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Zero Emission

Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

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Project ID #

FC085

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Overview

Timeline

- Project start date: Sept. 1st 2010*
- Project end date: Aug. 31st 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^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
- 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 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 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^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 (RSO or SRO))
- **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) (RTO or TRO)
- **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

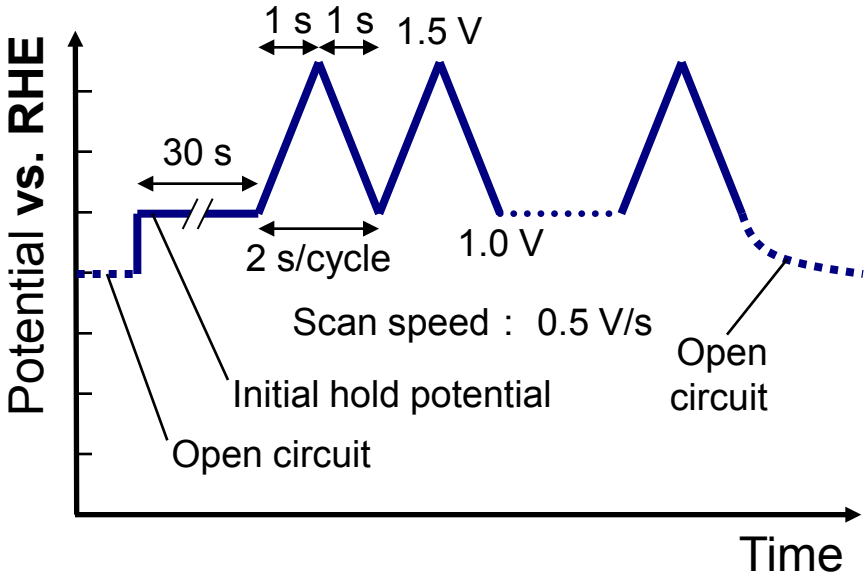
- Milestone 1 (End of Phase 1; Q1; 2012 [calender year])
  - Synthesize a support that demonstrates at least:
    - 70 mS/cm proton conductivity [Current status ~ >120 mS/cm; stand-alone]
    - 2 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m^2/g BET surface area [Current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

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

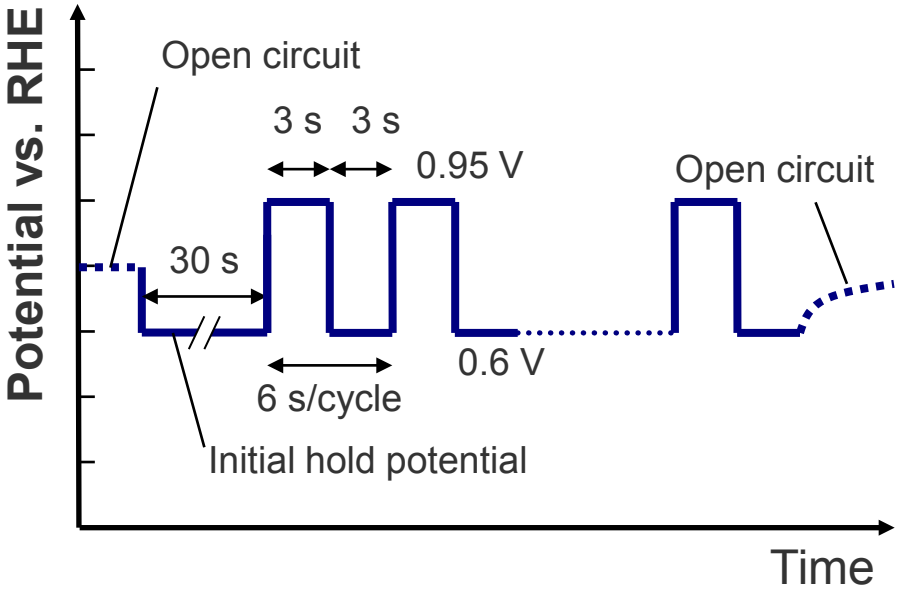
- Milestone 2 (End of Phase 2; Q3; 2013)
  - Synthesize a support that demonstrates at least:
    - 100 mS/cm proton conductivity [Current status > 120 mS/cm; stand-alone]
    - 5 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m^2/g BET surface area [Current status > 250m^2/g]
    - Durability* in acidic electrolyte [Current status – durable, further tests ongoing]
  - Prepare and evaluate Pt-catalyzed supports [Current Status: ongoing]
  - Identify optimal ionomer loading in electrode [Current Status: Not yet started]
  - Prepare 6 100 cm^2 MEAs w/ optimal support formulation [Not yet started]
- GNG criterion (applied at end of Q1; 2012)

"At the end of Phase I, IIT and Nissan North America Inc. will have prepared or showed significant progress towards preparing a support material with a surface area of 50 m^2/g; an electron conductivity of 2 S/cm, a proton conductivity of 0.07S/cm and durability in acidic electrolyte of 1000 cycles per the defined accelerated test protocols*"

Approach: Potential Cycling to Estimate Support and Electrocatalyst Durability



Support Durability—Support corrosion



Catalyst Durability– Pt Dissolution

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

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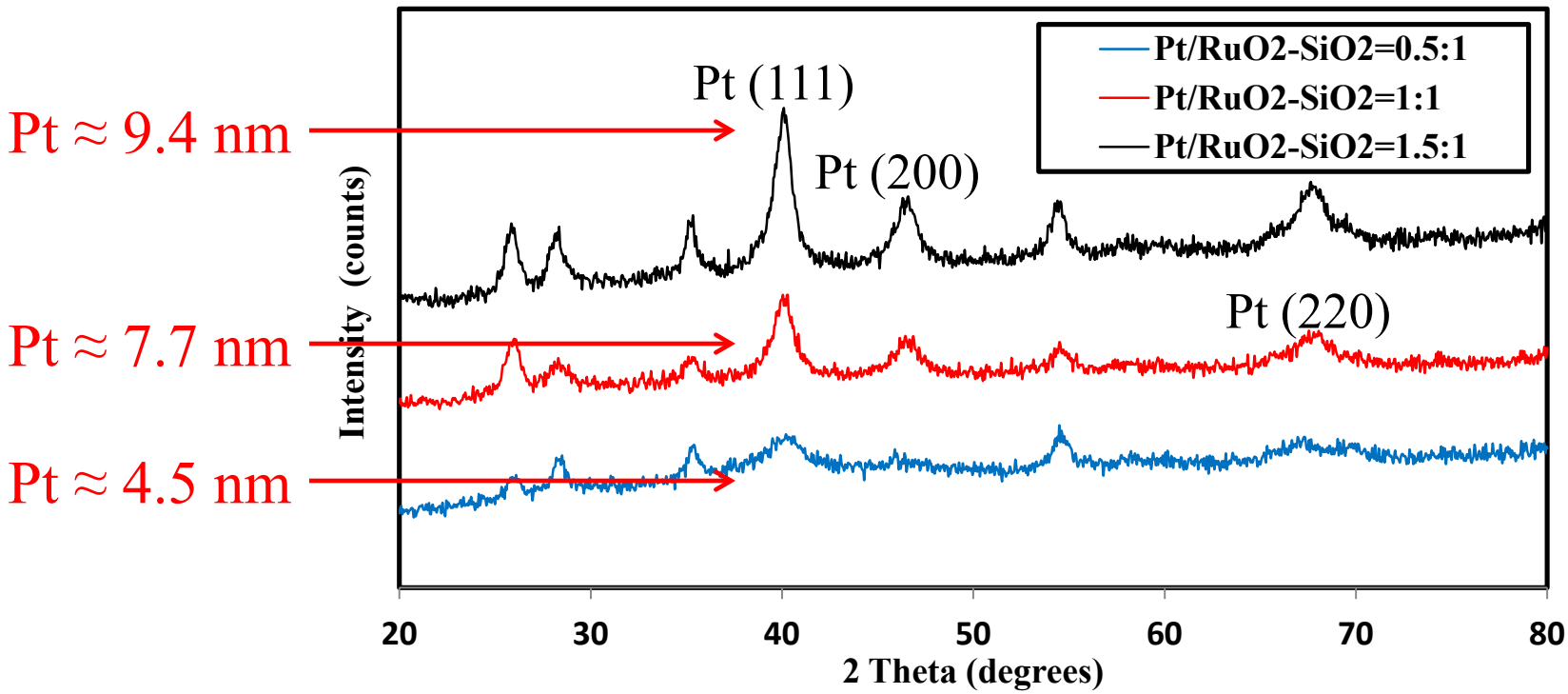
Technical Accomplishments: XRD of RuO_2- SiO_2

Crystallite sizes were estimated using the Scherrer equation.

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

K(shape factor)=0.94; λ (x-ray wavelength)=1.54Å;
β(the line broadening at half the maximum intensity in radians)=0.01571;
Θ(Bragg angle)=40.1;
τ(crystallite size)= 0.94*1.54/0.01571/cos(40.1/2/360*2*π)=93.96Å

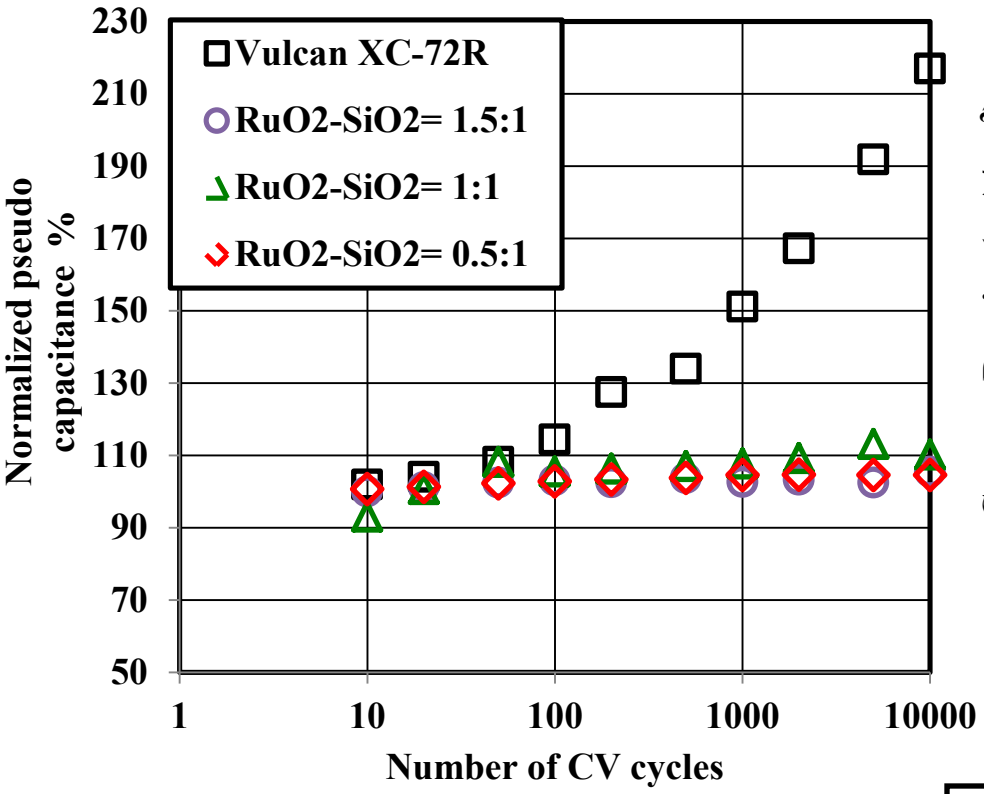


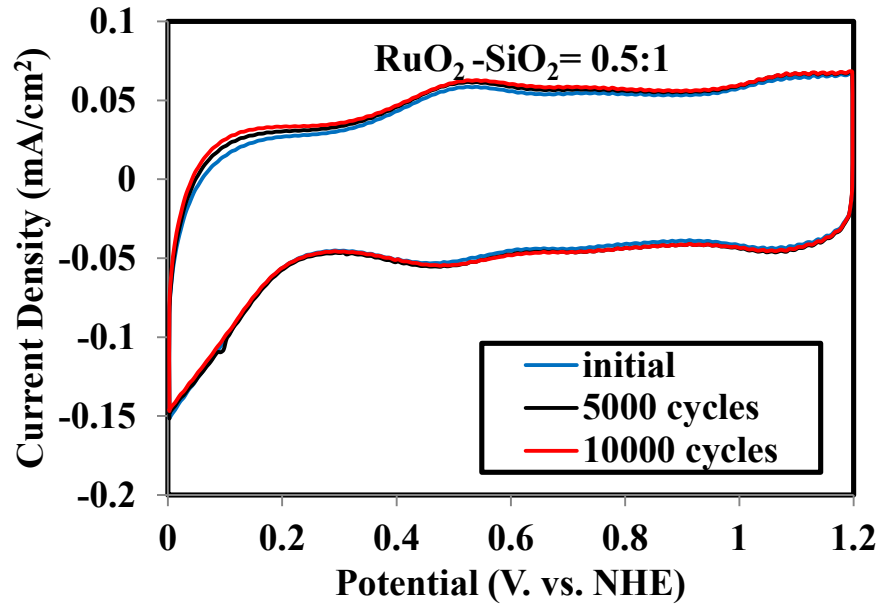
Supports with higher BET surface area resulted in well-dispersed Pt particles with smaller crystallite size.

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

Technical Accomplishments: Electrochemical Stability of RuO_2 -SiO_2

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



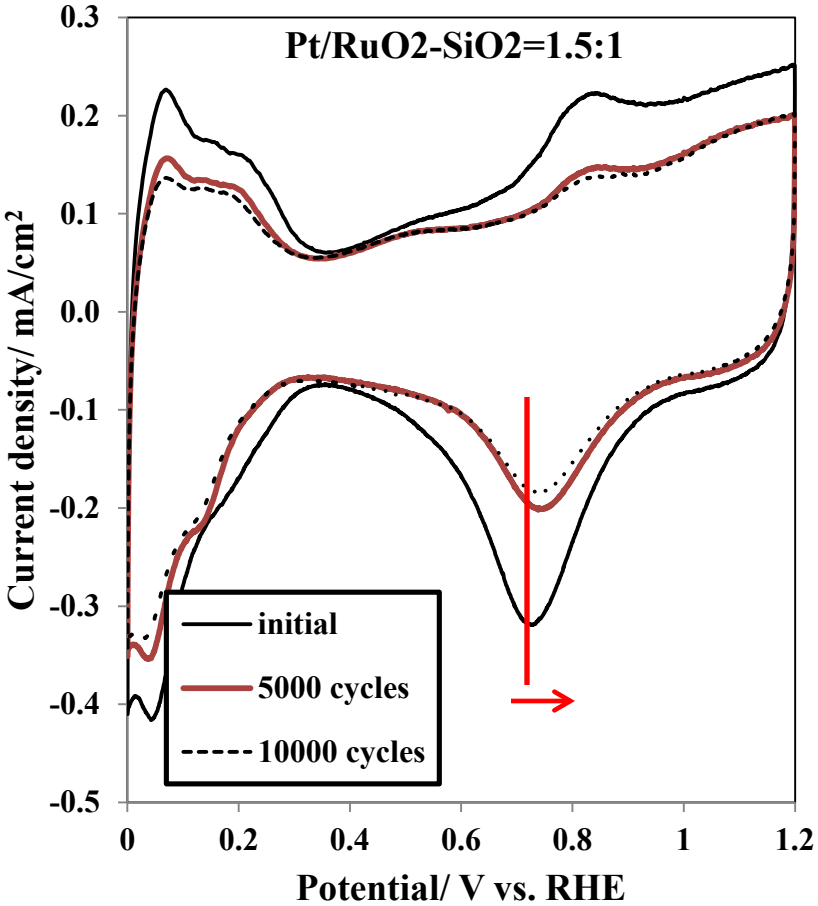


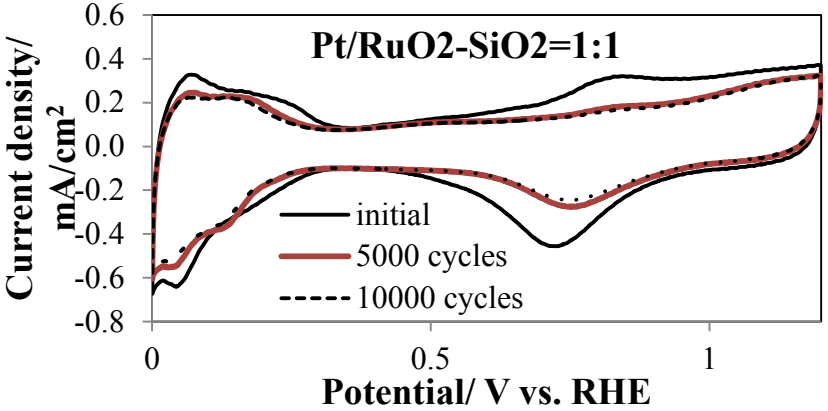
All RuO_2-SiO_2 supports exhibited higher stability than Vulcan carbon.

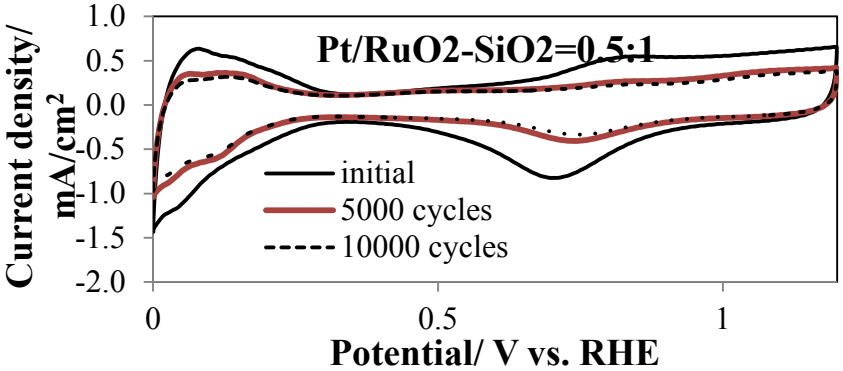
Ru(II)→Ru(III) between 0.244V and 0.444V vs. NHE
Ru(III)→Ru(IV) between 0.444V and 1.044V vs. NHE
Ru(IV)→Ru(VI) between 1.044V and 1.444V vs. NHE

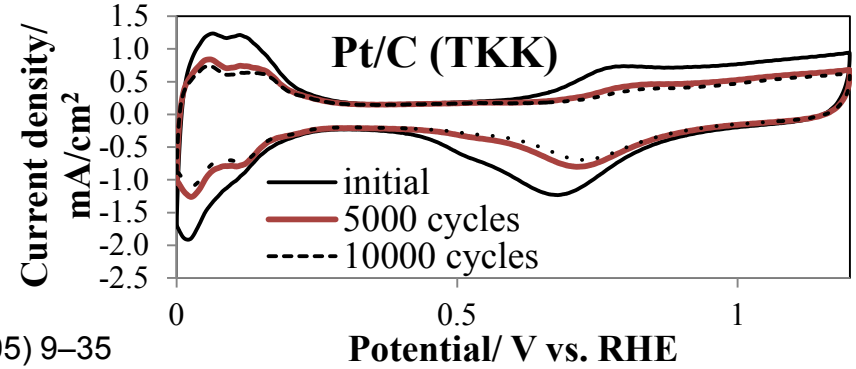
Technical Accomplishments: Stability of Pt/SRO Electrocatalysts

0.1 M $HClO_4$ under N_2 atmosphere; sweep rate of 20 mV/S; room temperature





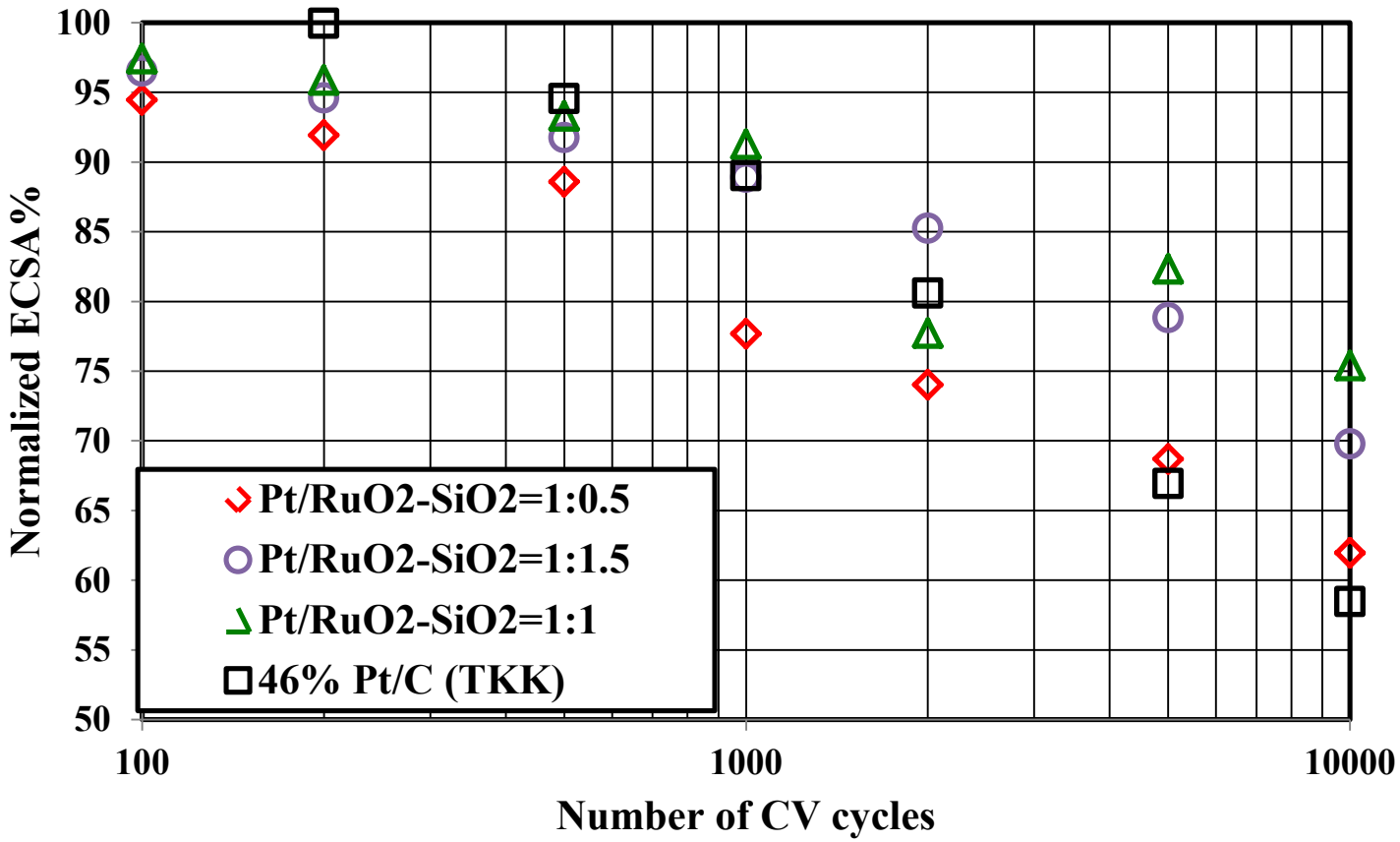




The positive shift of this peak suggests that Pt particle size increased.

H. A. Gasteiger et. a.l., Applied Catalysis B: Environmental 56 (2005) 9–35

Technical Accomplishments: Stability of Pt/SRO Electrocatalysts



- All Pt/RuO_2-SiO_2 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_2-RuO_2 =1: 0.5 → 4.5nm

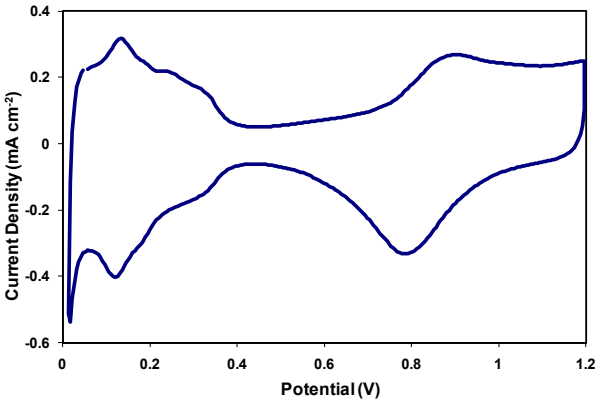
Pt/SiO_2-RuO_2 =1: 1 → 7.7nm

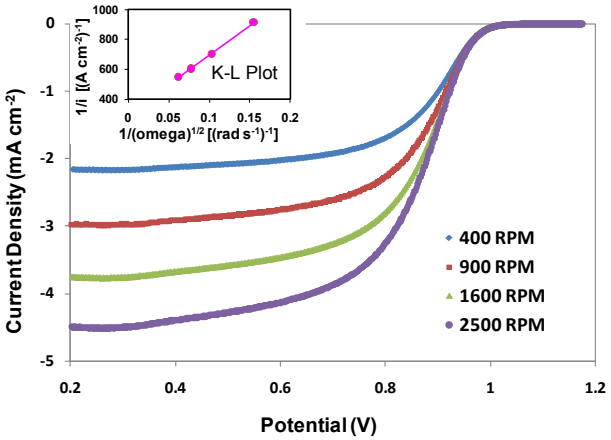
Pt/SiO_2-RuO_2 =1: 1.5 → 9.4nm

ORR Activity-RDE

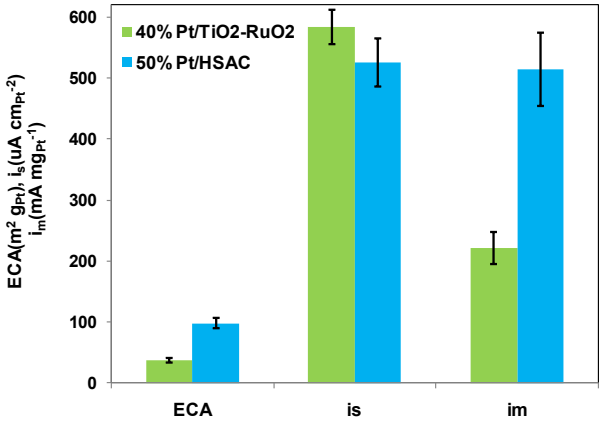
- The ORR activity of the catalyst was evaluated in RDE with optimized ink formulation (I:S=0.58).
  - The results were compared with TKK baseline catalyst TEC10E50E (50% Pt/HSAC).

Example of CV and iV of 40%Pt/TiO_2-RuO_2





Activity Benchmarking with Pt/C



- The catalyst showed the similar H_2 adsorption and desorption characteristic as TEC10E50E
  - ECA was ~ 38 m^2/g_{Pt} (40% of TEC10E50E)
  - Resulted in higher specific activity than TEC10E50E due to lower ECA
- ORR mass specific activity was around 220 mA/mg_{Pt} (40% of TEC10E50E)
  - Low mass activity may be due to the larger Pt particle sizes *(6-9 nm)* than expected ~3 nm

Catalyst Load-cycling Durability-RDE

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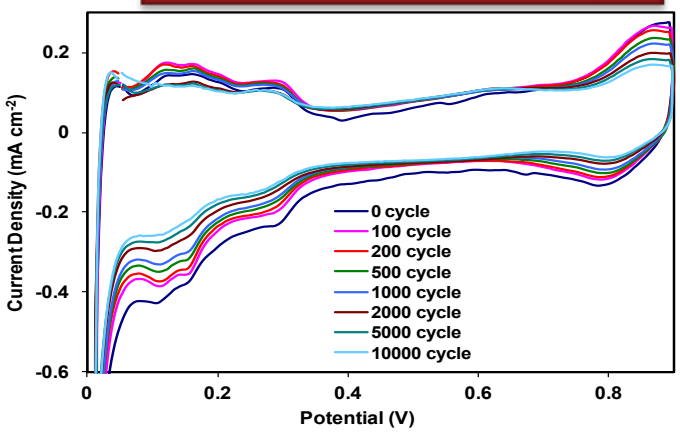
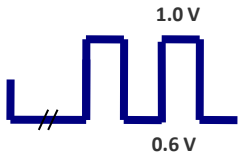
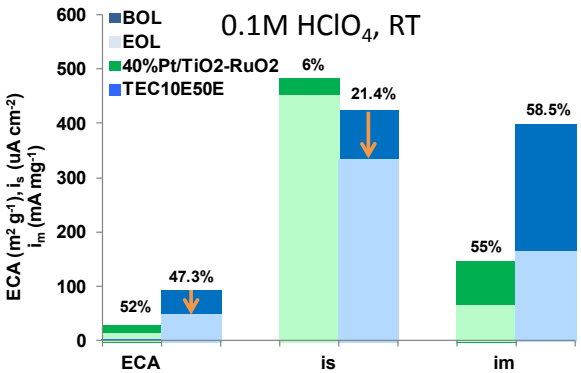
- The Pt stability of the catalyst was tested under Nissan load cycling protocol.
  - The results were compared with TKK baseline catalyst TEC10E50E (50% Pt/HSAC).

CV of 40% Pt/TiO_2-RuO_2

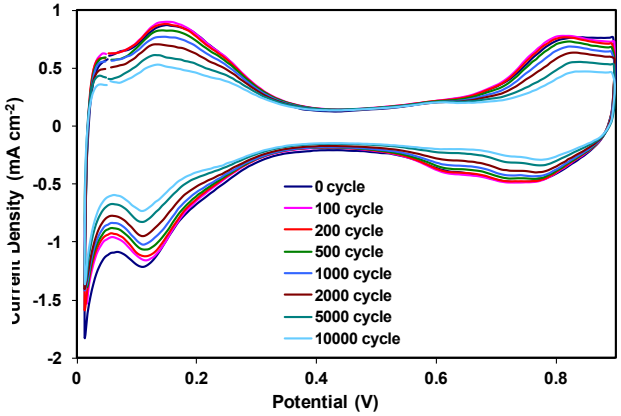


0.1M $HClO_4$, N_2 saturated, 60°C





CV of 50% Pt/HSAC



- 40% Pt/TiO_2-RuO_2 showed similar Pt dissolution stability as TEC10E50E
  - ECA loss was ~ 52% (~47% for TEC10E50E)
  - Mass specific activity loss was ~55% (58% for TEC10E50E)

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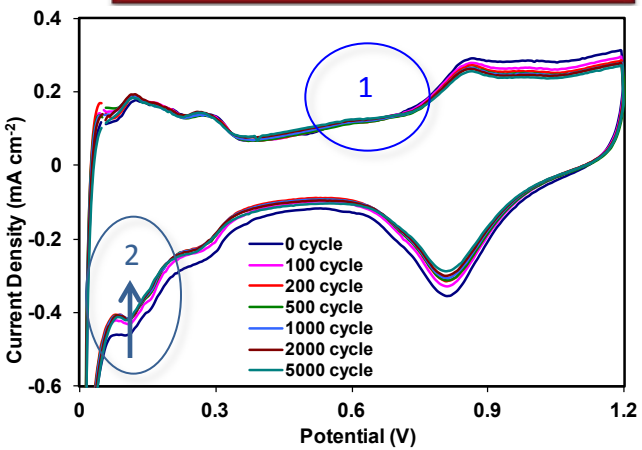
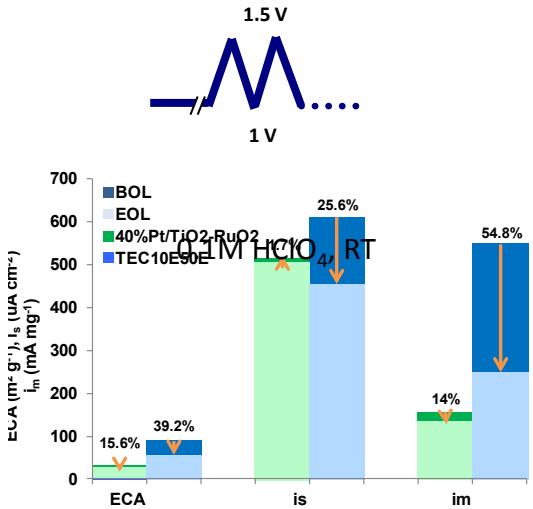
Catalyst Start-stop Durability-RDE

- 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).

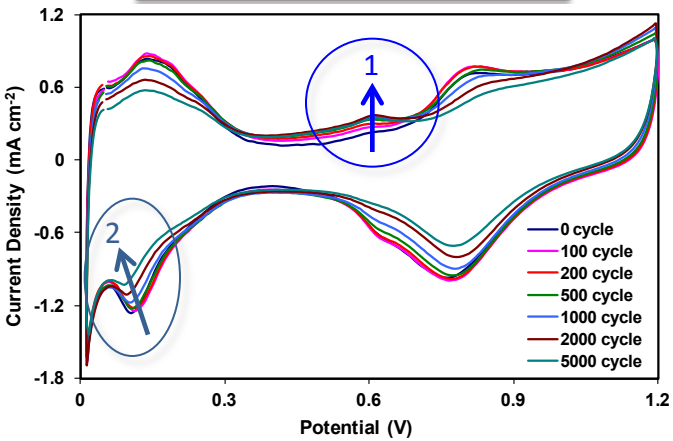
CV of 40% Pt/TiO_2-RuO_2



0.1M $HClO_4$, N_2 saturated, 60°C



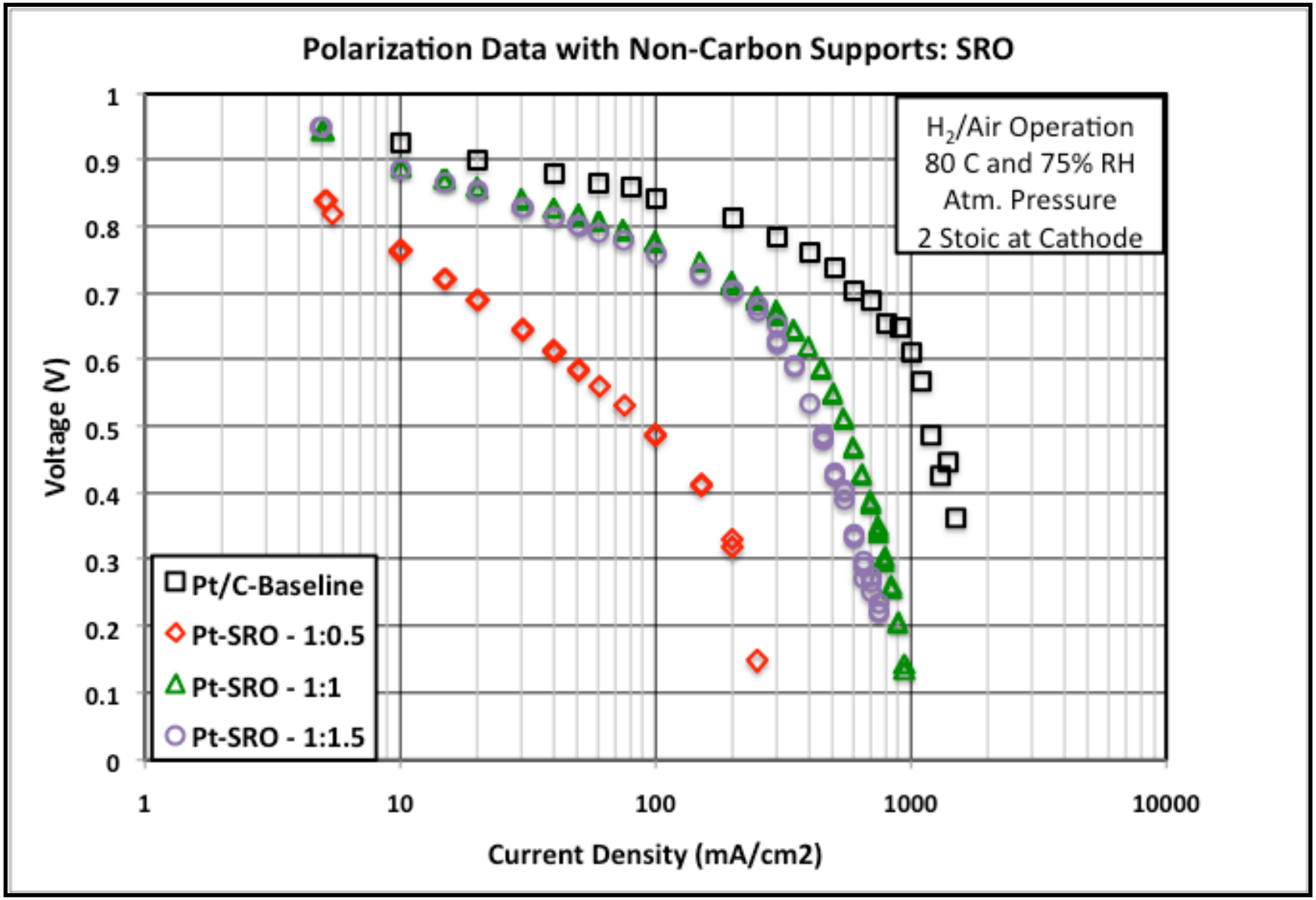
CV of 50% Pt/HSAC



- The TiO_2-RuO_2 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)

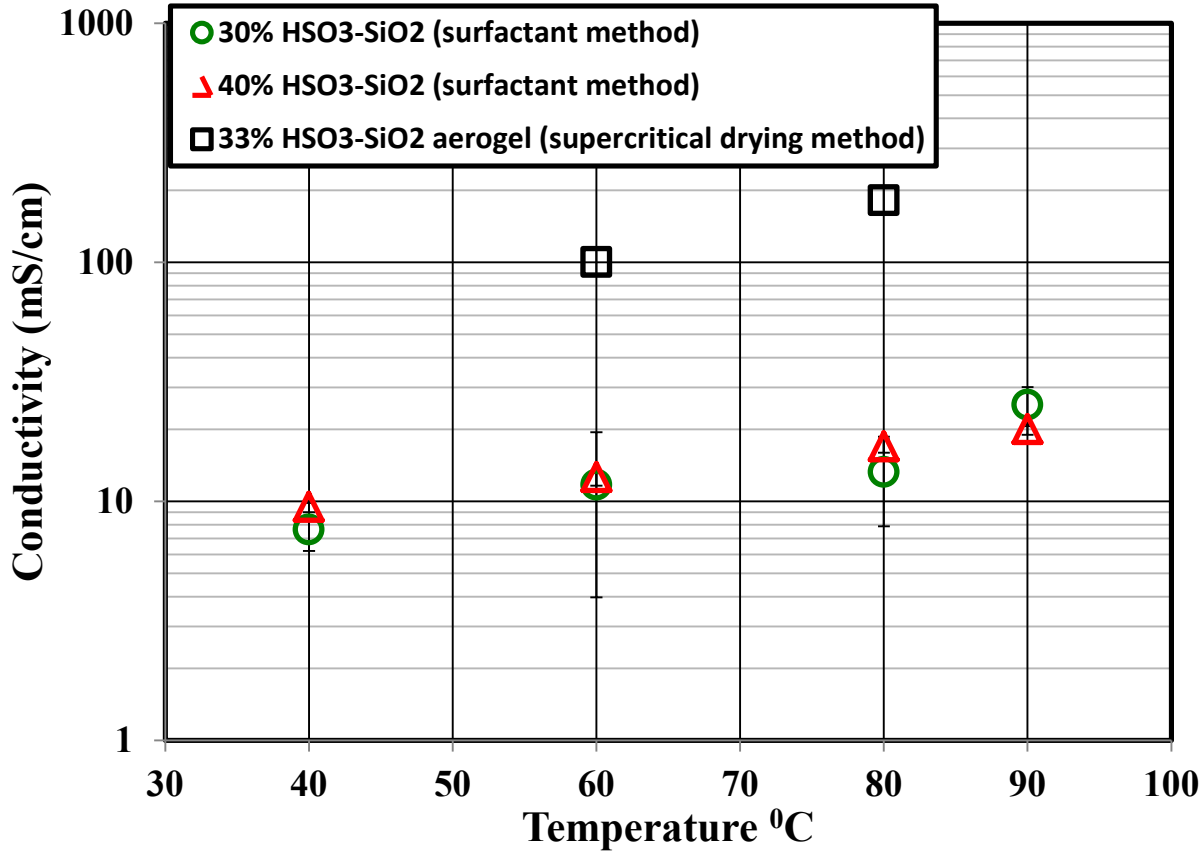
1. TiO_2-RuO_2 did not show any sign of surface oxides as observed for TEC10E50E.
2. H_2 adsorption peak potential did not shift like TEC10E50E, which confirms its stability during potential cycling.

Technical Accomplishments: Performance with Pt/SRO Electrocatalysts



Pt loading: 0.4 mg/cm^2 at the cathode; 0.2 mg/cm^2 at the anode

Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO_2 Aerogels



33% HSO_3-SiO_2 aerogel possesses

- ❑ High proton conductivity
  - ▪Improvement attributed to the exceptional network structure of the aerogel
- ❑ High BET surface area: 500 m^2/g.
- ❑ High thermal stability: Conductivity retained upon annealing at 250 ^oC for 4 hours.

Technical Accomplishments: Properties of RuO_2 - 33% Sulfonic acid Functionalized SiO_2 aerogels

Weight ratio of RuO_2 - 33% HSO_3-SiO_2 aerogel	1:1	1.2 :1
Electrical conductivity (S/cm)	3±1	8±3
BET surface area (m^2/g)	130±5	100±7
IEC (mmol/g)	0.55±0.1	0.5±0.1

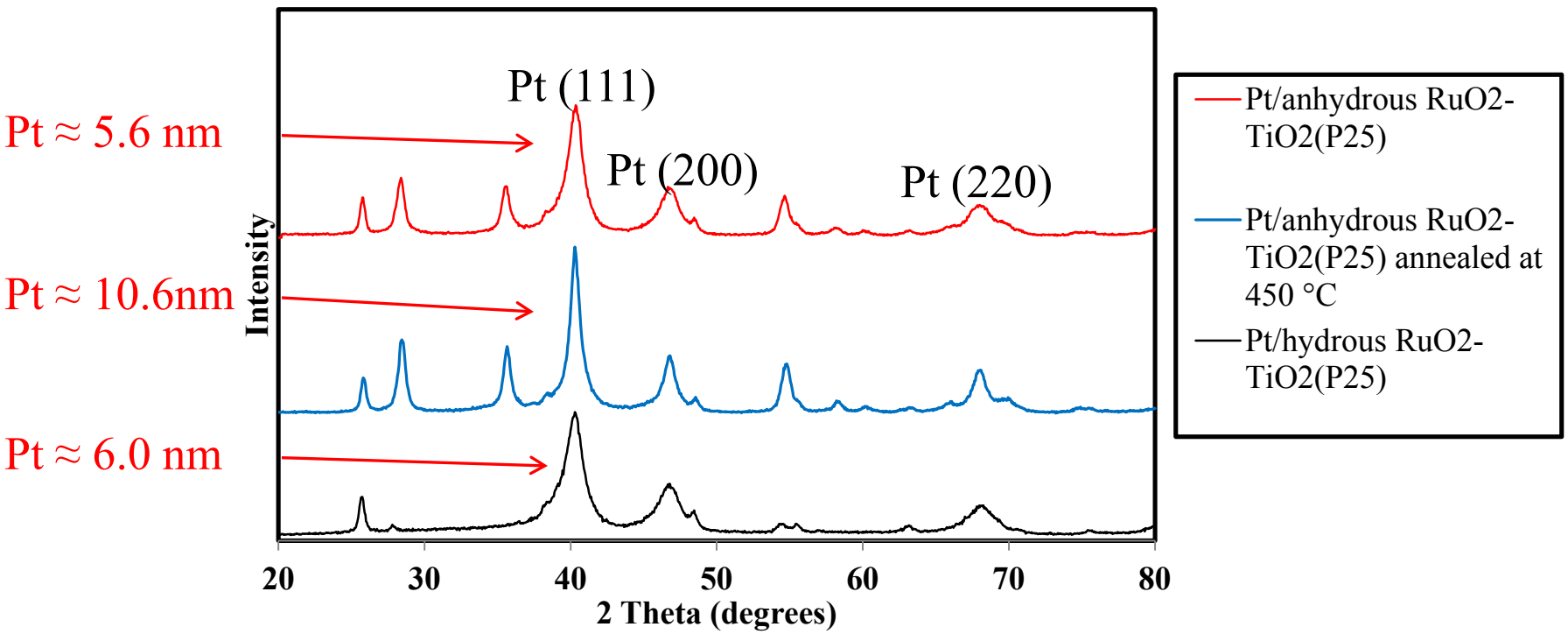
- ❑ RuO_2/HSO_3- SiO_2 aerogels possess relatively high electrical conductivity and moderate BET surface area.
- ❑ IEC results suggest that only 20~30% of the HSO_3 group was blocked by deposited RuO_2.
- ❑ This lends credence to the concept of a *mixed-conducting* support
- ❑ Note: Difficult to independently 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.

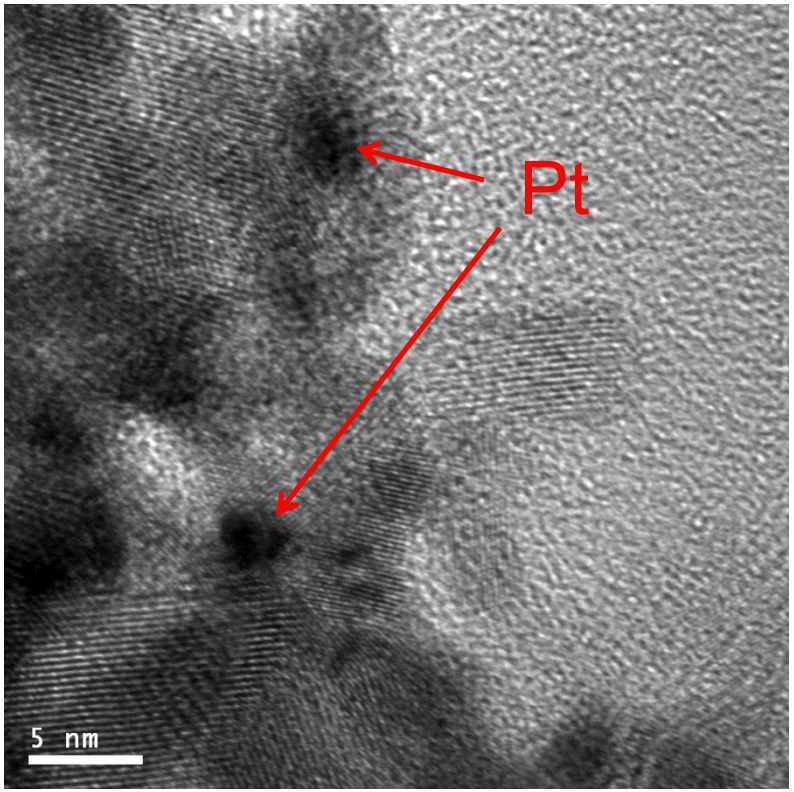
$$\tau = K^* \lambda / \beta \cos \Theta$$

K(shape factor)=0.94; λ (x-ray wavelength)=1.54Å;
β(the line broadening at half the maximum intensity in radians)=0.02618;
Θ(Bragg angle)=40.35;
τ(crystallite size)= 0.94*1.54/0.02618/cos(40.35/2/360*2*π)=56.4Å

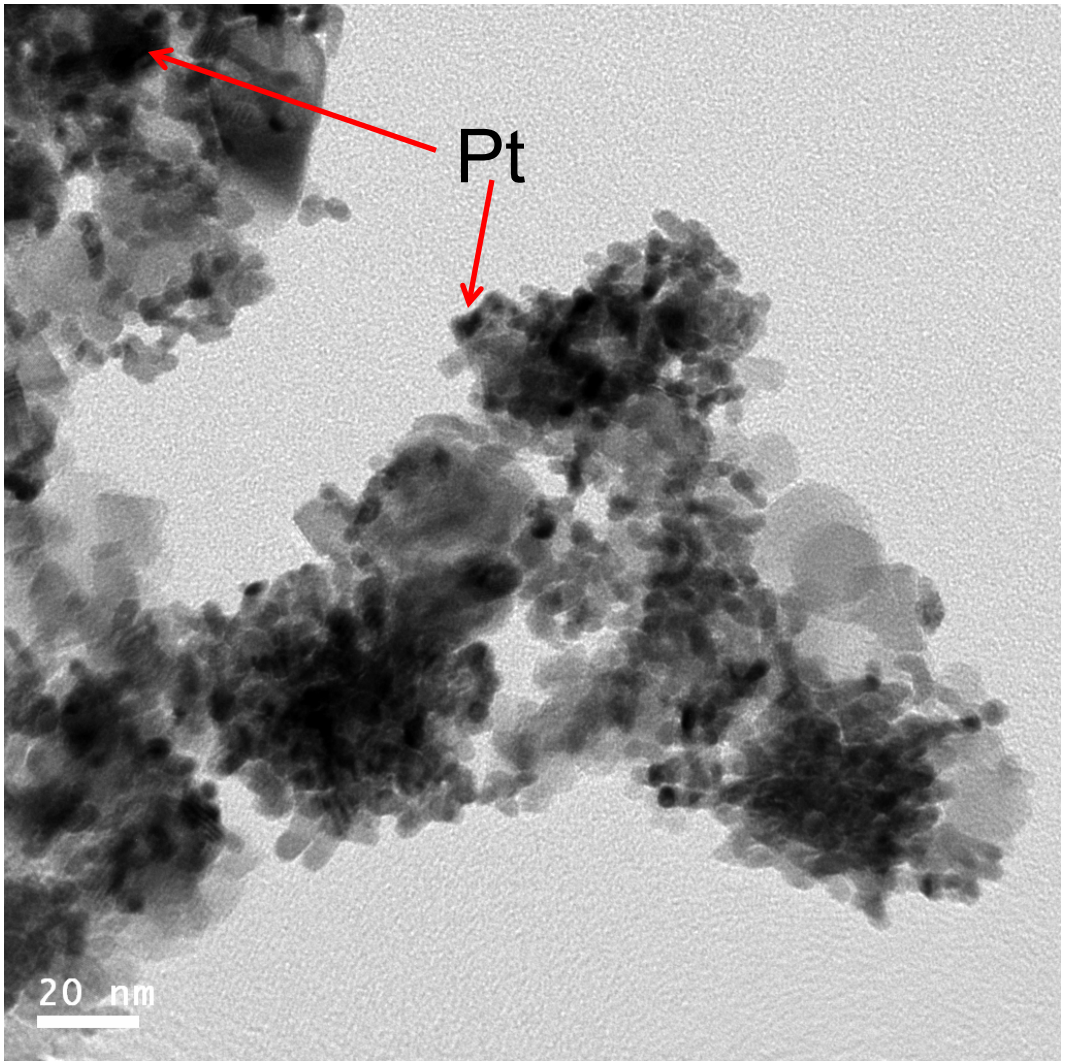


A, Patterson, *Phys. Rev.* **56** (1939) 978–982

Technical Accomplishments: TEM of Pt/RTO-anhydrous



Pt particle size: 3~6 nm

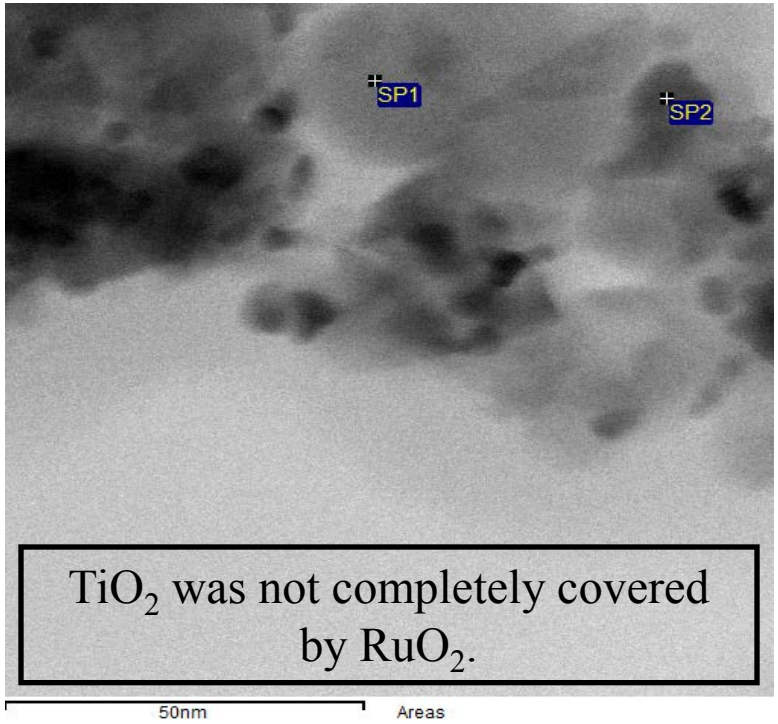


BET surface area of RuO_2-TiO_2 : 30±3 m^2/g

Technical Accomplishments: Characterization of RTO

RuO_2- TiO_2	anhydrous	hydrous
Electrical conductivity (S/cm)	22±4	10±3
BET surface area (m^2/g)	30±3	83±5

Anhydrous RuO_2-TiO_2 has higher degree of crystalline than hydrous RuO_2-TiO_2 and has higher electrical conductivity.



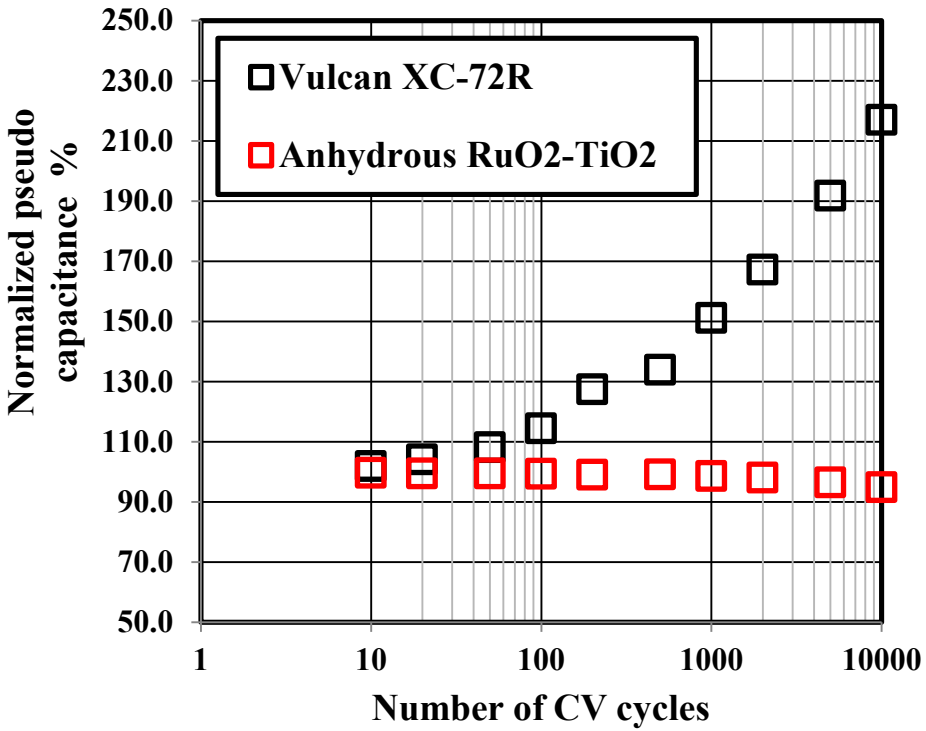
TiO_2 was not completely covered by RuO_2.

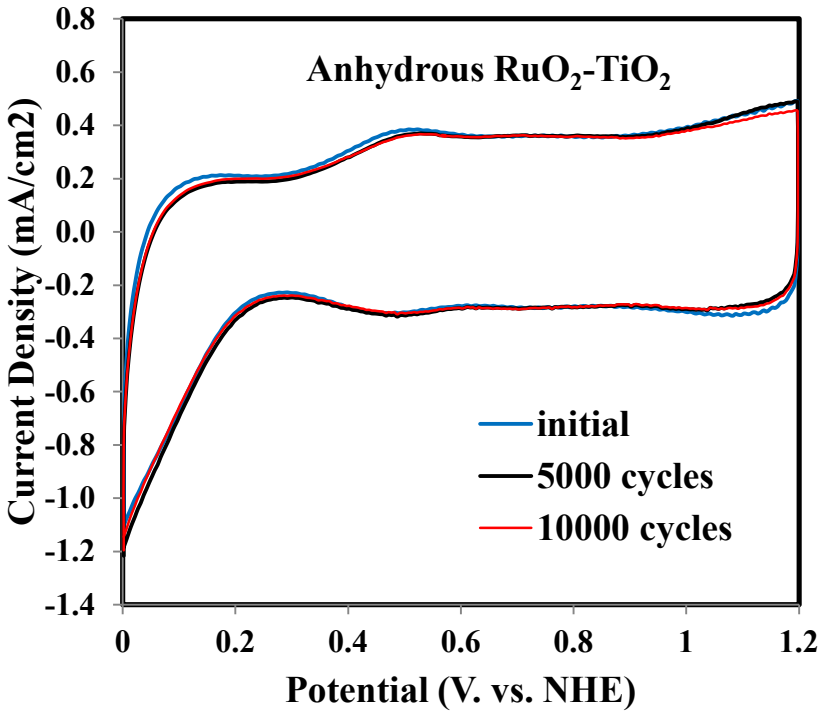
Spectrum	In stats.	O	Ti	Ru	Pt
SP1	Yes	59.70	39.14	0.00	1.16
SP2	Yes	63.27	29.55	7.18	0.00
Mean		61.49	34.35	3.59	0.58
Std. deviation		2.53	6.79	5.08	0.82
Max.		63.27	39.14	7.18	1.16
Min.		59.70	29.55	0.00	0.00

Technical Accomplishments: Stability of RTO Supports (IIT)

0.1 M $HClO_4$ under N_2 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.



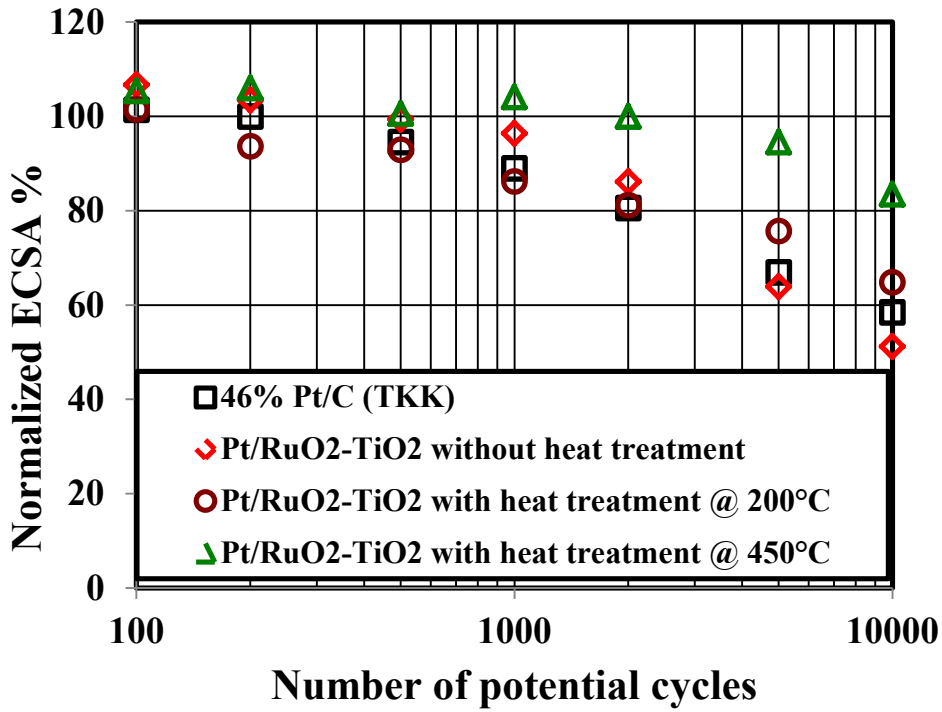


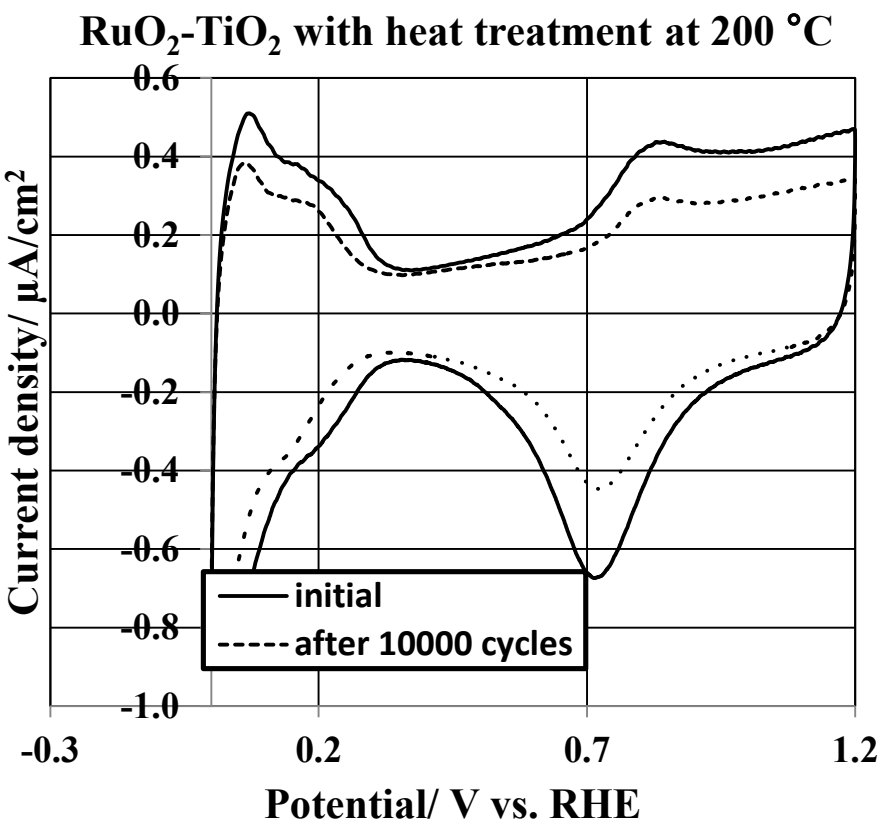
RuO_2-TiO_2 support exhibited higher stability than Vulcan carbon.

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 $HClO_4$ under N_2 atmosphere; sweep rate of 20 mV/S; room temperature

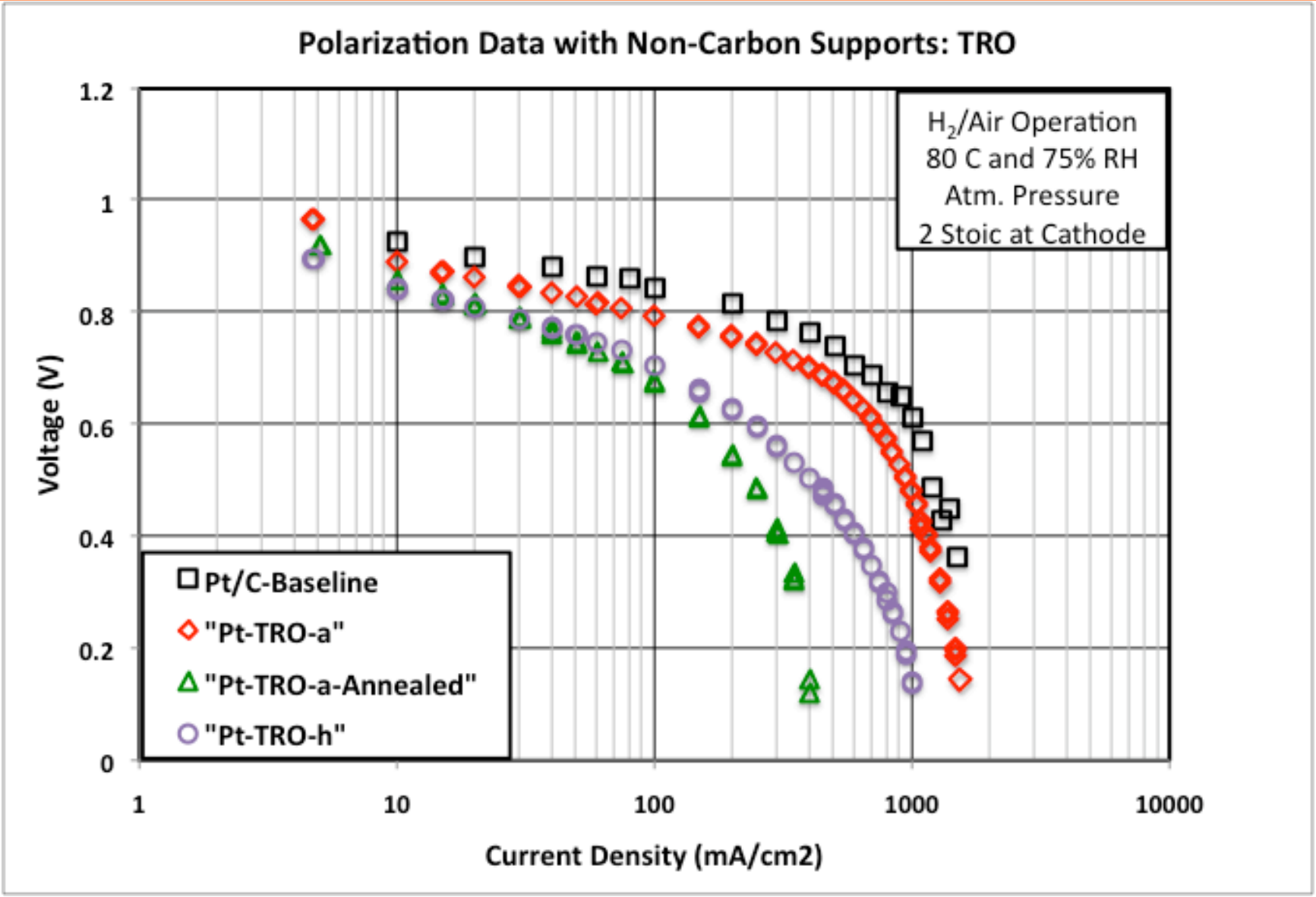




Electrocatalyst stability can be improved by heat treatment.
Catalyst with heat treatment at 450 °C exhibited high stability. However, the Pt crystallite size increased (5.6nm → 10.6 nm) and ECSA/performance decreased.

Journal of The Electrochemical Society, 158 (11) B1439-B1445 (2011)

Technical Accomplishments: Performance of Pt/RTO Electrocatalysts



Pt loading: 0.4 mg/cm^2 at the cathode; 0.2 mg/cm^2 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^2/g
    (50 m^2/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_2 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, 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

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, $Si(OC_2H_5)_4$
TMOS	Tetramethyl orthosilicate, $Si(OCH_3)_4$
MPTMS	3-mercaptopropyl trimethoxysilane, $HS(CH_2)_3Si(OCH_3)_3$
SBA-15	Santa Barbara Amorphous type SiO_2
P123	Pluronic P®-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_2)	SBA-15
RuO_2	Ruthenium dioxide	RuO_2
Pt/ RuO_2-SiO_2	Pt deposited on RuO_2-SiO_2. The mole ratio of RuO_2:SiO_2 is x:1	Pt/ RuO_2-SiO_2 =x:1 Pt/SRO-x Where x=0.5, 1, 1.5
X % sulfonic acid functionalized SiO_2	Sulfonic acid functionalized silica. The mol % of the functionalized domain is X.	X% HSO_3-SiO_2 where X= 20, 30, or 40
TiO_2-SiO_2	RuO_2 deposited on TiO_2 (P25). The mole ratio of RuO_2:TiO_2 is 1:1. RuO_2 is in anhydrous form.	Anhydrous RuO_2-TiO_2 TRO-a
TiO_2-SiO_2	RuO_2 deposited on TiO_2 (P25). The mole ratio of RuO_2:TiO_2 is 1:1. RuO_2 is in hydrous form.	Hydrous RuO_2-TiO_2 TRO-h
Pt/ RuO_2-TiO_2	Pt deposited on RuO_2-TiO_2.	Pt/ RuO_2-TiO_2

Notation of Samples Discussed in Presentation

Samples prepared	Description	Notation
Pt/ RuO_2-TiO_2	Pt deposited on TRO-a followed by heat treatment.	Pt/ RuO_2-TiO_2 with heat treatment Pt/TRO-a-450
33% HSO_3-SiO_2 aerogel	Sulfonic acid functionalized silica prepared by supercritical dryer method. The mol % of the functionalized domain is 33.	33% HSO_3-SiO_2 aerogel
RuO_2/33% sulfonic acid functionalized SiO_2 aerogel support	Pt deposited on 33% HSO_3-SiO_2 aerogel. The weight % of RuO_2 to 33% HSO_3-SiO_2 aerogel =1.2 or 1	Pt/RuO_2-$SSiO_2$
SO_4^{2-}/SnO_2	Sulfated tin oxide	SO_4^{2-}/SnO_2
Pt/SO_4^{2-}/SnO_2	Pt deposited on SO_4^{2-}/SnO_2	Pt/SO_4^{2-}/SnO_2
Pt/SO_4^{2-}/SnO_2-RuO_2	Pt deposited on SO_4^{2-}/SnO_2-RuO_2. The mole ratio of SnO_2-RuO_2 =1:1.	Pt/SO_4^{2-}/SnO_2-RuO_2
ITO	Tin-doped indium oxide	ITO

Literature Review: Non-Carbon Supports

Non-carbon catalyst supports in literature

SiO_2

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_2, doped TiO_2, 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_x

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.

$RuO_2.xH_2O$

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° to 80° 2θ 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.

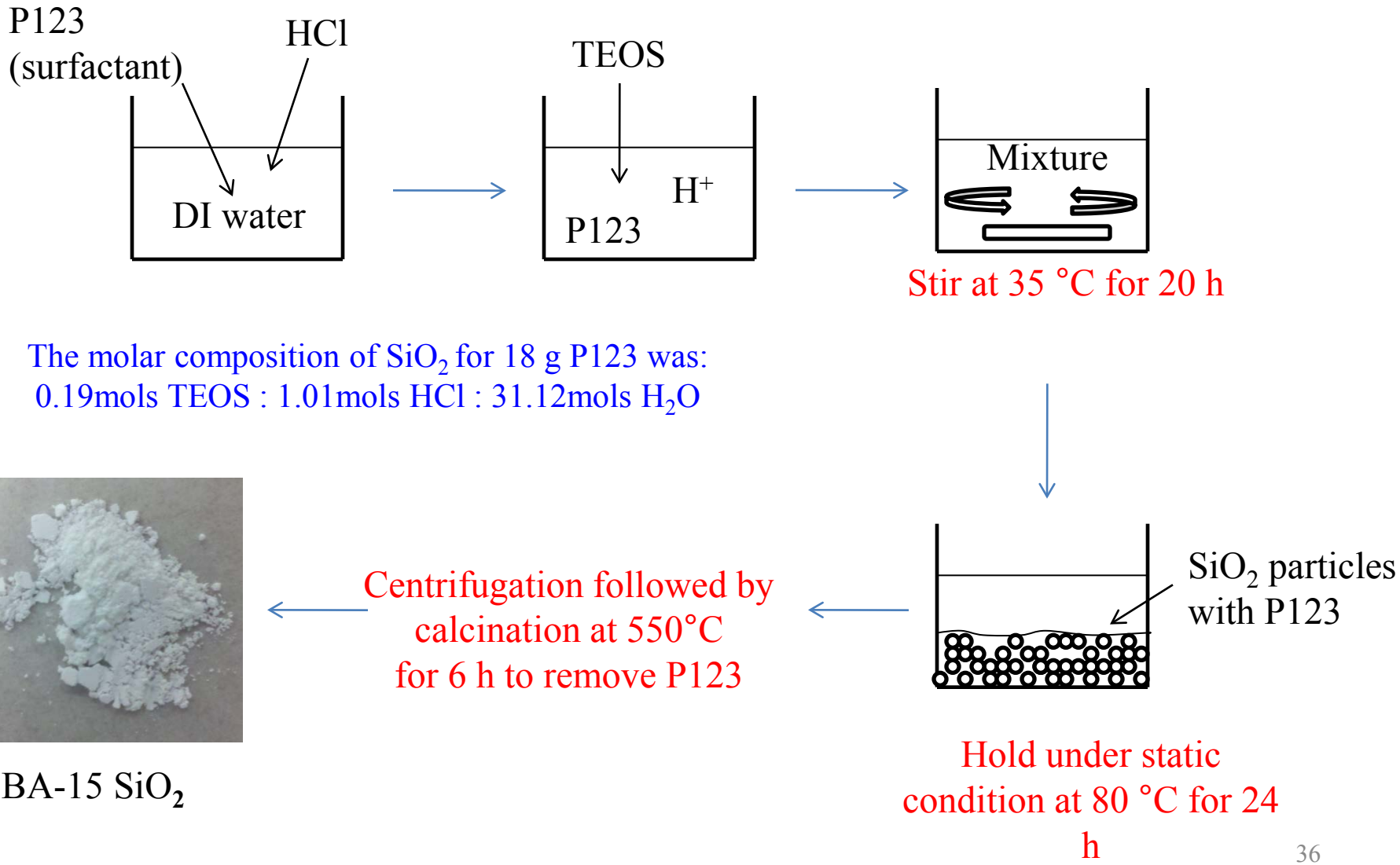
- **Two-point probe technique:**
  - To measure electrical conductivity. All experiments were conducted at room temperature.

- **Ion exchange capacity (IEC):**
  - To calculate the proton exchange capacity of materials ($mmol_{H+}/g$)

- **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

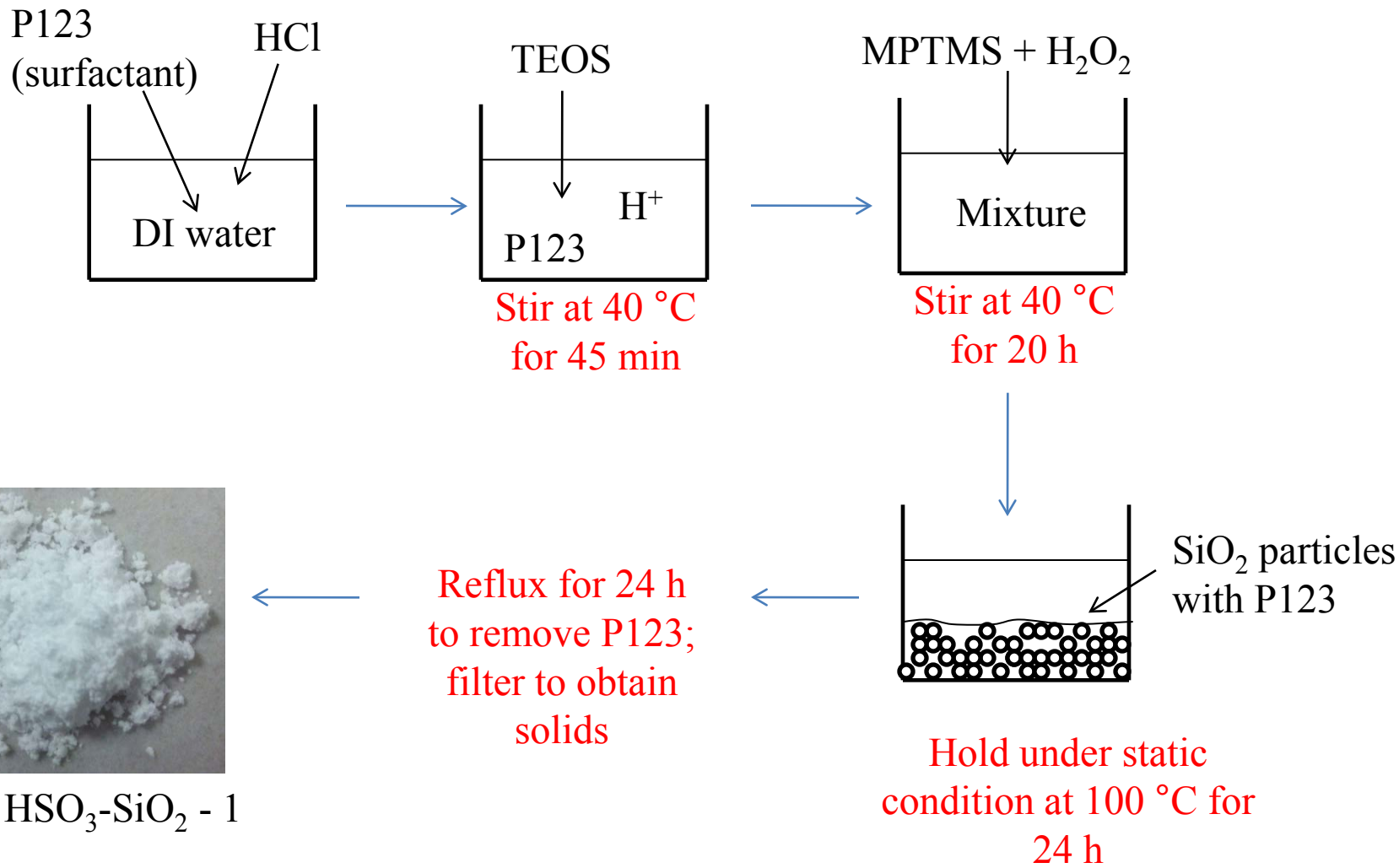


The molar composition of SiO_2 for 18 g P123 was:
0.19mols TEOS : 1.01mols HCl : 31.12mols H_2O

D.Y. Zhao, et al., J. Am. Chem. Soc. 120 (1998) 6024.

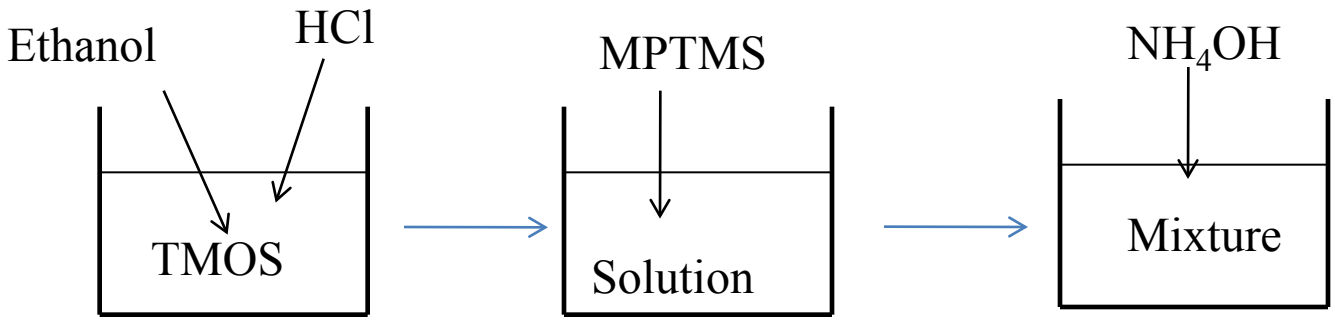
Approach: Synthesis of Sulfonic Acid Functionalized SiO_2 – Method 1

The molar composition used to prepare 20% functionalized SiO_2 with 4 g P123 was:
0.0328 mols TEOS : 0.0082 mols MPTMS: 0.0369 mols H_2O_2 : 0.24 mols HCl :~6.67 mols H_2O



Juan A. Melero, et. al., J. Mater. Chem., 2002, 12, 1664–167

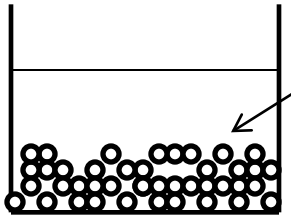
Approach: Synthesis of Sulfonic Acid Functionalized SiO_2 – Method 2



Stir for 18 hours

Stir for 30 min, centrifuge and wash with ethanol

Ratio of starting materials is:
(TMOS+MPTMS):H_2O:C_2H_5OH:HCl= 1:30:10:6
For 25% HSO_3-SiO_2-2, ratio of TMOS:MPTMS=0.25:0.75



Thiol functionalized SiO_2 particles

Dry overnight at 50^0C

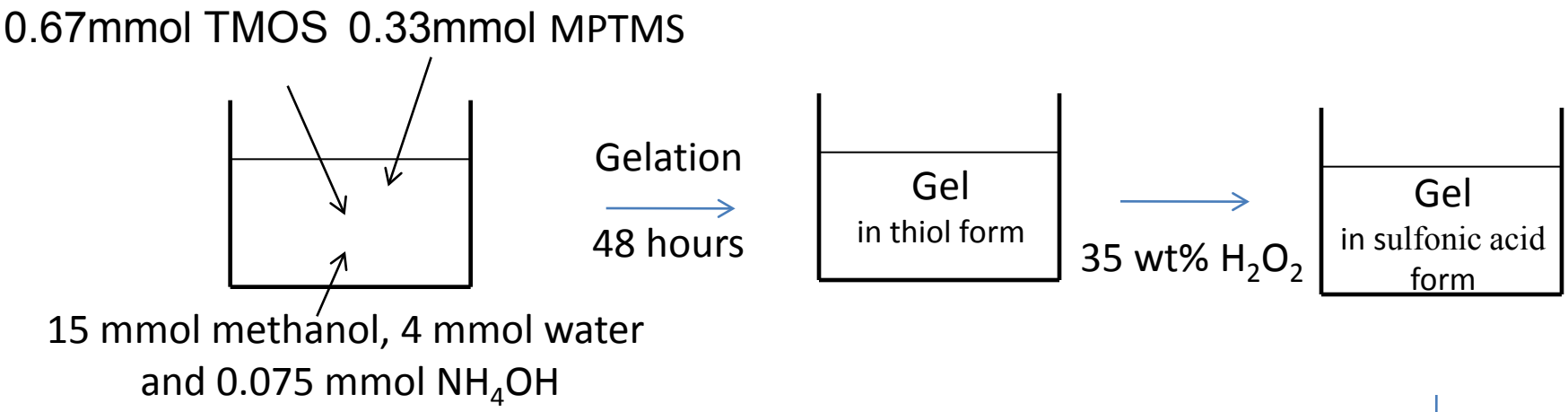
Oxidize the thiol group to sulfonic acid using 35% H_2O_2

X%HSO_3-SiO_2-2

25%HSO_3-SiO_2-2

C.R. Miller, et al Langmuir 21 (2005) 9733–9740

Approach: Synthesis of Sulfonic Acid Functionalized SiO_2 – Aerogel

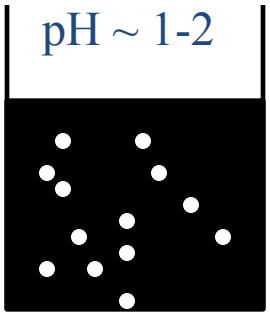


33% HSO_3-SiO_2 aerogel

Approach: Synthesis of RuO_2-SiO_2 Composites: RuO_2 deposition

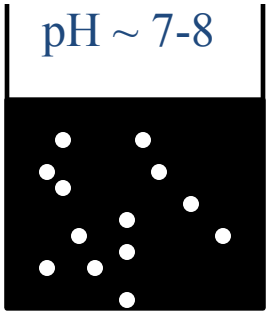
RuO_2-SiO_2 composites were prepared by depositing RuO_2 on SBA-15.

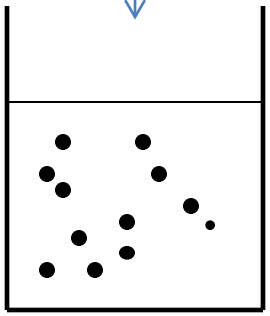
The mole ratio of RuO_2:SiO_2 was: 0~0.6 :1



SBA-15 was immersed in 0.1 M $RuCl_3$(aq)

0.1 M KOH(aq) was added





RuO_2 particles deposit on the support

Powder heat treatment

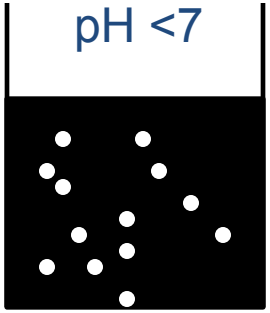
Dry at 100 °C

Calcine at 450 °C

J.C. Hicks, C.W. Jones, Langmuir 22 (2006) 2676.

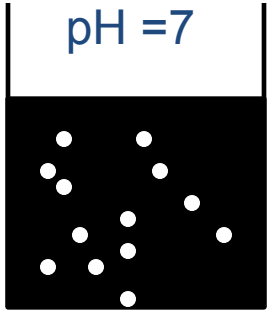
Approach: Synthesis of Pt/RuO_2-SiO_2 (SBA15)

RuO_2-SiO_2 was prepared by depositing RuO_2 on SBA-15.

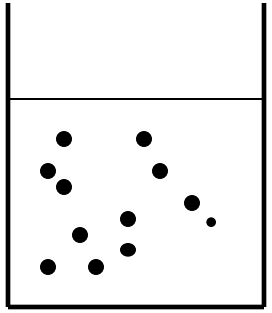


SBA-15 was immersed in 0.1 M $RuCl_3$(aq)

add 0.1 M KOH(aq)



The mole ratio of RuO_2:SiO_2 was: 0~0.6 :1



RuO_2 deposition

Powder heat treatment

Dry at 120 °C

Calcination at 450 °C

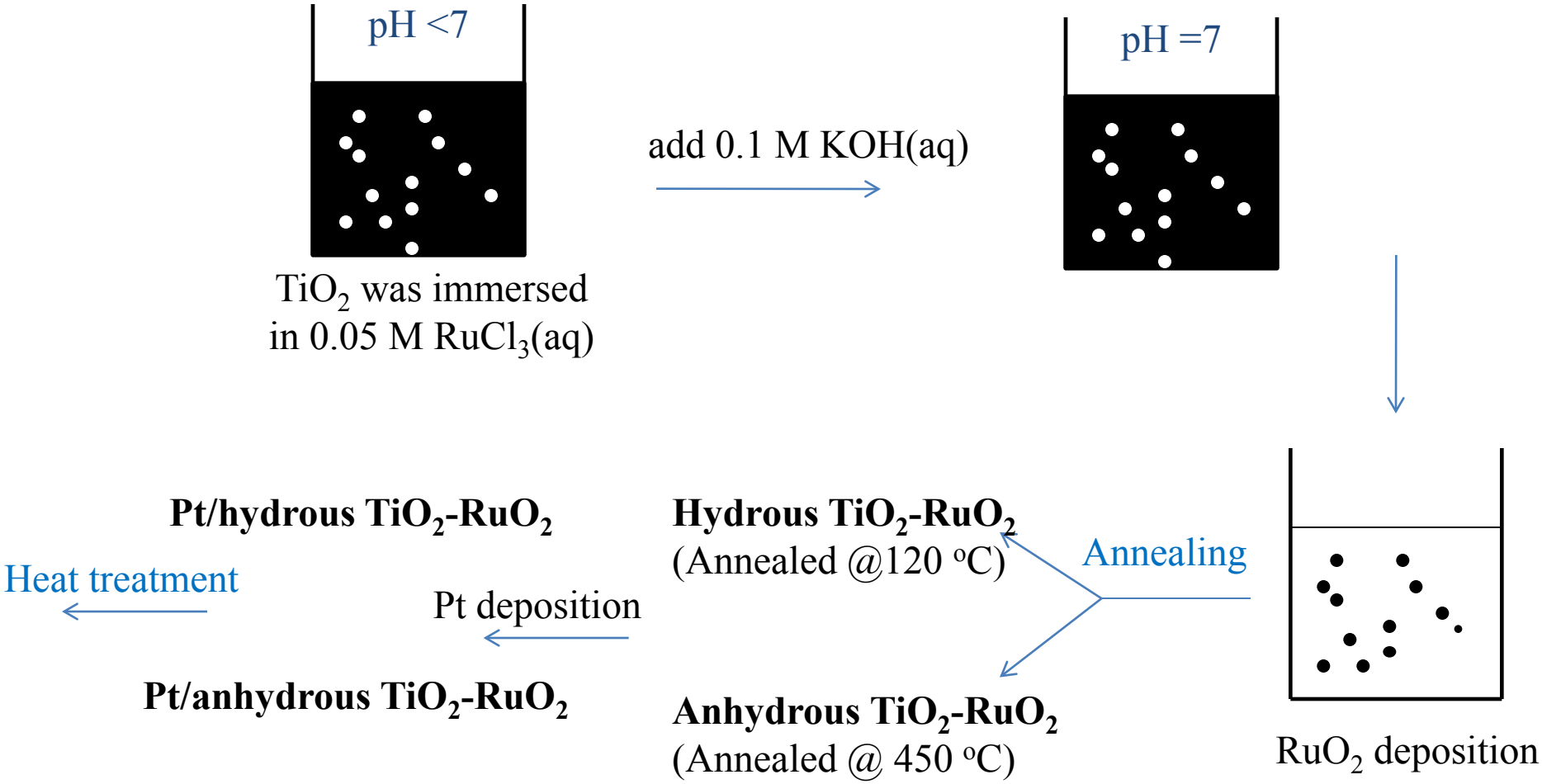
Pt deposition

Pt/RuO_2-SiO_2

J.C. Hicks, C.W. Jones, Langmuir 22 (2006) 2676.

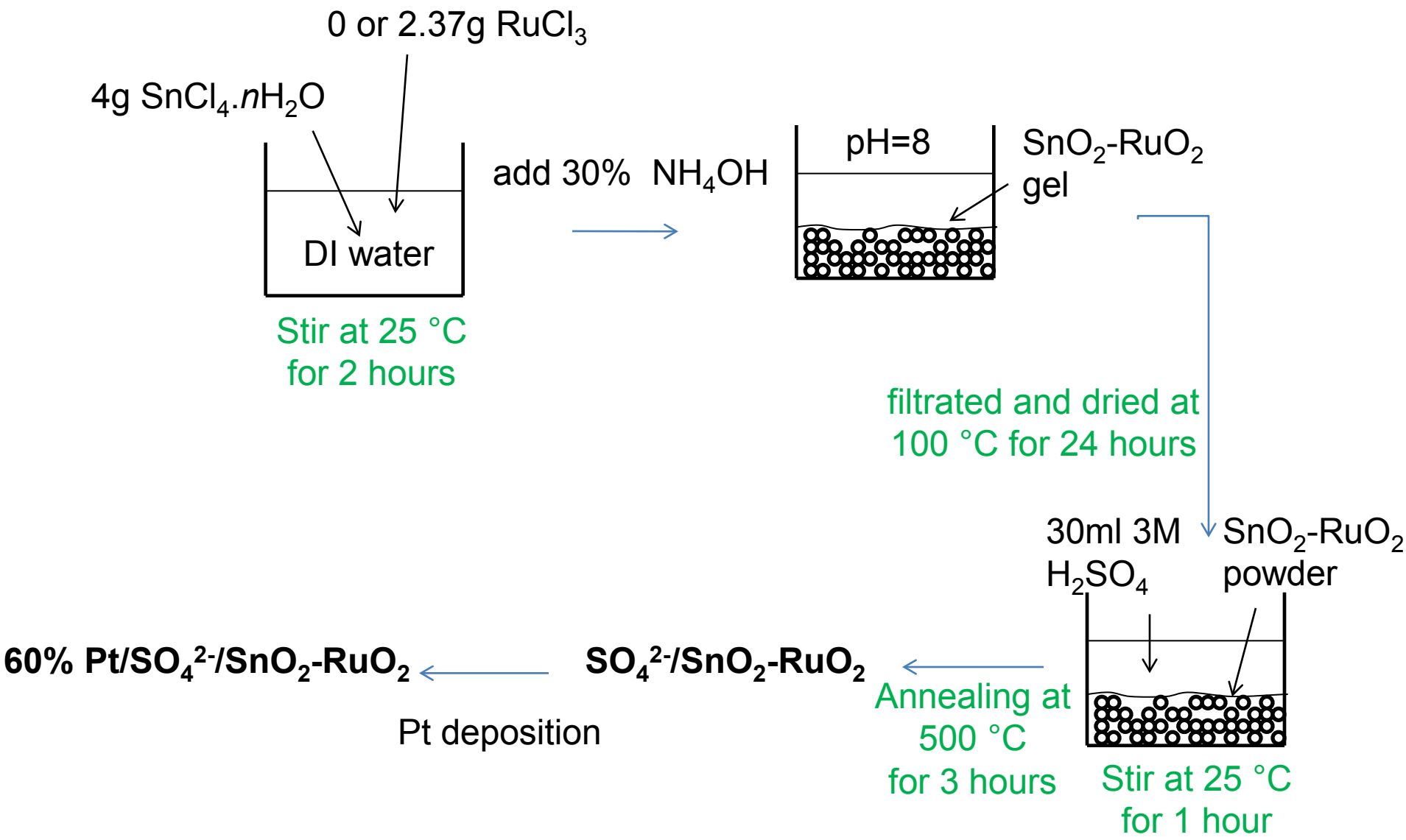
Approach: Synthesis of Pt/RuO_2-TiO_2

RuO_2-TiO_2 were prepared by depositing RuO_2 on TiO_2 (P25).
The mole ratio of TiO_2:RuO_2 was: 1 :1



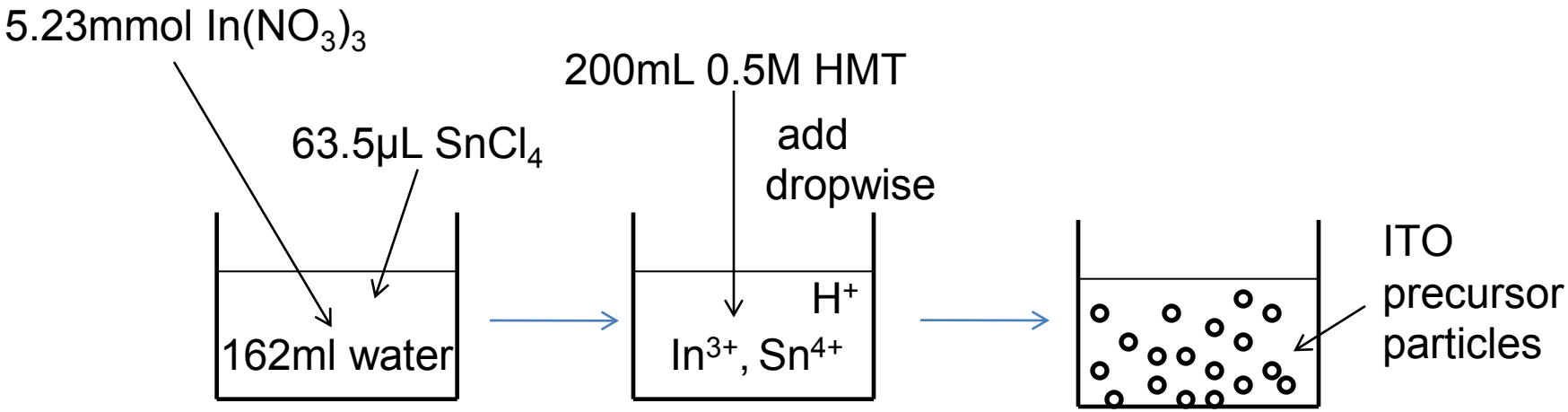
J.C. Hicks, C.W. Jones, Langmuir 22 (2006) 2676.

Approach: Synthesis of $Pt/SO_4^{2-}/SnO_2$-RuO_2



Hiromi Matsuhashi et. al., Chem.,Mater. 2001, 13, 3038-3042

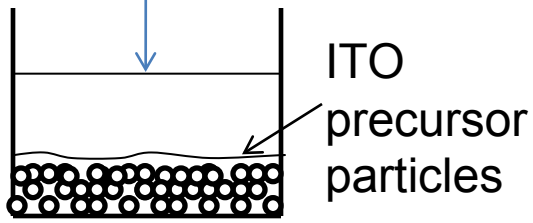
Approach: Synthesis of Indium tin oxide (ITO) (wet chemical method)



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

stir 25 °C overnight

The mass composition of 1g ITO was: 0.9 In_2O_3 and 0.1 SnO_2



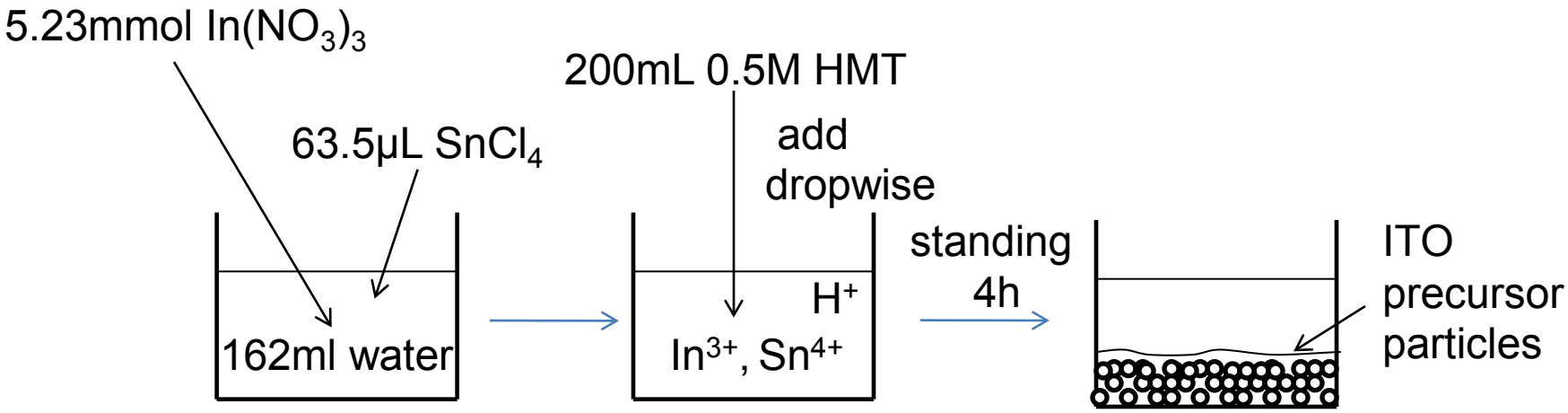
the precipitate was recovered by centrifuge

washed twice with isopropanol and dry overnight at 60°C .

Pulverize and heat the powders at 820 ℃ for 2 hours

Indium tin oxide

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



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

stir at 25°C overnight

The mass composition of 1g ITO was: 0.9 In_2O_3 and 0.1 SnO_2

the precipitate was recovered by centrifuge

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

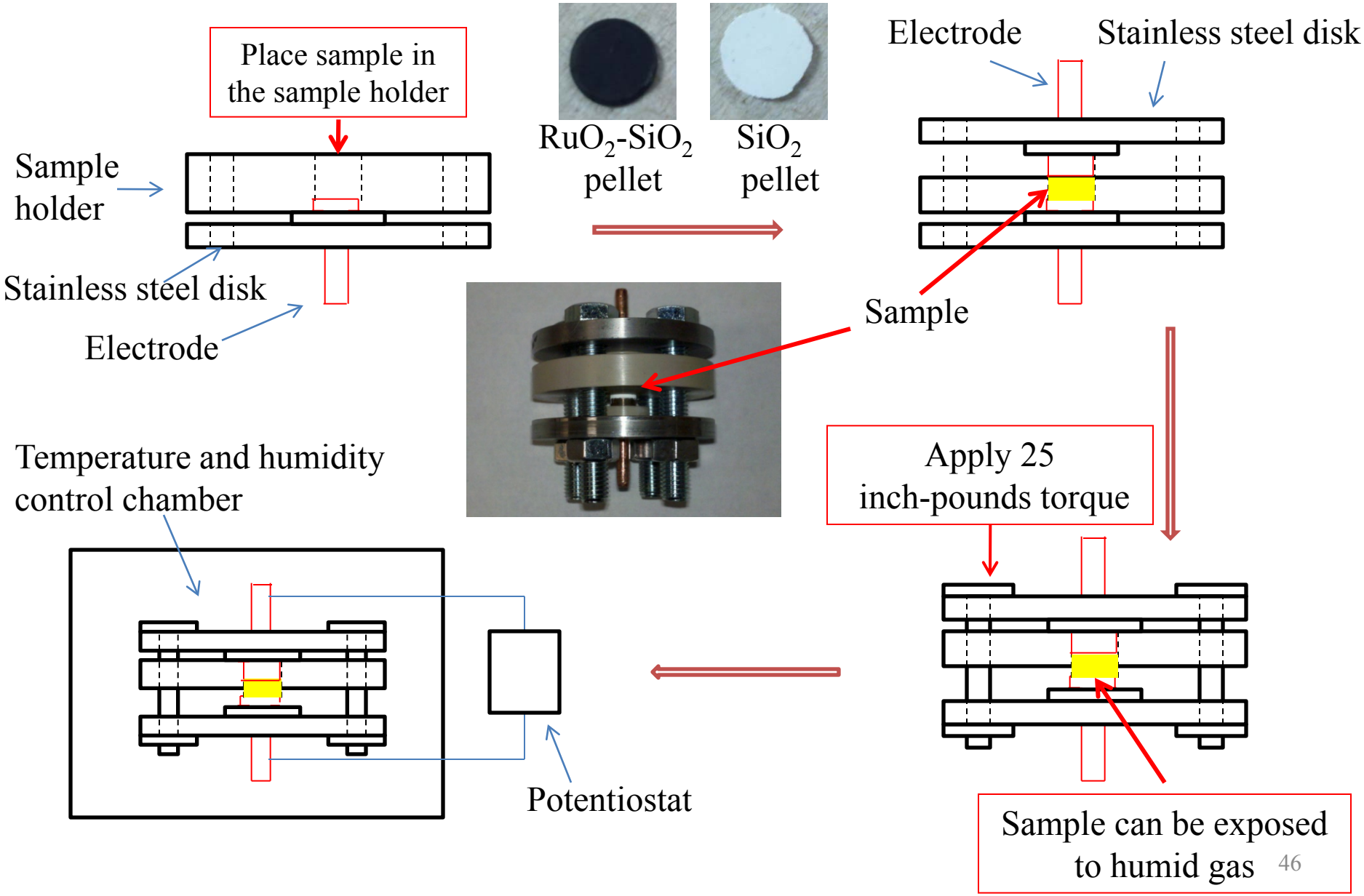
Supercritical drying

Indium tin oxide precursor

pulverize and heat at 820℃ for 2 hours

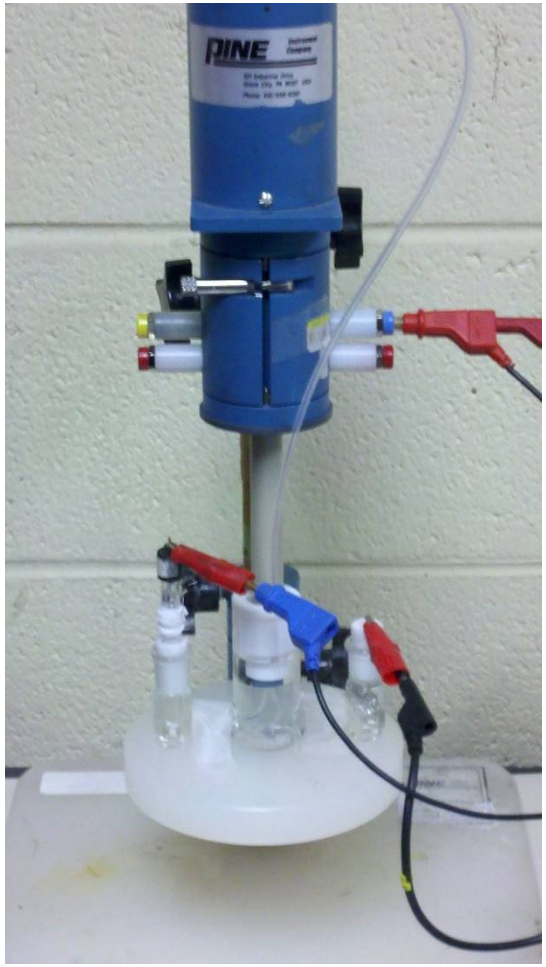
Indium tin oxide

Approach: Conductivity Measurements

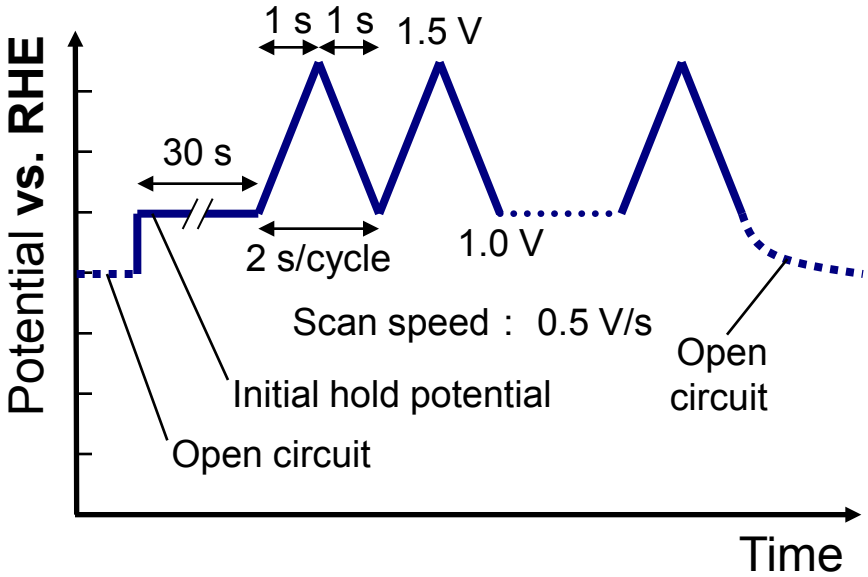


Approach: Potential Cycling to Estimate Support Stability

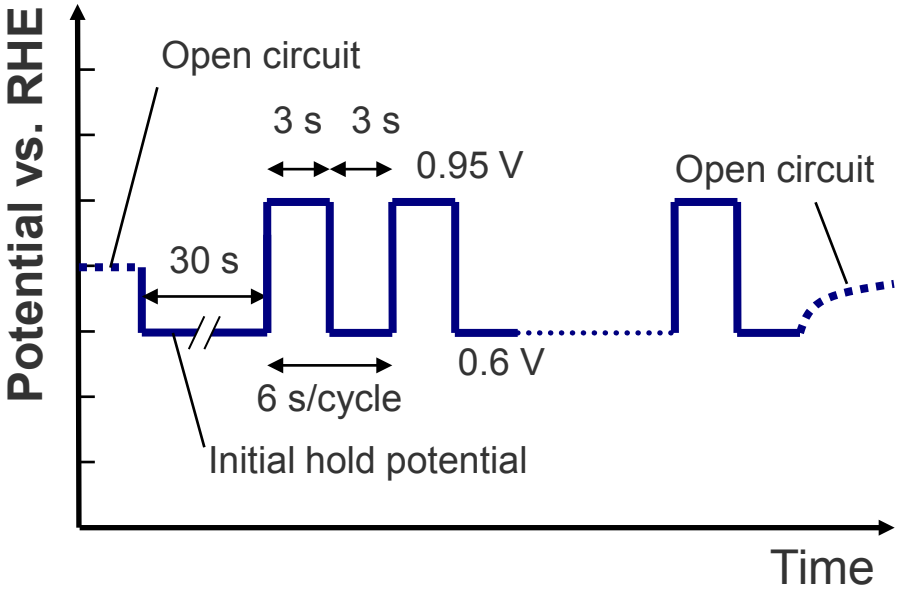
- Three Electrode Cell with Rotating Disk Electrode
  - Working Electrode : Glassy carb coated with catalyst support
  - Counter Electrode : Pt foil
  - Reference Electrode : Saturated Calomel Electrode (SCE)
  - Electrolyte : N_2 saturated 0.1M $HClO_4$
- Support loading on W.E.: 200 $\mu g/cm^2_{geo}$
- Pt loading: 50 $\mu g/cm^2_{geo}$
- Potential cycling protocol
  - See following slides



Approach: Potential Cycling to Estimate Support and Electrocatalyst Durability



Support Durability—Support corrosion



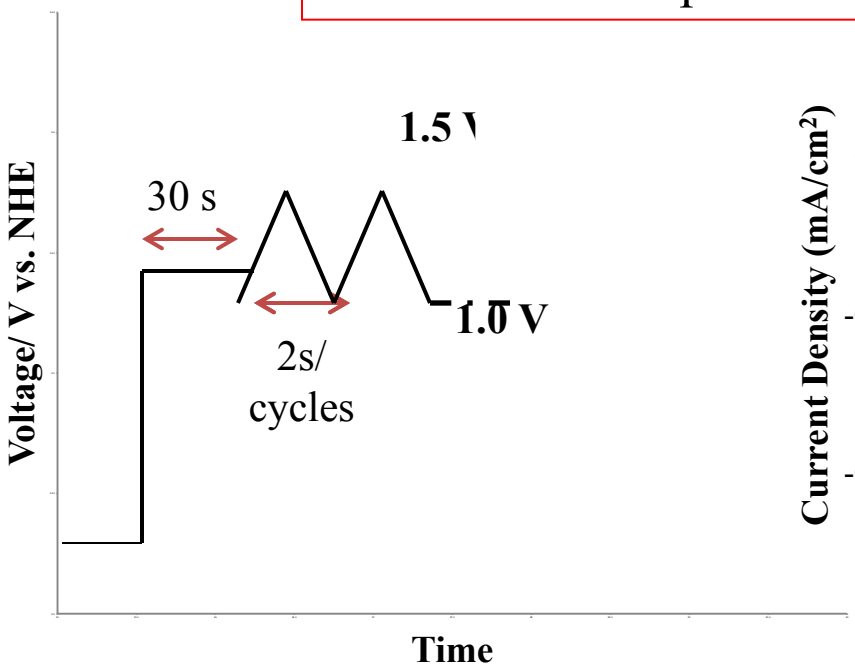
Catalyst Durability– Pt Dissolution

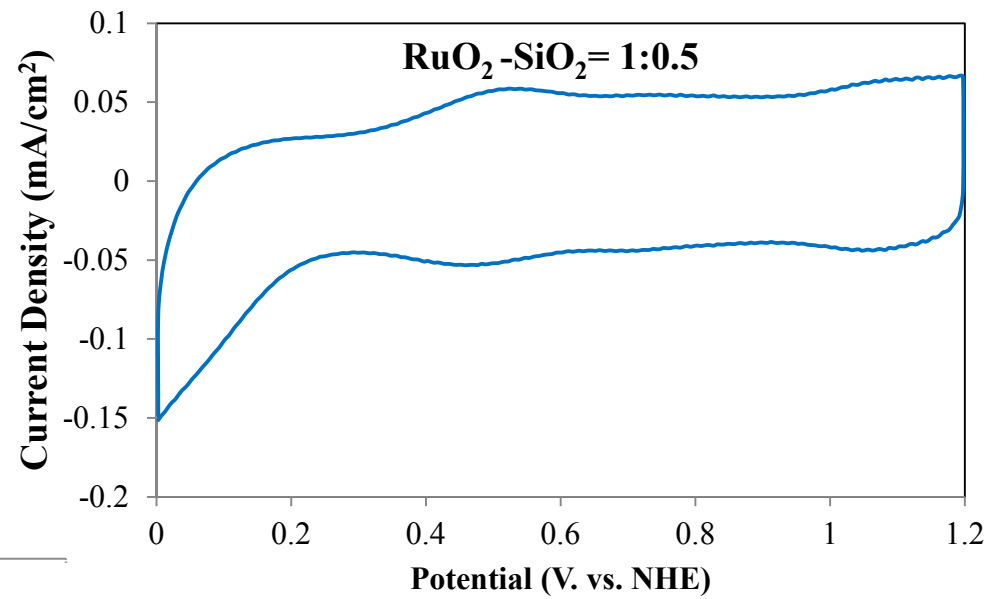
NISSAN
R&D AMERICAS

Approach: Stability of supports - Example

0.1 M $HClO_4$ under N_2 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.





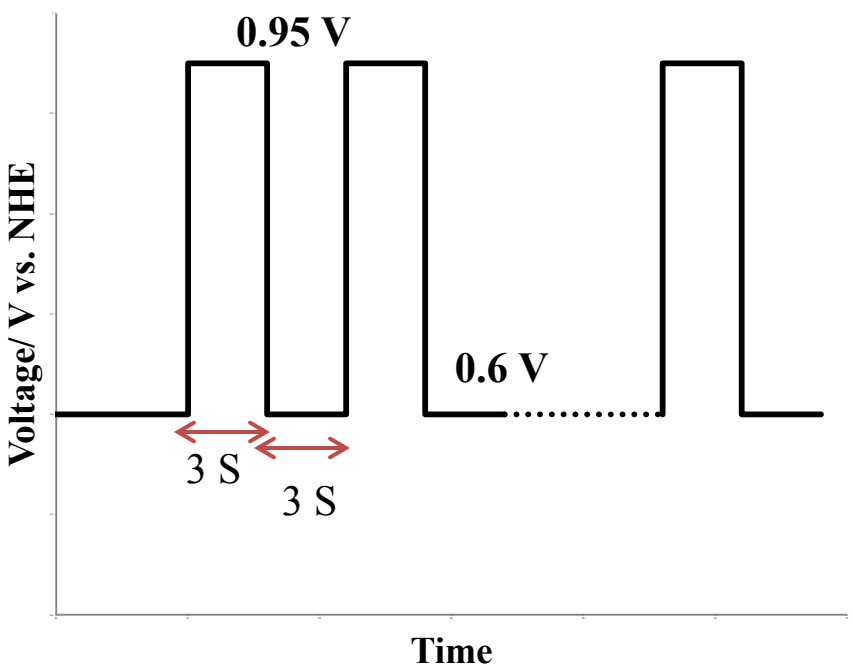
$$(0.044+0.056)/2/20=2.5\ \text{mF/cm}^2 \quad (\text{pseudo capacitance } (C_{DL}))$$

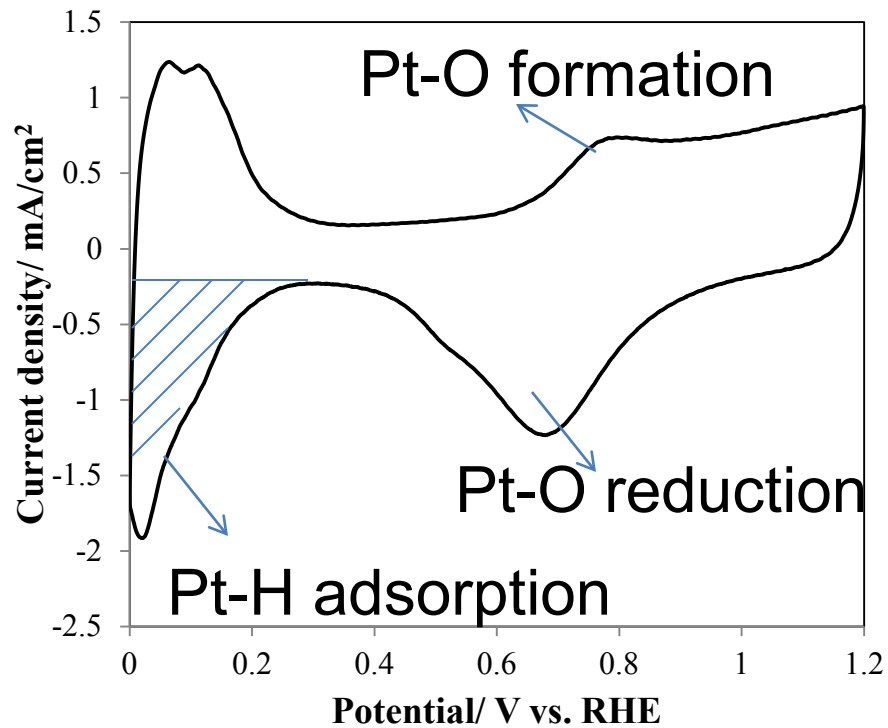
Average current density at 0.4V (mA/cm^2)

Scan rate: mV/s

Approach: Stability of Catalysts - Example

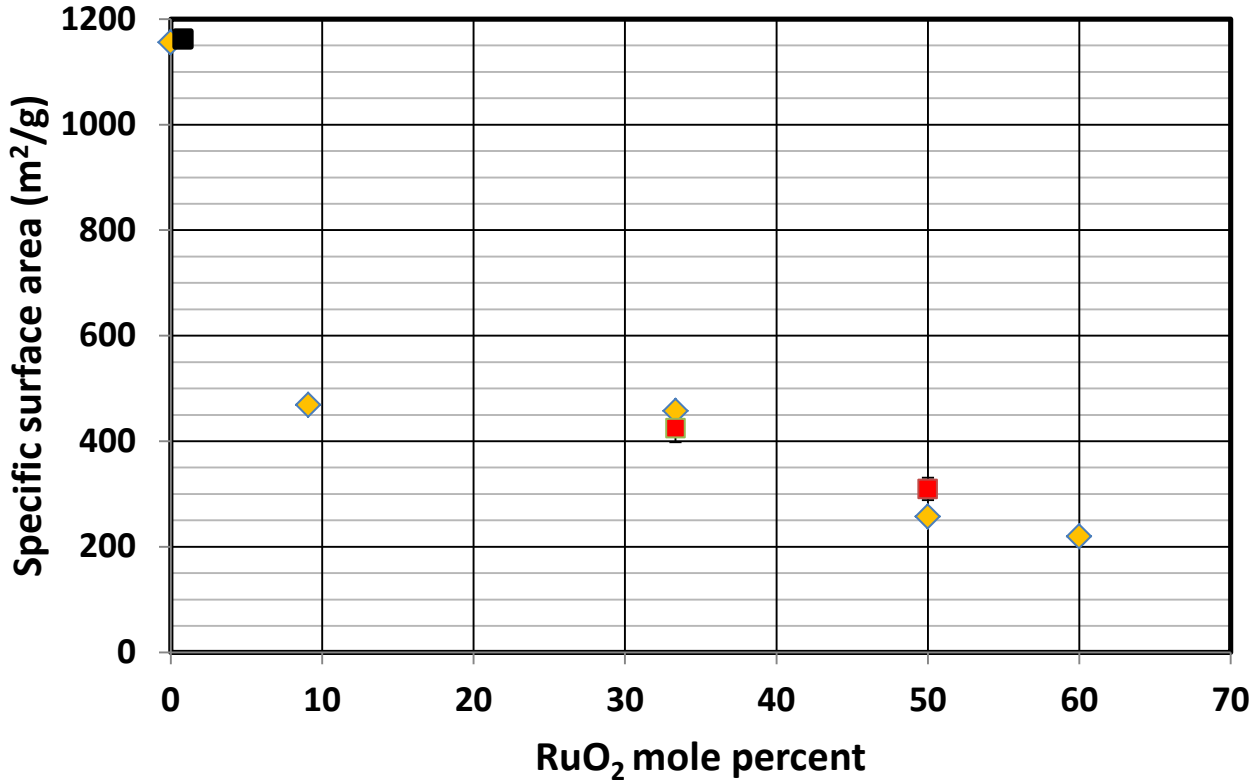
The stability of catalyst was evaluated by monitoring the change of ECSA.





0.1 M $HClO_4$ under N_2 atmosphere; CV sweep rate of 20 mV/S; room temperature (NTCNA runs potential cycling at 60C; CVs at 50 mV/s)

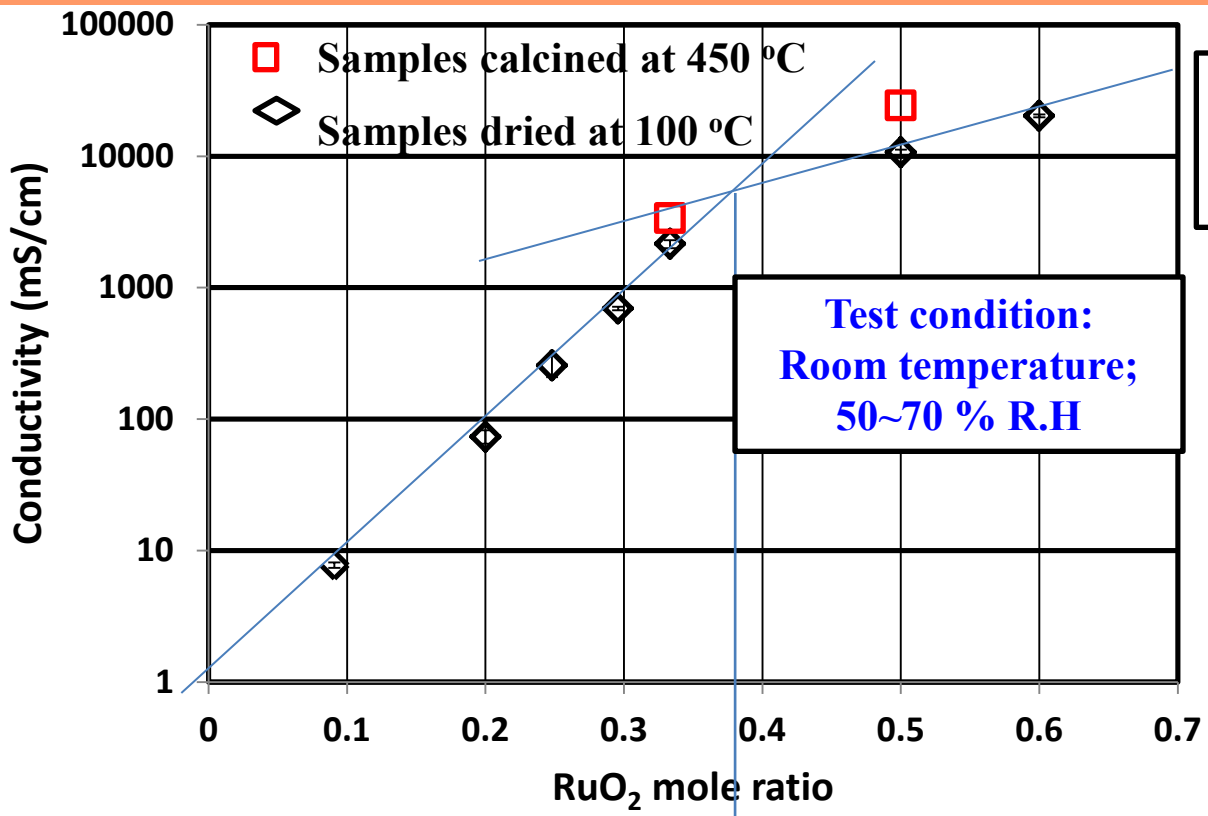
Technical Accomplishments: BET Surface Area of SiO_2 and RuO_2-SiO_2



- RuO_2- SiO_2 samples calcined at 450 °C
- RuO_2- SiO_2 samples dried at 100 °C
- Pure SBA-15

- Surface area decreases with mol% RuO_2
- Trend is consistent with expectation – RuO_2 has low specific surface area (14 m^2/g)
- Even with high RuO_2 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

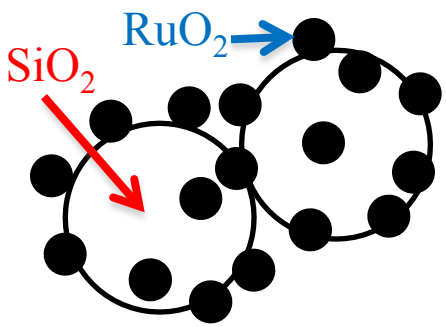
Technical Accomplishments: Electrical Conductivity of RuO_2 -SiO_2



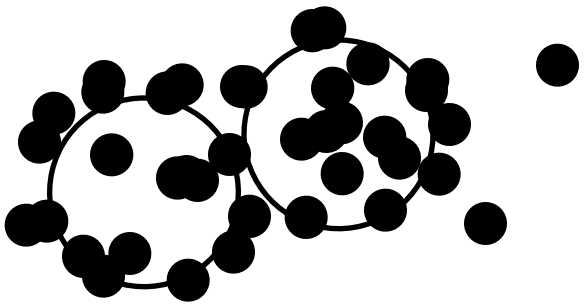
•Samples calcined at 450 °C have higher conductivity.

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

RuO_2 particles are dispersed without contacting each other.

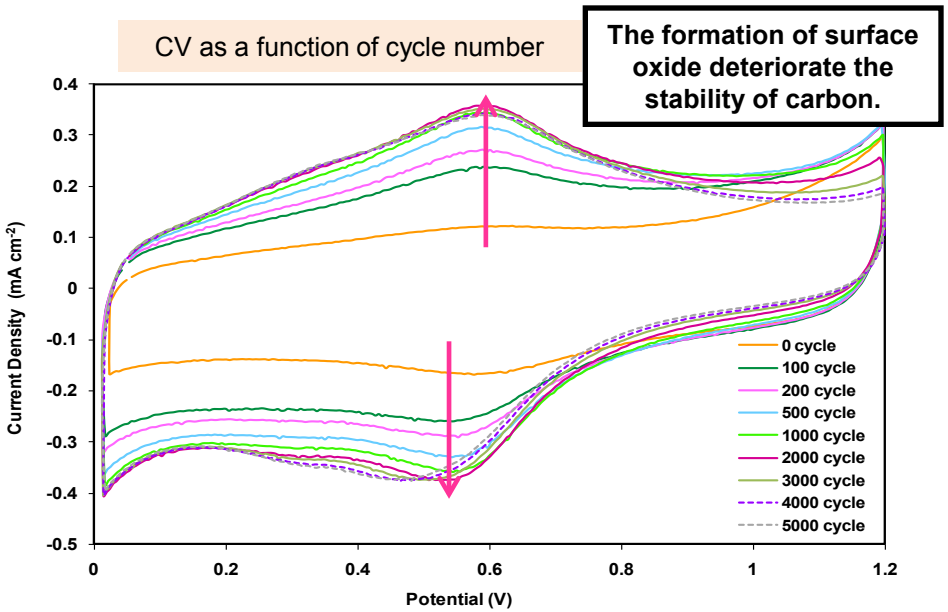


RuO_2 particles are in good contact with each other.

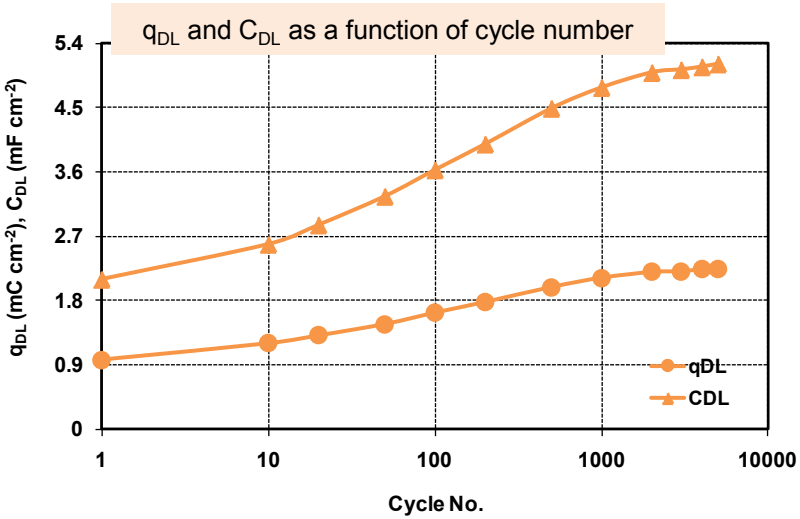


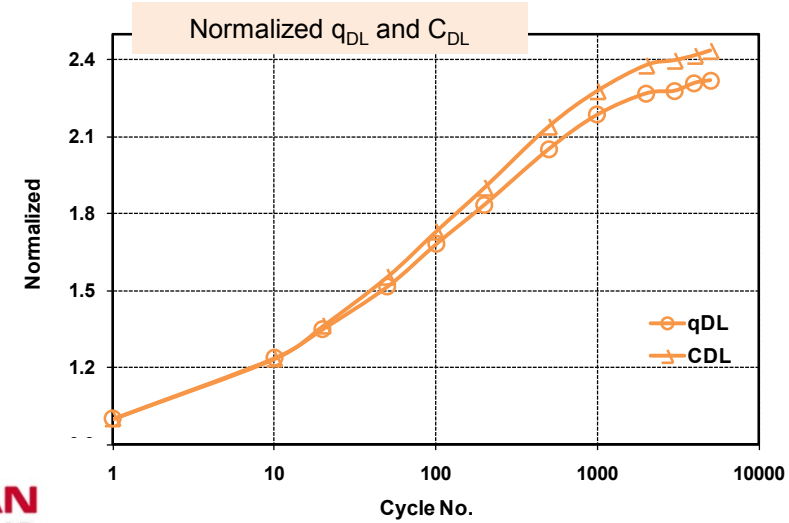
Technical Accomplishments: Electrochemical Stability of RuO_2 -SiO_2

Stability of Vulcan-Benchmark data



- Baseline CV data (0 cycle)for Vulcan match very well with the literature data*
- C_{DL} calculated by dividing apparent double layer normalized for loading by BET surface area (220 m^2/g) resulted in 6~7 $\mu F/cm^2$ capacitance at 0.4 V. (Literature value is 8 $\mu F/cm^2$)*
- Reported C_{DL} and q_{DL} (0.05-0.4 V) include pseudo capacitance and charge due to surface oxides





Kim Kinoshita, Carbon, 1988. Pg: 299

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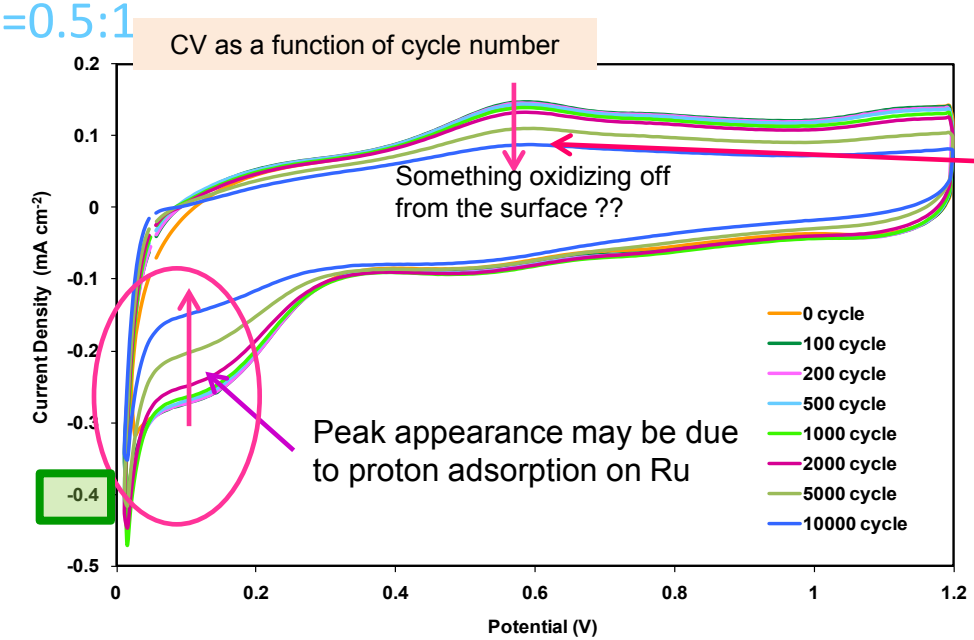
Technical Accomplishments: Electrochemical Stability of RuO_2 -SiO_2

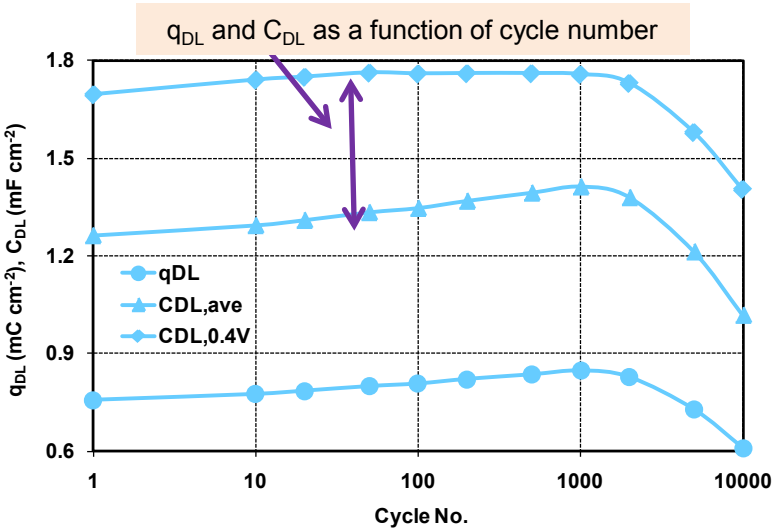
Stability of RuO_2:SiO_2=0.5:1

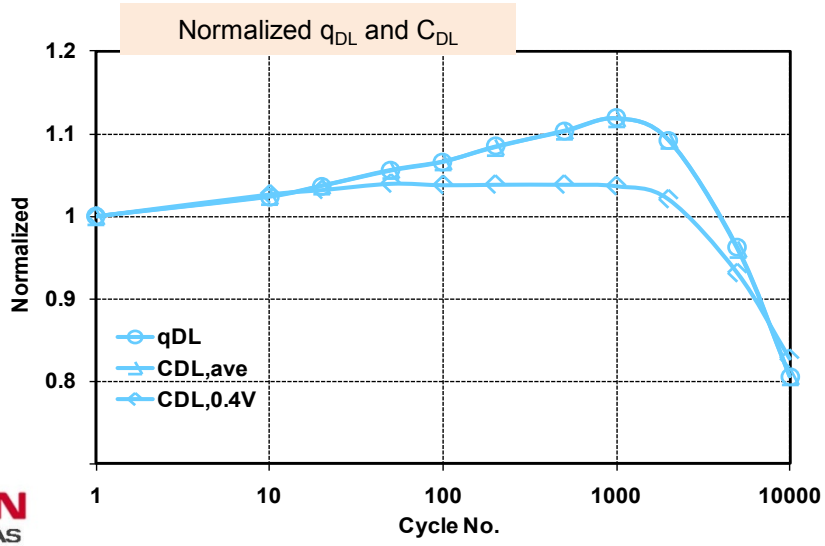


Peak @ 0.6 V disappears with cycling as against to **carbon support** where it become prominent with cycling (result of surface oxides shown in slide #4)

Difference in the C_{DL} values is due to difference in current values for i_{ave} and i_{dl} used for these calculation

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





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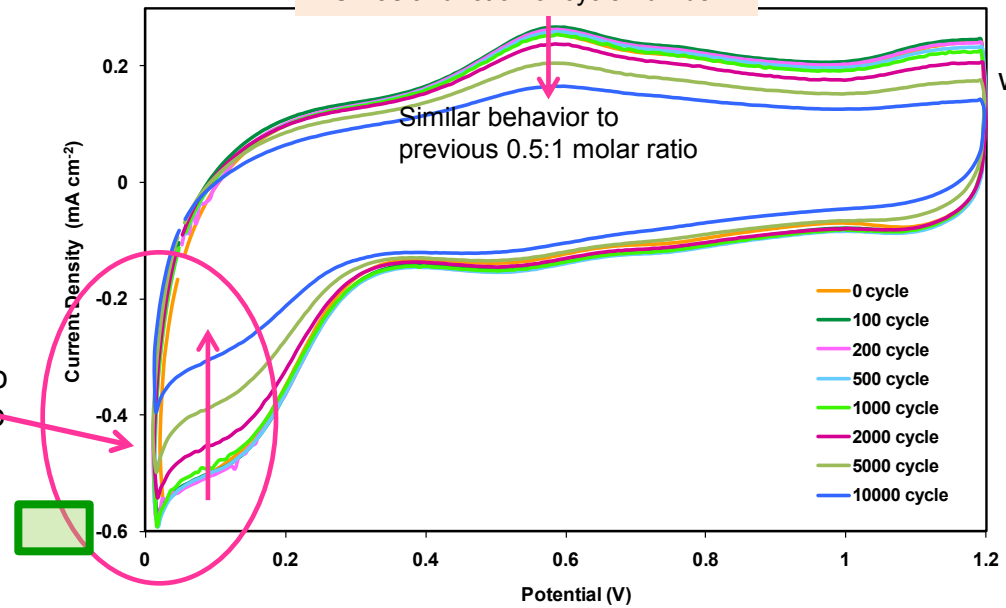
Technical Accomplishments: Electrochemical Stability of RuO_2 -SiO_2

Stability of RuO_2:SiO_2=1:1

CV as a function of cycle number



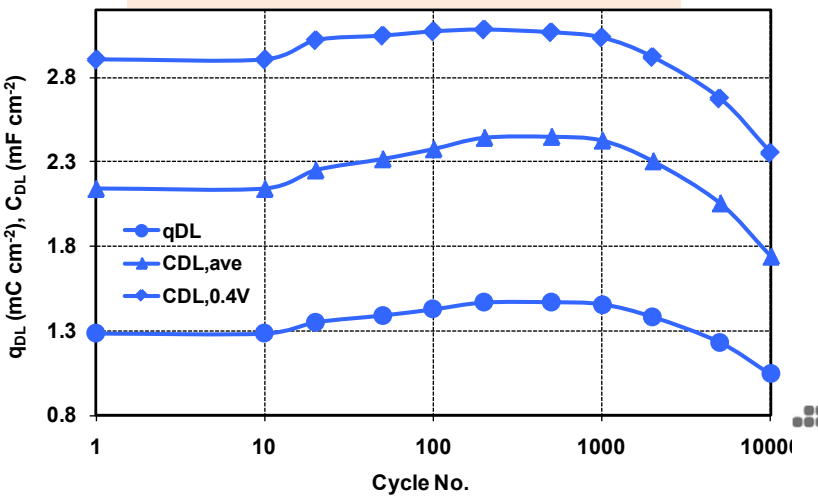
Similar behavior to previous 0.5:1 molar ratio

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

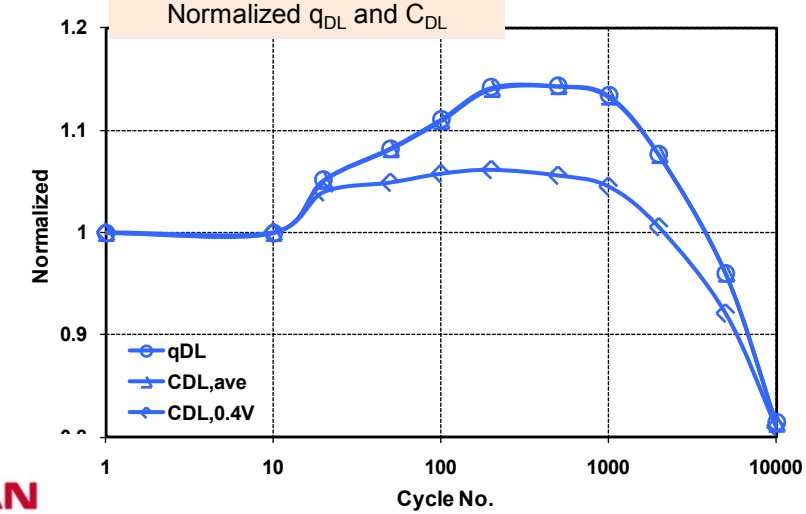
This peak is more prominent at this ratio than 0.5:1 molar ratio

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

q_{DL} and C_{DL} as a function of cycle number



Normalized q_{DL} and C_{DL}



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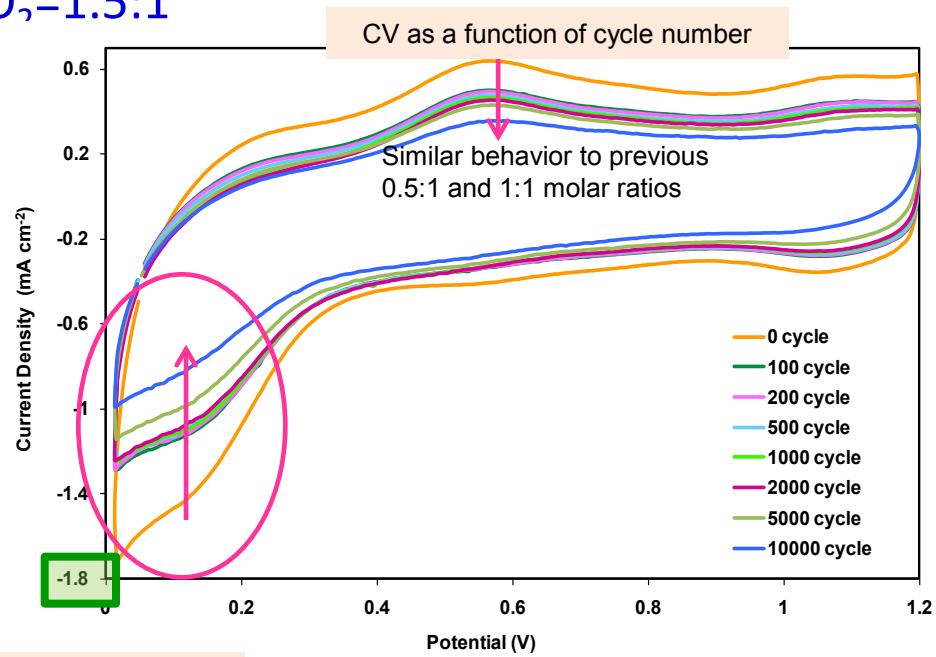
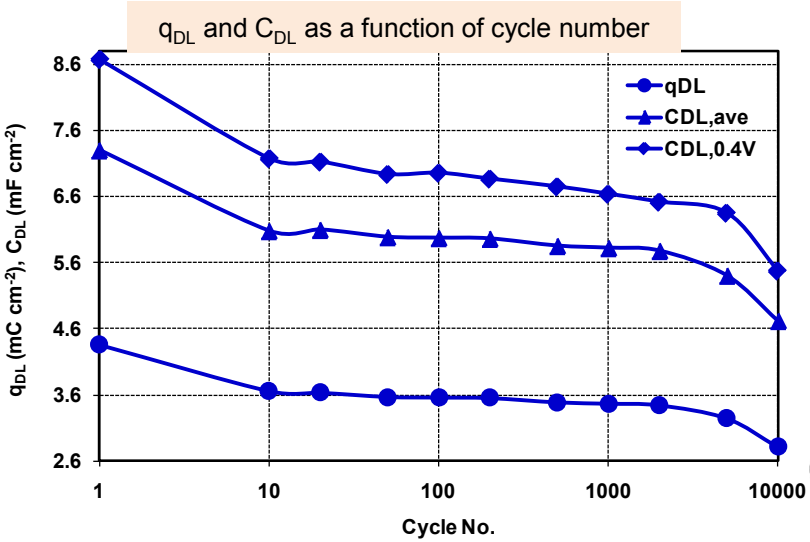
Technical Accomplishments: Electrochemical Stability of RuO_2 -SiO_2

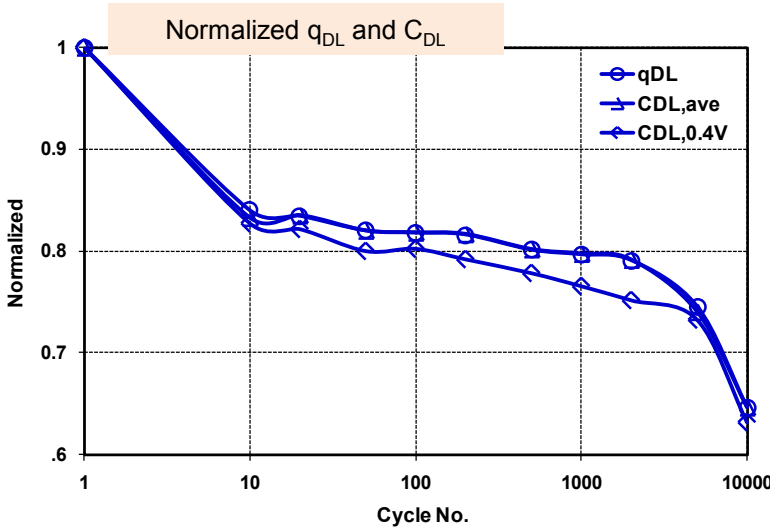
Stability of RuO_2:SiO_2=1.5:1



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

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





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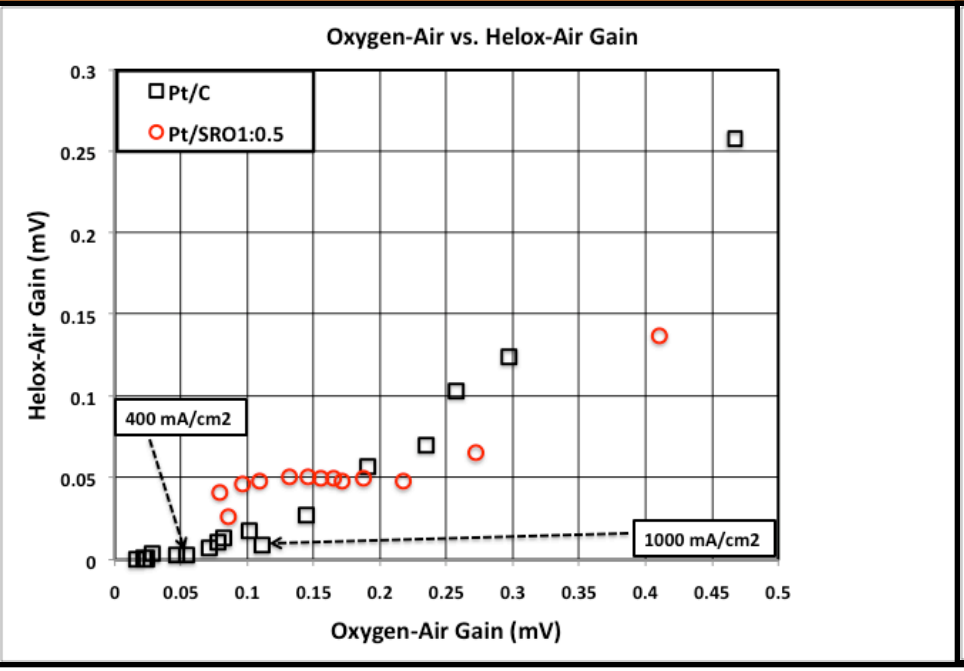
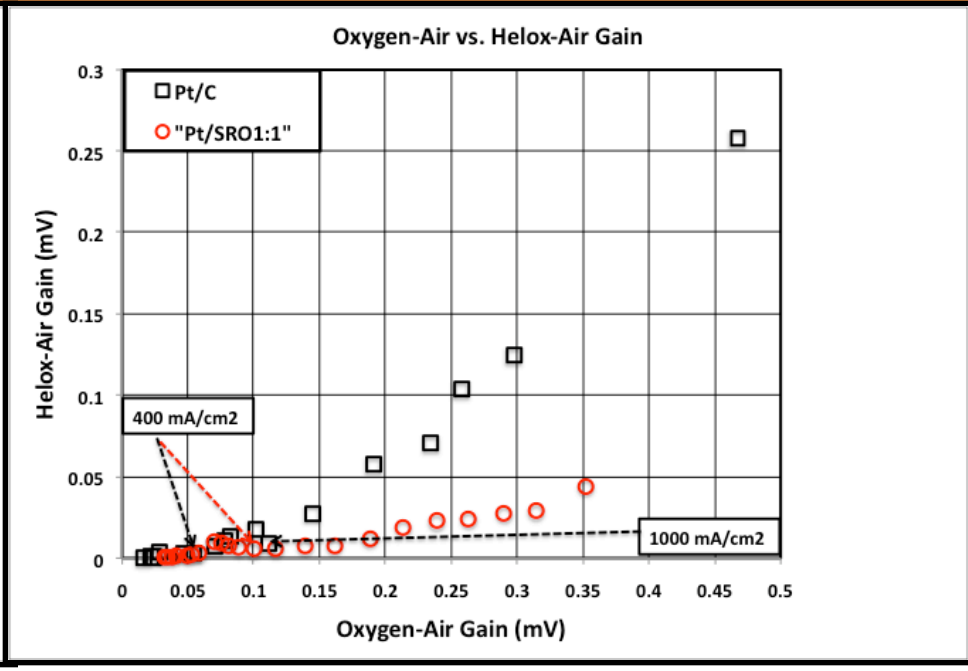
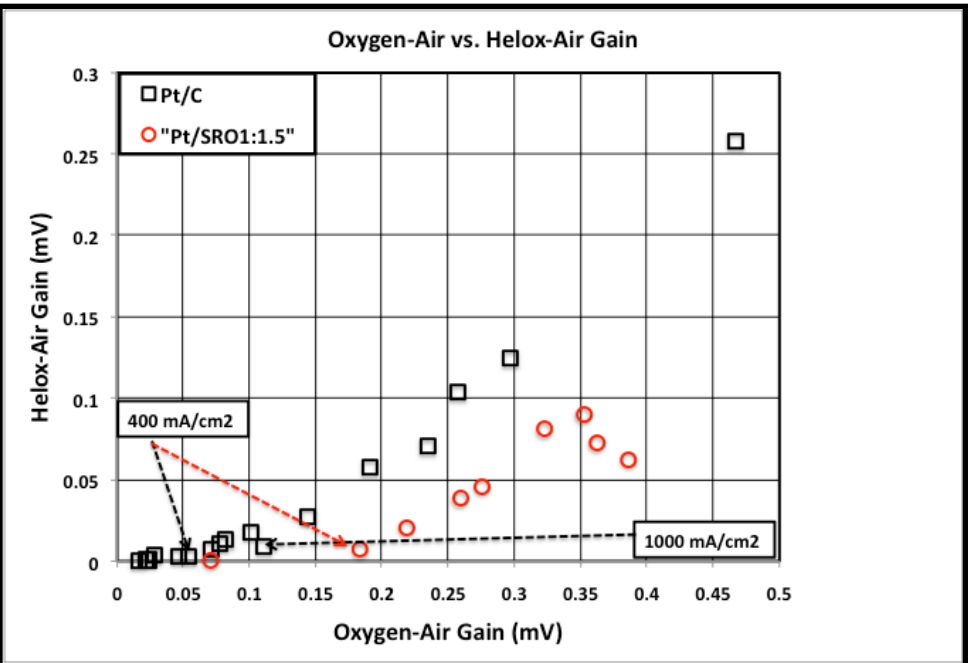
Technical Accomplishments: Performance with Pt/SRO Electrocatalysts







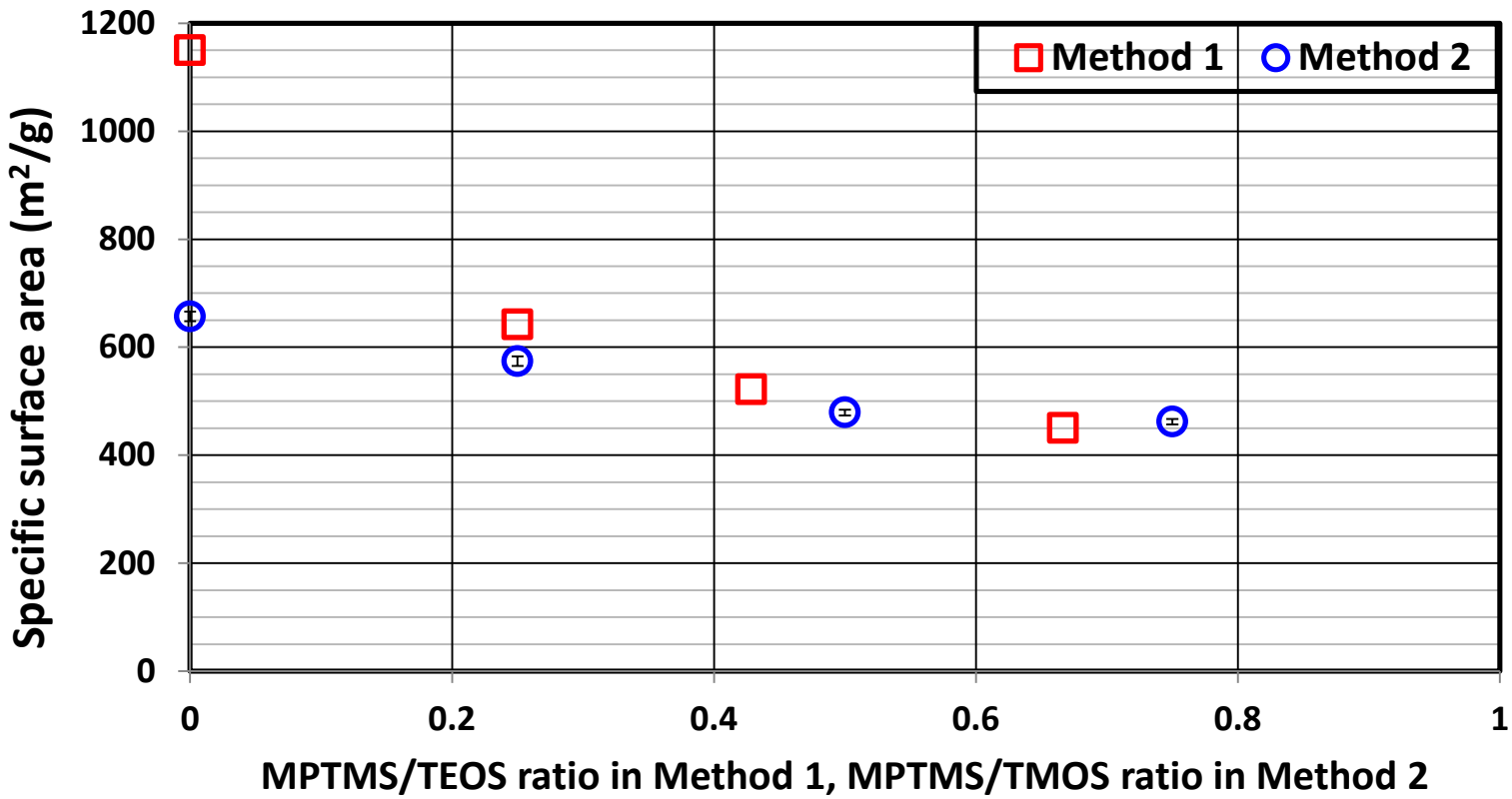
- Plot of O_2-Air vs. Helox-Air gain indicates extent and nature of mass transport limitations

- 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

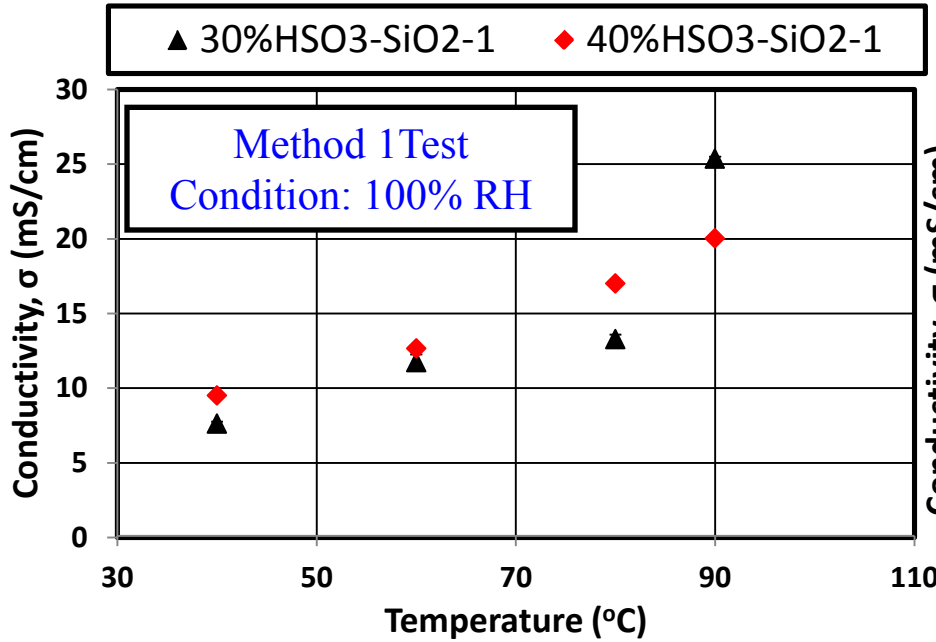
Technical Accomplishments: BET Surface Area of Sulfonic Acid Functionalized SiO_2

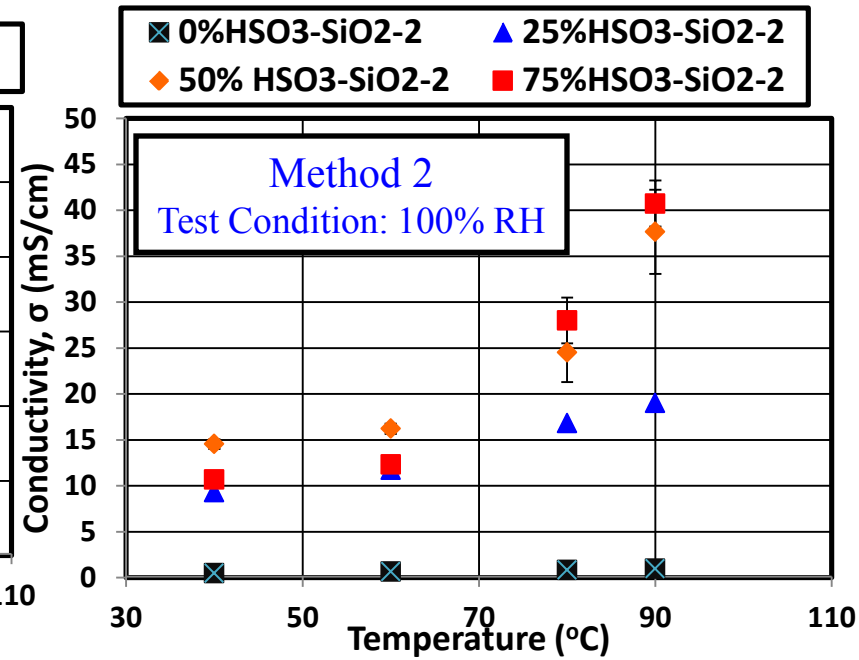


- BET surface area decreases with increasing extent of functionalization in both methods
- This is consistent with expectation based on results in the literature*
- Surface areas obtained are well above that of Vulcan XC-72, and higher than the milestones set for this project
- PIs will continue to improve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

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

Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO_2 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%

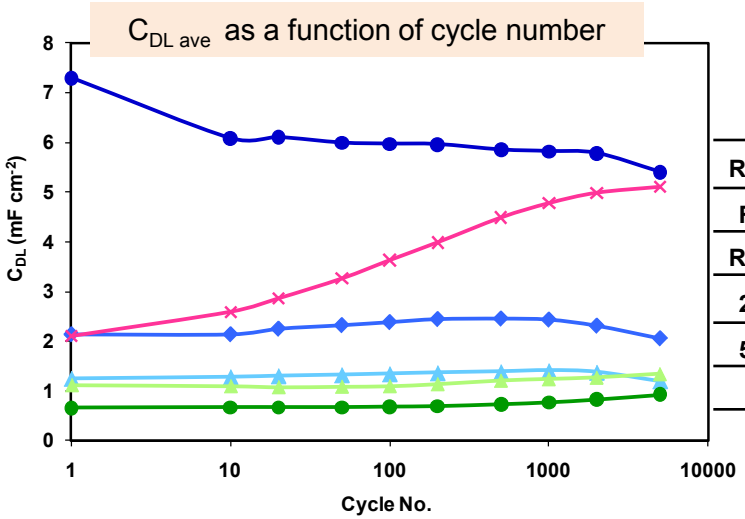
-Supercritical drying procedures in conjunction with study of alternate precursors (e.g. functionalized POSS) should further enhance surface functionalization and surface area.

-

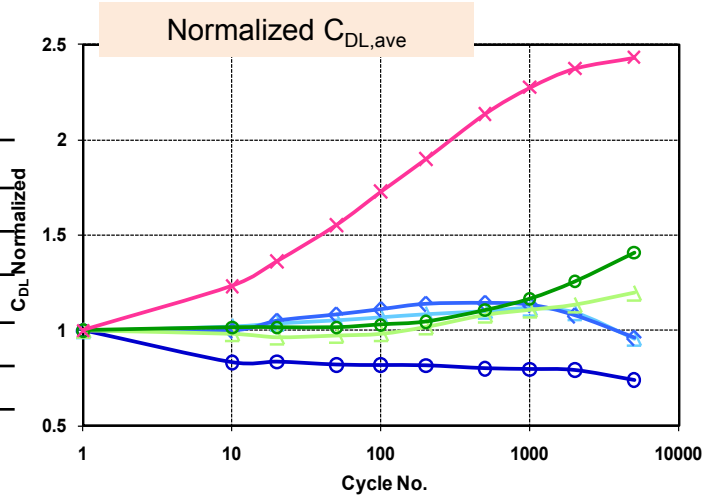
Technical Accomplishments: Stability of Functionalized Silica

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_2:SiO_2=0.5:1	4
RuO_2:SiO_2=1:1	3.7
RuO_2:SiO_2=1.5:1	26
25%SO_3H-SiO_2	19.6
50%SO_3H-SiO_2	40.9
Vulcan	143.3



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

  RuO_2:SiO_2=1:1 ≈ RuO_2:SiO_2=0.5:1 > 25%HSO_3-SiO_2 > RuO_2:SiO_2=1.5:1 > 50%HSO_3-SiO_2 >> Vulcan

- Based on these results RuO_2 functionalized silica with low RuO_2 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 μF/cm^2)

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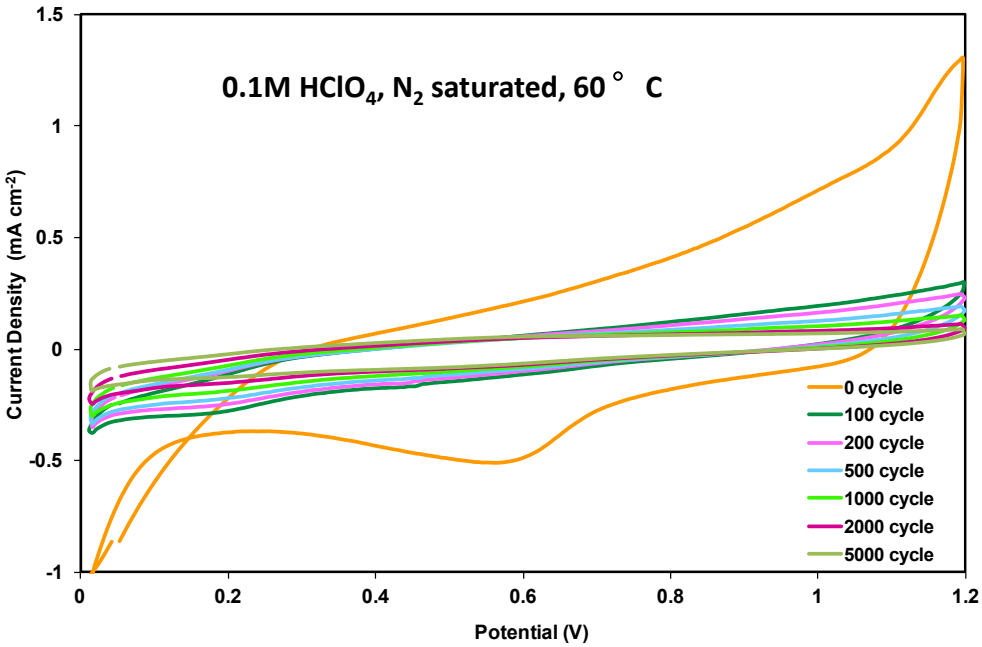
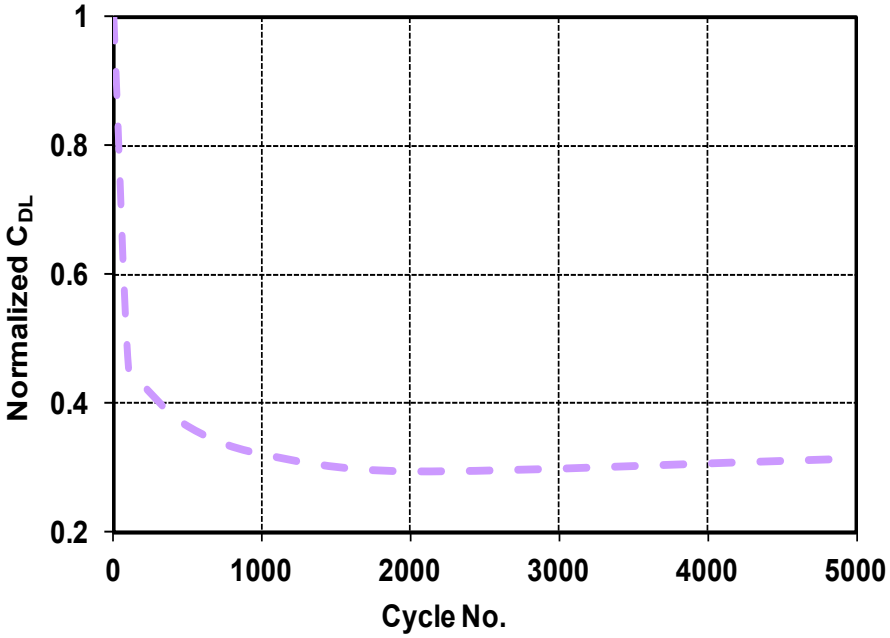
Technical Accomplishments: Stability of Functionalized Silica – RuO_2

Start-Stop Stability of SO_3H-SiO_2-RuO_2 (1:1)





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

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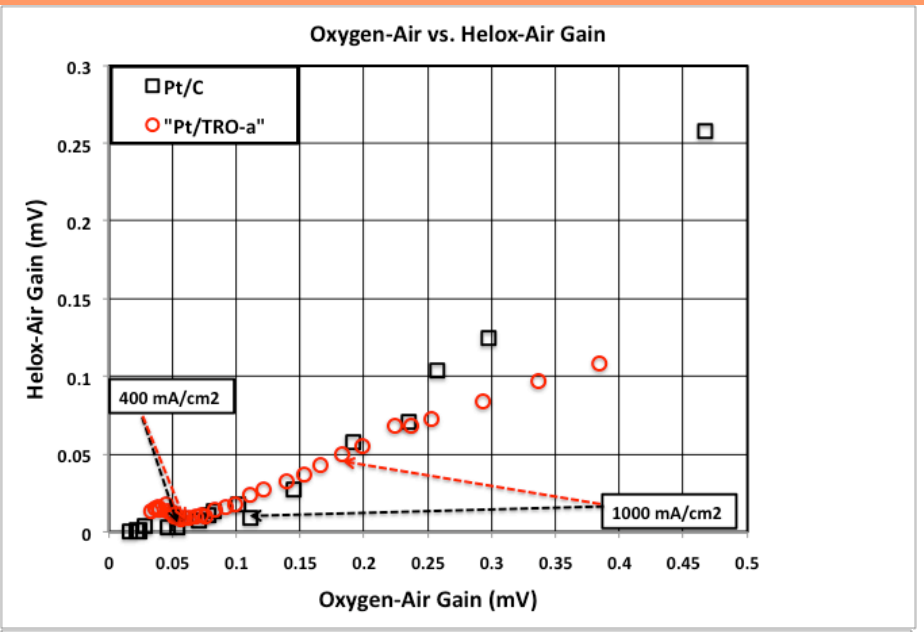
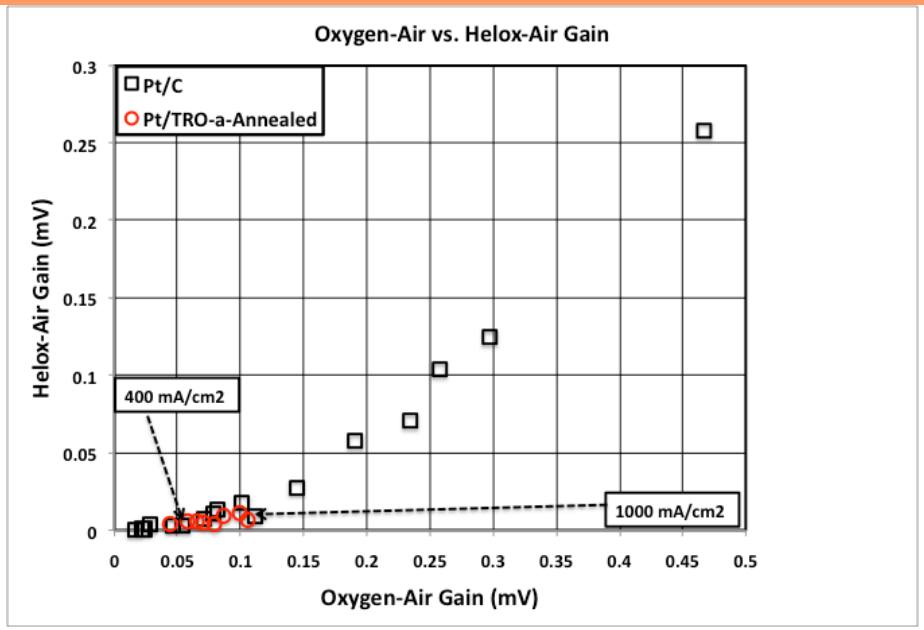
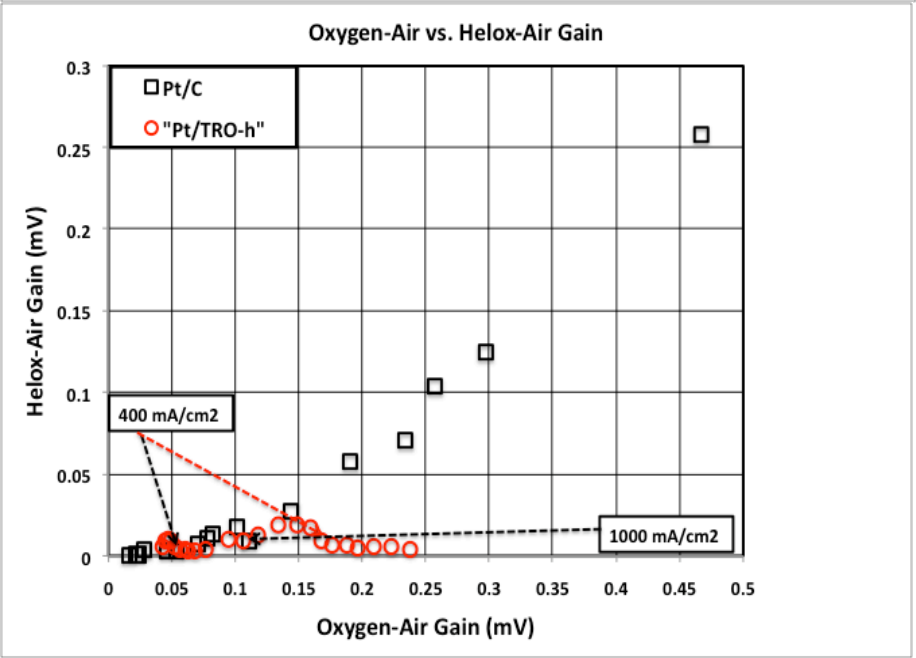
Technical Accomplishments: Performance of Pt/RTO Electrocataysts







- Plot of O_2-Air vs. Helox-Air gain indicates extent and nature of mass transport limitations

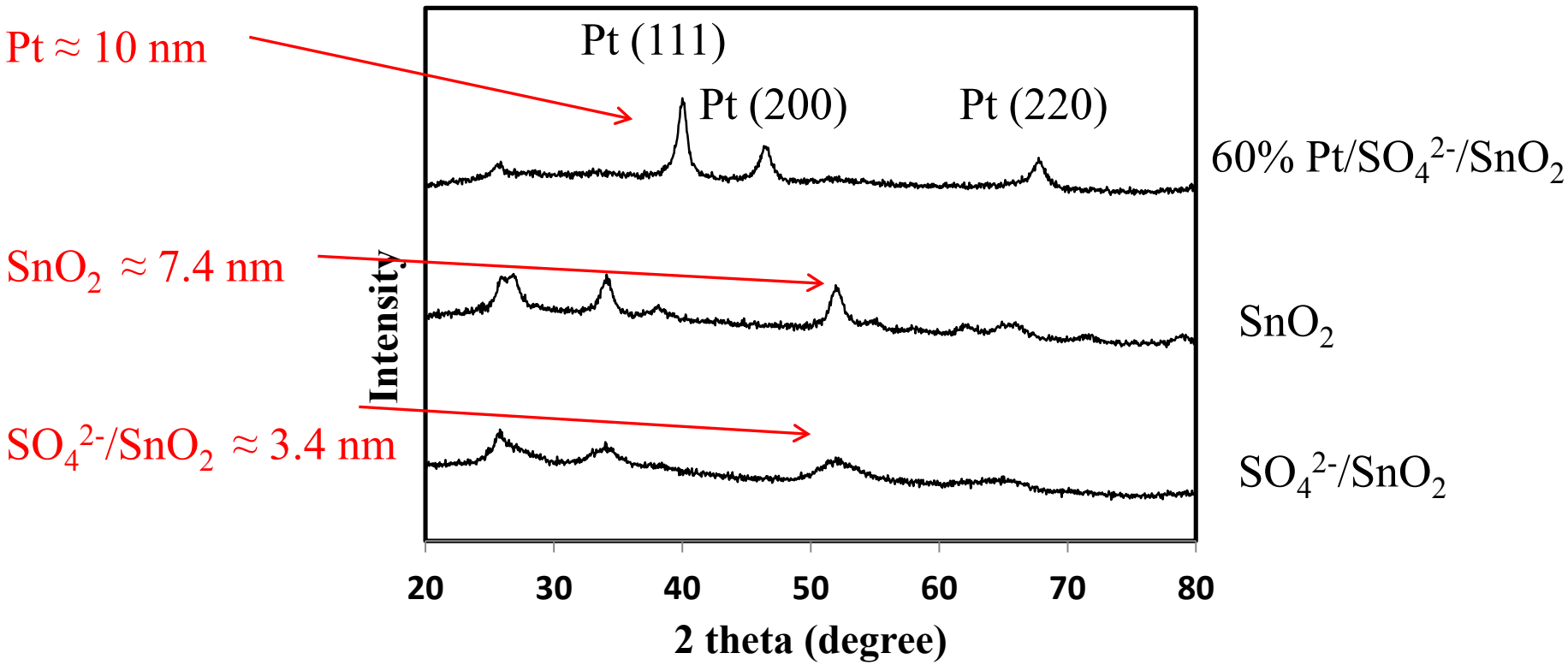
- Transport limitations (in addition to Ohmic limitations) observed in all TRO supports

- RTO supports when annealed or prepared with hydrous ruthenium oxide show tendency towards condensed phase transport limitations

Technical Accomplishments: XRD of $Pt/SO_4^{2-}/SnO_2$

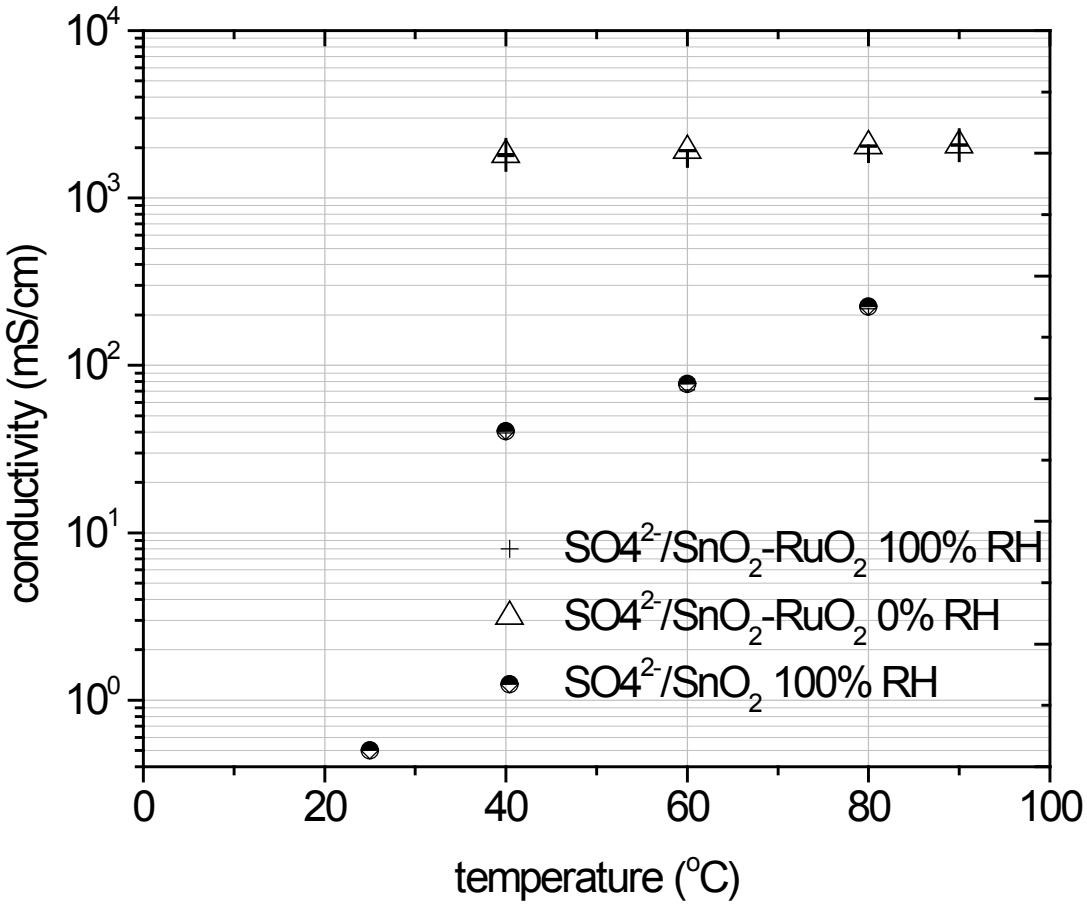
The SO_4^{2-} group on the surface of SnO_2 inhibits the degree of crystallization.

The crystallite sizes estimated by the Scherrer equation were around 7.4 nm and 3.4 nm for SnO_2 and SO_4^{2-}/SnO_2, respectively.



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

Technical Accomplishments: Conductivity of $Pt/SO_4^{2-}/SnO_2$-RuO_2



A maximum proton conductivity of 220 mS/cm was obtained for SO_4^{2-}/SnO_2 at 80 ° C. Moreover, the SO_4^{2-}/SnO_2 was annealed at 500 ° C, which means that SO_4^{2-} group on SnO_2 was more thermally stable than sulfonic acid functionalized silica aerogel.

Technical Accomplishments: Properties of $Pt/SO_4^{2-}/SnO_2$-RuO_2

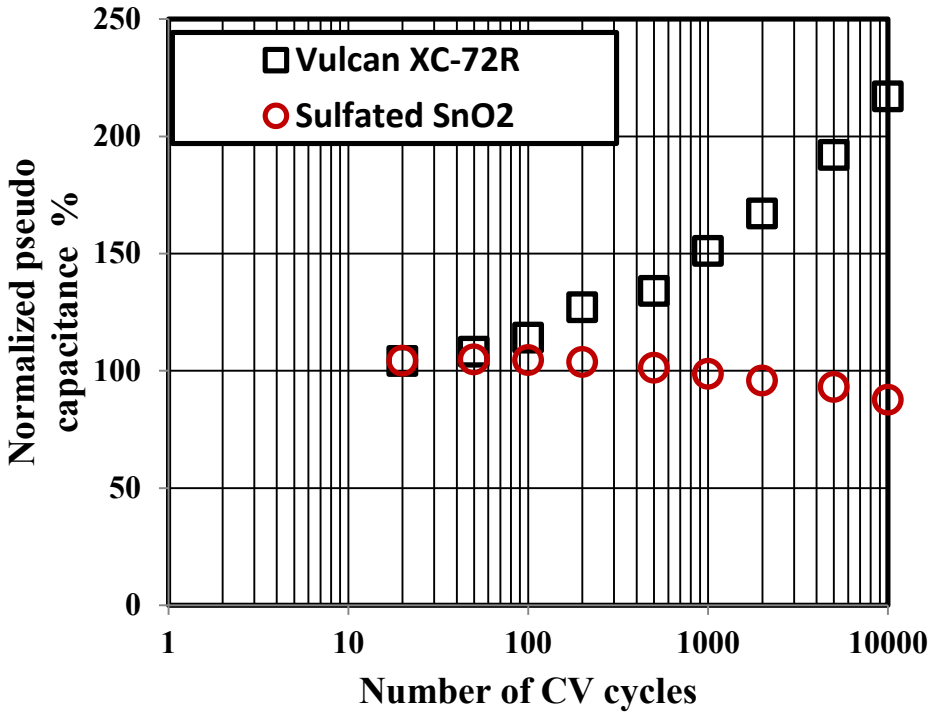
Sample	BET surface area(m^2/g)	IEC (mmol/g)	Electrical conductivity (S/cm)
SnO_2	21	~0	~0
SO_4^{2-}/SnO_2	96	0.65	~0
SO_4^{2-}/SnO_2 -RuO_2 (mole ratio of Sn:Ru=1:1)	?	?	2-3
60%$Pt/SO_4^{2-}/SnO_2$	?	0.175	23±3

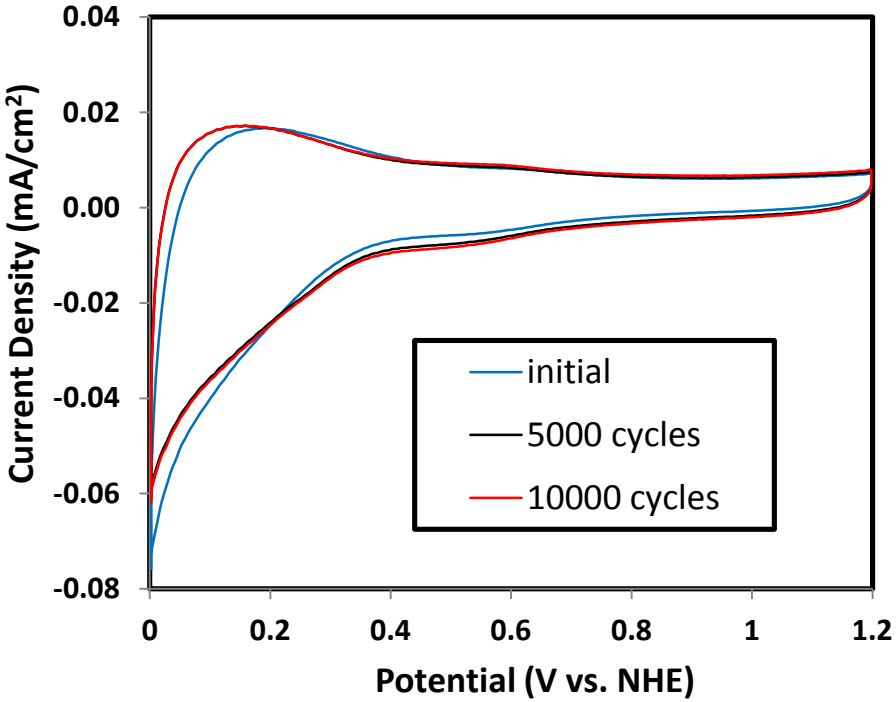
- ❑ IEC results suggested that SO_4^{2-}/SnO_2 -RuO_2 was almost completely covered by RuO_2 and no sulfonic acid group was exposed on the surface (IEC ≈0).
- ❑ The IEC results was consistent with conductivity results. The high conductivity of SO_4^{2-}/SnO_2 -RuO_2 was contributed by the electrical conductivity of RuO_2
- ❑60%$Pt/SO_4^{2-}/SnO_2$ exhibited high electrical conductivity, where Pt served as electrical conductor.
- ❑ IEC results suggested that about 33% of the SO_4^{2-} group of 60%$Pt/SO_4^{2-}/SnO_2$ sample was blocked by deposited Pt (1-0.175/0.4/0.65=0.67).

Technical Accomplishments: Stability of SO_4^{2-}/SnO_2

0.1 M $HClO_4$ under N_2 atmosphere; CV sweep rate of 20 mV/S; RT

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

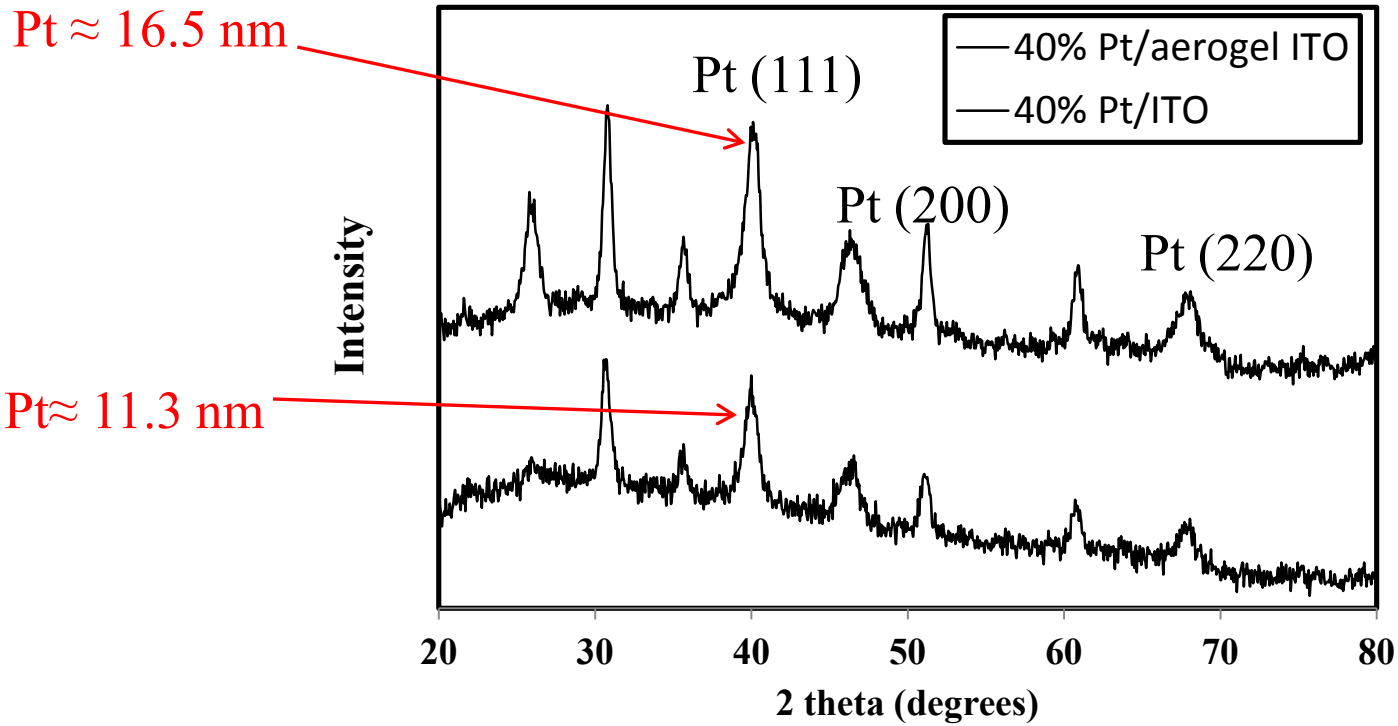




Sulfated SnO_2 support exhibited higher stability than Vulcan carbon.

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.



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

Technical Accomplishments: Properties of ITO

	ITO	Aerogel ITO	Commercial-ITO
Electrical conductivity (S/cm)	1.5	0.8	0.6
BET (m^2/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.

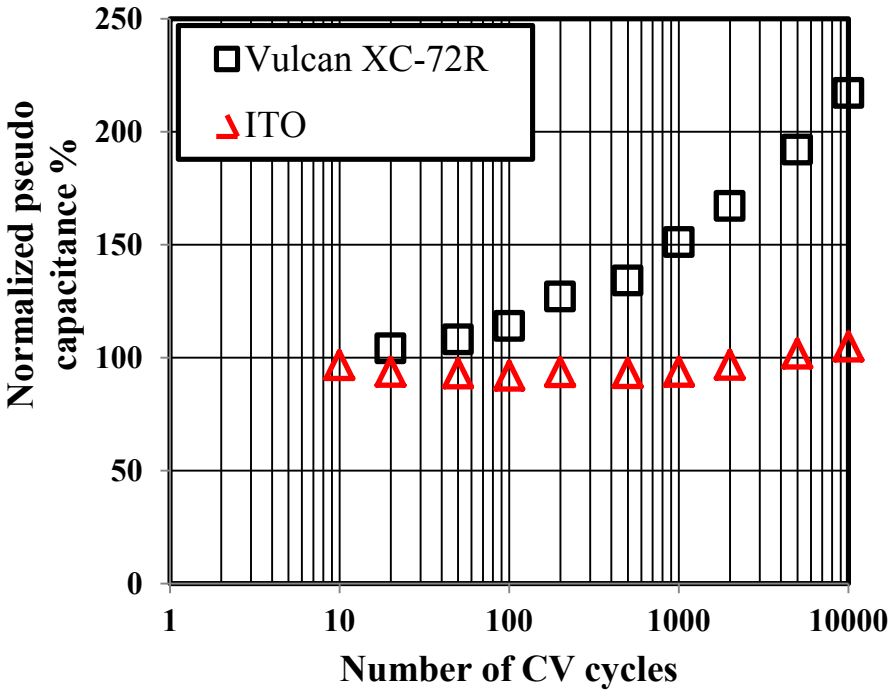
- The BET surface area of aerogel ITO was less than ITO. The result indicated that the aerogel network was not formed properly. Work is still ongoing in this area.

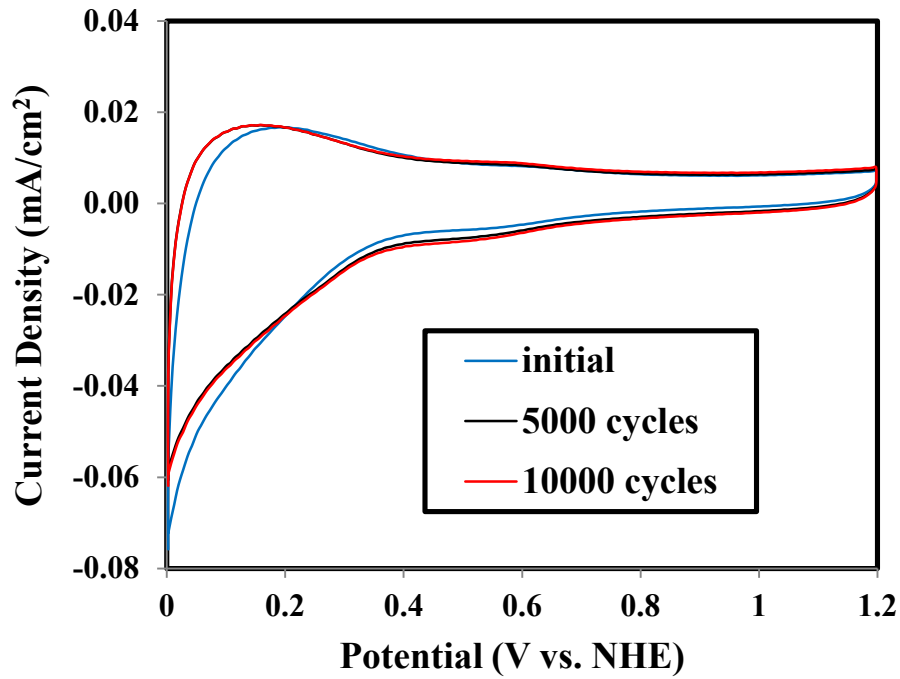
Thin Solid Films **411**:1(1-5); 2002

Technical Accomplishments: Stability of ITO

0.1 M $HClO_4$ under N_2 atmosphere; CV sweep rate of 20 mV/S; RT

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





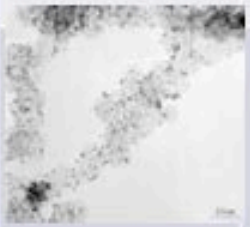
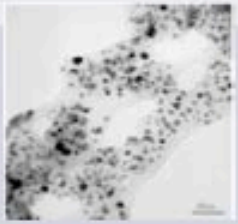
ITO support exhibited better stability than Vulcan carbon.

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

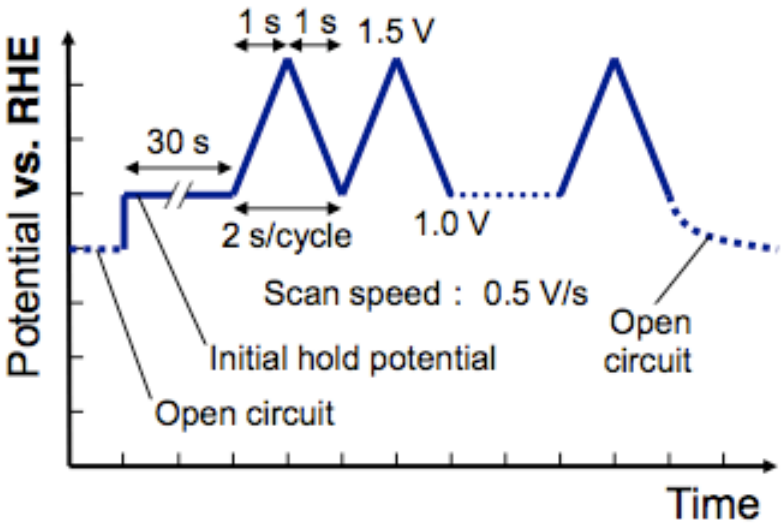
Catalyst Information

	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^2/g)	310.5	395.7	97.6	NA	84.6
TEM Images				NA	NA

HSAC = Ketjen Black®

Collaboration with Nissan, North America - Benchmarking

Catalyst Support Durability Evaluation
RDE Protocol: Carbon Corrosion



Temperature / °C		60
Solution	Electrolyte	0.1 M $HClO_4$
	Dissolved gas	Saturated with N_2 or Ar
	Reference Electrode	RHE
	Counter Electrode	Pt gauze

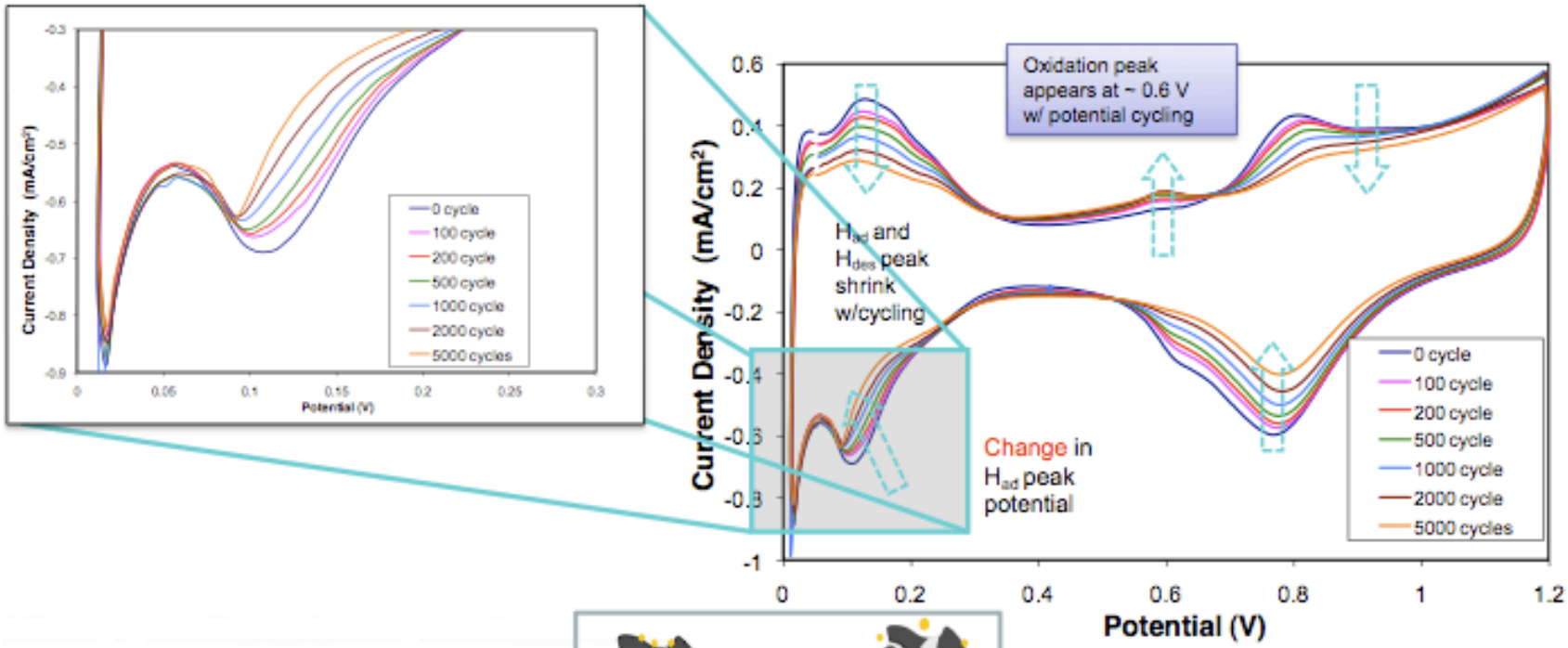
Diagnosis: CV at 0, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000 cycles

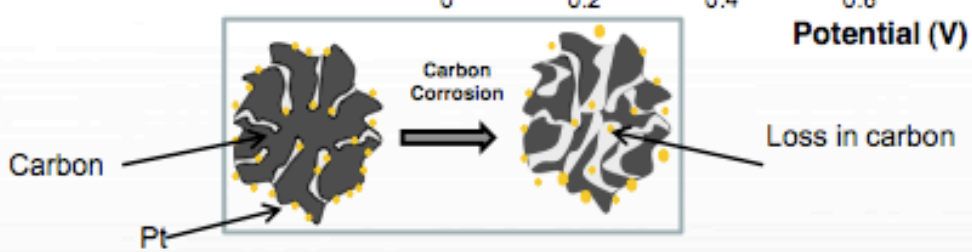
(Indispensable item: Electrochemical area)

Collaboration with Nissan, North America - Benchmarking

Catalyst Support Durability Evaluation

Example RDE: Vulcan Support

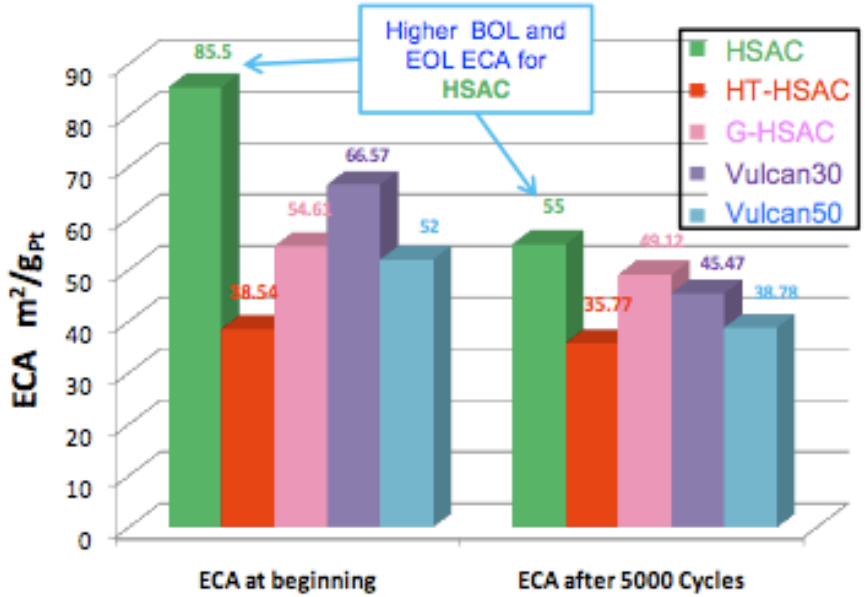


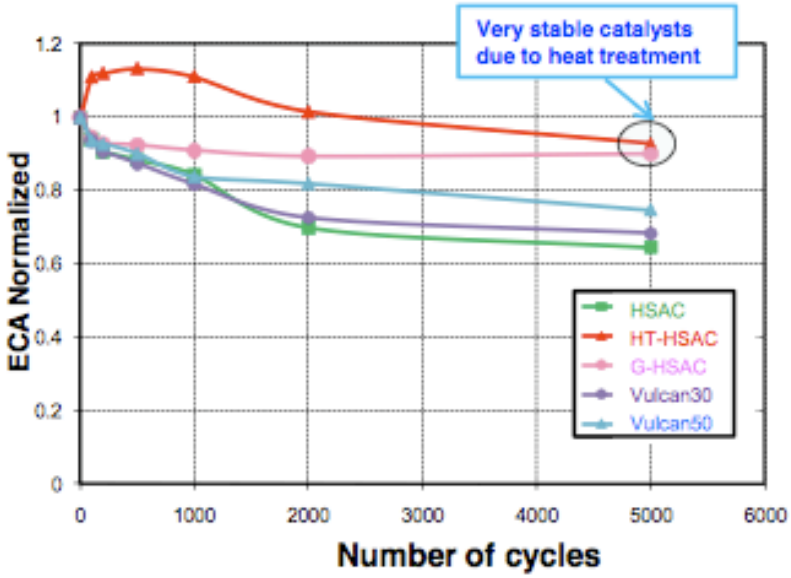


- H_{ads} peaks and oxidation peaks decreased with potential cycling.
- Double layer increased slightly with more potential cycling, as opposed to other catalyst

Collaboration with Nissan, North America - Benchmarking

Carbon Support Corrosion Evaluation
Comparison RDE



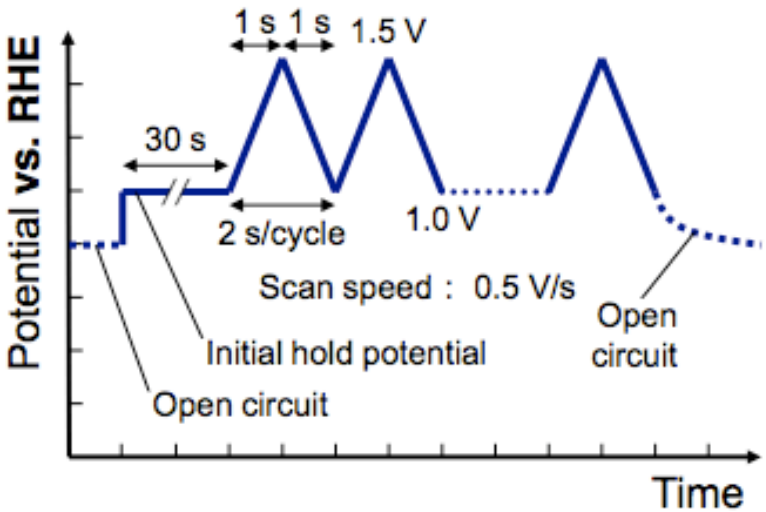


Catalyst	% ECA Loss
HSAC	~ 36%
HT-HSAC	~ 7%
G-HSAC	~ 10%
Vulcan30	~ 32%
Vulcan50	~ 25%

- 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_2
	Dew point / °C	80
	Flow rate / NL min^{-1}	0.5
WE (Cathode)	Gas	N_2
	Dew point / °C	≧ 80
	Flow rate / NL min^{-1}	0.5

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

(Indispensable item: Electrochemical area)

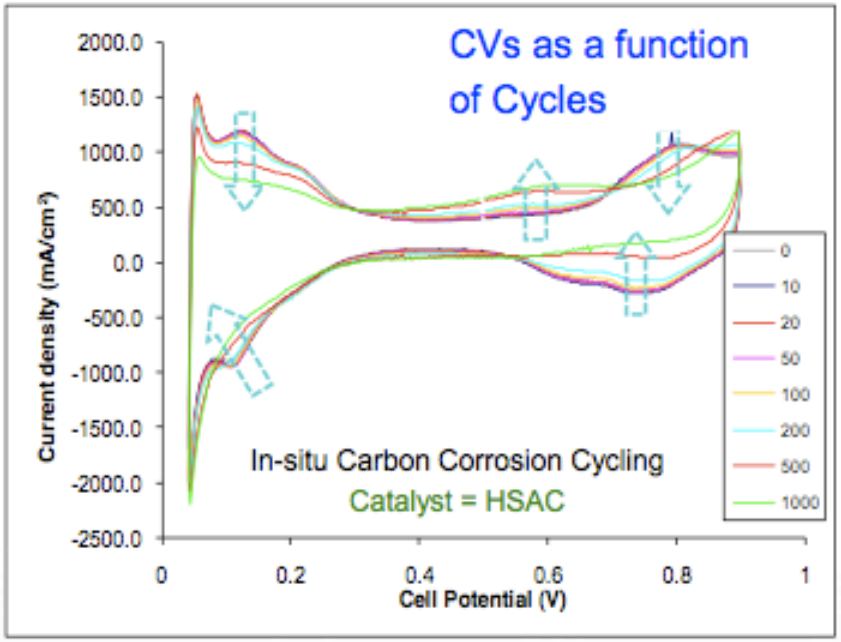
At high voltage, carbon oxidation reaction (carbon corrosion) accompanies the H_2O consumption. To prevent drying of cathode, the dew point should be set slightly above 80 °C.

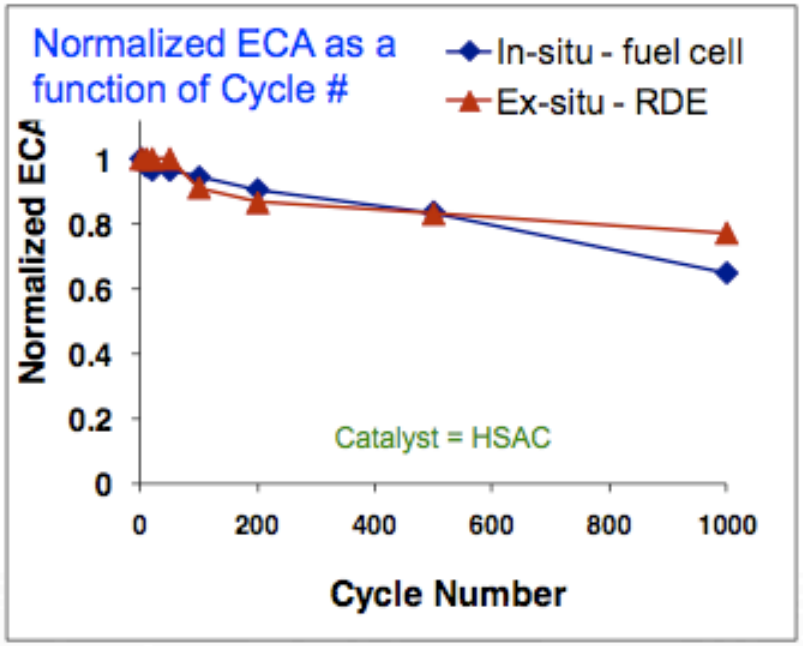
Collaboration with Nissan, North America - Benchmarking

Carbon Support Corrosion Evaluation
Comparison RDE & Fuel Cell Single Cell

NISSAN INFINITI.

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





✓ Excellent correlation between RDE and Fuel Cell

NTCNA-FH
Fuel Cell Laboratory

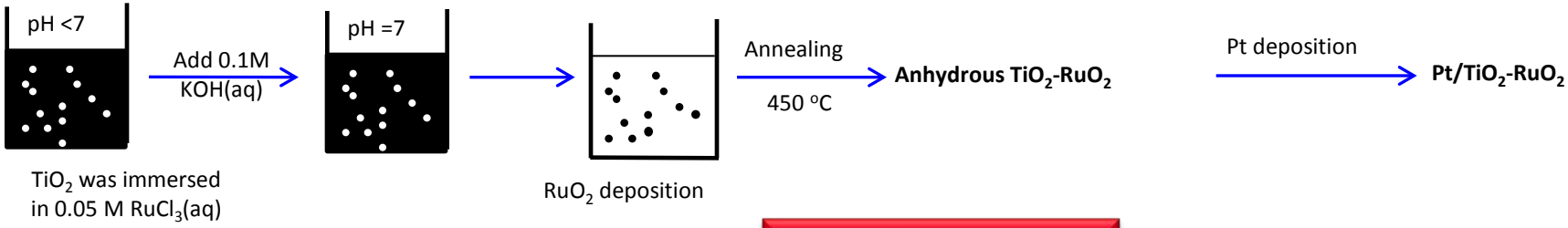
Summary

- 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

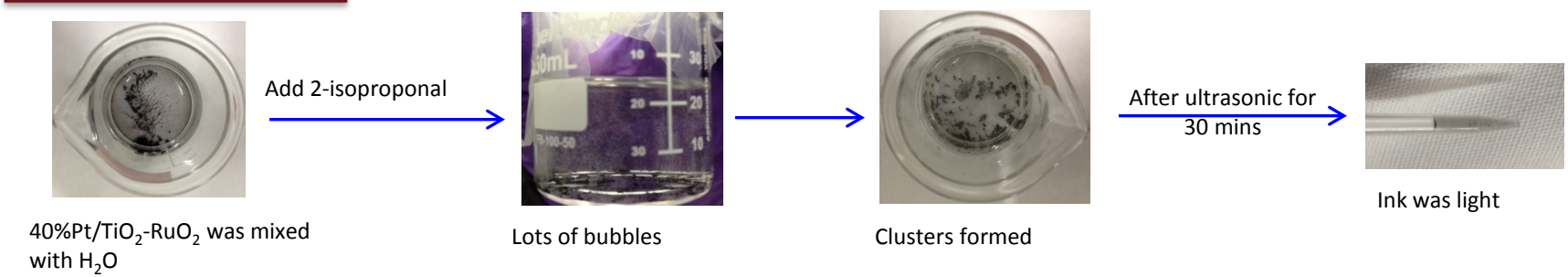
Synthesis of Pt/TiO_2-RuO_2



Characterization

	TiO_2-RuO_2	Pt/TiO_2-RuO_2	TEC10E50E
BET (m^2/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.

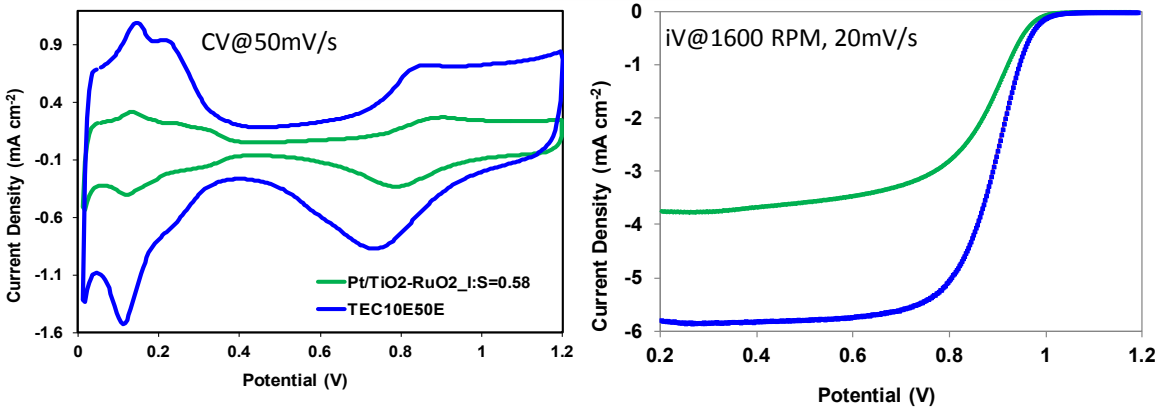
Collaboration with Nissan, North America - Benchmarking

ORR Activity-RDE

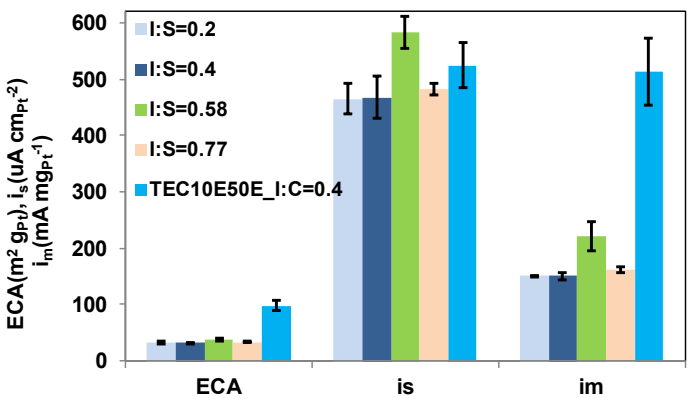
Ink optimization

- 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 TKK baseline catalyst TEC10E50E(50% Pt/HSAC).

Example of CV and iV of 40%Pt/TiO_2-RuO_2



Activity as a function of I:S ratio



- 40%Pt/TiO_2-RuO_2 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_2 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

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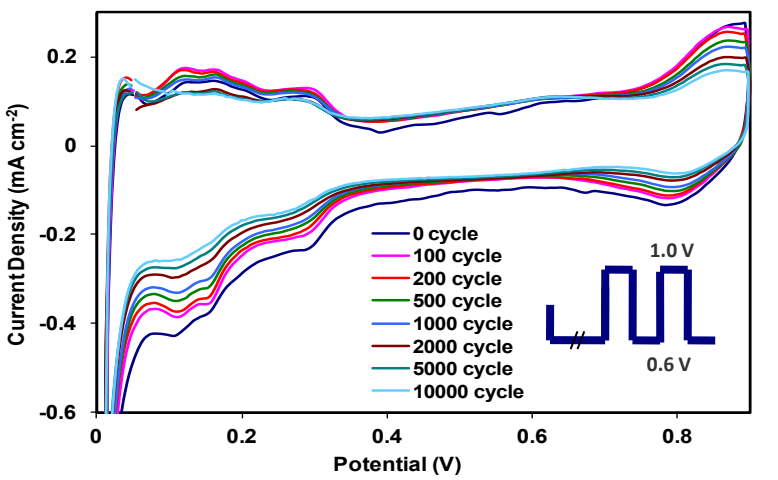
- The stability of the catalyst was tested under Nissan load cycling and start-stop cycling. The losses were compared with those of TEC10E50E(50% Pt/HSAC).

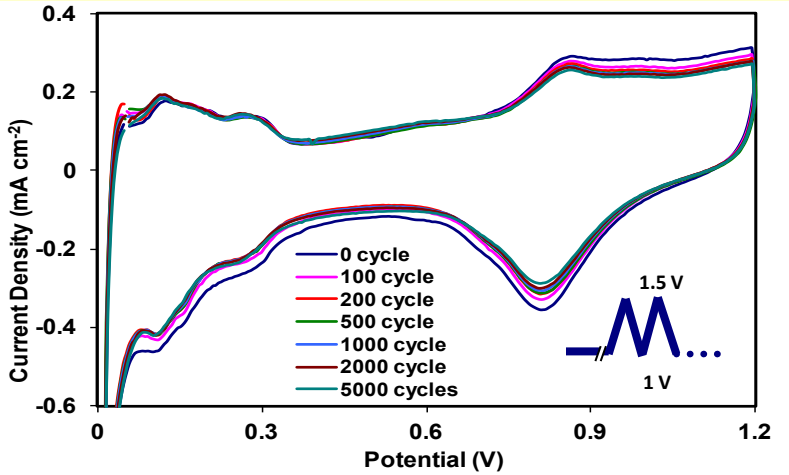
Load Cycling 0.1M $HClO_4$, N_2 saturated, 60°C

Start-stop Cycling

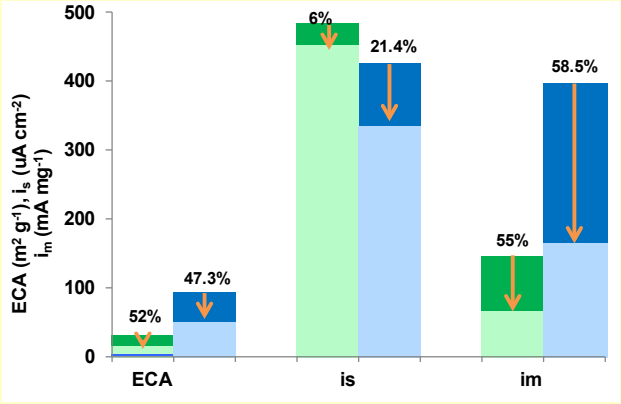
Effect of Load Cycling on CV



Effect of Start-stop Cycling on CV



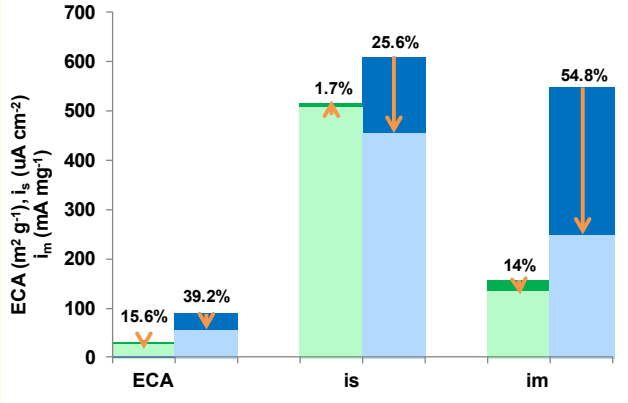
Losses in Load Cycling



0.1M $HClO_4$, RT

- BOL
- EOL
- 40%Pt/TiO2-RuO2
- 50% Pt/HSAC

Losses in Start-stop Cycling



- The Pt/TiO_2-RuO_2 was quite stable under start-stop cycling, however, it lost the stability in load cycling, comparable to TEC10E50E.