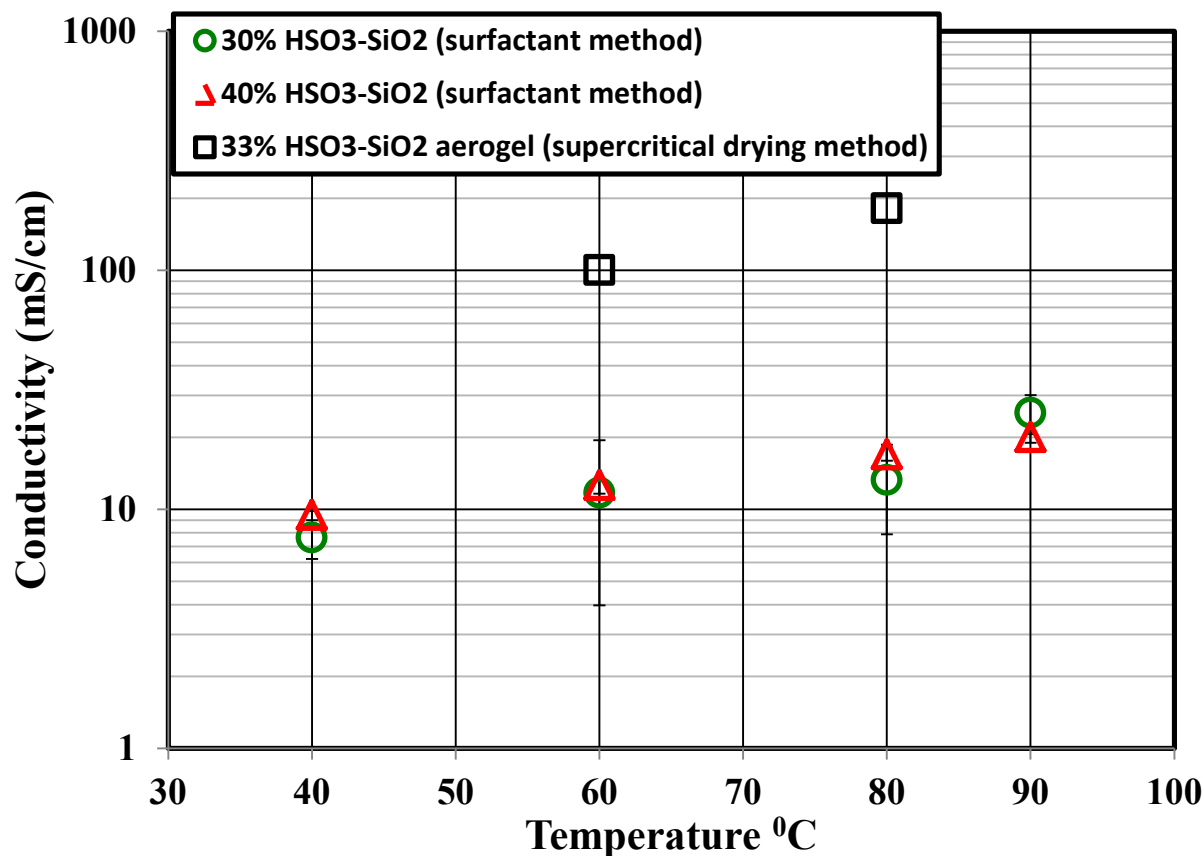
# Technical Accomplishments: Performance with Pt/SRO Electro catalysts

## Polarization Data with Non-Carbon Supports: SRO



Pt loading: **0.4 mg/cm<sup>2</sup>** at the cathode; **0.2 mg/cm<sup>2</sup>** at the anode

# Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO<sub>2</sub> Aerogels



33% HSO<sub>3</sub>-SiO<sub>2</sub> aerogel possesses

□ High proton conductivity

▪ Improvement attributed to the exceptional network structure of the aerogel

□ High BET surface area: 500 m<sup>2</sup>/g.

□ High thermal stability: Conductivity retained upon annealing at 250 °C for 4 hours.

# Technical Accomplishments: Properties of RuO<sub>2</sub> - 33% Sulfonic acid Functionalized SiO<sub>2</sub> aerogels

Weight ratio of RuO <sub>2</sub> - 33% HSO <sub>3</sub> - SiO <sub>2</sub> aerogel	1:1	1.2 :1
Electrical conductivity (S/cm)	3±1	8±3
BET surface area (m <sup>2</sup> /g)	130±5	100±7
IEC (mmol/g)	0.55±0.1	0.5±0.1

□ RuO<sub>2</sub>/HSO<sub>3</sub>- SiO<sub>2</sub> aerogels possess relatively high electrical conductivity and moderate BET surface area.

□ IEC results suggest that only 20~30% of the HSO<sub>3</sub> group was blocked by deposited RuO<sub>2</sub>.

□ This lends credence to the concept of a *mixed-conducting* support

□ Note: Difficult to independently estimate proton and electron conductivity – working on impedance methods to isolate the two.

# Technical Accomplishments: XRD of Pt / RTO

Crystallite sizes were estimated using Scherrer equation.

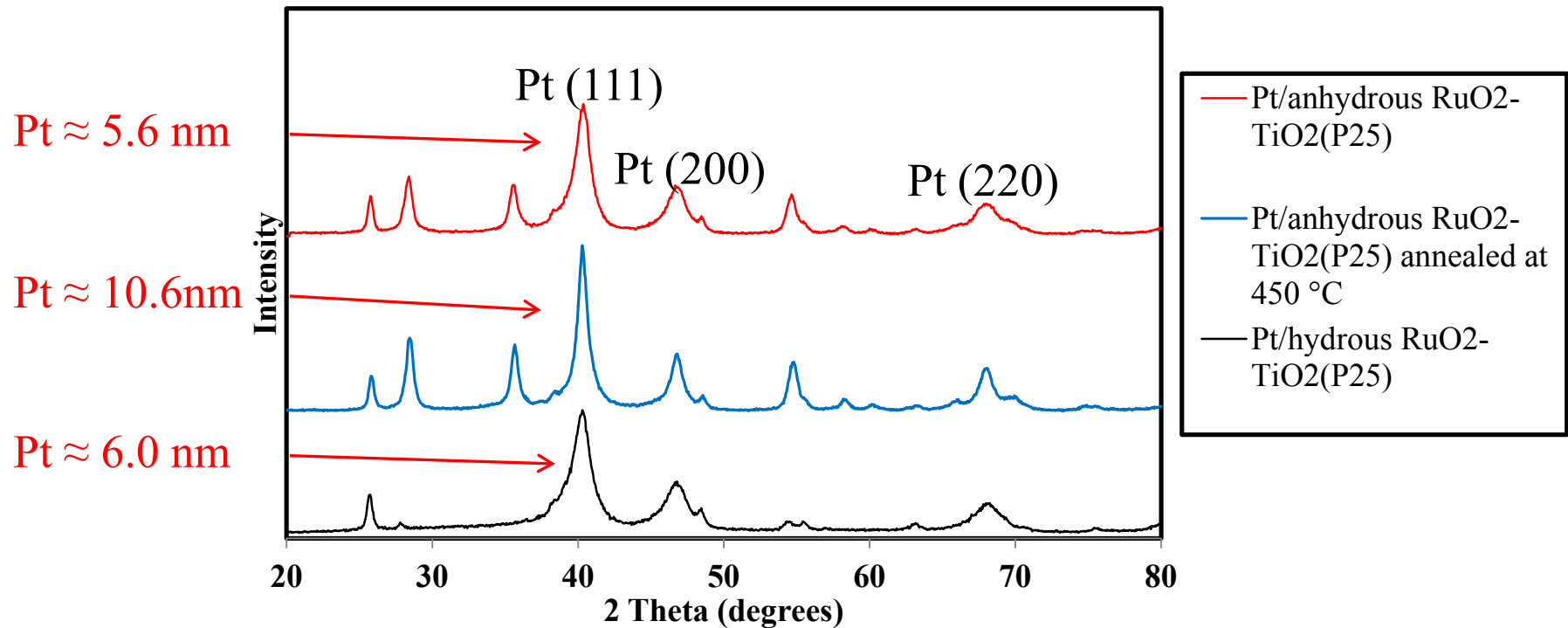
$$\tau = K * \lambda / \beta \cos \Theta$$

$K$ (shape factor)=0.94;  $\lambda$  (x-ray wavelength)=1.54Å;

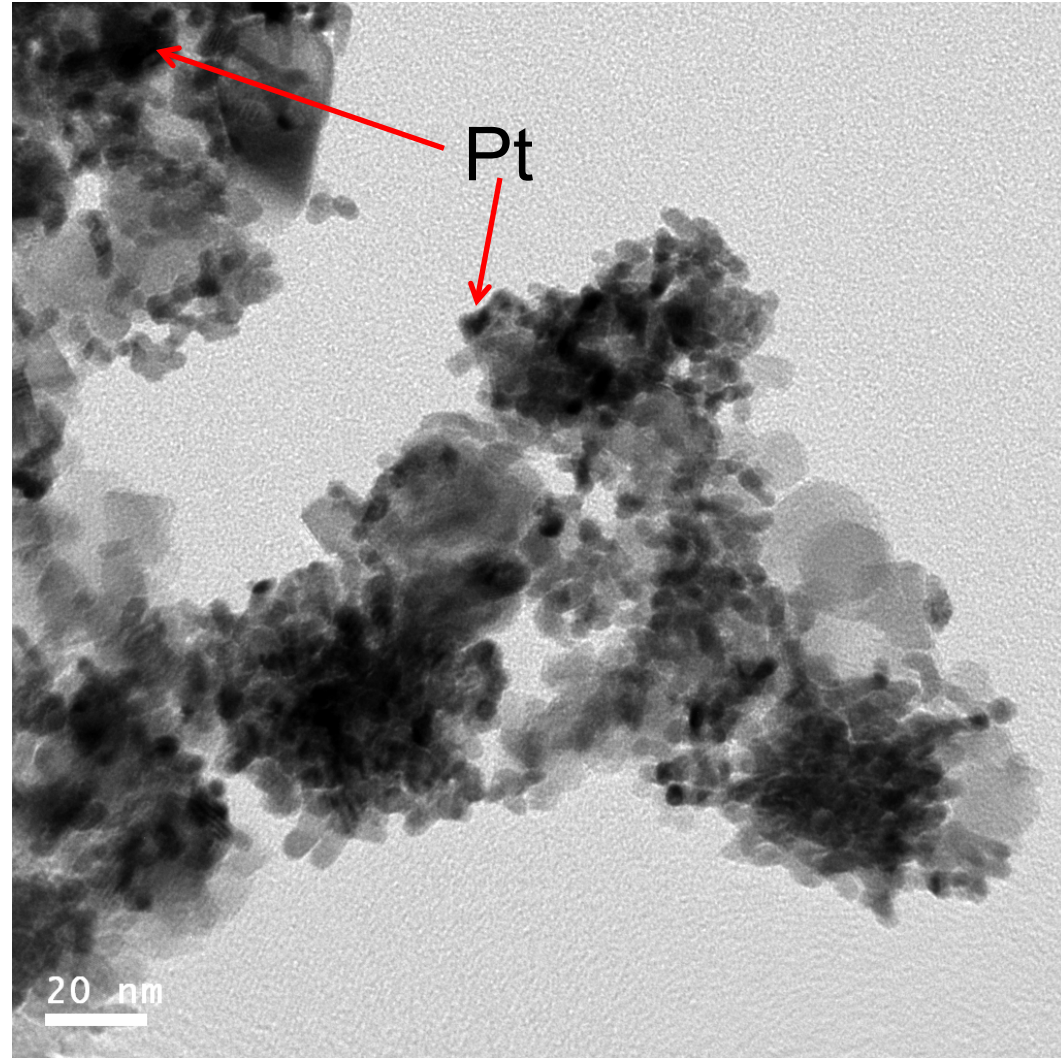
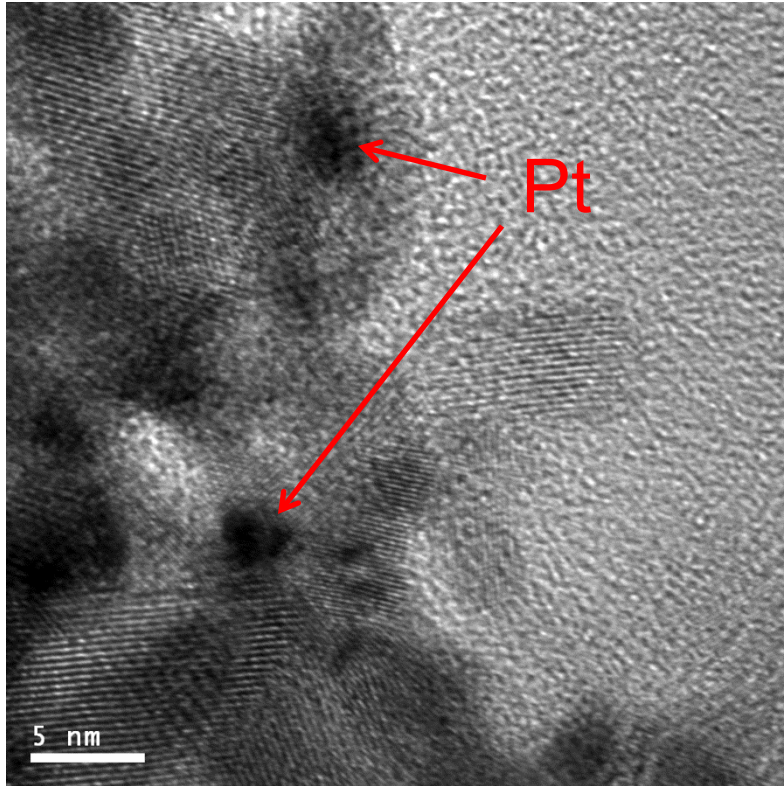
$\beta$ (the line broadening at half the maximum intensity in radians)=0.02618;

$\Theta$ (Bragg angle)=40.35°;

$\tau$ (crystallite size)=  $0.94 * 1.54 / 0.02618 / \cos(40.35 / 2 / 360 * 2 * \pi) = 56.4 \text{ \AA}$



# Technical Accomplishments: TEM of Pt/RTO-anhydrous



Pt particle size: 3~6 nm

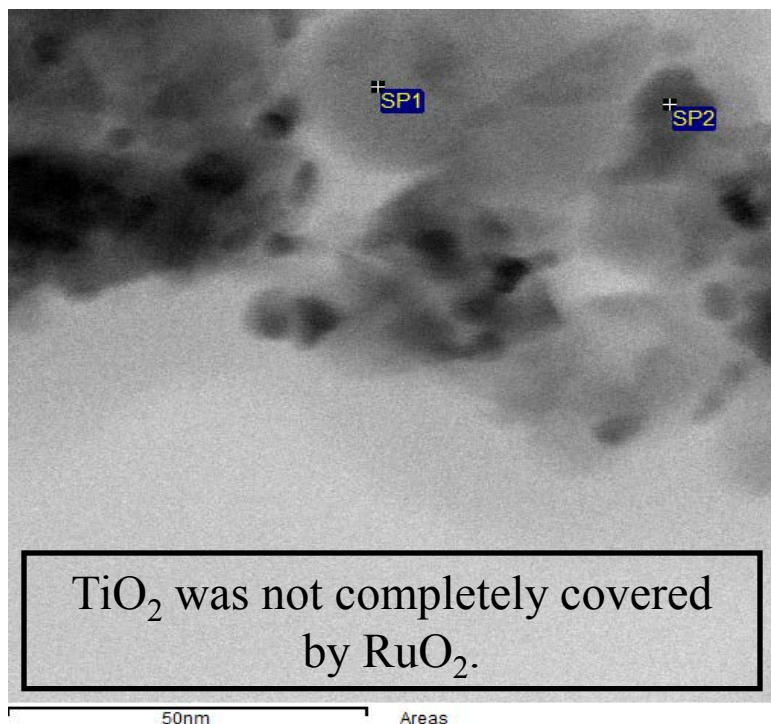
BET surface area of  $\text{RuO}_2\text{-TiO}_2$   
:  $30 \pm 3 \text{ m}^2/\text{g}$



# Technical Accomplishments: Characterization of RTO

RuO <sub>2</sub> -TiO <sub>2</sub>	anhydrous	hydrous
Electrical conductivity (S/cm)	22±4	10±3
BET surface area (m <sup>2</sup> /g)	30±3	83±5

Anhydrous RuO<sub>2</sub>-TiO<sub>2</sub> has higher degree of crystalline than hydrous RuO<sub>2</sub>-TiO<sub>2</sub> and has higher electrical conductivity.

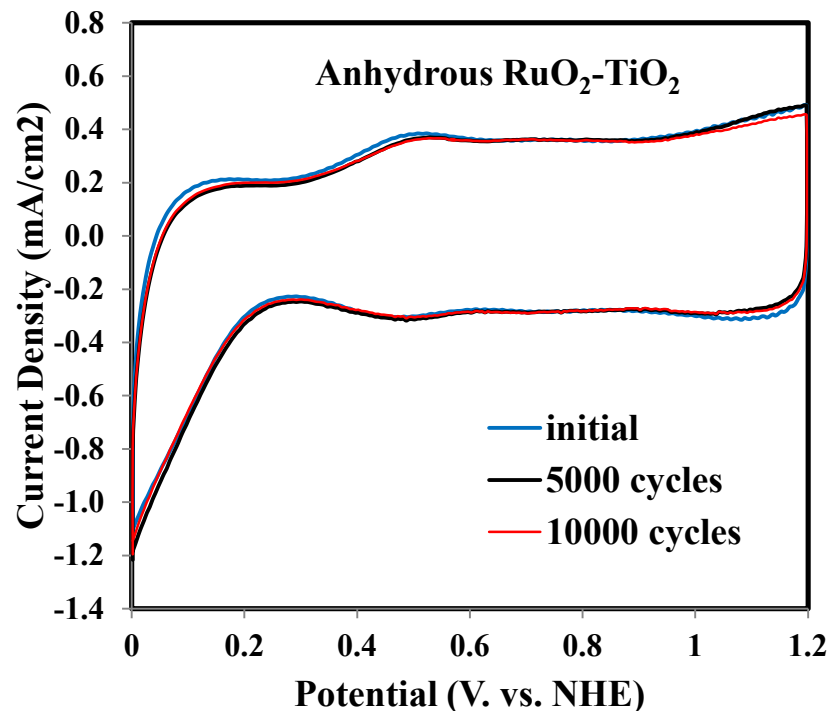
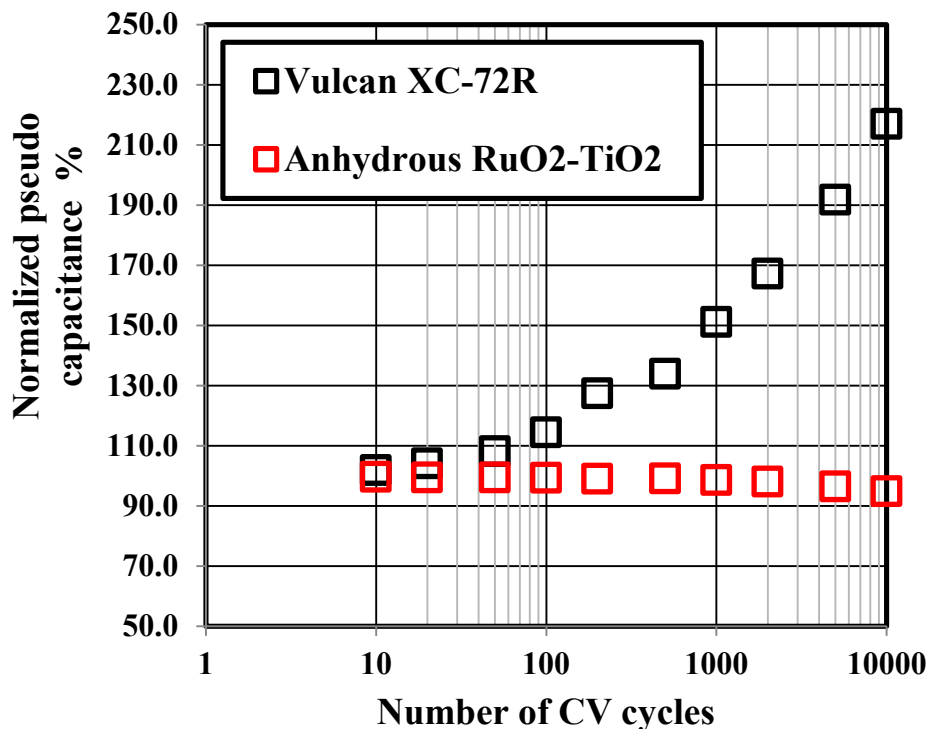


Spectrum	In stats.	O	Ti	Ru	Pt
SP1	Yes	59.70	39.14	0.00	1.16
SP2	Yes	63.27	29.55	7.18	0.00
Mean		61.49	34.35	3.59	0.58
Std. deviation		2.53	6.79	5.08	0.82
Max.		63.27	39.14	7.18	1.16
Min.		59.70	29.55	0.00	0.00

# Technical Accomplishments: Stability of RTO Supports (IIT)

0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; sweep rate of 20 mV/S; room temperature

The support stability is evaluated by monitoring the pseudo capacitance ( $C_{DL}$ ) at 0.4 V.

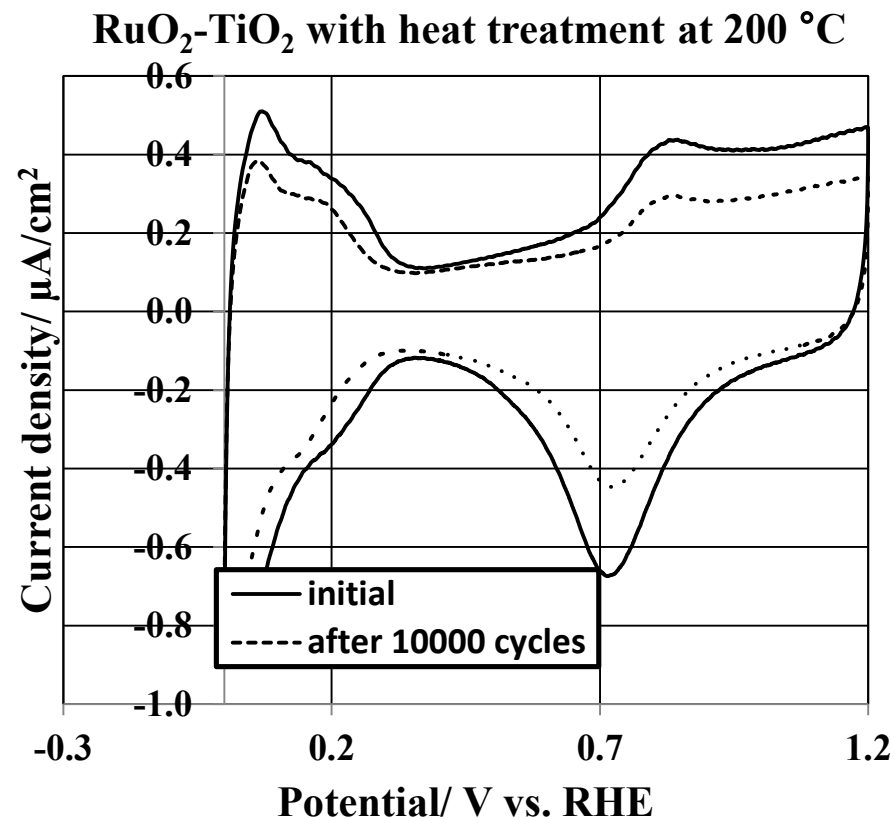
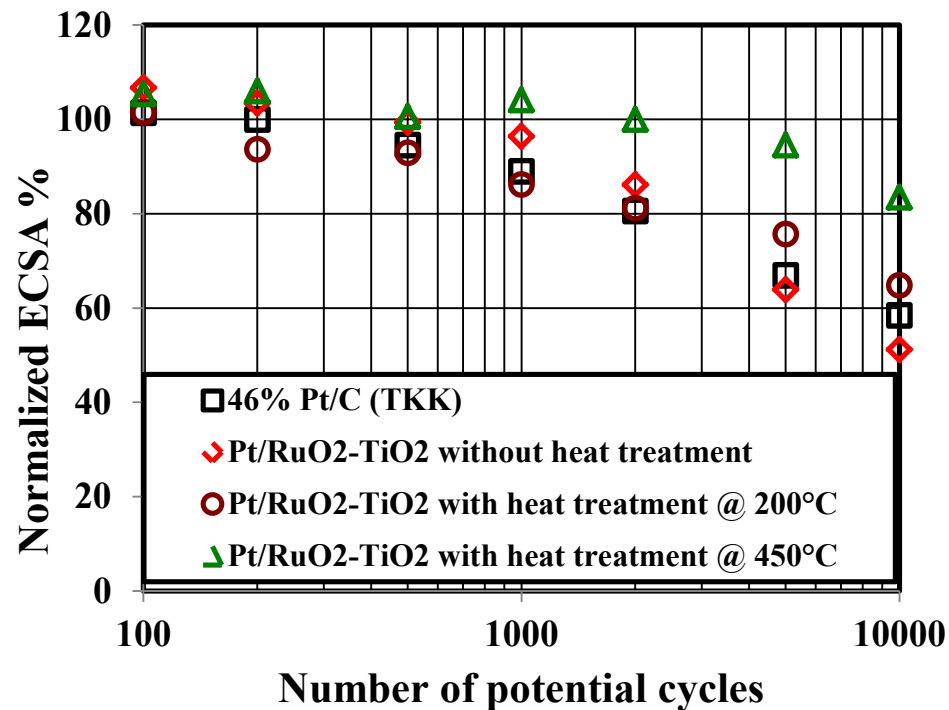


RuO<sub>2</sub>-TiO<sub>2</sub> support exhibited higher stability than Vulcan carbon.

Ru(II)→Ru(III) between 0.244V and 0.444V vs. NHE  
Ru(III)→Ru(IV) between 0.444V and 1.044V vs. NHE  
Ru(IV)→Ru(VI) between 1.044V and 1.444V vs. NHE

# Technical Accomplishments: Stability of Pt/RTO Catalysts (IIT)

0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; sweep rate of 20 mV/S; room temperature

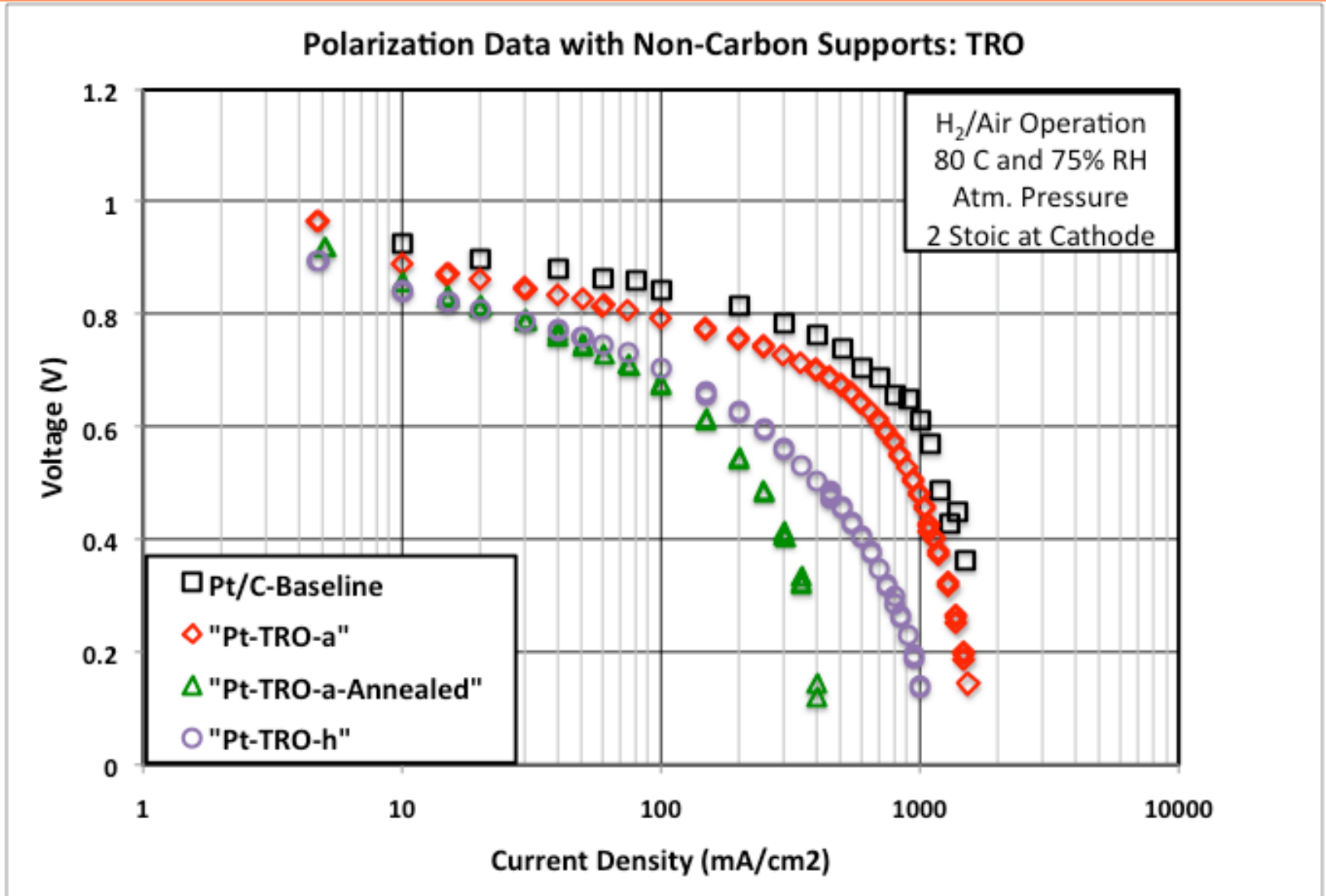


Electrocatalyst stability can be improved by heat treatment.

Catalyst with heat treatment at 450 °C exhibited high stability. However, the Pt crystallite size increased (5.6nm  $\rightarrow$  10.6 nm) and ECSA/performance decreased.



# Technical Accomplishments: Performance of Pt/RTO Electrocatalysts



**Pt loading: 0.4 mg/cm<sup>2</sup> at the cathode; 0.2 mg/cm<sup>2</sup> at the anode**

# Summary of Technical Accomplishments

- Proton and electron conducting metal oxides (SRO; RTO) 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<sup>2</sup>/g  
(50 m<sup>2</sup>/g overall target)
  - High durability upon aggressive potential cycling  
(NTCNA protocol, performed at IIT and at NTCNA)
  - Moderate to high performance
- A number of non-RuO<sub>2</sub> supports have been evaluated and found to be stable
- New stable of non-carbon supports (ITO, sulfated tin oxide) under study.
- In collaboration with Nissan North America Inc., extensive benchmarking of state-of-the-art electrocatalysts and electrocatalyst supports has been performed.

# Summary of Collaboration with NTCNA

- Nissan North America Inc. is a key project partner from industry
  - Dr. Kev Adjemian is PI 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
    - 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 contributions.

# Proposed Future Work

- **Future directions in FY 12:**
  - Continue work on alternate precursors in conjunction with supercritical drying and precursor ratio optimization to support stability and mixed-conductivity **(Task 1)**
  - Quantify mixed-conductivity (as opposed to stand-alone proton/electron conductivities) in all supports **(Task 1)**
  - Work in conjunction with Nissan North America Inc. to finish durability testing on catalyzed samples as well as initial MEA testing **(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)**
- **Future directions in Phase 2**
  - Continue work on incorporating Pt nanoparticles onto durable supports using standard and supercritical impregnation methods **(Task 1,3)**
  - Initiate and 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 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, SnO<sub>2</sub> 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<sup>2</sup>/g (50 m<sup>2</sup>/g overall target)
- Excellent support durability upon aggressive potential cycling + good MEA performance

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

## Proposed work for FY12 and beyond

- Explore alternate precursors in conjunction with supercritical drying and precursor ratio optimization to enhance mixed conductivity and surface area (Task 1)
- Study and quantify mixed-conductivity in synthesized supports (Task 1)
- Work in conjunction with Nissan North America Inc. to complete durability testing (Task 2)
- Introduce platinum nanoparticles onto durable mixed-conducting supports; evaluate specific and mass activities, and stability under cycling using RDE and MEA studies (Task 1,3)
- Initiate ionomer reduction studies, eventually leading to scale up of MEAs and formulation of cost model for downselected formulations (Tasks 3-5).

# Supplementary Slides

# Acronyms Used in Presentation

TEOS	Tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$
TMOS	Tetramethyl orthosilicate, $\text{Si}(\text{OCH}_3)_4$
MPTMS	3-mercaptopropyl trimethoxysilane, $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
SBA-15	Santa Barbara Amorphous type $\text{SiO}_2$
P123	Pluronic P <sup>®</sup> -123, a triblock copolymer
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
CV	Cyclic voltammetry

# Notation of Samples Discussed in Presentation

Samples prepared	Description	Notation
SBA-15	Silica (SiO <sub>2</sub> )	SBA-15
RuO <sub>2</sub>	Ruthenium dioxide	RuO <sub>2</sub>
Pt/ RuO <sub>2</sub> -SiO <sub>2</sub>	Pt deposited on RuO <sub>2</sub> -SiO <sub>2</sub> . The mole ratio of RuO <sub>2</sub> :SiO <sub>2</sub> is x:1	Pt/ RuO <sub>2</sub> -SiO <sub>2</sub> =x:1 Pt/SRO-x Where x=0.5, 1, 1.5
X % sulfonic acid functionalized SiO <sub>2</sub>	Sulfonic acid functionalized silica. The mol % of the functionalized domain is X.	X% HSO <sub>3</sub> -SiO <sub>2</sub> where X= 20, 30, or 40
TiO <sub>2</sub> -SiO <sub>2</sub>	RuO <sub>2</sub> deposited on TiO <sub>2</sub> (P25). The mole ratio of RuO <sub>2</sub> :TiO <sub>2</sub> is 1:1. RuO <sub>2</sub> is in anhydrous form.	Anhydrous RuO <sub>2</sub> -TiO <sub>2</sub> TRO-a
TiO <sub>2</sub> -SiO <sub>2</sub>	RuO <sub>2</sub> deposited on TiO <sub>2</sub> (P25). The mole ratio of RuO <sub>2</sub> :TiO <sub>2</sub> is 1:1. RuO <sub>2</sub> is in hydrous form.	Hydrous RuO <sub>2</sub> -TiO <sub>2</sub> TRO-h
Pt/ RuO <sub>2</sub> -TiO <sub>2</sub>	Pt deposited on RuO <sub>2</sub> -TiO <sub>2</sub> .	Pt/ RuO <sub>2</sub> -TiO <sub>2</sub>



# Notation of Samples Discussed in Presentation

Samples prepared	Description	Notation
Pt/ RuO <sub>2</sub> -TiO <sub>2</sub>	Pt deposited on TRO-a followed by heat treatment.	Pt/ RuO <sub>2</sub> -TiO <sub>2</sub> with heat treatment Pt/TRO-a-450
33% HSO <sub>3</sub> -SiO <sub>2</sub> aerogel	Sulfonic acid functionalized silica prepared by supercritical dryer method. The mol % of the functionalized domain is 33.	33% HSO <sub>3</sub> -SiO <sub>2</sub> aerogel
RuO <sub>2</sub> /33% sulfonic acid functionalized SiO <sub>2</sub> aerogel support	Pt deposited on 33% HSO <sub>3</sub> -SiO <sub>2</sub> aerogel. The weight % of RuO <sub>2</sub> to 33% HSO <sub>3</sub> -SiO <sub>2</sub> aerogel =1.2 or 1	Pt/RuO <sub>2</sub> -SSiO <sub>2</sub>
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	Sulfated tin oxide	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>
Pt/SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	Pt deposited on SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	Pt/SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>
Pt/SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -RuO <sub>2</sub>	Pt deposited on SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -RuO <sub>2</sub> . The mole ratio of SnO <sub>2</sub> -RuO <sub>2</sub> =1:1.	Pt/SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -RuO <sub>2</sub>
ITO	Tin-doped indium oxide	ITO

# Literature Review: Non-Carbon Supports

## Non-carbon catalyst supports in literature

### SiO<sub>2</sub>

- X. Zhu, H. et. al., *Electrochem. Solid State Lett.* 9 (2006) A49.  
L.Wang, D.M. et. al., *J. Power Sources* 161 (2006) 61.  
B. Seger, et. al., *J. Electroanal. Chem.* 621 (2008) 198.

### Ti-based oxides (TiO<sub>2</sub>, doped TiO<sub>2</sub>, and sub-stoichiometric Ti oxides)

- D.V. Bavykin, et. al., *Adv. Mater.* 18 (2006) 2807.  
R.F. Bartholomew, et. al., *Phys. Rev.* 187 (1969) 828.  
K.-W. Park, et. al., *Electrochem. Comm.* 9 (2007) 2256.  
O.E. Haas, et. al., *J. New Mater. Electrochem. Syst.* 11 (2008) 9

### Sn-based oxides

- M.M. Gadgil, et. al., *J. Mol. Cat.* 87 (1994) 297.  
D.R. Schryer, et. al., *J.Catal.* 122 (1990) 193.  
J.C.C. Fan, et. al., *J. Appl. Phys.* 48 (1977) 3524.

### WO<sub>x</sub>

- L.W. Niedrach, et. al., *J. Electrochem. Soc.* 116 (1969) 152.  
P.J. Kulesza, et. al., *J. Electroanal. Chem.* 259 (1989) 81.  
P.J. Kulesza, et. al., *J. Electrochem. Soc.* 136 (1989) 707.

### WC

- Y. Hara, et. al., *Appl. Catal. A* 332 (2007) 289.  
R. Ganesan, et. al., *Electrochem. Comm.* 9 (2007) 2576.  
D.J. Ham, et. al., *Catal. Today* 132 (2008) 117.

### RuO<sub>2</sub>·xH<sub>2</sub>O

- Z. Chen, X. et. al., *Electrochem. Comm.* 7 (2005) 593.  
H.A. Gasteiger, et. al., *J. Electrochem. Soc.* 141 (1994) 1795.

# Approach: Characterization Techniques

- **X-ray diffraction (XRD):**

- To confirm crystal structure and to estimate crystallite size. Diffractograms were recorded from  $20^\circ$  to  $80^\circ$   $2\theta$  with a step of 2 min/degree.

- **Transmission electron microscopy (TEM):**

- To determine the surface morphology, the size and distribution of the metal particles. TEM micrographs were obtained using a Jeol 2100F microscope at an acceleration voltage of 200 kV equipped with a liquid nitrogen Si(Li) EDX detector.

- **Brunauer-Emmett-Teller (BET) surface area analyzer:**

- To calculate the BET specific surface area by a multipoint analysis of nitrogen desorption isotherms.

- **Two-point probe technique:**

- To measure electrical conductivity. All experiments were conducted at room temperature.

- **Ion exchange capacity (IEC):**

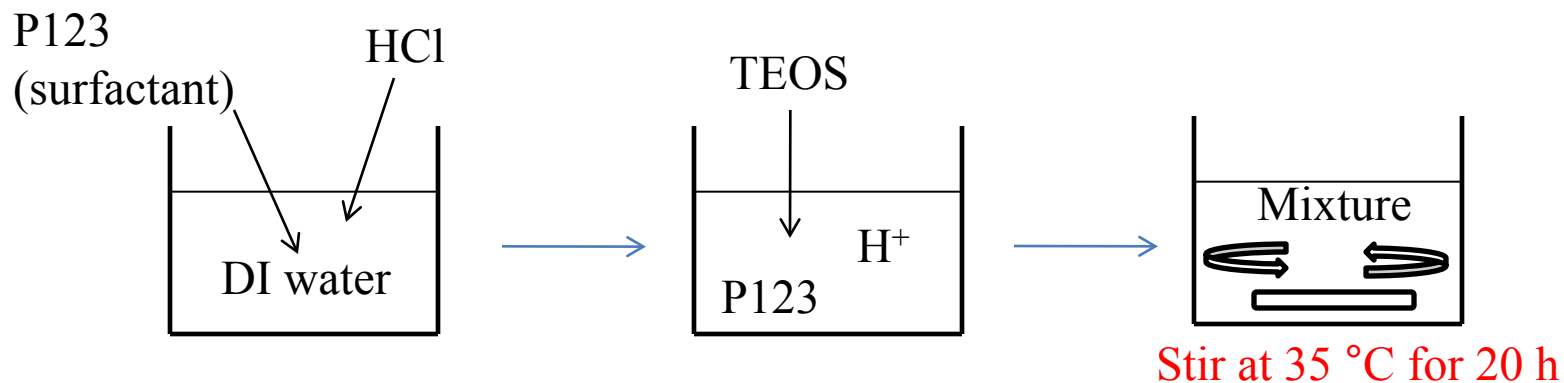
- To calculate the proton exchange capacity of materials ( $\text{mmol}_{\text{H}^+}/\text{g}$ )

- **Rotating disc electrode (RDE):**

- To calculate and evaluate the ECSA, ORR and stability of catalyst/support materials

# Approach: Synthesis of SBA-15

SBA-15 was synthesized as follows

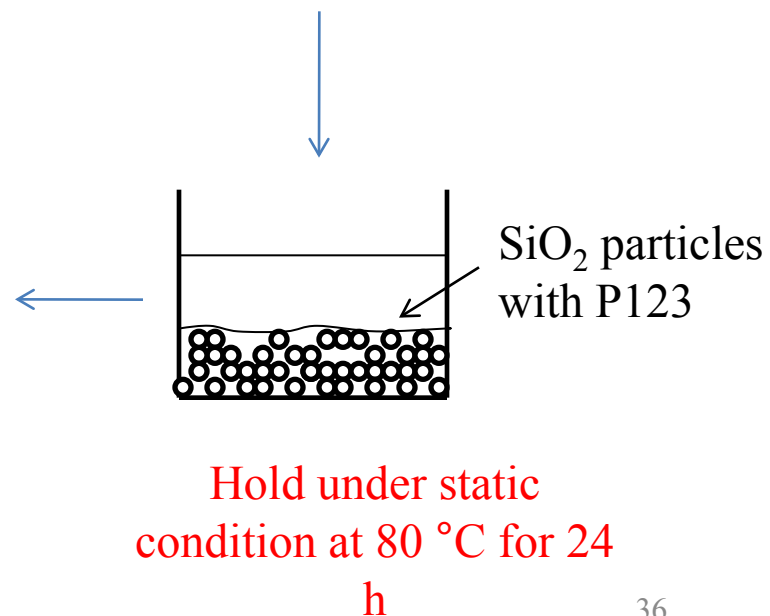


The molar composition of SiO<sub>2</sub> for 18 g P123 was:  
0.19mols TEOS : 1.01mols HCl : 31.12mols H<sub>2</sub>O



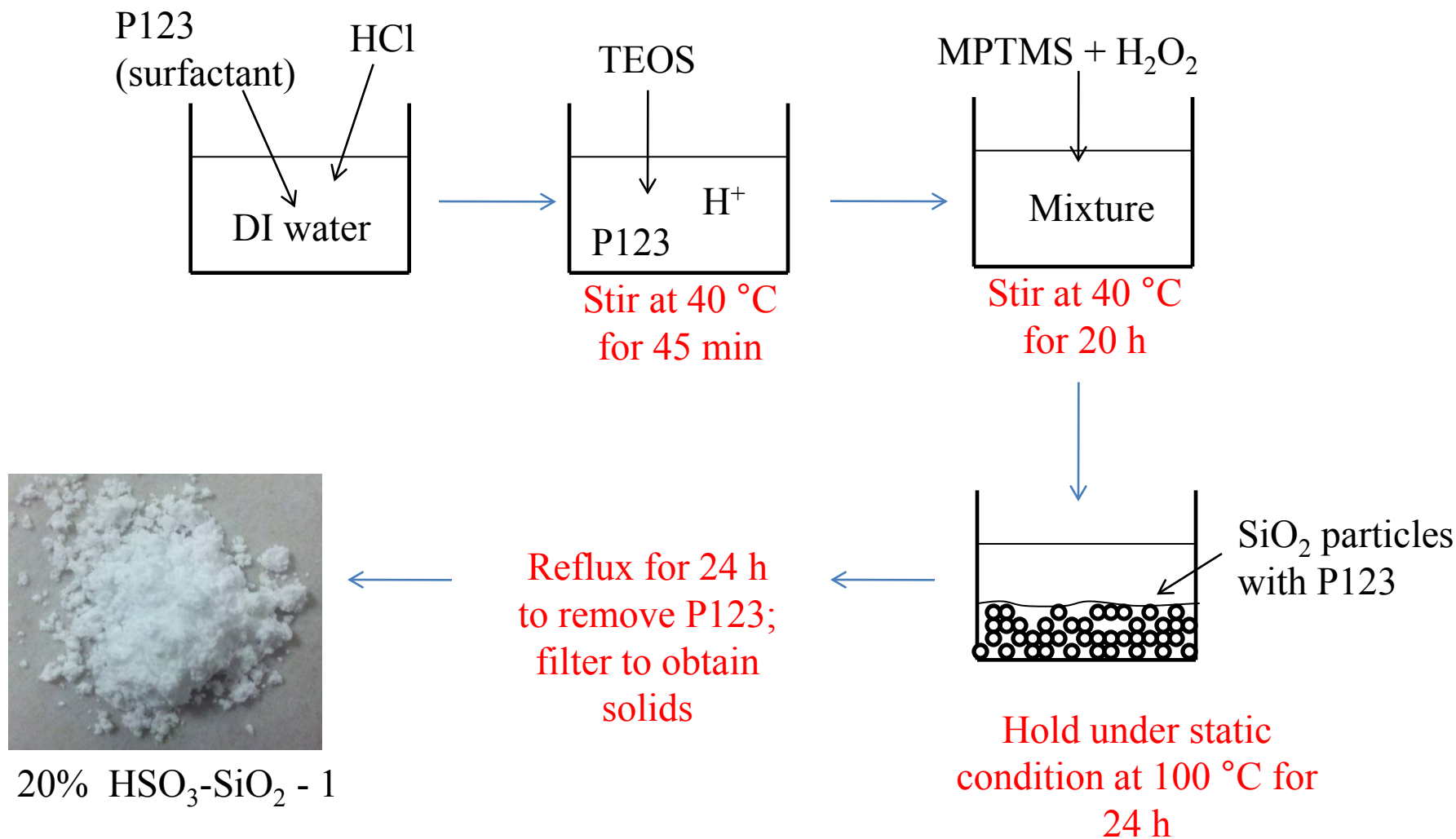
SBA-15 SiO<sub>2</sub>

Centrifugation followed by  
calcination at 550°C  
for 6 h to remove P123

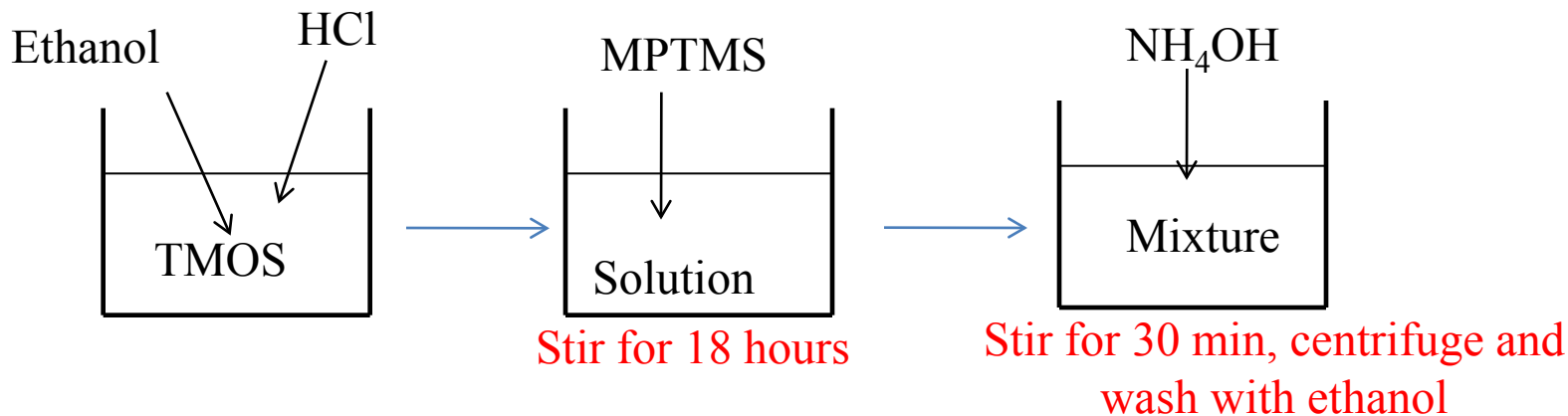


# Approach: Synthesis of Sulfonic Acid Functionalized SiO<sub>2</sub> – Method 1

The molar composition used to prepare 20% functionalized SiO<sub>2</sub> with 4 g P123 was:  
0.0328 mols TEOS : 0.0082 mols MPTMS: 0.0369 mols H<sub>2</sub>O<sub>2</sub> : 0.24 mols HCl : ~6.67 mols H<sub>2</sub>O



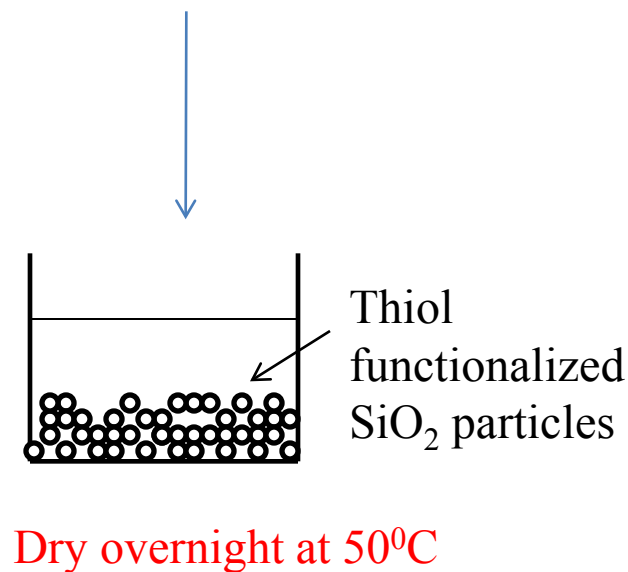
# Approach: Synthesis of Sulfonic Acid Functionalized SiO<sub>2</sub> – Method 2



Ratio of starting materials is:

(TMOS+MPTMS):H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH:HCl= 1:30:10:6

For 25% HSO<sub>3</sub>-SiO<sub>2</sub>-2, ratio of TMOS:MPTMS=0.25:0.75



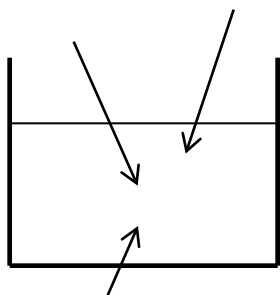
X%HSO<sub>3</sub>-SiO<sub>2</sub>-2



25%HSO<sub>3</sub>-SiO<sub>2</sub>-2

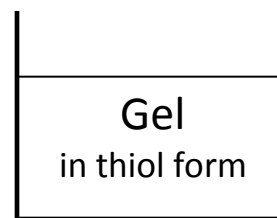
# Approach: Synthesis of Sulfonic Acid Functionalized SiO<sub>2</sub> – Aerogel

0.67mmol TMOS 0.33mmol MPTMS

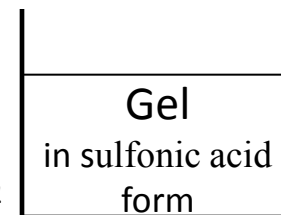


15 mmol methanol, 4 mmol water  
and 0.075 mmol NH<sub>4</sub>OH

Gelation  
→  
48 hours

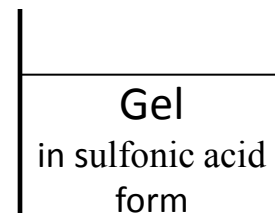


→  
35 wt% H<sub>2</sub>O<sub>2</sub>



8-12 times with acetone  
over 3-4 days

←  
supercritical drying

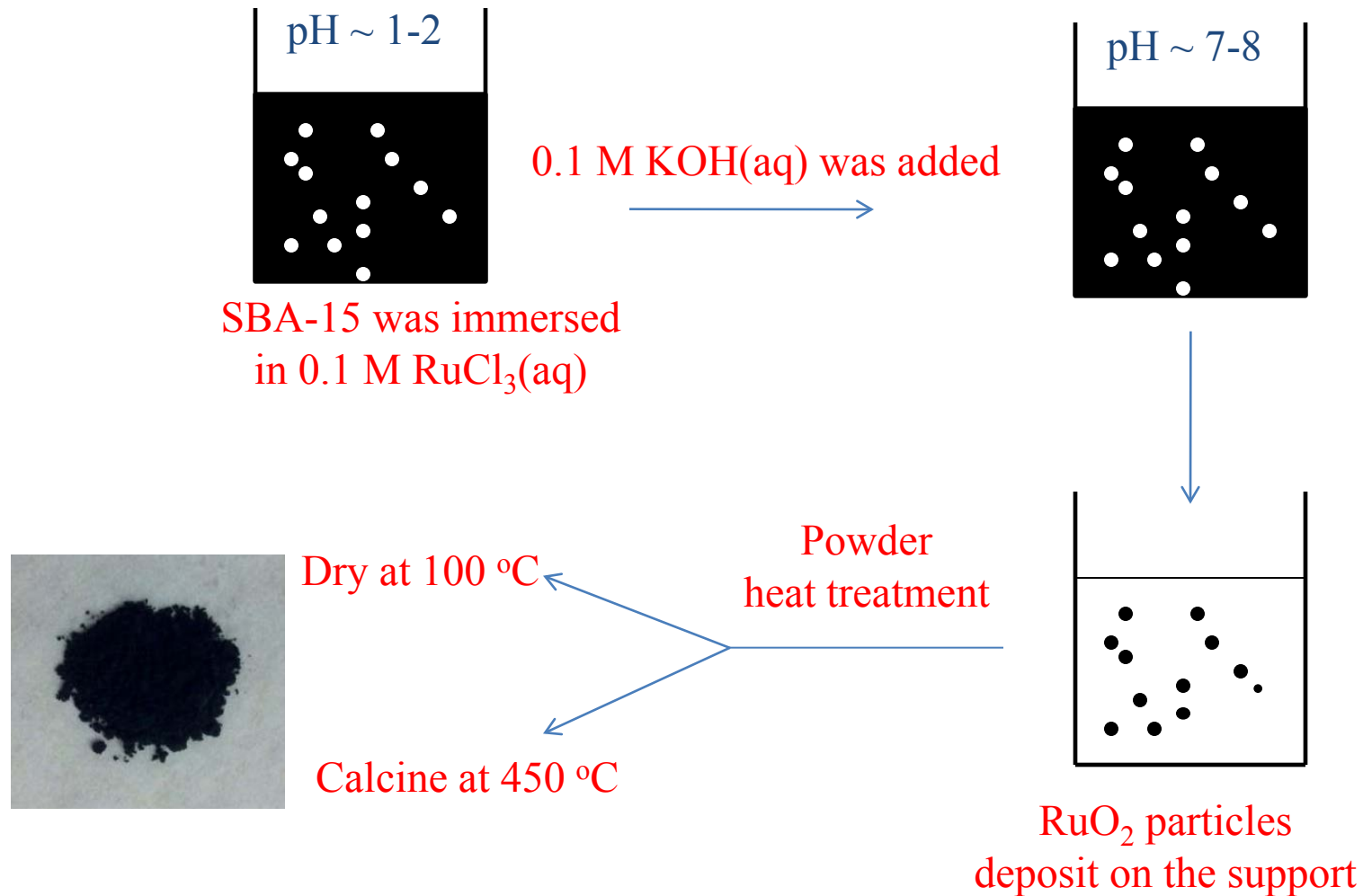


33% HSO<sub>3</sub>-SiO<sub>2</sub>  
aerogel

# Approach: Synthesis of RuO<sub>2</sub>-SiO<sub>2</sub> Composites: RuO<sub>2</sub> deposition

RuO<sub>2</sub>-SiO<sub>2</sub> composites were prepared by depositing RuO<sub>2</sub> on SBA-15.

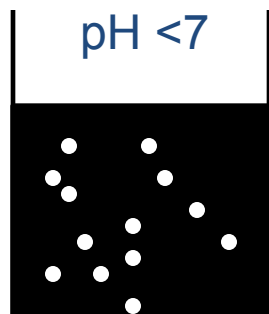
The mole ratio of RuO<sub>2</sub>:SiO<sub>2</sub> was: 0~0.6 :1





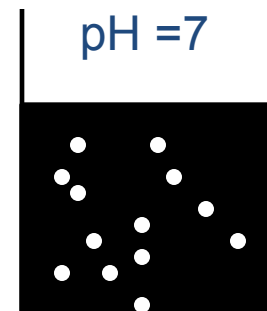
# Approach: Synthesis of Pt/RuO<sub>2</sub>-SiO<sub>2</sub> (SBA15)

RuO<sub>2</sub>-SiO<sub>2</sub> was prepared by depositing RuO<sub>2</sub> on SBA-15.

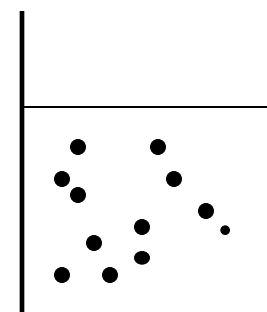


SBA-15 was immersed  
in 0.1 M RuCl<sub>3</sub>(aq)

add 0.1 M KOH(aq)



The mole ratio of RuO<sub>2</sub>:SiO<sub>2</sub> was: 0~0.6 :1



RuO<sub>2</sub> deposition

Dry at 120 °C

Powder  
heat treatment



Calcination at 450 °C

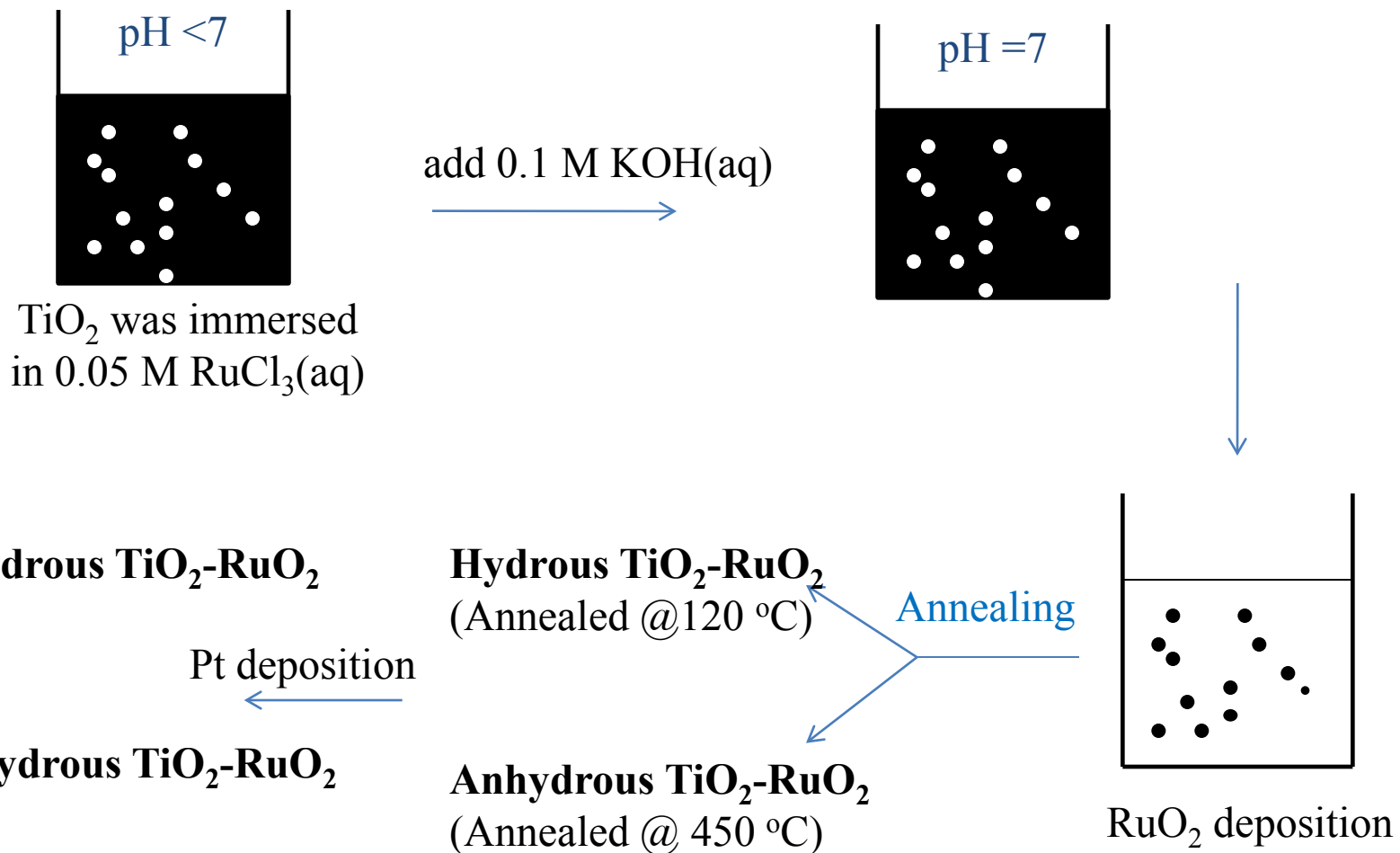
Pt deposition



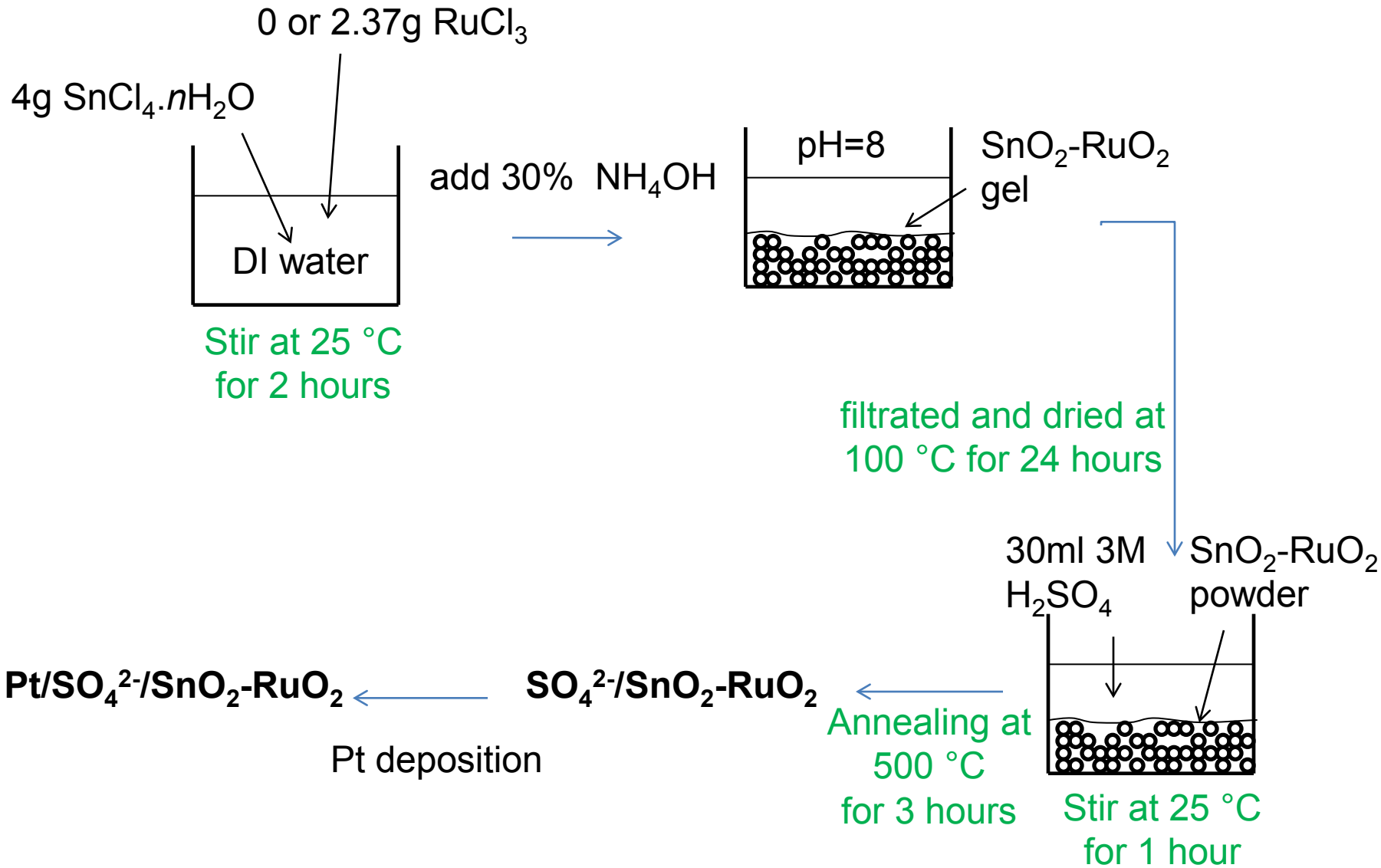
Pt/RuO<sub>2</sub>-SiO<sub>2</sub>

# Approach: Synthesis of Pt/RuO<sub>2</sub>-TiO<sub>2</sub>

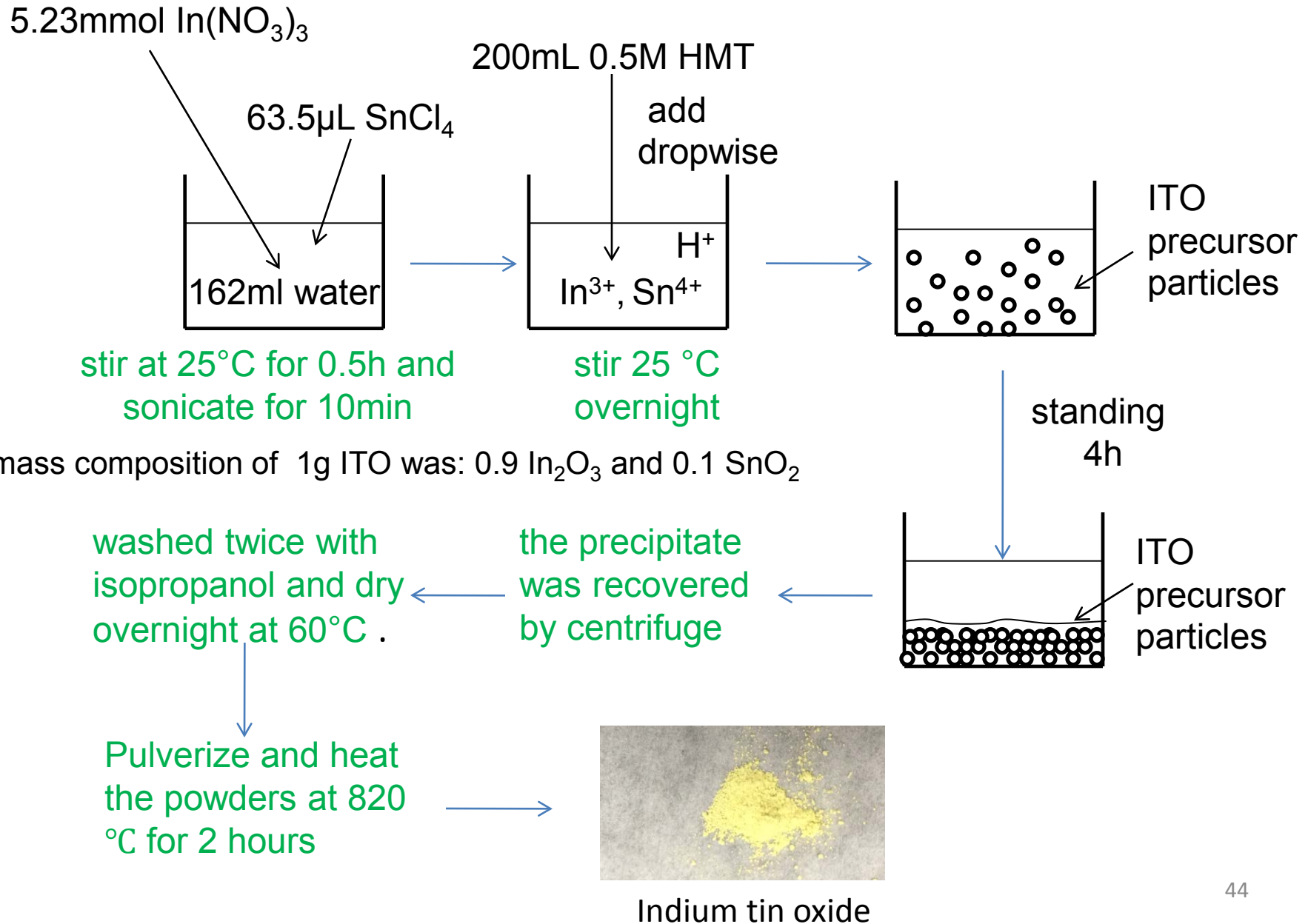
RuO<sub>2</sub>-TiO<sub>2</sub> were prepared by depositing RuO<sub>2</sub> on TiO<sub>2</sub> (P25).  
The mole ratio of TiO<sub>2</sub>:RuO<sub>2</sub> was: 1 :1



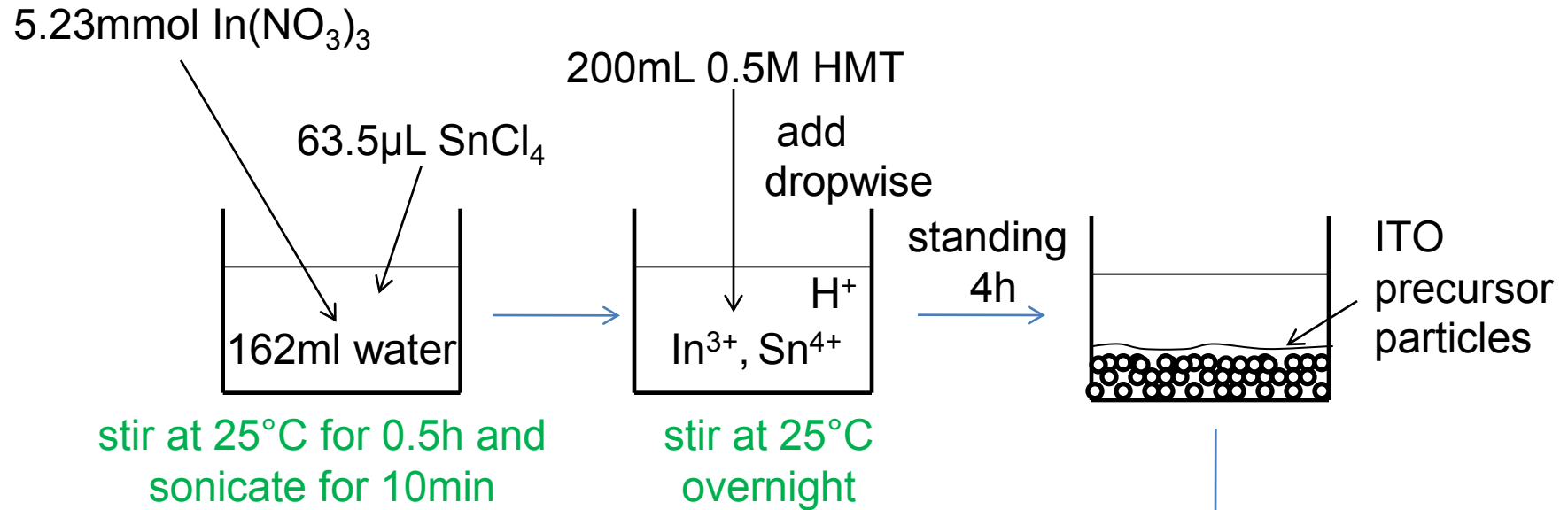
# Approach: Synthesis of Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-RuO<sub>2</sub>



# Approach: Synthesis of Indium tin oxide (ITO) (wet chemical method)



# Approach: Synthesis of Indium tin oxide (ITO) (supercritical drying method)



stir at 25°C for 0.5h and  
sonicate for 10min

stir at 25°C  
overnight

ITO  
precursor  
particles

The mass composition of 1g ITO was: 0.9  $\text{In}_2\text{O}_3$  and 0.1  $\text{SnO}_2$

Supercritical drying

Washed twice with  
isopropanol, then 8-  
12 times with acetone  
over 3-4 days

the precipitate  
was recovered  
by centrifuge



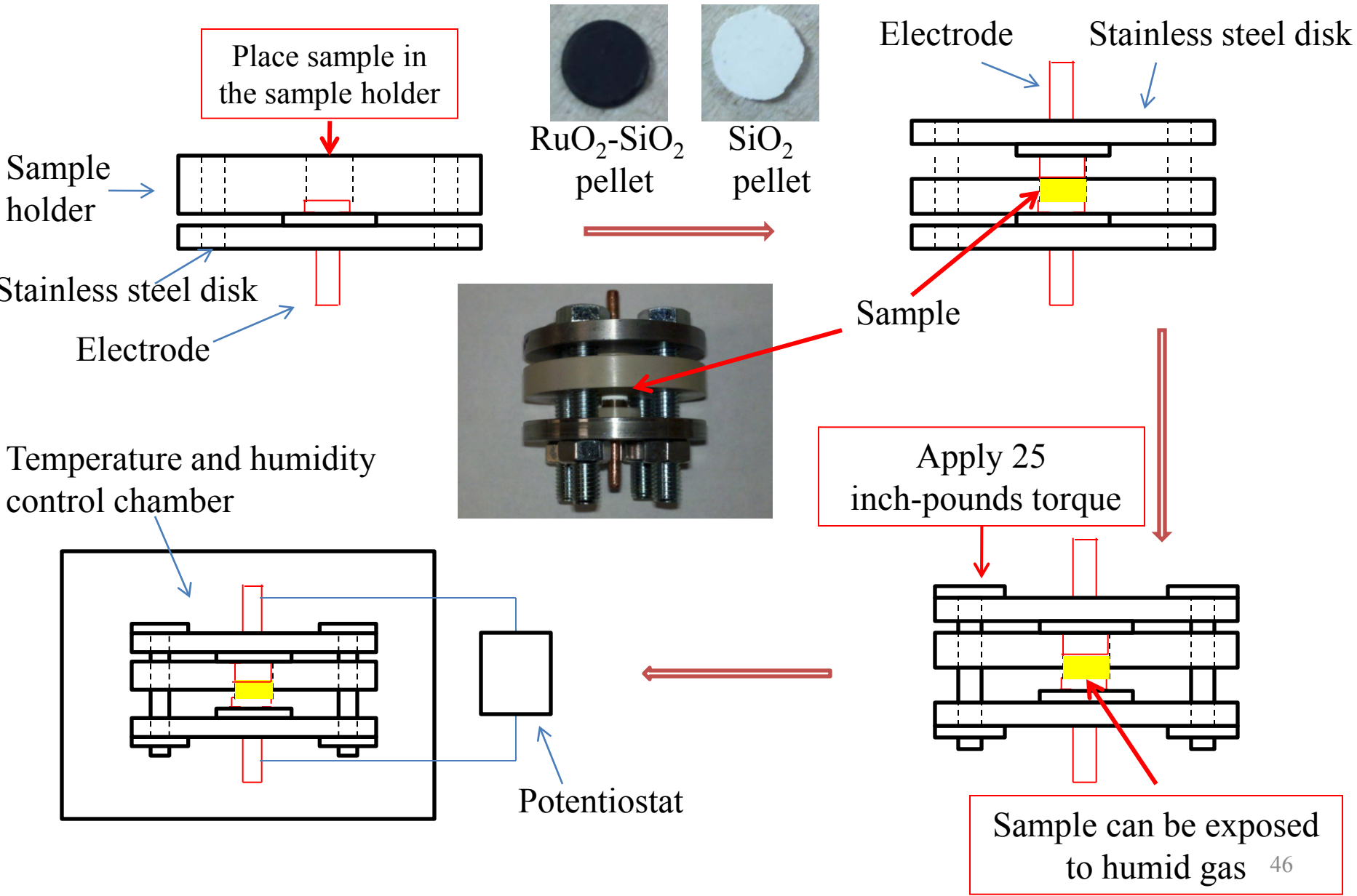
Indium tin oxide precursor

pulverize and  
heat at 820°C  
for 2 hours



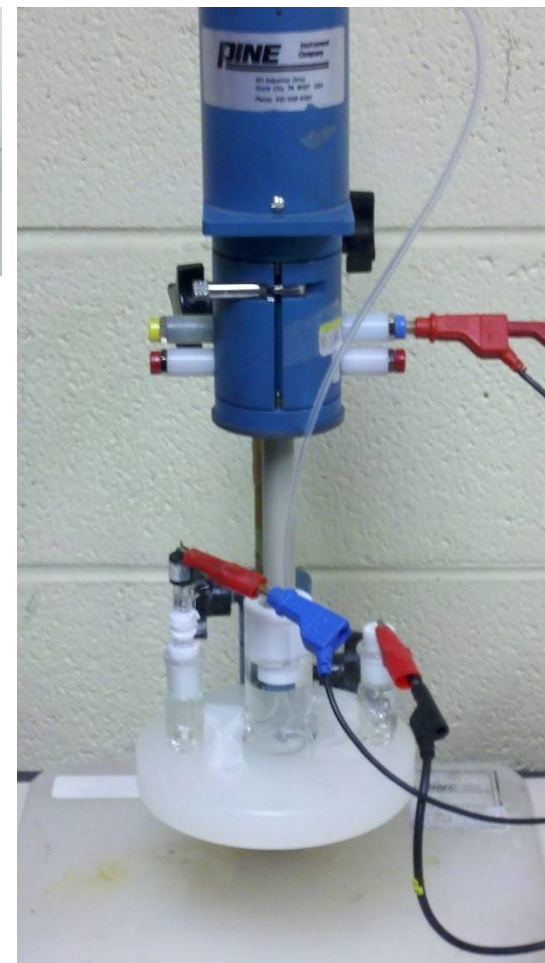
Indium tin oxide

# Approach: Conductivity Measurements

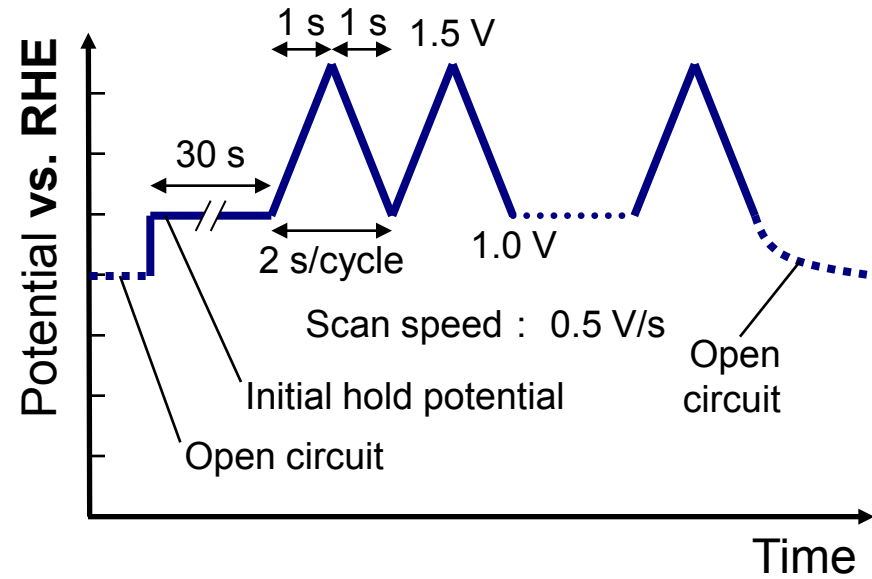


# Approach: Potential Cycling to Estimate Support Stability

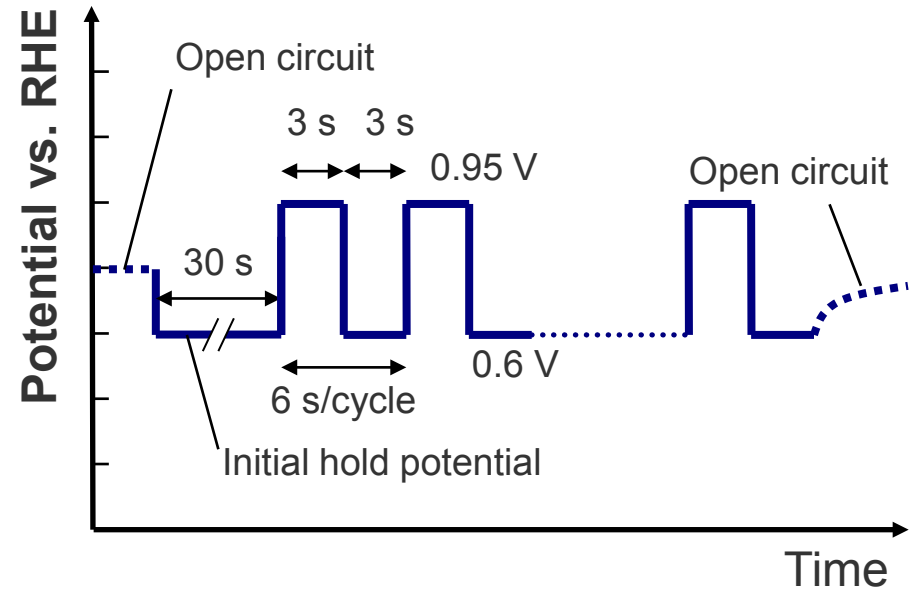
- Three Electrode Cell with Rotating Disk Electrode
  - Working Electrode : Glassy carb coated with catalyst support
  - Counter Electrode : Pt foil
  - Reference Electrode : Saturated Calomel Electrode (SCE)
  - Electrolyte :  $\text{N}_2$  saturated 0.1M  $\text{HClO}_4$
- Support loading on W.E.: 200  $\mu\text{g}/\text{cm}^2_{\text{geo}}$
- Pt loading: 50  $\mu\text{g}/\text{cm}^2_{\text{geo}}$
- Potential cycling protocol
  - See following slides



# Approach: Potential Cycling to Estimate Support and Electrocatalyst Durability



Support Durability—Support corrosion



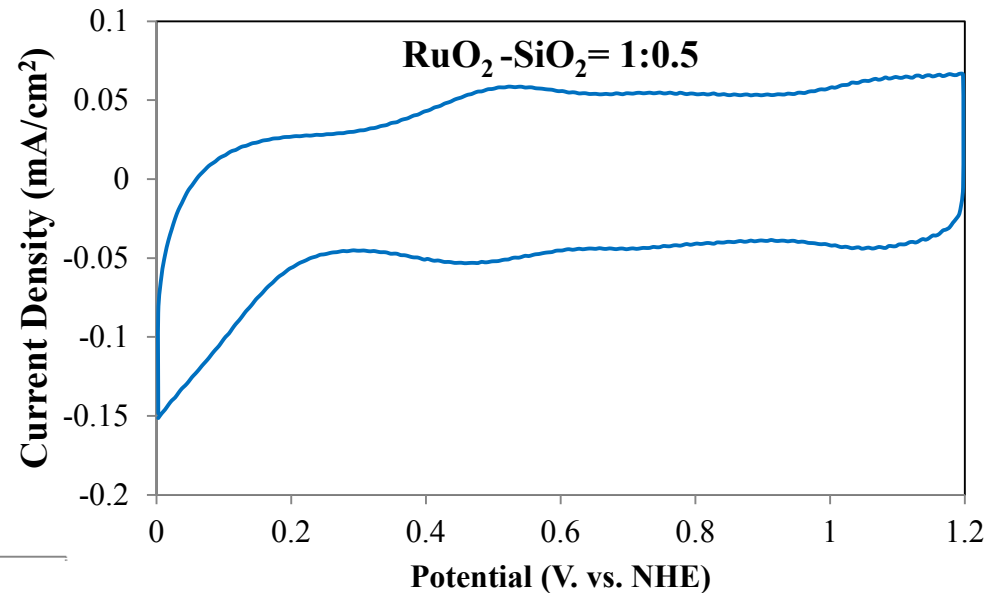
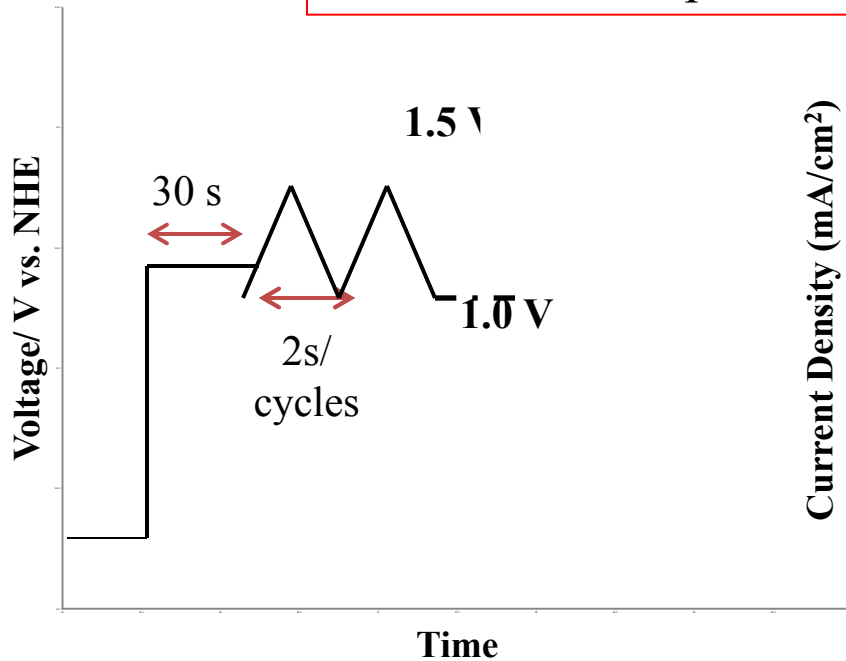
Catalyst Durability—Pt Dissolution



# Approach: Stability of supports - Example

0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; CV sweep rate of 20 mV/s; room temperature; NTCNA uses 60C test during potential cycling and 50 mV/s during CV

The support stability is evaluated from the pseudo-capacitance ( $C_{DL}$ ) at 0.4 V.



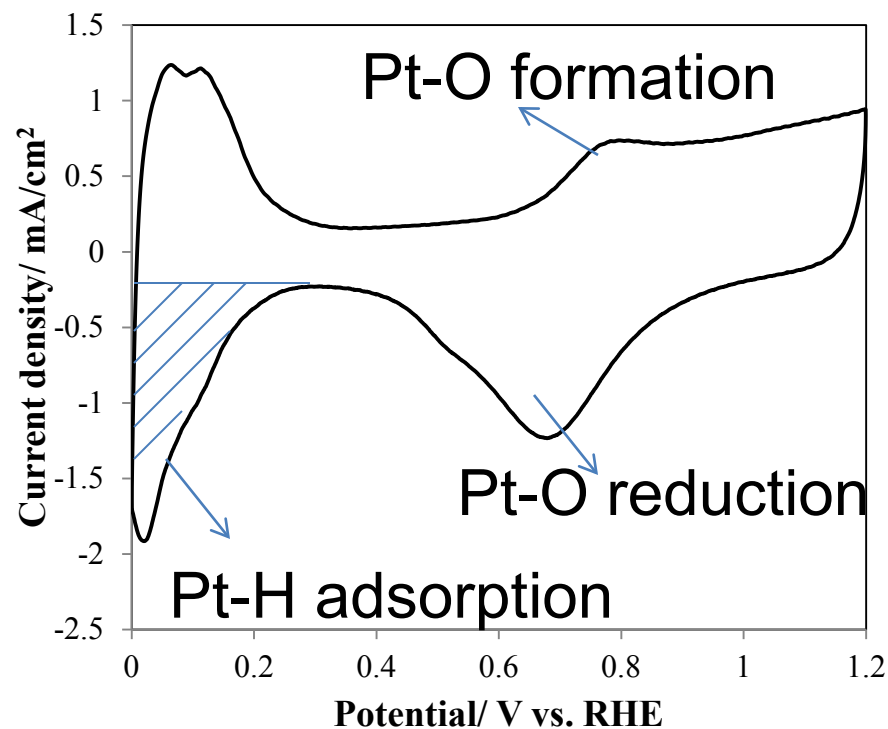
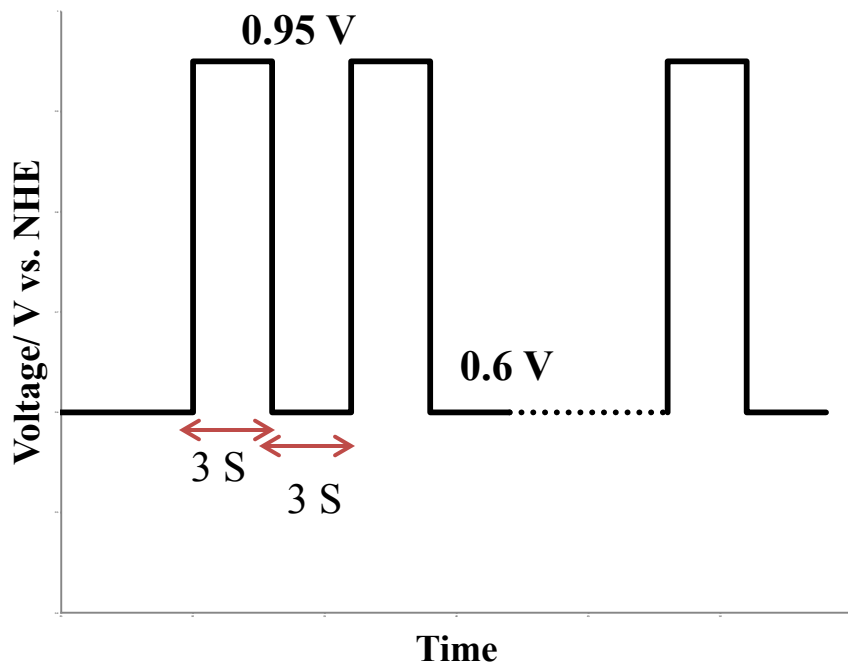
$$(0.044+0.056)/2/20=2.5 \text{ mF/cm}^2 \text{ (pseudo capacitance (} C_{DL} \text{))}$$

Average current density  
at 0.4V (mA/cm<sup>2</sup>)

Scan rate: mV/s

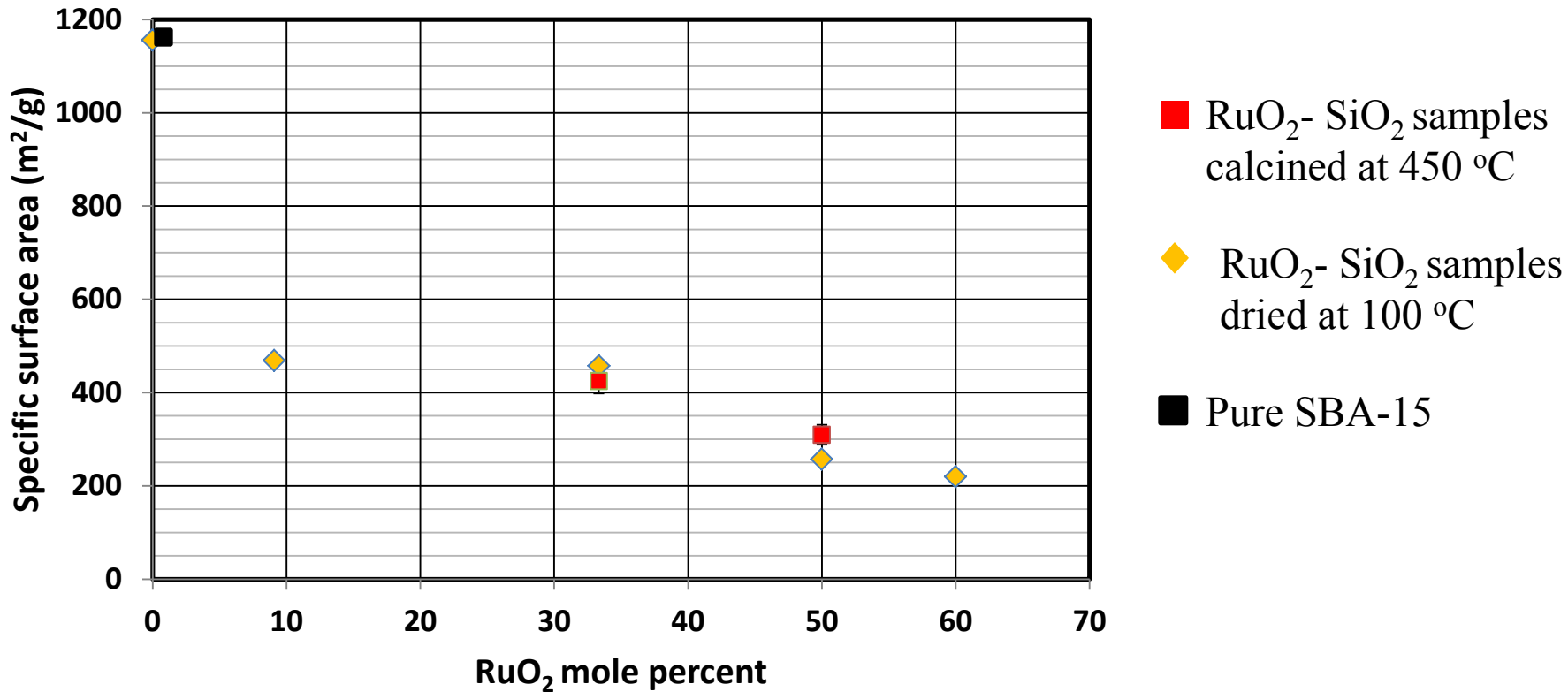
# Approach: Stability of Catalysts - Example

The stability of catalyst was evaluated by monitoring the change of ECSA.



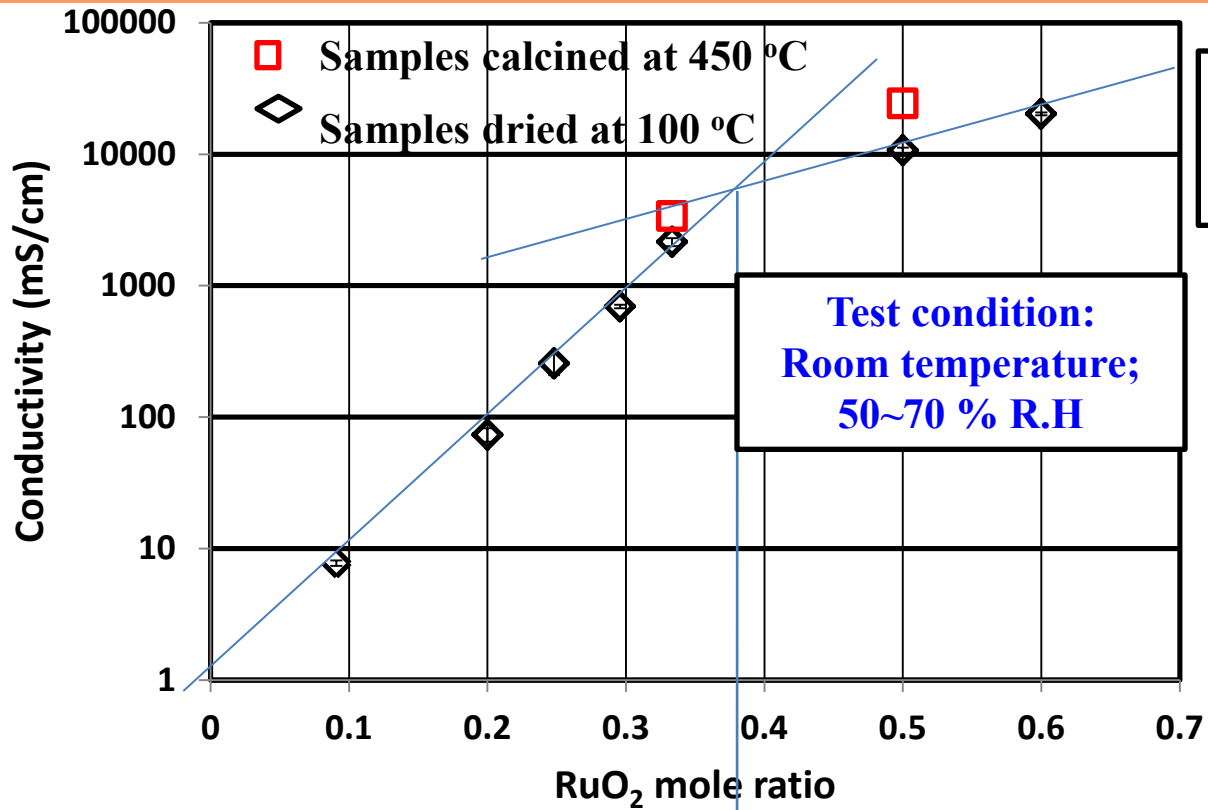
0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; CV sweep rate of 20 mV/S; room temperature (NTCNA runs potential cycling at 60C; CVs at 50 mV/s)

# Technical Accomplishments: BET Surface Area of SiO<sub>2</sub> and RuO<sub>2</sub>-SiO<sub>2</sub>



- Surface area decreases with mol% RuO<sub>2</sub>
- Trend is consistent with expectation – RuO<sub>2</sub> has low specific surface area (14 m<sup>2</sup>/g)
- Even with high RuO<sub>2</sub> loading, BET surface areas obtained are comparable to Vulcan XC-72 and higher than the milestones set for this project
- PIs will continue to improve on this metric through advanced processing methods

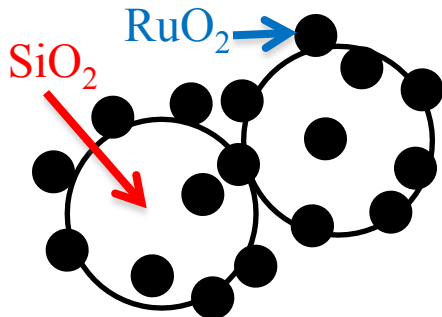
# Technical Accomplishments: Electrical Conductivity of RuO<sub>2</sub>-SiO<sub>2</sub>



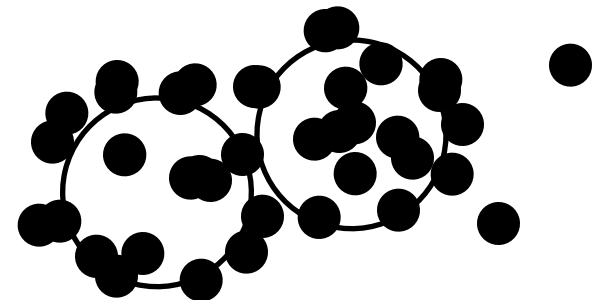
• Samples calcined at 450 °C have higher conductivity.

Test condition:  
Room temperature;  
50~70 % R.H

RuO<sub>2</sub> particles are dispersed without contacting each other.

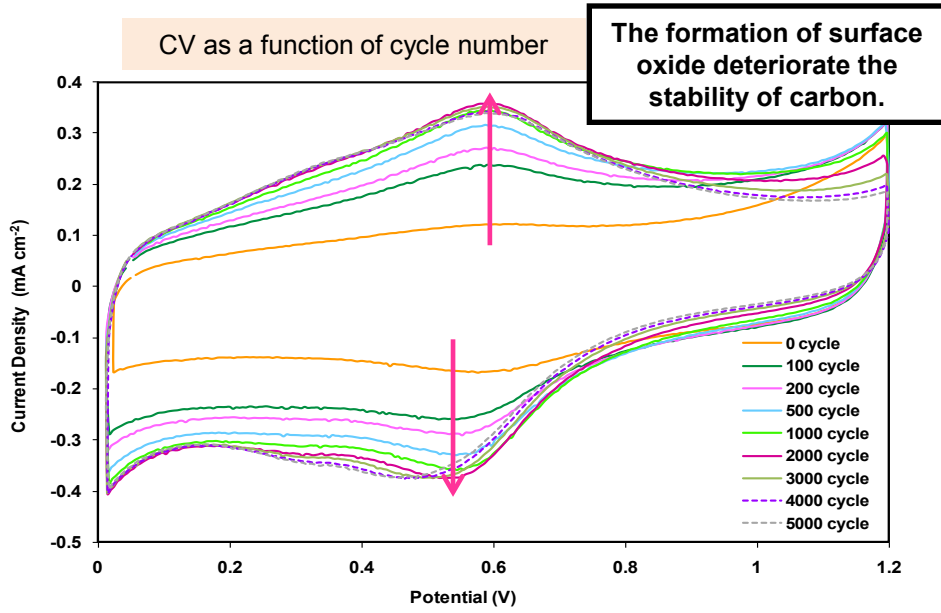


RuO<sub>2</sub> particles are in good contact with each other.



# Technical Accomplishments: Electrochemical Stability of RuO<sub>2</sub>-SiO<sub>2</sub>

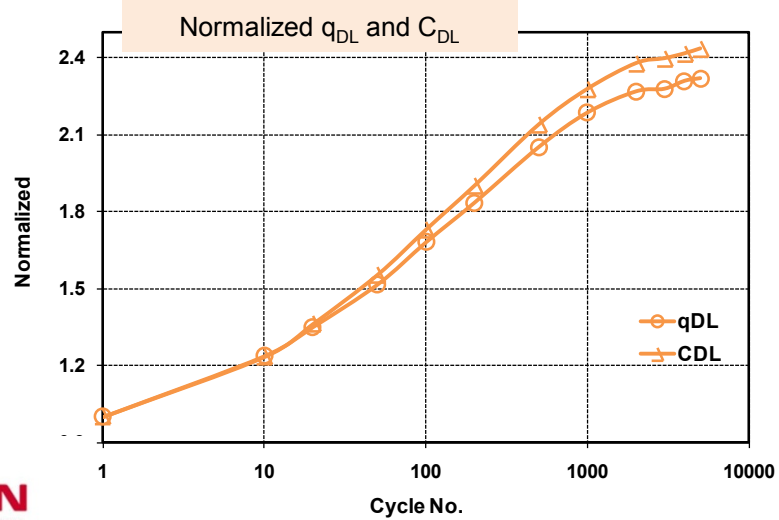
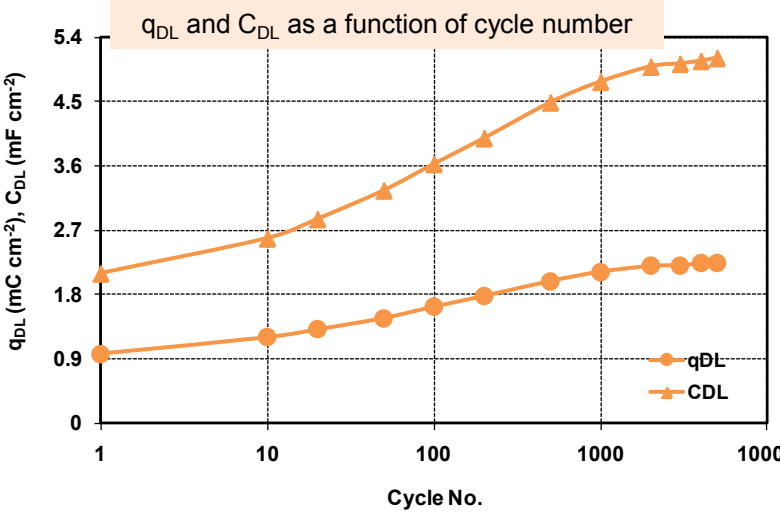
## Stability of Vulcan-Benchmark data



□ Baseline CV data (0 cycle) for Vulcan match very well with the literature data\*

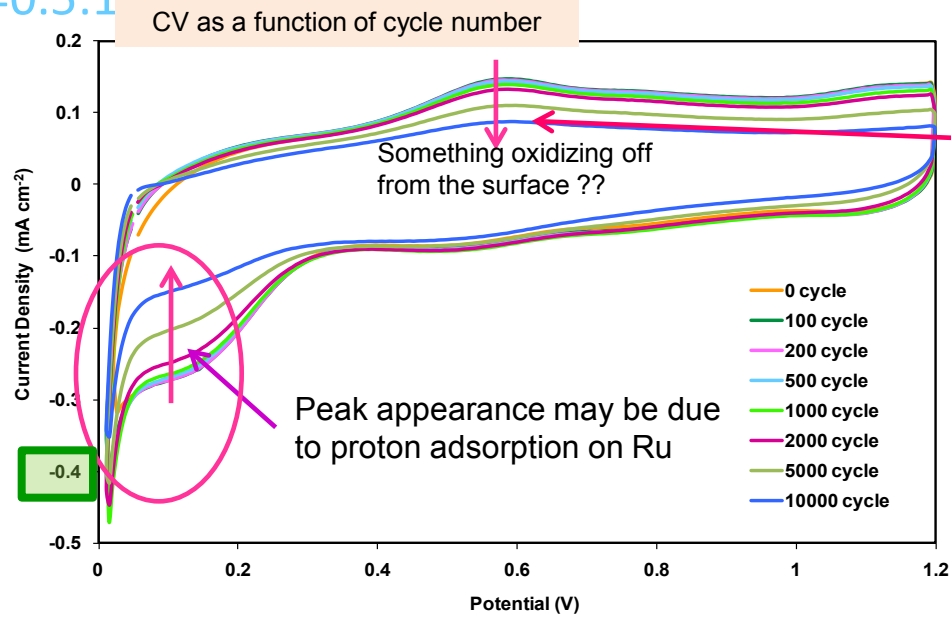
□ C<sub>DL</sub> calculated by dividing apparent double layer normalized for loading by BET surface area (220 m<sup>2</sup>/g) resulted in 6~7 μF/cm<sup>2</sup> capacitance at 0.4 V. (Literature value is 8 μF/cm<sup>2</sup>)\*

□ Reported C<sub>DL</sub> and q<sub>DL</sub> (0.05-0.4 V) include pseudo capacitance and charge due to surface oxides



# Technical Accomplishments: Electrochemical Stability of RuO<sub>2</sub>-SiO<sub>2</sub>

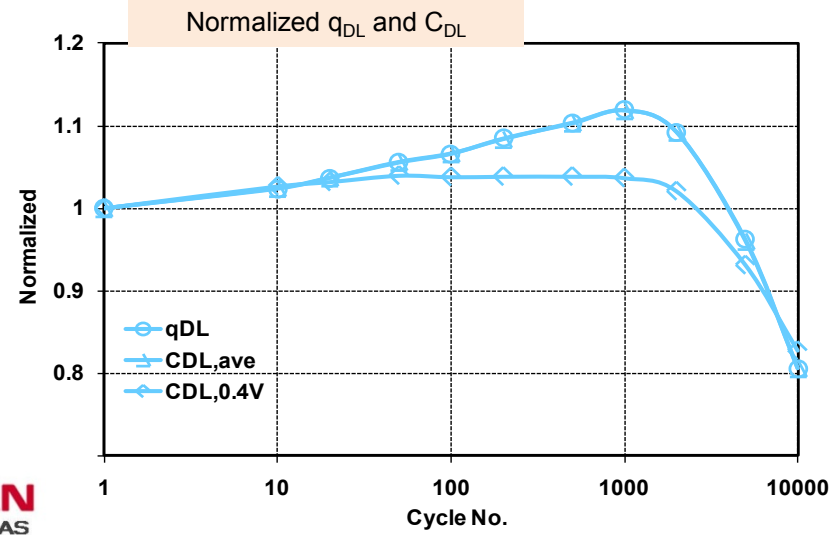
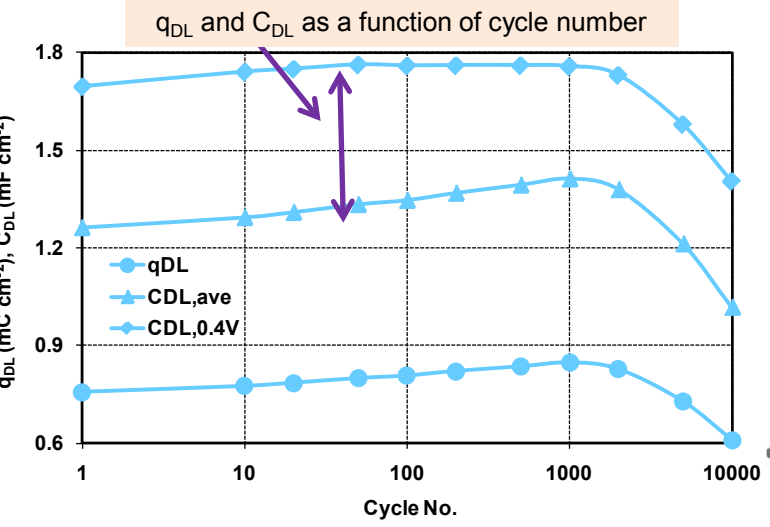
Stability of RuO<sub>2</sub>:SiO<sub>2</sub>=0.5:1



Peak @ 0.6 V disappears with cycling as against to **carbon support** where it become prominent with cycling (result of surface oxides shown in slide #4)

Difference in the C<sub>DL</sub> values is due to difference in current values for i<sub>ave</sub> and i<sub>dl</sub> used for these calculation

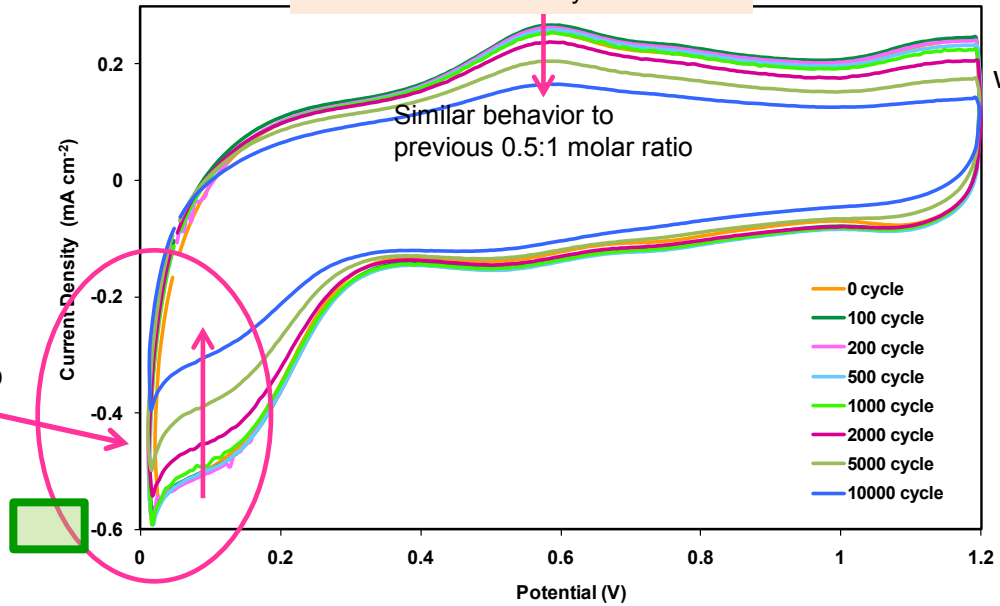
**Double-layer capacitance decreases ~19% post 10000 cycles.**



# Technical Accomplishments: Electrochemical Stability of RuO<sub>2</sub>-SiO<sub>2</sub>

## Stability of RuO<sub>2</sub>:SiO<sub>2</sub>=1:1

CV as a function of cycle number

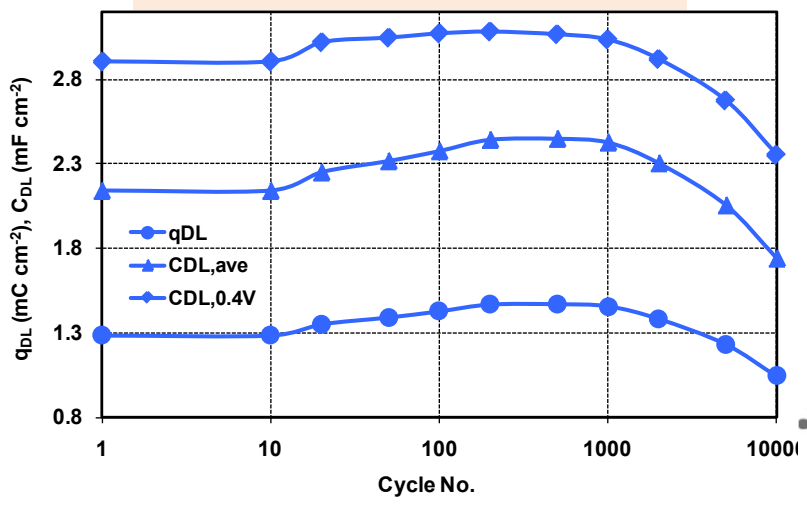


Peak @ 0.6 V disappears with cycling similar to 0.5:1 molar ratio sample

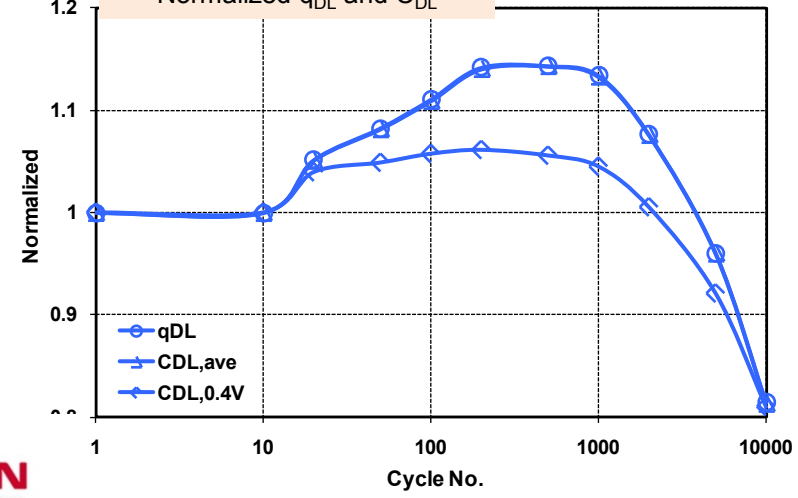
This peak is more prominent at this ratio than 0.5:1 molar ratio

Double-layer capacitance reduces ~20% post 10000 cycles.

q<sub>DL</sub> and C<sub>DL</sub> as a function of cycle number

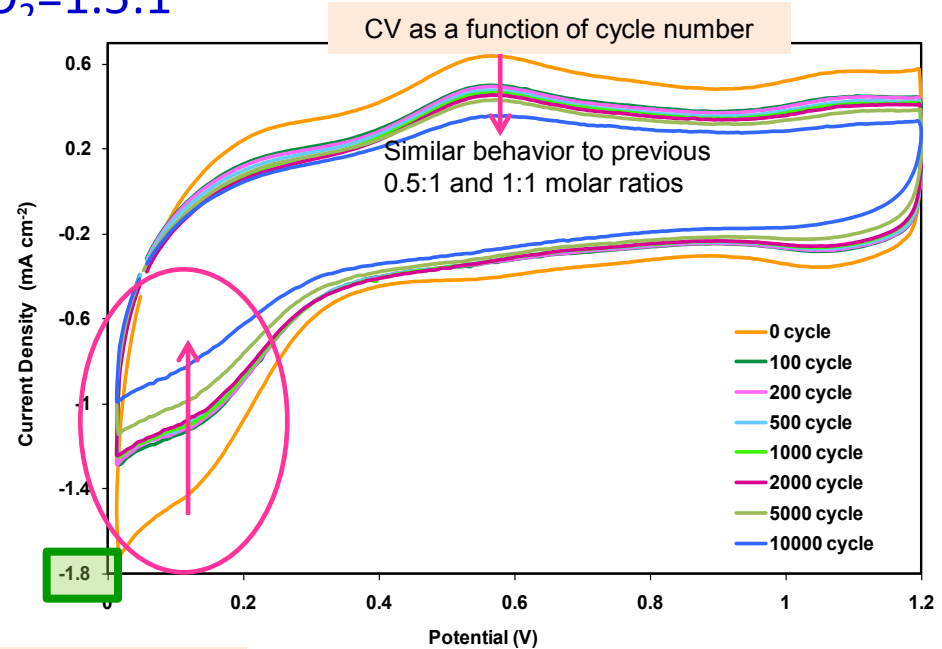


Normalized q<sub>DL</sub> and C<sub>DL</sub>



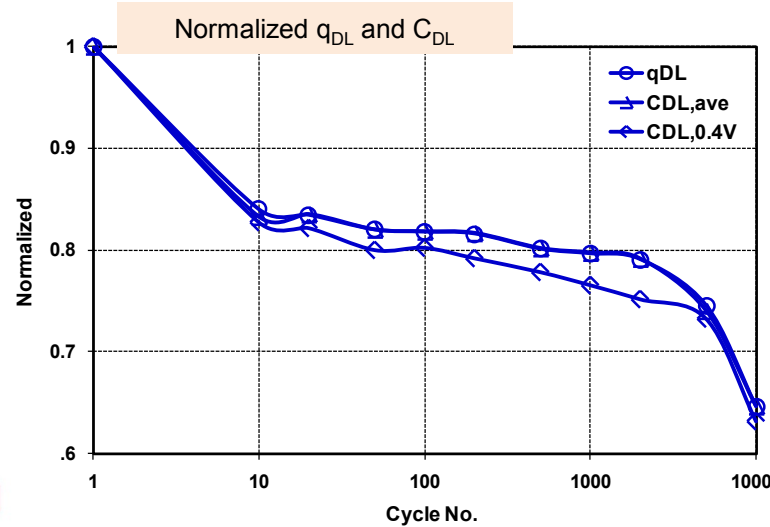
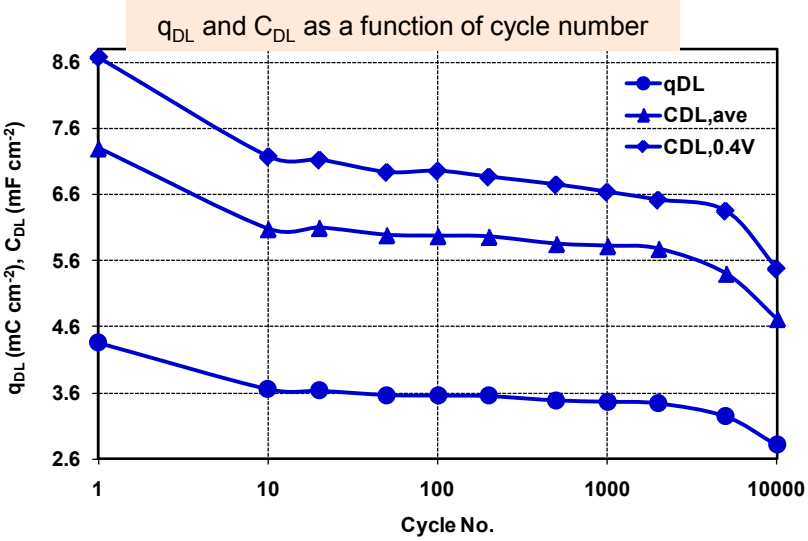
# Technical Accomplishments: Electrochemical Stability of RuO<sub>2</sub>-SiO<sub>2</sub>

## Stability of RuO<sub>2</sub>:SiO<sub>2</sub>=1.5:1



Similar to other molar ratios, peak @ 0.6 V disappears with more cycling

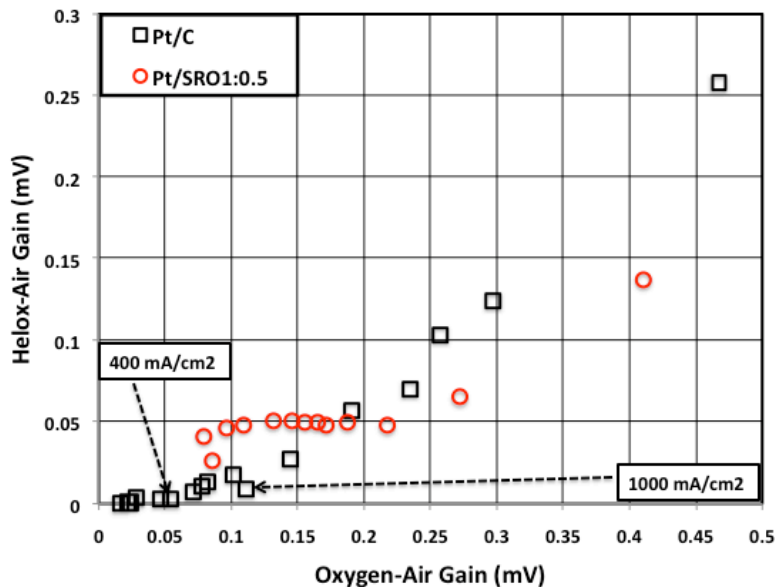
**Double-layer capacitance reduces ~36% post 10000 cycles.**



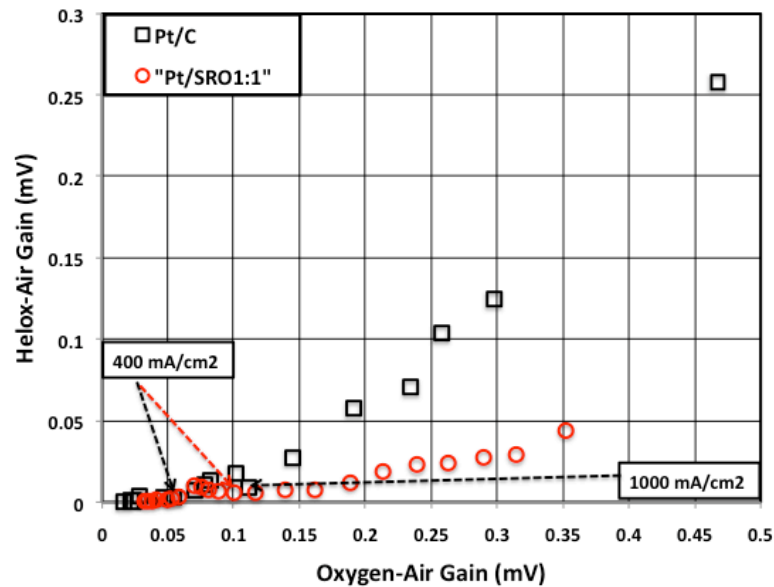


# Technical Accomplishments: Performance with Pt/SRO Electro catalysts

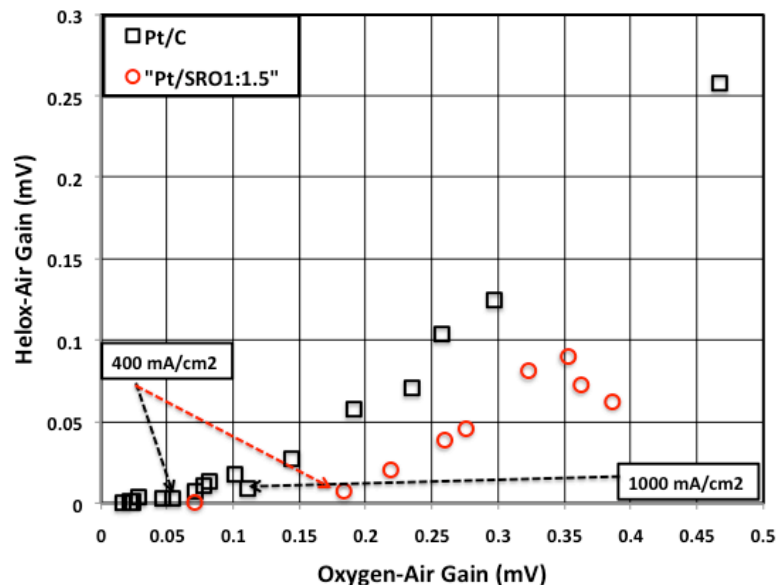
Oxygen-Air vs. Helox-Air Gain



Oxygen-Air vs. Helox-Air Gain

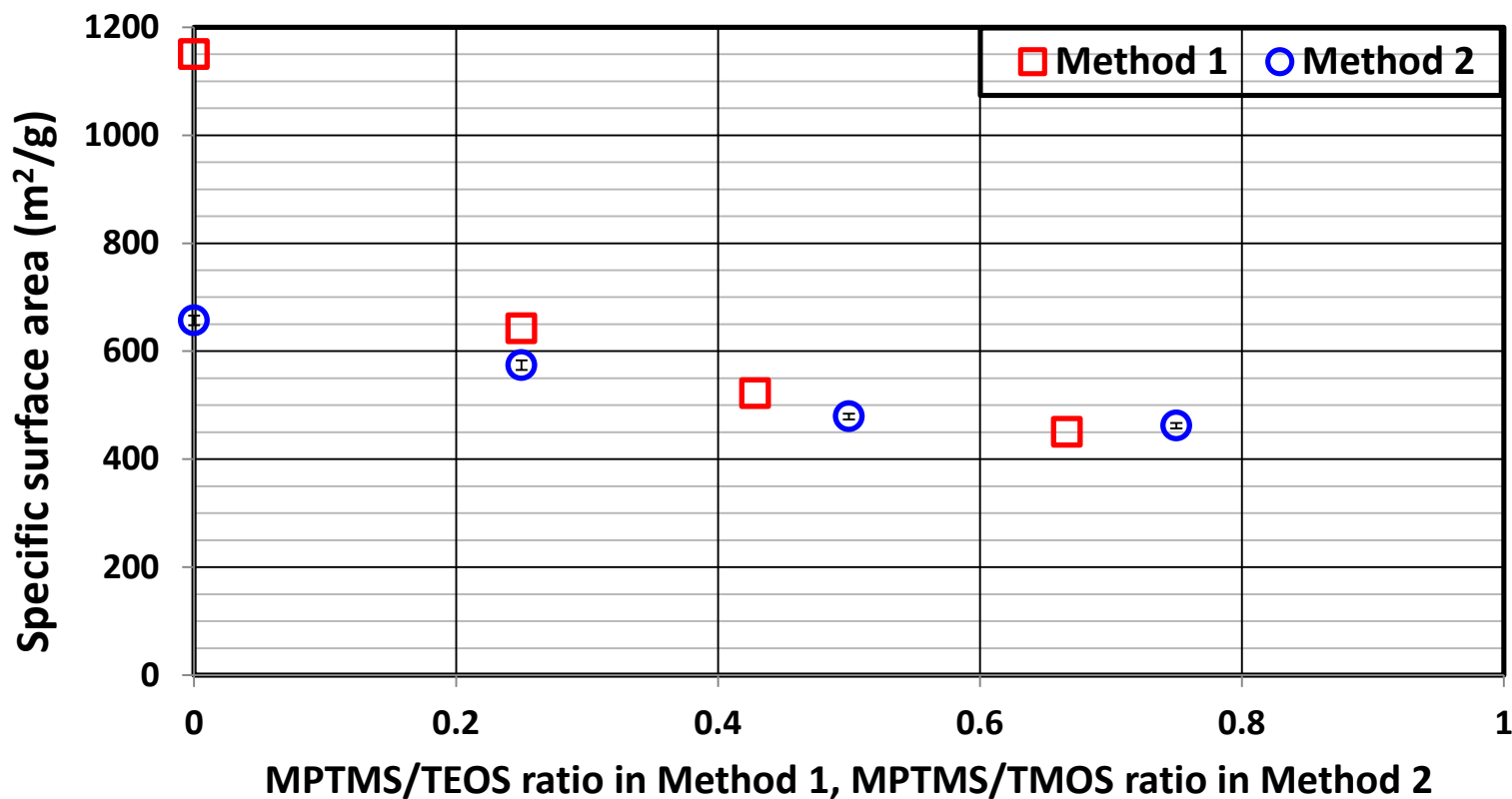


Oxygen-Air vs. Helox-Air Gain



- Plot of O<sub>2</sub>-Air vs. Helox-Air gain indicates extent and nature of mass transport limitations
- Severe transport limitations (in addition to Ohmic limitations) in SRO 1:0.5
- All SRO electrocatalysts demonstrate more transport limitations than Pt/C
- SRO supports (esp. 1:1) show tendency towards condensed phase transport limitations

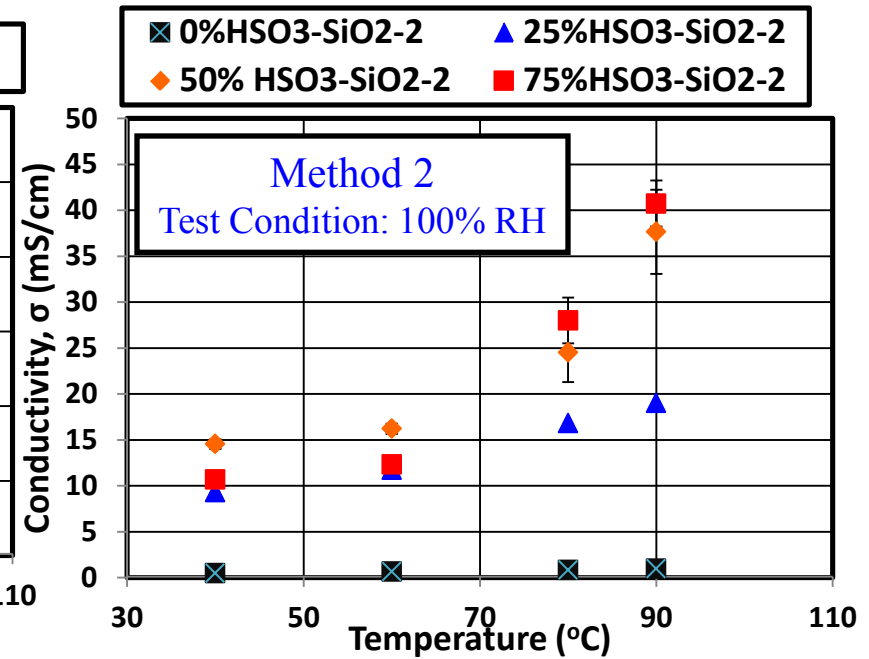
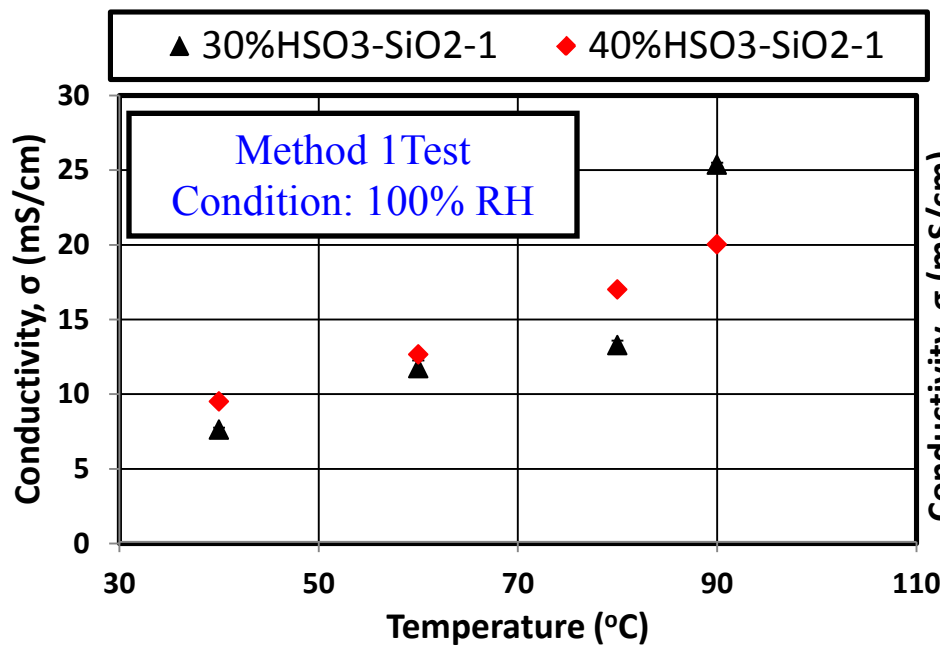
## Technical Accomplishments: BET Surface Area of Sulfonic Acid Functionalized SiO<sub>2</sub>



- BET surface area decreases with increasing extent of functionalization in both methods
- This is consistent with expectation based on results in the literature\*
- Surface areas obtained are well above that of Vulcan XC-72, and higher than the milestones set for this project
- PIs will continue to improve on this metric through advanced processing methods

\*Marschall *et al.*, Small, 5 (2009) 854

# Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO<sub>2</sub> Prepared by Methods 1 and 2



-The stand-alone proton conductivity currently tops out at 40 mS/cm at 90C and 100% RH (Method 2)

-Still working to optimize the precursor formulation employed, and to extend the degree of surface and interior functionalization to 100%

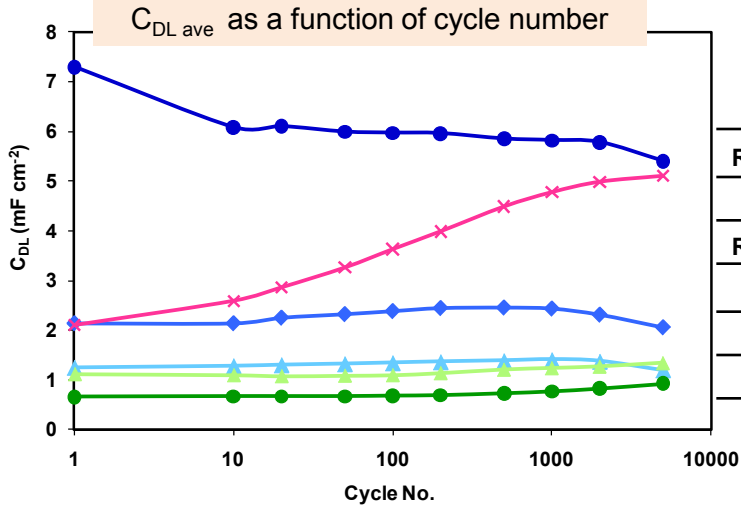
-Supercritical drying procedures in conjunction with study of alternate precursors (e.g. functionalized POSS) should further enhance surface functionalization and surface area.

-

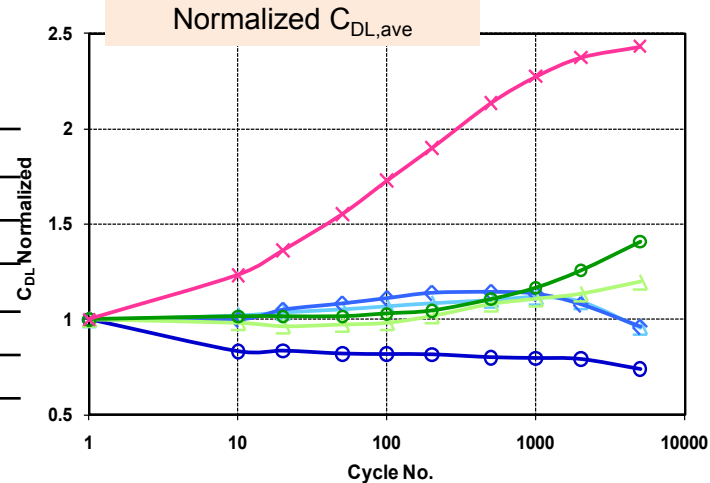
# Technical Accomplishments: Stability of Functionalized Silica

## Summary of the Stability of Functionalized Silica Supports

- The stability of functionalized silica supports was compared with that of Vulcan support.



Support	$C_{DL}$ change(%)
RuO <sub>2</sub> :SiO <sub>2</sub> =0.5:1	4
RuO <sub>2</sub> :SiO <sub>2</sub> =1:1	3.7
RuO <sub>2</sub> :SiO <sub>2</sub> =1.5:1	26
25%SO <sub>3</sub> H-SiO <sub>2</sub>	19.6
50%SO <sub>3</sub> H-SiO <sub>2</sub>	40.9
Vulcan	143.3



- The stability based on  $C_{DL}$  change(%):

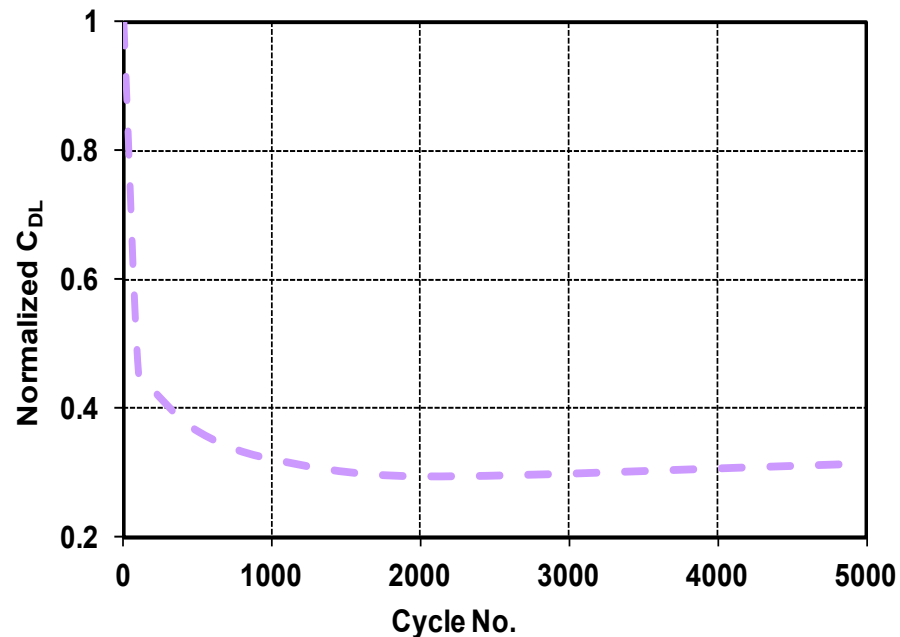
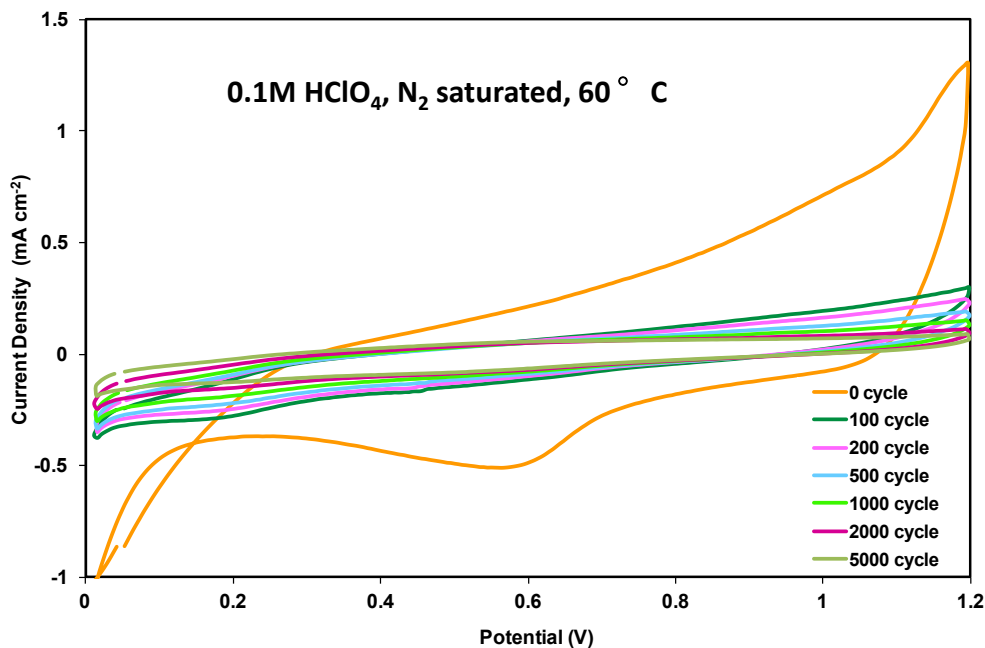
$RuO_2:SiO_2=1:1 \approx RuO_2:SiO_2=0.5:1 > 25\%HSO_3-SiO_2 > RuO_2:SiO_2=1.5:1 > 50\%HSO_3-SiO_2 \gg Vulcan$

- Based on these results RuO<sub>2</sub> functionalized silica with low RuO<sub>2</sub> content can be a stable non- carbon support.
- NTCNA's benchmark data for Vulcan support matches well with literature values for double layer capacitance ( 6 – 7  $\mu F/cm^2$ )



# Technical Accomplishments: Stability of Functionalized Silica – RuO<sub>2</sub>

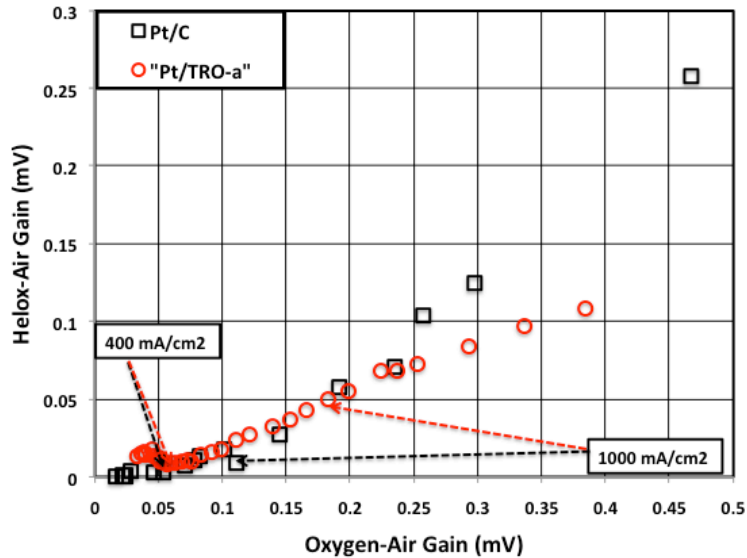
## Start-Stop Stability of SO<sub>3</sub>H-SiO<sub>2</sub>-RuO<sub>2</sub> (1:1)



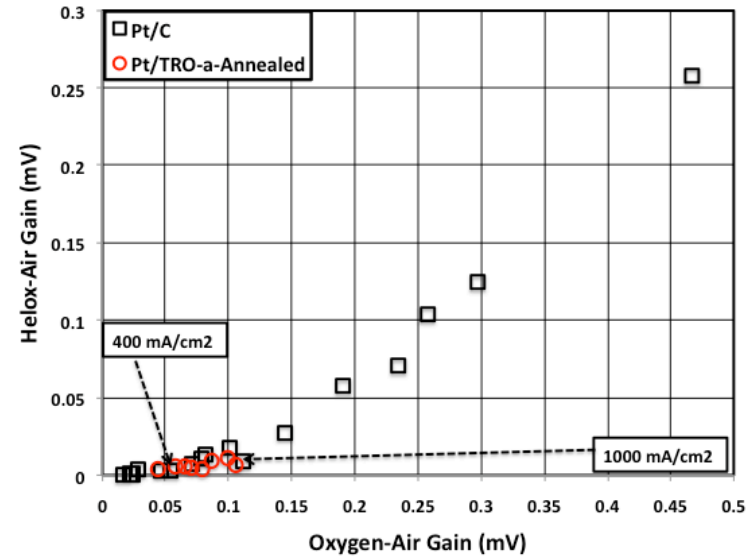
- After the first CV cycle, the support material is quite stable.

# Technical Accomplishments: Performance of Pt/RTO Electrocatalysts

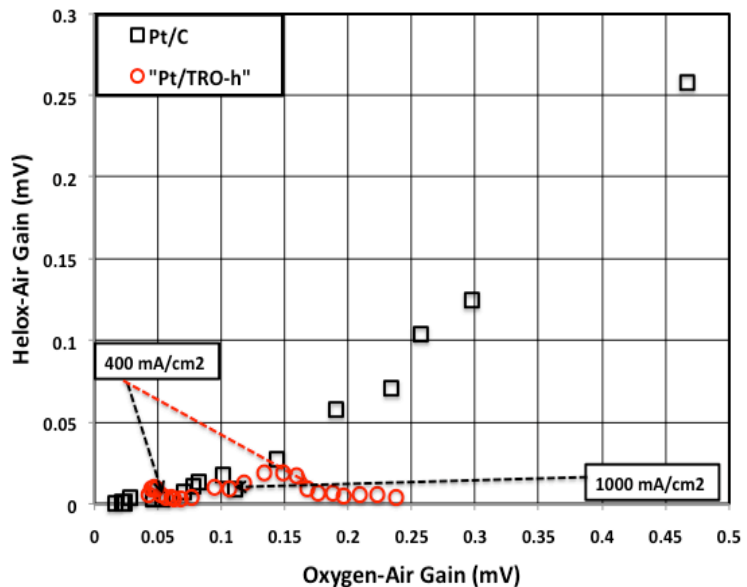
Oxygen-Air vs. Helox-Air Gain



Oxygen-Air vs. Helox-Air Gain



Oxygen-Air vs. Helox-Air Gain

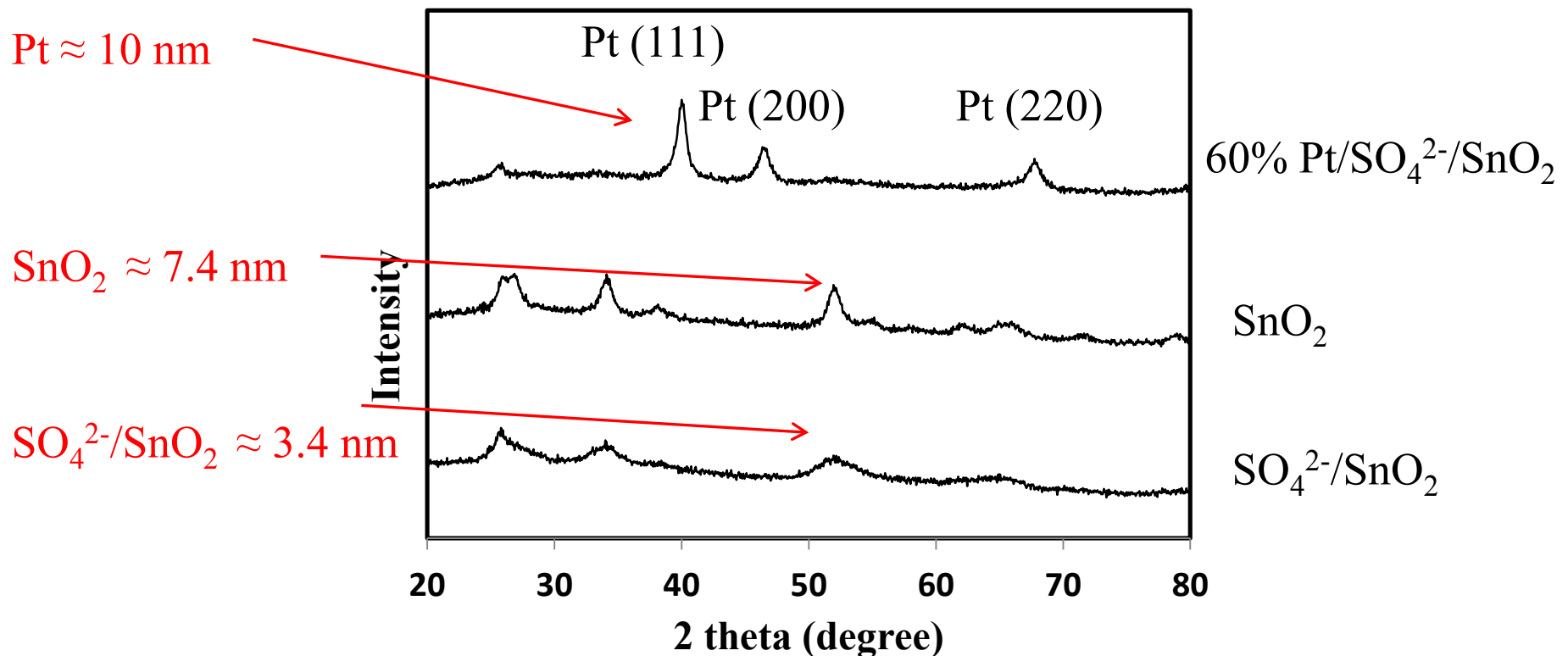


- Plot of O<sub>2</sub>-Air vs. Helox-Air gain indicates extent and nature of mass transport limitations
- Transport limitations (in addition to Ohmic limitations) observed in all TRO supports
- RTO supports when annealed or prepared with hydrous ruthenium oxide show tendency towards condensed phase transport limitations

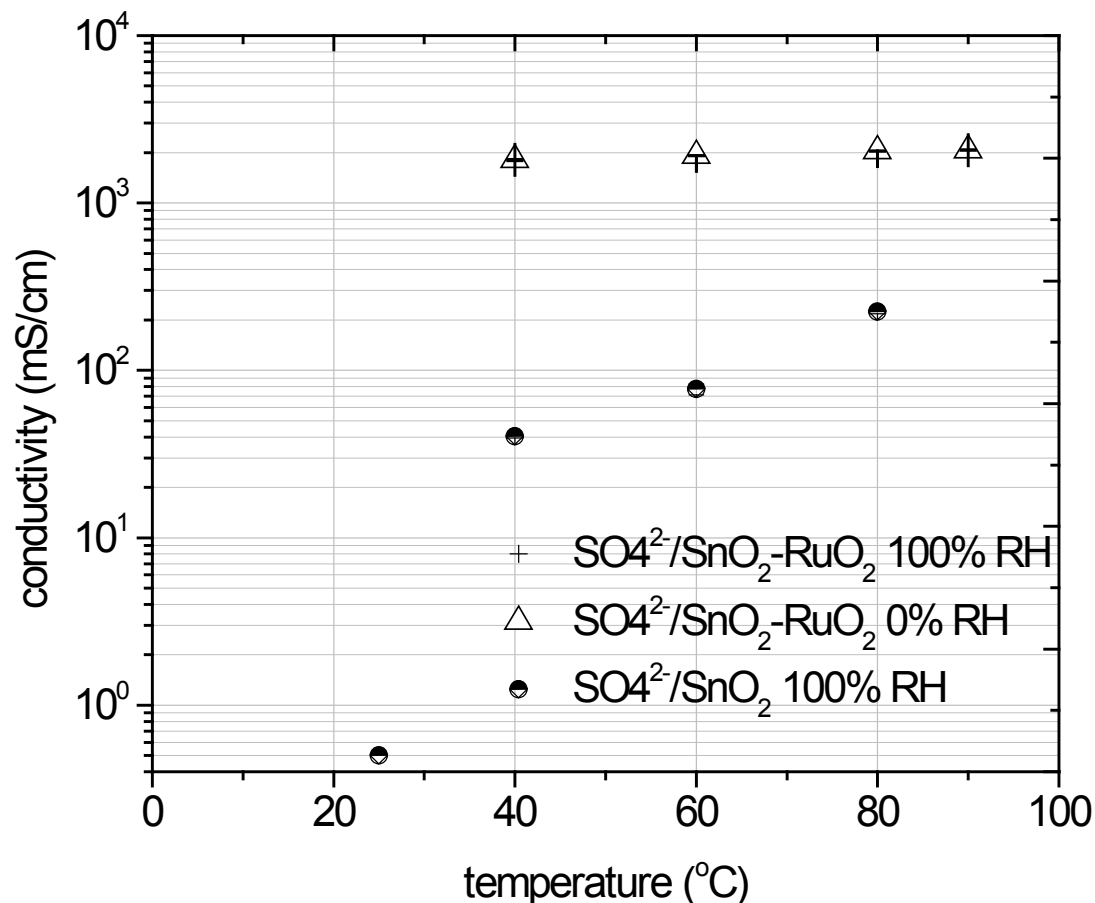
# Technical Accomplishments: XRD of Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>

The SO<sub>4</sub><sup>2-</sup> group on the surface of SnO<sub>2</sub> inhibits the degree of crystallization.

The crystallite sizes estimated by the Scherrer equation were around 7.4 nm and 3.4 nm for SnO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>, respectively.



# Technical Accomplishments: Conductivity of Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-RuO<sub>2</sub>



A maximum proton conductivity of 220 mS/cm was obtained for SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> at 80 ° C. Moreover, the SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> was annealed at 500 ° C, which means that SO<sub>4</sub><sup>2-</sup> group on SnO<sub>2</sub> was more thermally stable than sulfonic acid functionalized silica aerogel.



# Technical Accomplishments: Properties of Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-RuO<sub>2</sub>

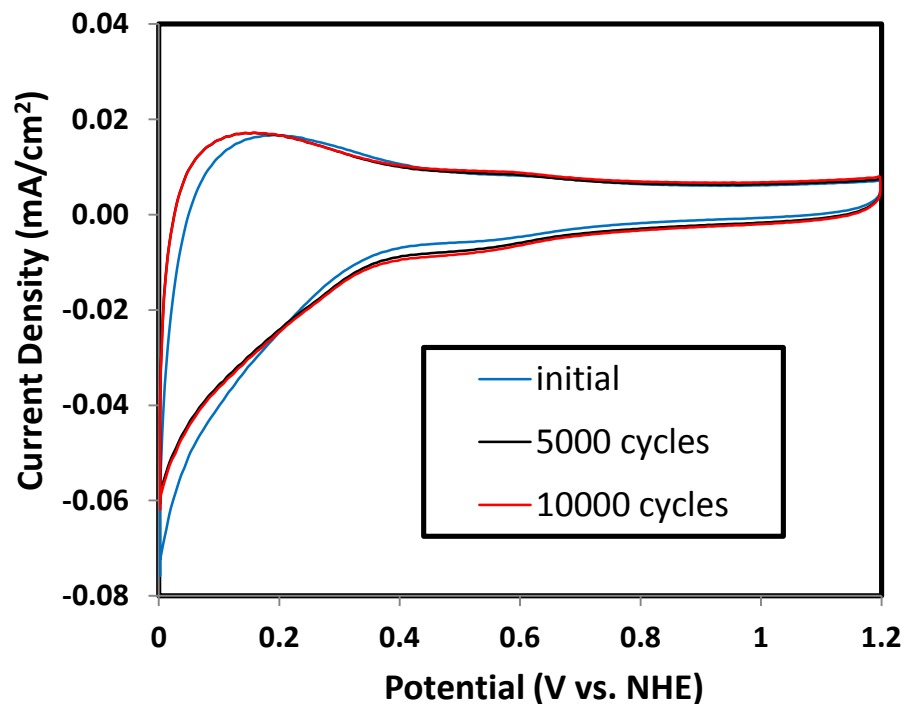
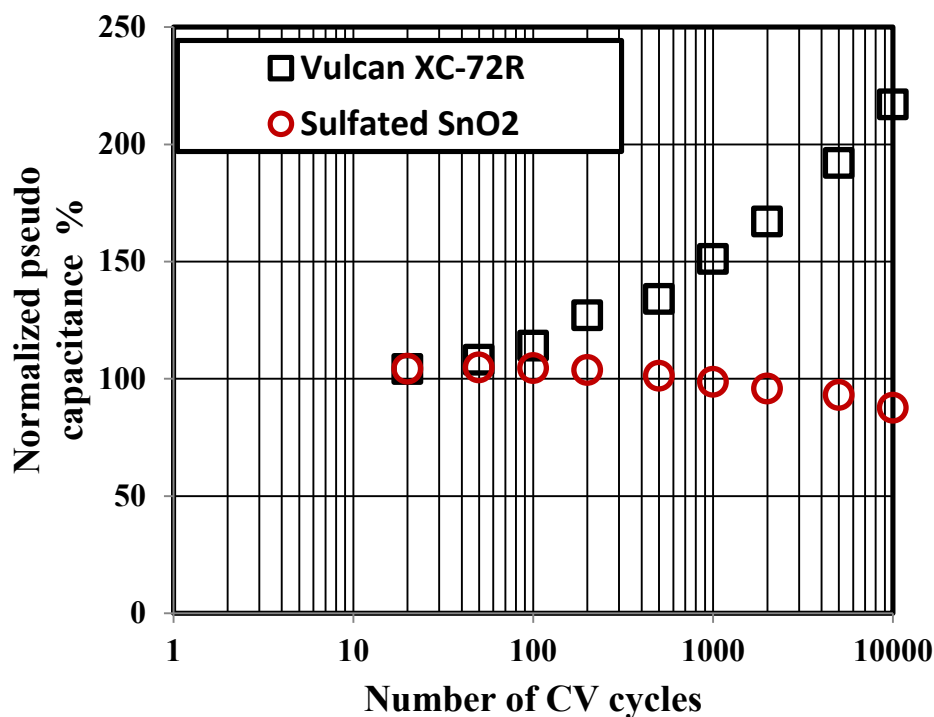
Sample	BET surface area(m <sup>2</sup> /g)	IEC (mmol/g)	Electrical conductivity (S/cm)
SnO <sub>2</sub>	21	~0	~0
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	96	0.65	~0
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -RuO <sub>2</sub> (mole ratio of Sn:Ru=1:1)	?	?	2-3
60%Pt/SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	?	0.175	23 ± 3

- ❑ IEC results suggested that SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-RuO<sub>2</sub> was almost completely covered by RuO<sub>2</sub> and no sulfonic acid group was exposed on the surface (IEC ≈ 0).
- ❑ The IEC results was consistent with conductivity results. The high conductivity of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-RuO<sub>2</sub> was contributed by the electrical conductivity of RuO<sub>2</sub>
- ❑ 60%Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> exhibited high electrical conductivity, where Pt served as electrical conductor.
- ❑ IEC results suggested that about 33% of the SO<sub>4</sub><sup>2-</sup> group of 60%Pt/SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> sample was blocked by deposited Pt (1-0.175/0.4/0.65=0.67).

# Technical Accomplishments: Stability of $\text{SO}_4^{2-}/\text{SnO}_2$

0.1 M  $\text{HClO}_4$  under  $\text{N}_2$  atmosphere; CV sweep rate of 20 mV/S; RT

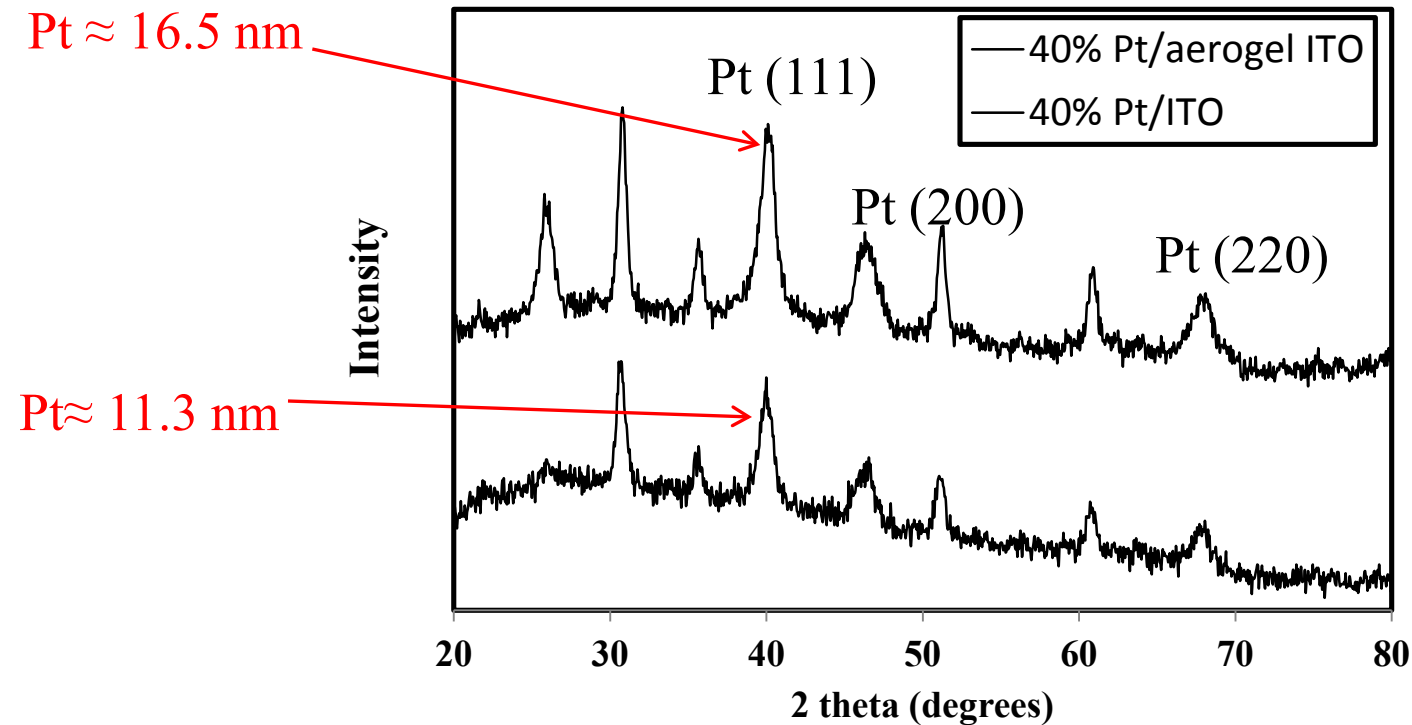
The support stability was evaluated from the pseudo capacitance ( $C_{\text{DL}}$ ) at 0.4 V.



Sulfated  $\text{SnO}_2$  support exhibited higher stability than Vulcan carbon.

# Technical Accomplishments: XRD of Pt/ITO

The crystallite sizes of Pt deposited on regular ITO and on ITO aerogels were around 11.3 and 16.5, respectively.



# Technical Accomplishments: Properties of ITO

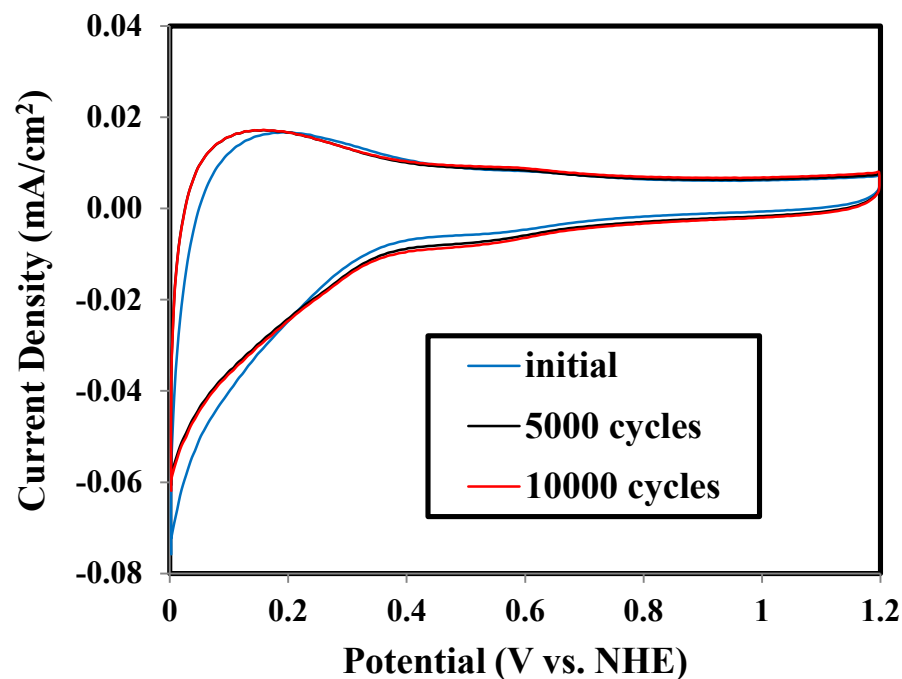
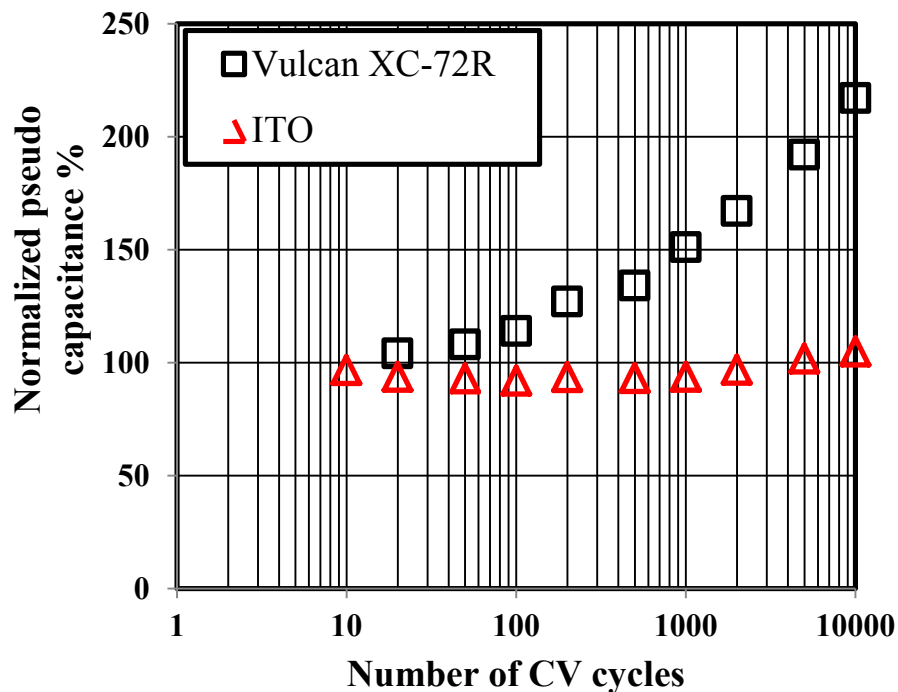
	ITO	Aerogel ITO	Commercial-ITO
Electrical conductivity (S/cm)	1.5	0.8	0.6
BET (m <sup>2</sup> /g)	45	35	27(32)

- ❑ The ITO synthesized in the lab was a powder in polycrystalline form; hence the conductivity was only around 1 S/cm; The conductivity of commercial ITO-film is around 500 S/cm.
- ❑ The BET surface area of aerogel ITO was less than ITO. The result indicated that the aerogel network was not formed properly. Work is still ongoing in this area.

# Technical Accomplishments: Stability of ITO

0.1 M HClO<sub>4</sub> under N<sub>2</sub> atmosphere; CV sweep rate of 20 mV/S; RT

The support stability was evaluated from the pseudo capacitance ( $C_{DL}$ ) at 0.4 V.



ITO support exhibited better stability than Vulcan carbon.

# Collaboration with NTCNA – Benchmarking of Baseline Materials

- Nissan North America Inc. is a key project partner from industry
  - Dr. Kev Adjemian is PI from Nissan North America Inc.
  - Will focus on providing an industry perspective and will perform benchmarking, durability testing, and large scale MEA fabrication and testing
  - The PIs from Nissan North America Inc. and IIT have visited each other's facility in the past 2 quarters. Regular visits are planned
  - Discussions are ongoing to house an IIT researcher (student) at Nissan North America Inc. for 1-2 weeks; with a reciprocal visit to IIT
  - The following few slides illustrate the benchmarking support provided by Nissan North America Inc. for this project
    - Outstanding correlations have been obtained between ex-situ and in-situ durability measurements
    - testing of project-related samples at Nissan North America Inc. using the methods described in the following slides scheduled to begin in March 2011

# Collaboration with Nissan, North America - Benchmarking

## Catalyst Information



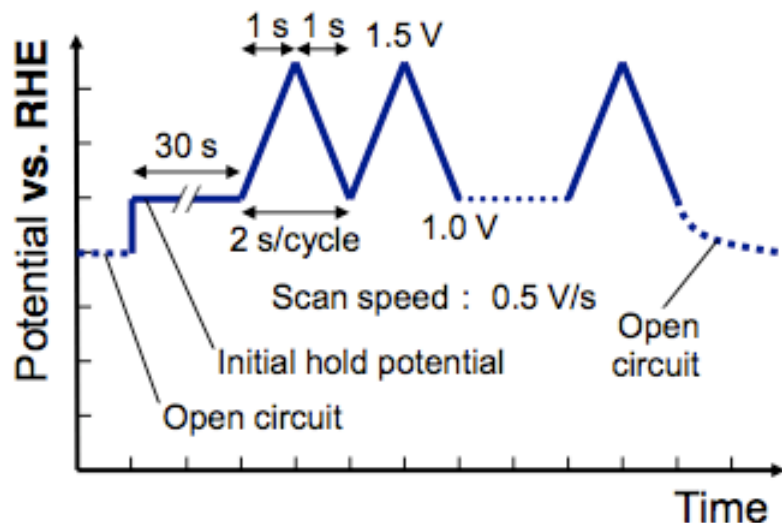
	High Surface Area Carbon (HSAC)	Heat Treated HSAC	Graphitized HSAC	Vulcan	Vulcan
Pt loading (wt%)	46.1% Pt	50.5 % Pt	46.3 % Pt	29.1 % Pt	45.7 % Pt
Carbon Support	HSAC	HSAC heat treated	Graphitized HSAC	Vulcan XC72	Vulcan XC72
Pt Particle Size (nm)	2.6	4.6	2.3	NA	2.3
BET Surface Area (m <sup>2</sup> /g)	310.5	395.7	97.6	NA	84.6
TEM Images				NA	NA

HSAC = Ketjen Black<sup>®</sup>

# Collaboration with Nissan, North America - Benchmarking

## Catalyst Support Durability Evaluation

### RDE Protocol: Carbon Corrosion



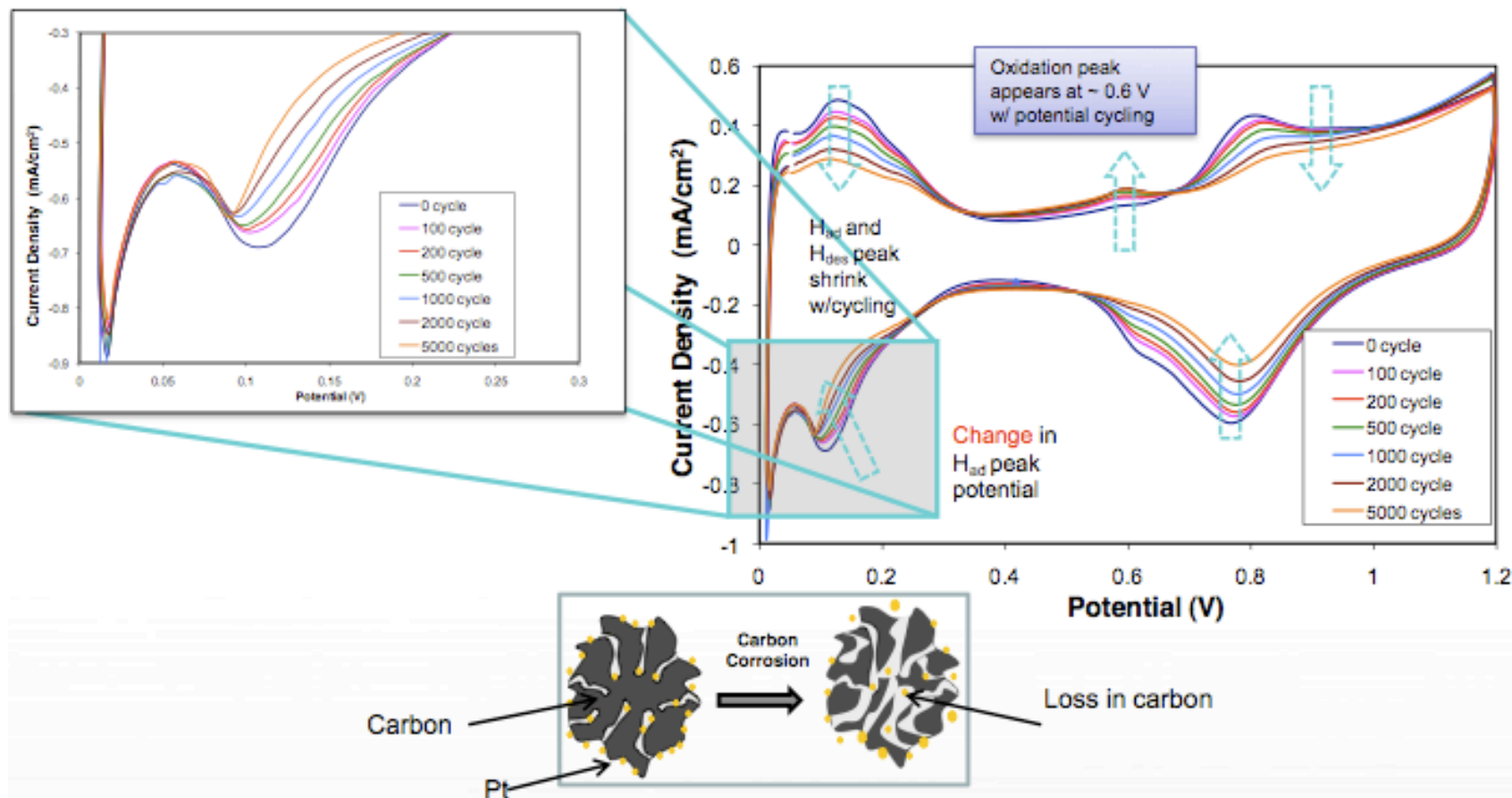
Temperature / °C		60
Solution	Electrolyte	0.1 M HClO <sub>4</sub>
	Dissolved gas	Saturated with N <sub>2</sub> or Ar
	Reference Electrode	RHE
	Counter Electrode	Pt gauze

**Diagnosis:** CV at 0, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000 cycles

(Indispensable item: Electrochemical area)

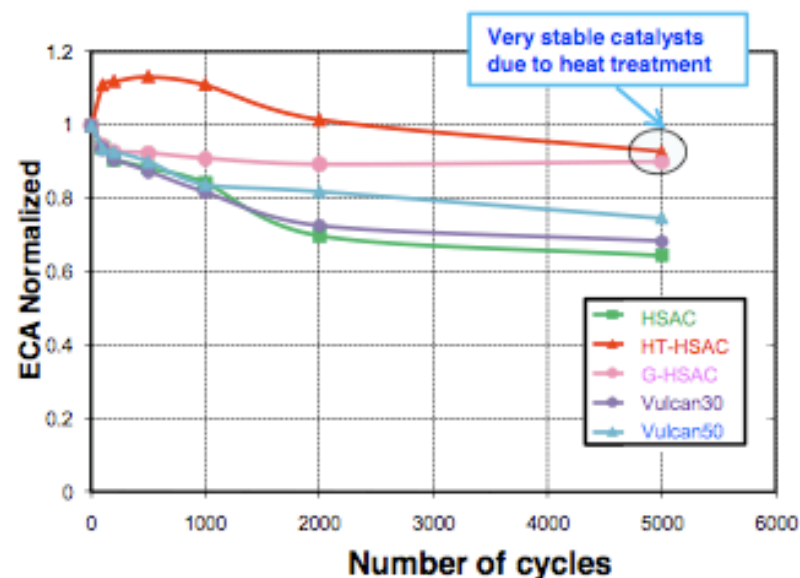
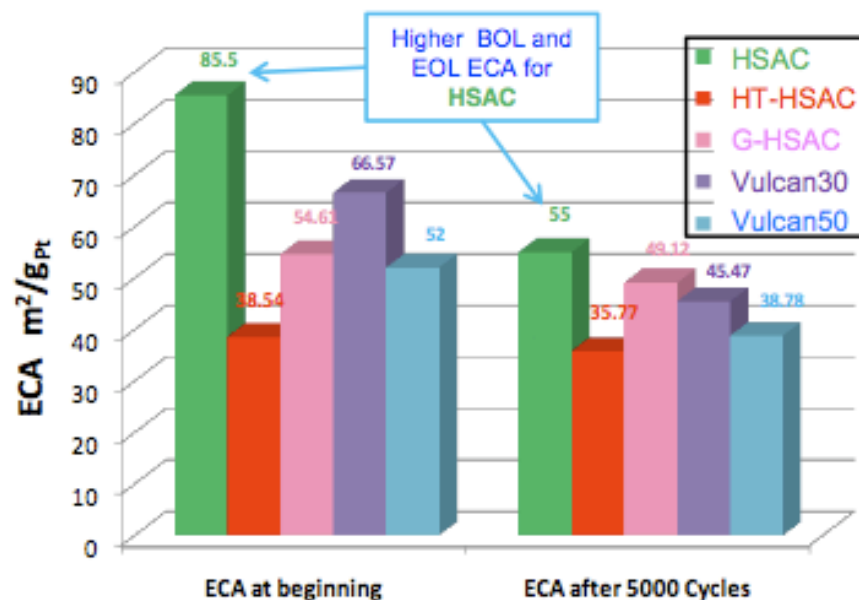


## Catalyst Support Durability Evaluation Example RDE: Vulcan Support



- H<sub>ads</sub> peaks and oxidation peaks decreased with potential cycling.
- Double layer increased slightly with more potential cycling, as opposed to other catalyst

## Carbon Support Corrosion Evaluation Comparison RDE

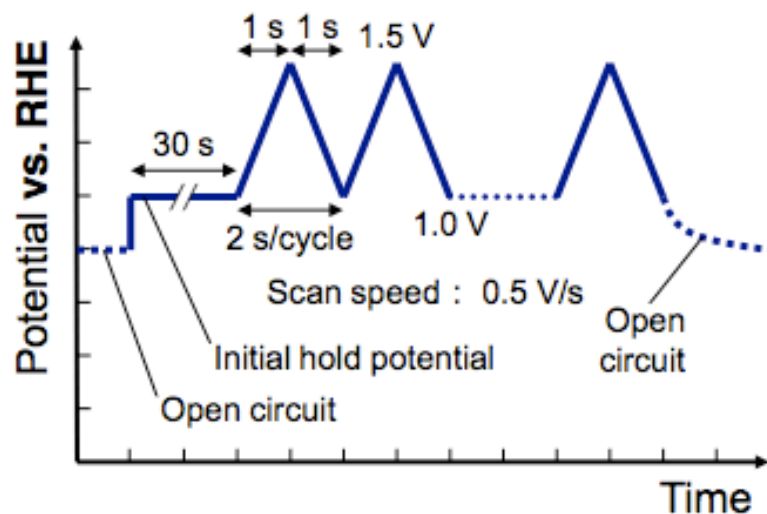


Catalyst	% ECA Loss
HSAC	~ 36%
HT-HSAC	~ 7%
G-HSAC	~ 10%
Vulcan30	~ 32%
Vulcan50	~ 25%

- HSAC Support provides the highest BoL and EoL ECA values
- HT-HSAC shows the highest durability (ECA loss) **but** BoL ECA is lower than EoL ECA for HSAC

# Collaboration with Nissan, North America - Benchmarking

## Catalyst Support Durability Evaluation Fuel Cell Protocol: Carbon Corrosion



Temperature / °C		80
RE/CE (Anode)	Gas	H <sub>2</sub>
	Dew point / °C	80
	Flow rate / NL min <sup>-1</sup>	0.5
WE (Cathode)	Gas	N <sub>2</sub>
	Dew point / °C	≥ 80
	Flow rate / NL min <sup>-1</sup>	0.5

**Diagnosis:** CV at 0, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000 cycles

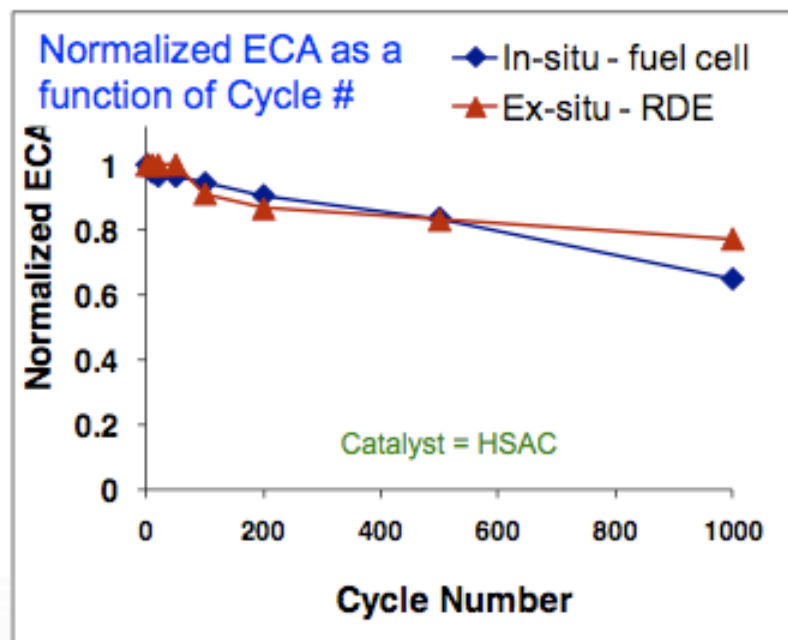
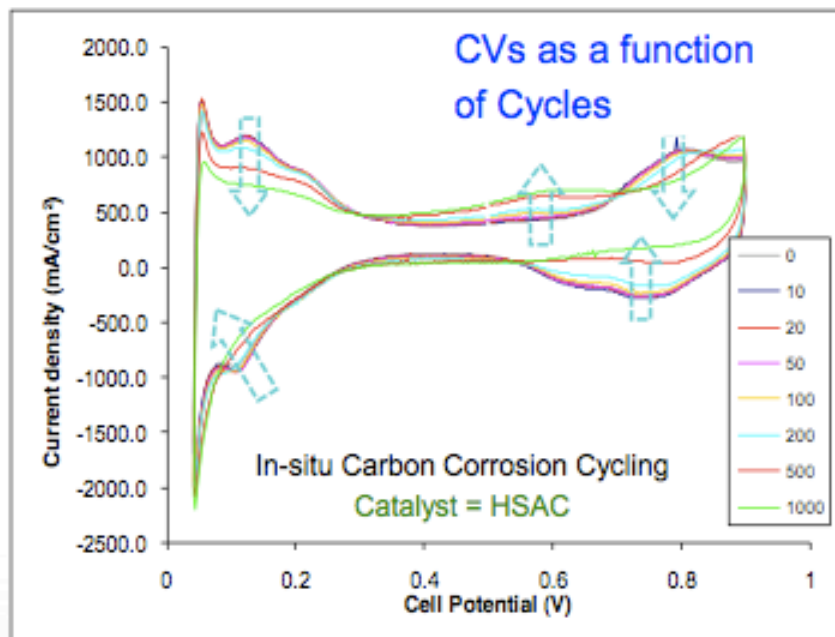
(Indispensable item: Electrochemical area)

At high voltage, carbon oxidation reaction (carbon corrosion) accompanies the H<sub>2</sub>O consumption. To prevent drying of cathode, the dew point should be set slightly above 80 °C.

## Carbon Support Corrosion Evaluation Comparison RDE & Fuel Cell Single Cell



### Baseline HSAC catalyst in-situ and ex-situ durability comparison



✓ Excellent correlation between RDE and Fuel Cell

## Summary



- **HSAC** Benchmark catalyst demonstrates highest BoL and EoL ECAs
- **HT-HSAC** shows the lowest amount of ECA loss after carbon corrosion testing
  - Still lower however than EoL of HSAC catalyst
- In-situ & Ex-situ testing protocols correlate very well when using the same catalyst

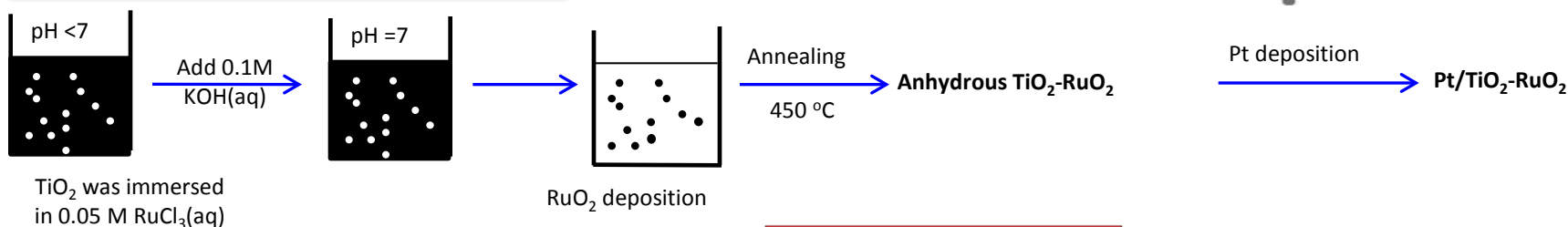


# Collaboration with Nissan, North America - Benchmarking



## Catalyst Observation

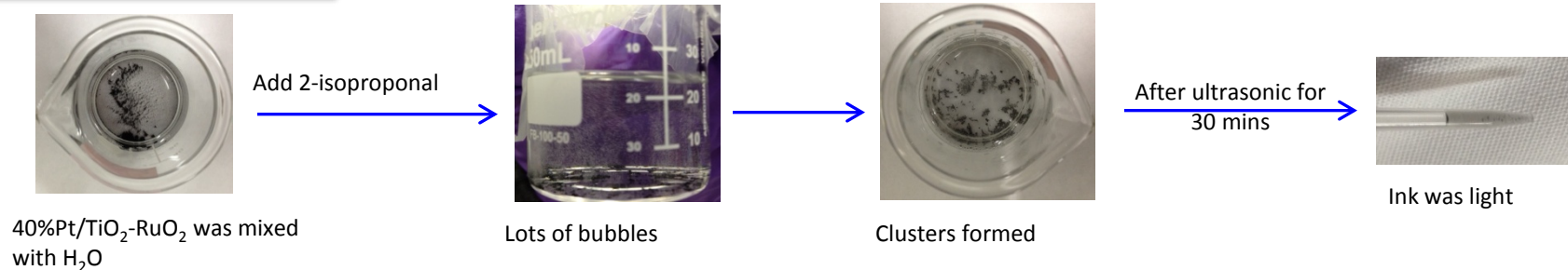
### Synthesis of Pt/TiO<sub>2</sub>-RuO<sub>2</sub>



### Characterization

	TiO <sub>2</sub> -RuO <sub>2</sub>	Pt/TiO <sub>2</sub> -RuO <sub>2</sub>	TEC10E50E
BET (m <sup>2</sup> /g)	33±4	30±5	310±10
Electrical conductivity (S/cm)	21±5	81±7	26±2
	Support	Catalyzed Support	TKK Baseline

### Ink preparation



- Pt distributed on the support surface might react with alcohol.
- Water-based ink was prepared with water-based Nafion to eliminate the reaction of the catalyst with alcohol. However, the activity was lower and deviated a lot due to the uneven dispersion of water-based ink on the disk.

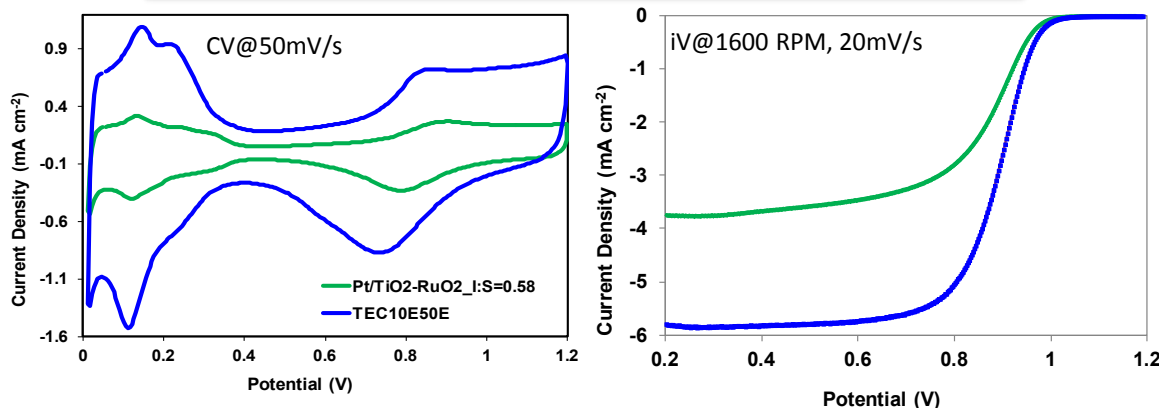


## ORR Activity-RDE

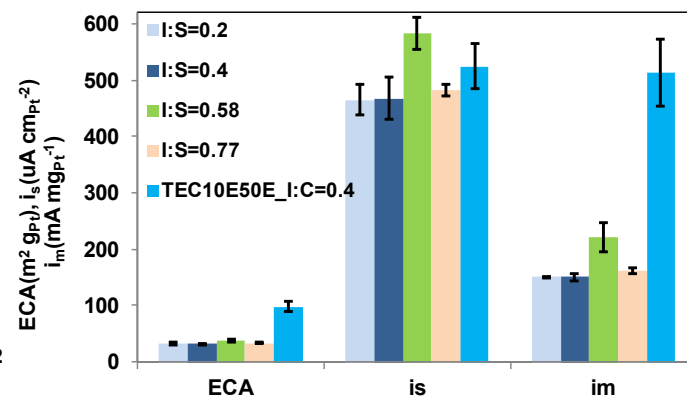
### Ink optimization

- The ORR activity of the catalyst was studied with different ionomer:support (I:S) ratio to optimize the ink formulation for the catalyst ex-situ performance.
  - The results were compared with TTK baseline catalyst TEC10E50E(50% Pt/HSAC).

Example of CV and iV of 40%Pt/TiO<sub>2</sub>-RuO<sub>2</sub>



Activity as a function of I:S ratio



- 40%Pt/TiO<sub>2</sub>-RuO<sub>2</sub> with a I:S ratio of 0.58 achieved the highest ORR mass specific activity, which was ~40% of the performance of TEC10E50E.
- The catalyst showed the similar H<sub>2</sub> adsorption and desorption characteristic as TEC10E50E.
- The catalyst had lower limiting current than TEC10E50E because of its low surface area and diffusion within catalyst layer (unoptimized micro-porosity).
- ORR activity for each I:S ratio is consistent and reproducible.

# Collaboration with Nissan, North America - Benchmarking Catalyst Durability-RDE



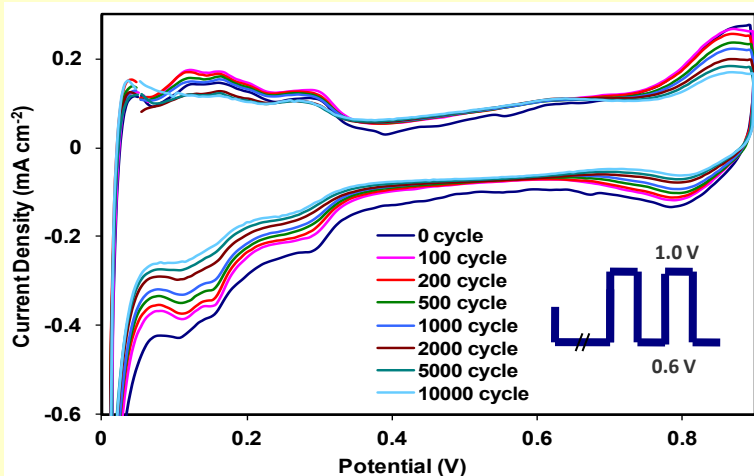
- The stability of the catalyst was tested under Nissan load cycling and start-stop cycling. The losses were compared with those of TEC10E50E(50% Pt/HSAC).

Load Cycling

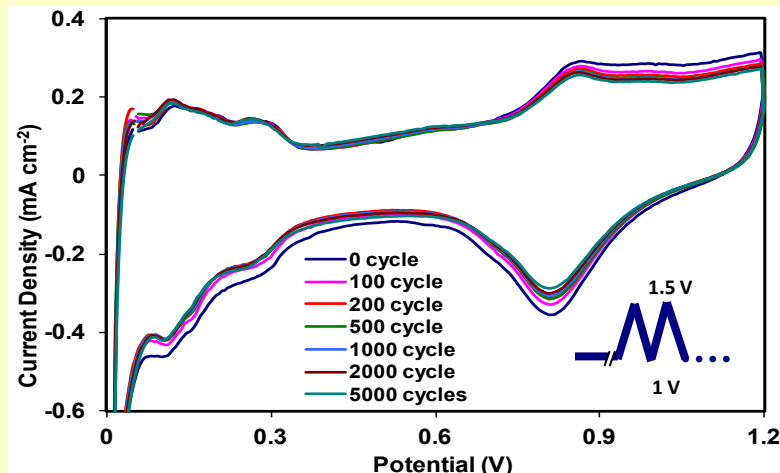
0.1M HClO<sub>4</sub>, N<sub>2</sub> saturated, 60°C

Start-stop Cycling

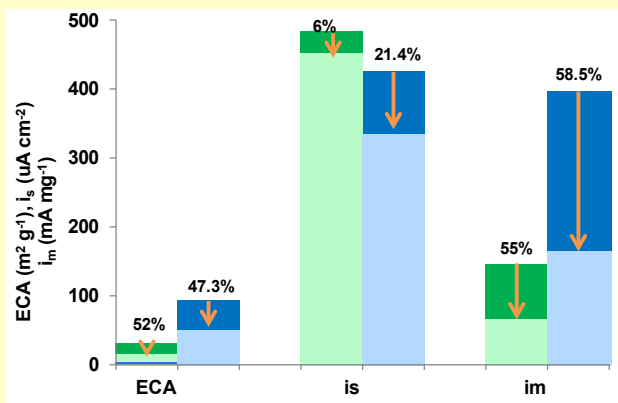
Effect of Load Cycling on CV



Effect of Start-stop Cycling on CV



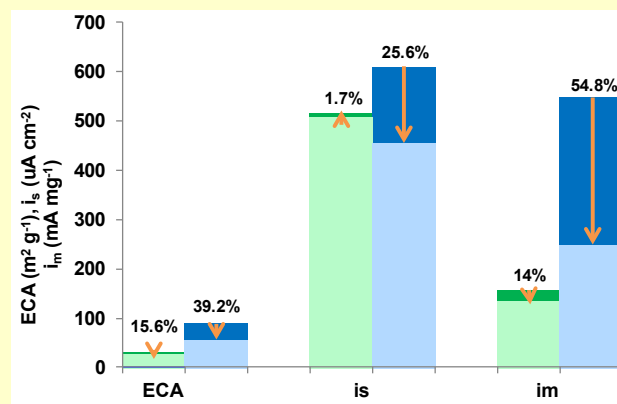
Losses in Load Cycling



0.1M HClO<sub>4</sub>, RT

- BOL
- EOL
- 40%Pt/TiO<sub>2</sub>-RuO<sub>2</sub>
- 50% Pt/HSAC

Losses in Start-stop Cycling



- The Pt/TiO<sub>2</sub>-RuO<sub>2</sub> was quite stable under start-stop cycling, however, it lost the stability in load cycling, comparable to TEC10E50E.