

Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

PI: Vijay K. Ramani

Department of Chemical and Biological Engineering
Illinois Institute of Technology

05.10.2011

Project ID #
FC085

Overview

Timeline

- Project start date: Aug. 1st 2010*
- Project end date: Jul. 30th 2013
- Percent complete: ~ 15%

Budget

- Total project funding
 - DOE share: \$ 1,476,230
 - Contractor share: \$ 415,775
- FY 2010 Funding: \$300,000
- FY 2011 Funding (planned): \$350,000

Barriers

- Barriers addressed:
 - Fuel Cell component durability to be improved
- Targets addressed
 - < 40% ECA Loss tested per GM protocol
 - < 30mV electrocatalyst support loss after 100 hrs at 1.2 mV; tested per GM protocol
 - Targets taken from Table 3.14.12, Multi-Year RDD plan

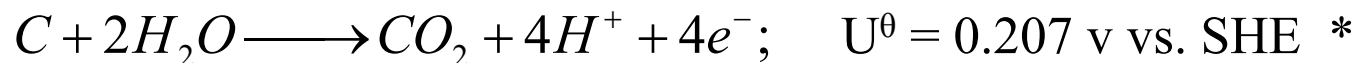
Partners

- Nissan North America Inc.
- Project lead: Illinois Institute of Technology

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

Relevance: Impact of Carbon Corrosion on PEFCs

- Carbon is mainly used as an electrocatalyst support due to its:
 - High electrical conductivity
 - High BET surface area : 200 - 300 m²/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 **Focus of Project Phase 2**
 - By virtue of surface proton conductivity of the electrocatalyst support
- Relevance to DOE Targets:
 - Addresses the issue of electrocatalyst and support stability, both of which are important in the context of fuel cell durability
 - The development of stable, non-carbon supports will help address technical targets for:
 - Operational lifetime (5000 hrs under cyclic operation),
 - ECA loss ($< 40\%$ per GM protocol) and
 - Electrocatalyst support loss ($< 30 \text{ mV}$ after 100 hrs at 1.2 V, per GM protocol).

Approach: Material Studied and Desired Properties

We are investigating mixed metal oxides ($\text{SiO}_2\text{-RuO}_2$) 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 cycling to 1.8V vs. RHE for 1000 cycles or higher
 - 1.8 V chosen as upper potential both to accelerate the durability test and to simultaneously assess suitability for PEM electrolyzers
- 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
- **Functionalize sequentially to introduce proton/electron conductivity**
 - Ruthenium oxide used as model electron conducting functionality
 - Sulfonic acid groups introduced to provide proton conductivity
 - Platinum will be deposited on durable supports that meet milestones [next slide]
 - Materials will be benchmarked against state-of-the-art carbon and Pt/C catalysts
- **Project sub-divided into 5 Tasks (T1-5)**
 - IIT: materials synthesis and characterization + ionomer reduction studies (T 1 , 3 and 5)
 - Synthesis and characterization of MMO supports (catalyzed and uncatalyzed)
 - Preliminary durability testing and catalytic activity measurements
 - Ionomer reduction studies in sub-scale MEAs
 - Provide materials and optimal electrode formulations to Nissan North America Inc.
 - Nissan North America Inc.: durability/performance testing + cost model (T 2, 4 and 5)
 - Accelerated test protocols on materials provided by IIT (Start-Stop + Load Cycling)
 - Fabrication / testing of sub-scale and 100 cm² MEAs
 - Development of cost model.

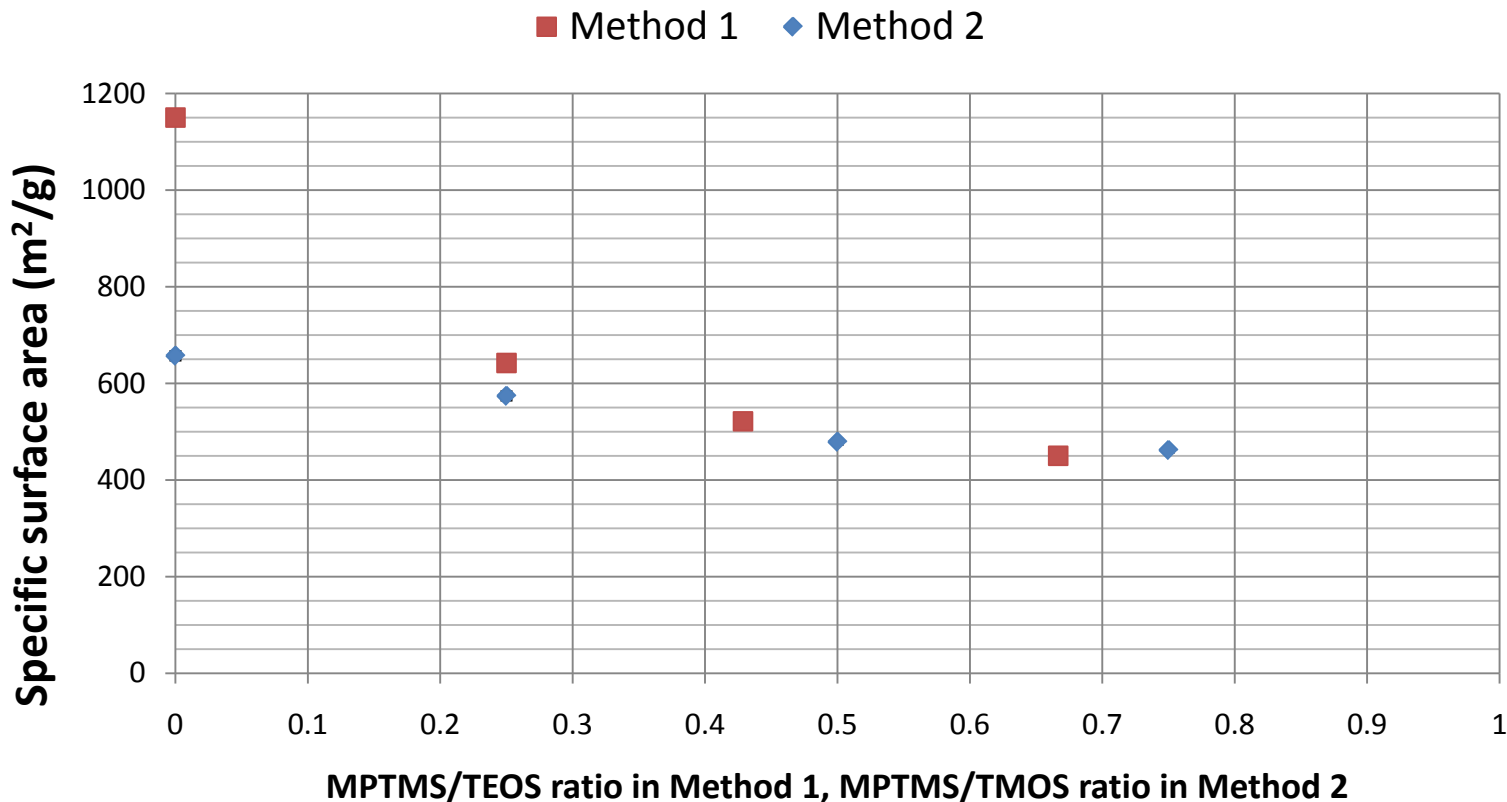
Approach: Milestones and GNG Criterion; Current Status

- Milestone 1 (End of Phase 1; Q1; 2012 [calendar year])
 - Synthesize a support that demonstrates at least:
 - 70 mS/cm proton conductivity [Current status ~ 40 mS/cm; stand-alone]
 - 2 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
 - 50 m²/g BET surface area [Current status > 250m²/g]
 - Durability* in acidic electrolyte [Current status - ongoing]
- Milestone 2 (End of Phase 2; Q3; 2013)
 - Synthesize a support that demonstrates at least:
 - 100 mS/cm proton conductivity [Current status ~ 40 -50 mS/cm; stand-alone]
 - 5 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
 - 50 m²/g BET surface area [Current status > 250m²/g]
 - Durability* in acidic electrolyte [Current status - ongoing]
 - Prepare Pt-catalyzed supports [Current Status: Not yet started]
 - Identify optimal ionomer loading in electrode [Current Status: Not yet started]
 - Prepare 6 100 cm² 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 m²/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”

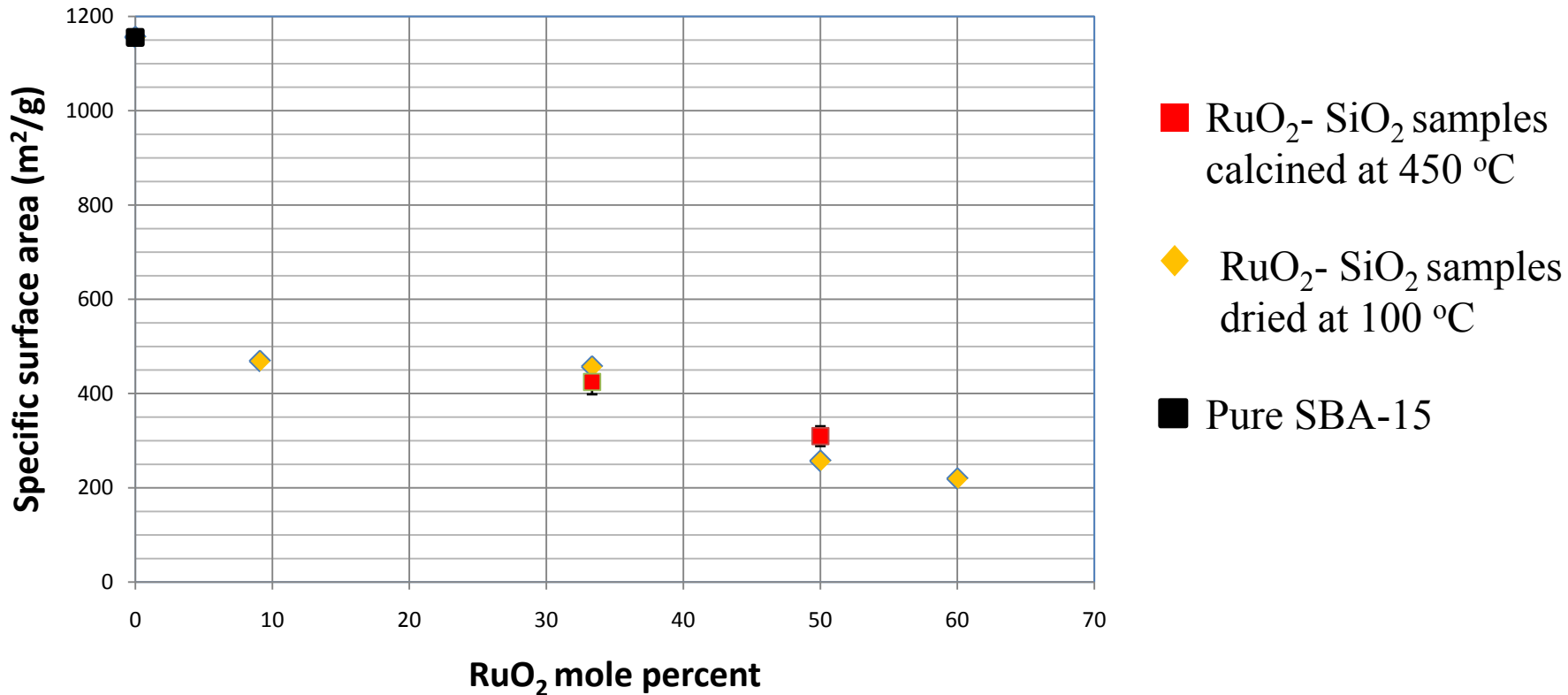
Technical Accomplishments: BET Surface Area of Sulfonic Acid Functionalized SiO₂



- 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

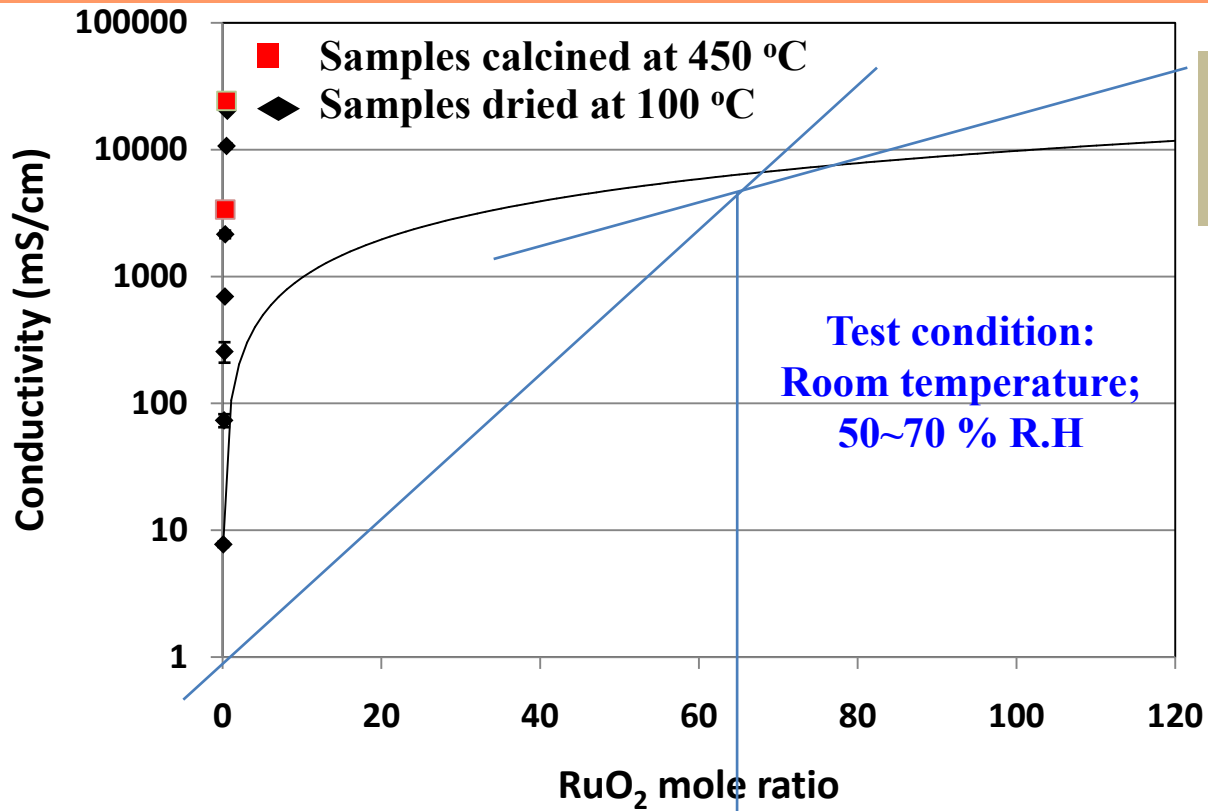
*Marschall *et al.*, Small, 5 (2009) 854

Technical Accomplishments: BET Surface Area of SiO₂ and RuO₂-SiO₂



- Surface area decreases with mol% RuO₂
- Trend is consistent with expectation – RuO₂ has low specific surface area (14 m²/g)
- Even with high RuO₂ 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

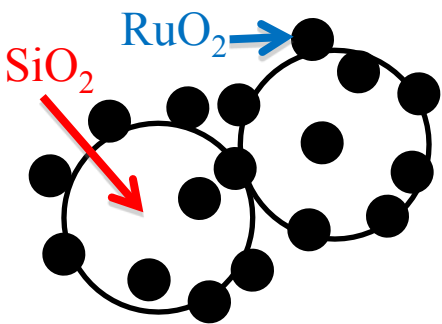
Technical Accomplishments: Electrical Conductivity of RuO₂-SiO₂



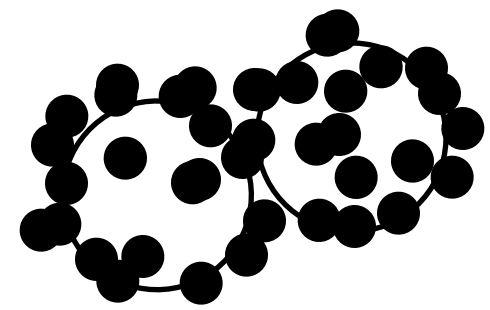
• Samples calcined at 450 °C have higher conductivity.

RuO₂ particles are dispersed without contacting each other.

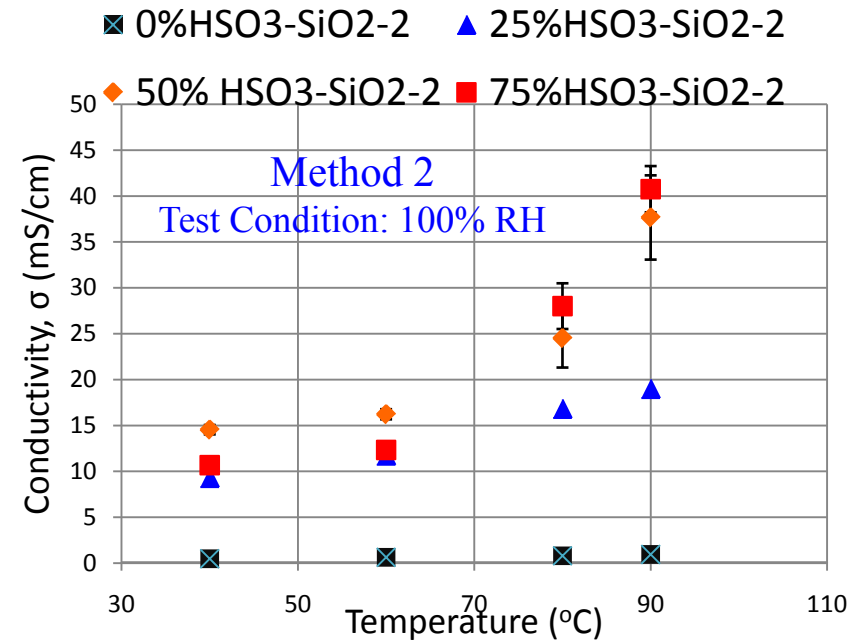
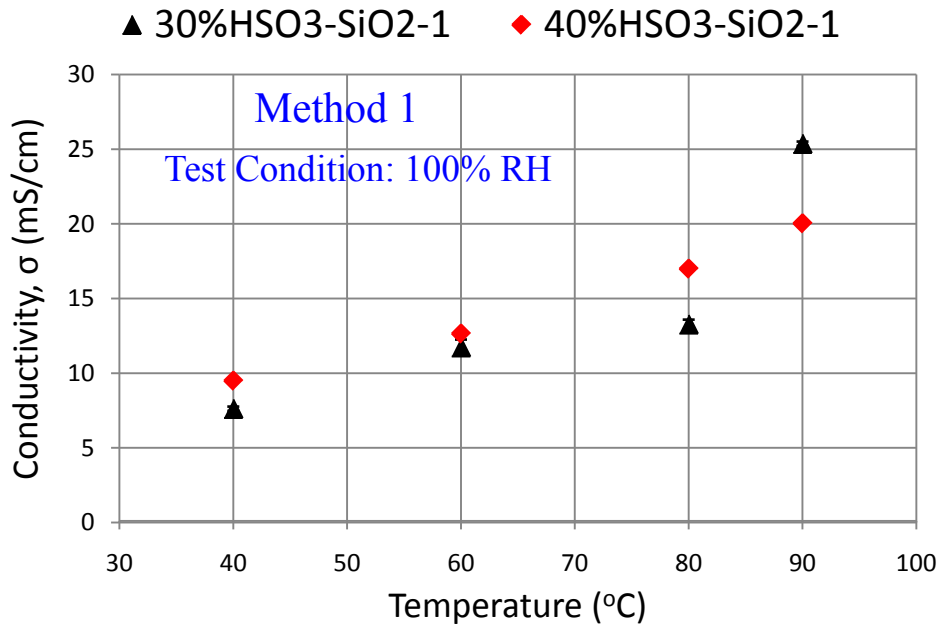
RuO₂ particles are in good contact with each other.



- The stand-alone electrical conductivity already exceeds milestones.
- The next step is to impregnate RuO₂ onto supports with sulfonic acid functionalization



Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO₂ Prepared by Methods 1 and 2



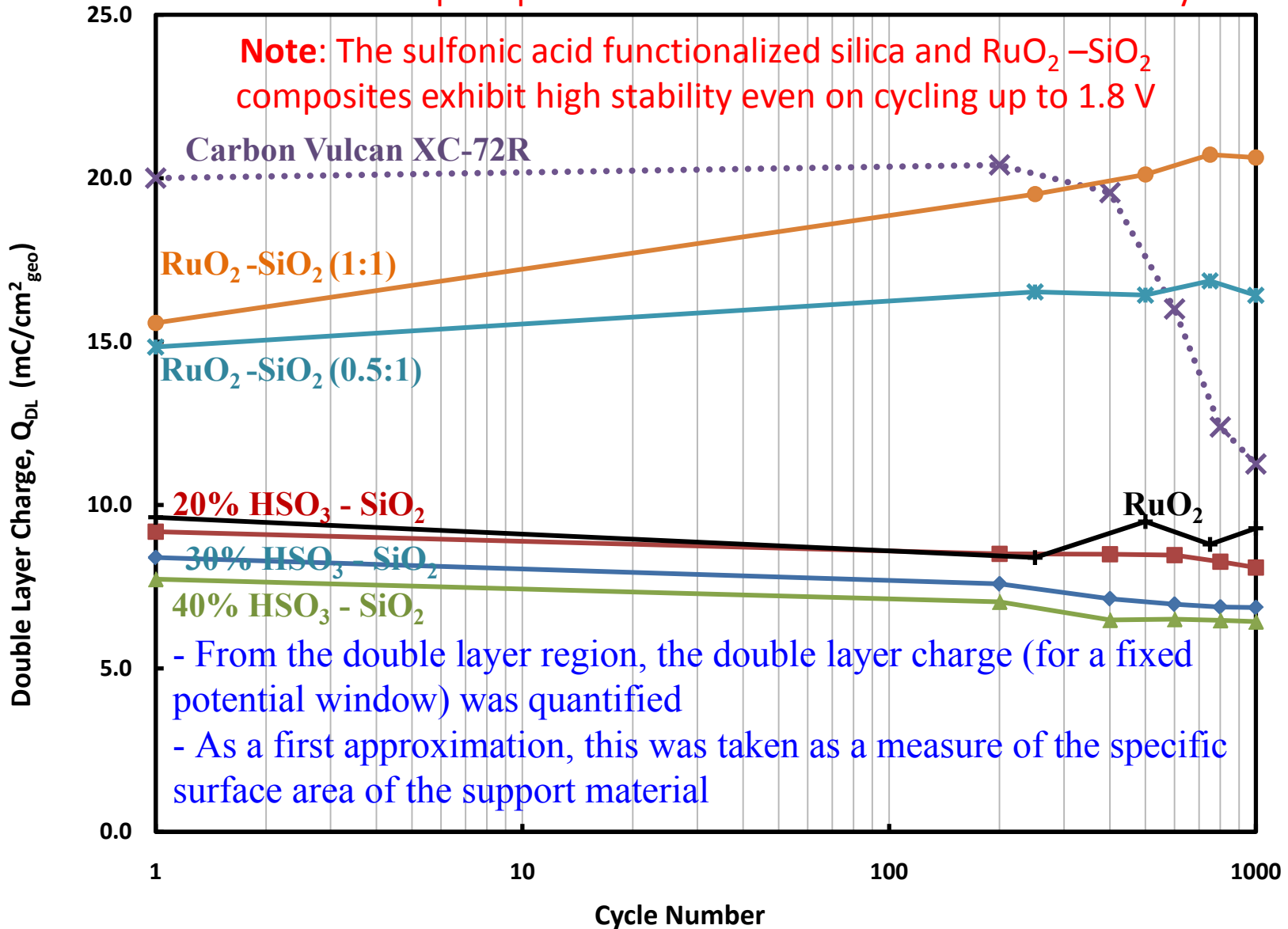
-The stand-alone proton conductivity currently tops out at 40 mS/cm at 90C and 100% RH (Method 2)

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

-Will introduce supercritical drying procedures in conjunction with study of alternate precursors (e.g. functionalized POSS) to further enhance surface functionalization and surface area

Technical Accomplishments: Stability of the Catalyst Supports Prepared Upon Potential Cycling (Tests done at IIT)

Note: 44% drop in specific surface area for carbon after 1000 cycles



Summary of Technical Accomplishments

- Proton and electron conducting metal oxides have been synthesized in support of project objectives with
 - Stand-alone proton conductivities > 40 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 m²/g
(50 m₂/g overall target)
 - Excellent durability upon aggressive potential cycling
(1000 cycles to 1.8V vs. RHE)
- In collaboration with Nissan North America Inc., extensive benchmarking of state-of-the-art electrocatalysts and electrocatalyst supports has been performed
 - This is further discussed under collaborations.

Collaboration with Nissan, North America

- Nissan North America Inc. is a key project partner from industry
 - Dr. Kev Adjemian is PI from Nissan North America Inc.
 - Will receive 50% of DOE share of the budget as a subcontract from IIT
 - 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

Catalyst Information



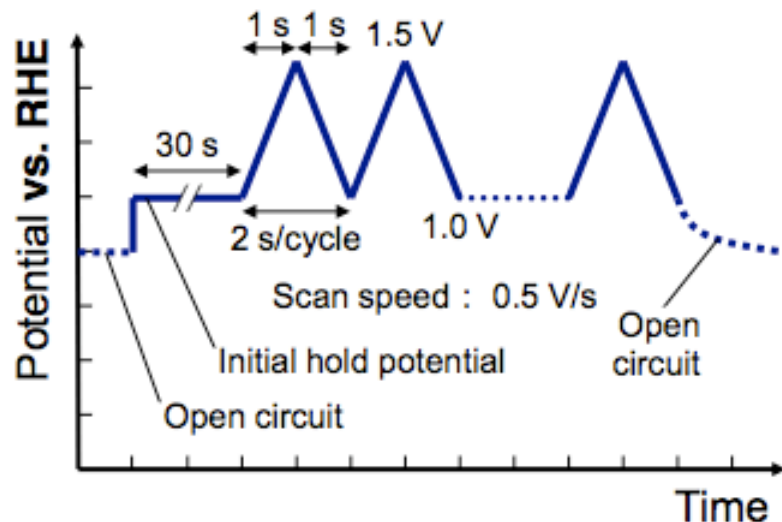
	High Surface Area Carbon (HSAC)	Heat Treated HSAC	Graphitized HSAC	Vulcan	Vulcan
Pt loading (wt%)	46.1% Pt	50.5 % Pt	46.3 % Pt	29.1 % Pt	45.7 % Pt
Carbon Support	HSAC	HSAC heat treated	Graphitized HSAC	Vulcan XC72	Vulcan XC72
Pt Particle Size (nm)	2.6	4.6	2.3	NA	2.3
BET Surface Area (m ² /g)	310.5	395.7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



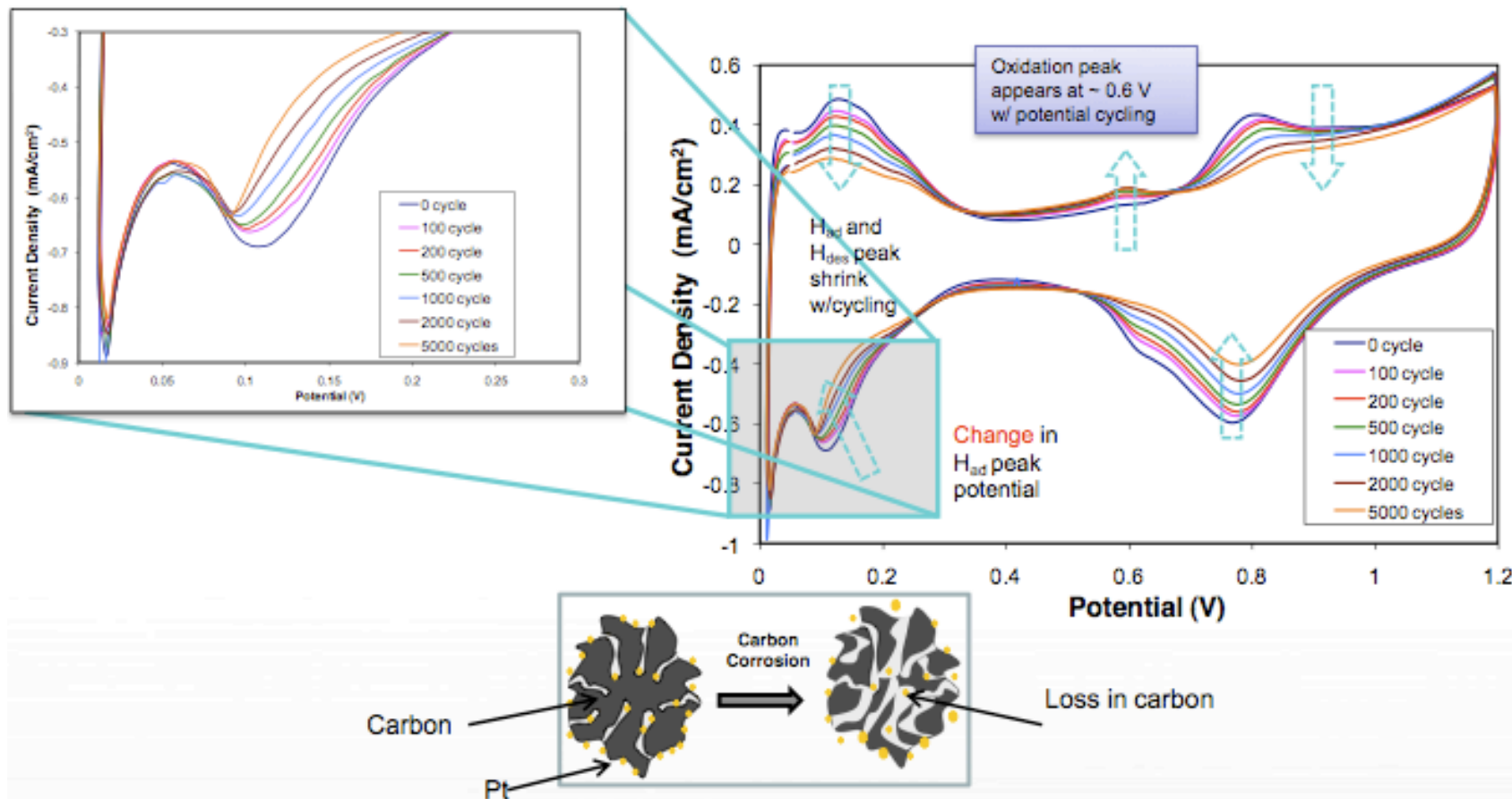
Temperature / °C		60
Solution	Electrolyte	0.1 M HClO ₄
	Dissolved gas	Saturated with N ₂ or Ar
	Reference Electrode	RHE
	Counter Electrode	Pt gauze

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

(Indispensable item: Electrochemical area)

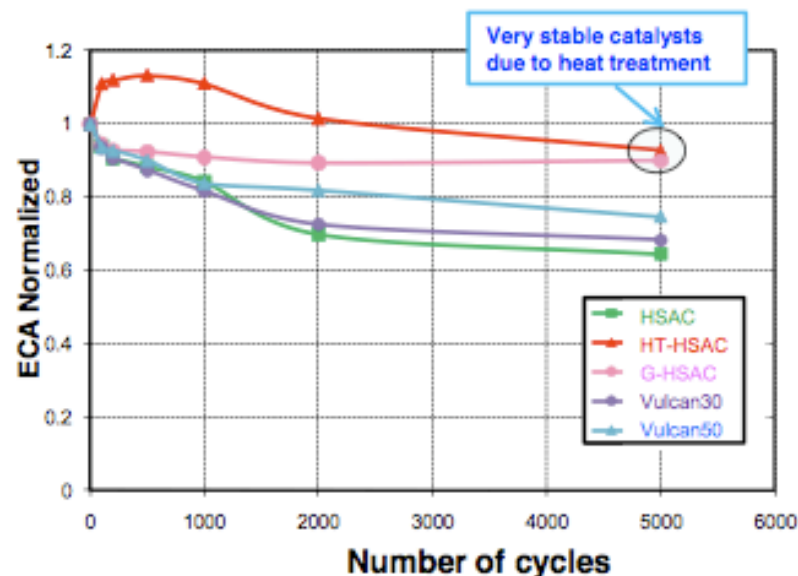
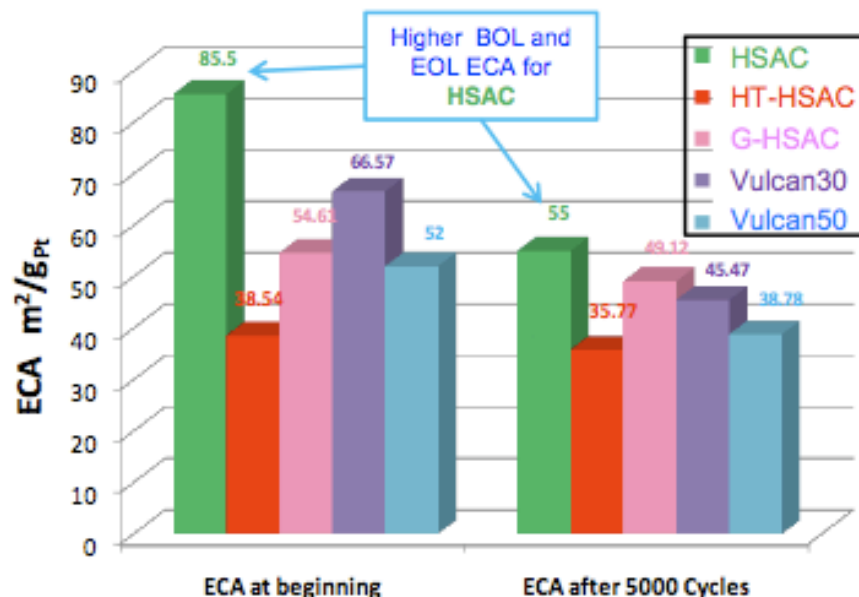
Collaboration with Nissan, North America - Benchmarking

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

Carbon Support Corrosion Evaluation Comparison RDE

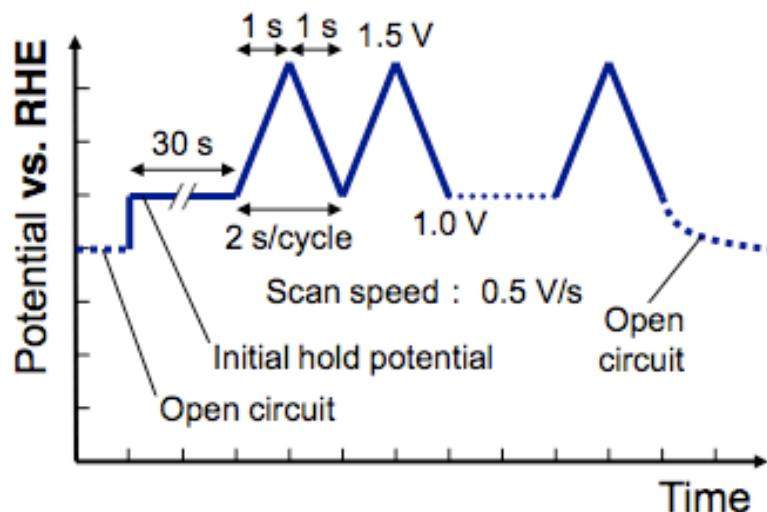


Catalyst	% ECA Loss
HSAC	~ 36%
HT-HSAC	~ 7%
G-HSAC	~ 10%
Vulcan30	~ 32%
Vulcan50	~ 25%

- **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

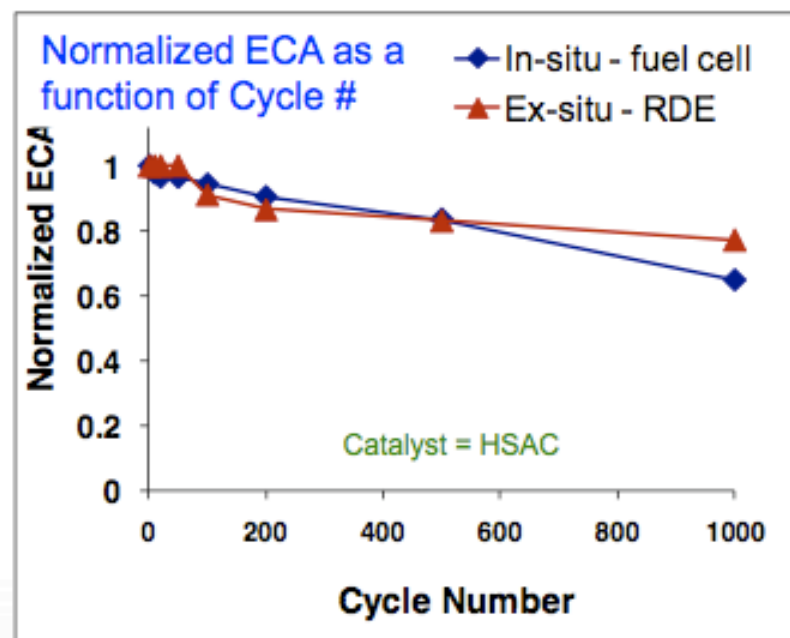
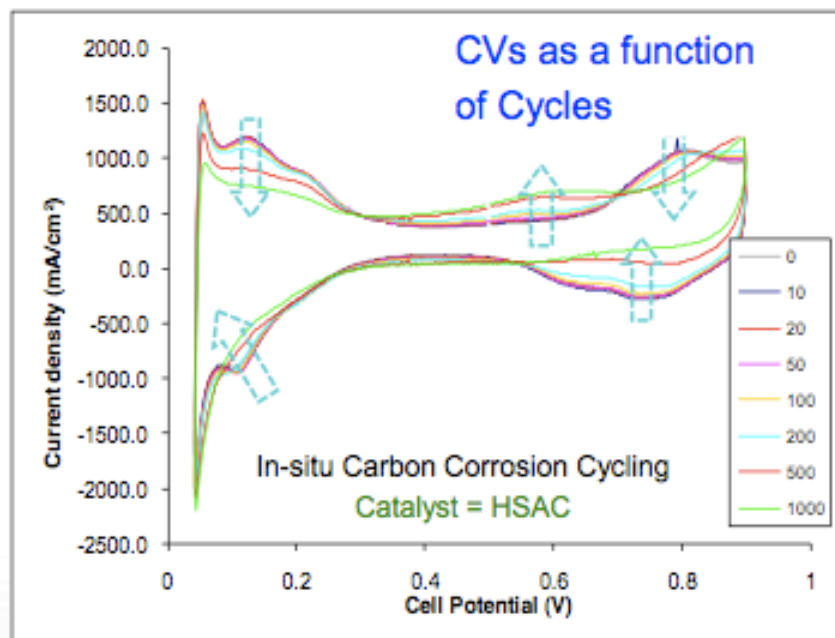
(Indispensable item: Electrochemical area)

At high voltage, carbon oxidation reaction (carbon corrosion) accompanies the H₂O 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

Proposed Future Work

- **Future directions in FY 11:**
 - **Explore alternate precursors in conjunction with supercritical drying and precursor ratio optimization to enhance proton conductivity of functionalized silica (Task 1)**
 - **Study and quantify mixed-conductivity (as opposed to stand-alone proton/electron conductivities) in $\text{SiO}_2:\text{SO}_3\text{H-RuO}_2$ composites (Task 1)**
 - **Work in conjunction with Nissan North America Inc. to finish durability testing (Task 2)**
 - **Introduce platinum nanoparticles onto durable mixed-conducting supports; evaluate specific and mass activities, and stability under cycling (Task 1,3)**
- **Future directions in FY 12**
 - **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 (Task 4)**

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 GM protocol
- < 30mV electrocatalyst support loss after 100 hrs at 1.2 mV; tested per GM protocol

Approach:

- Sequentially functionalize high surface area silica to introduce proton/electron conductivity
 - Ruthenium oxide used as model electron conducting functionality
 - Sulfonic acid groups introduced to provide proton conductivity
 - 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

Accomplishments/Progress

Proton/electron conducting metal oxides have been synthesized with

- Stand-alone proton conductivities > 40 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 m²/g (50 m₂/g overall target)
- Excellent durability upon aggressive potential cycling (1000 cycles to 1.8V vs. RHE)

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

Proposed work for FY11

- Explore alternate precursors in conjunction with supercritical drying and precursor ratio optimization to enhance proton conductivity of functionalized silica (Task 1)
- Study and quantify mixed-conductivity (as opposed to stand-alone proton/electron conductivities) in SiO₂:SO₃H-RuO₂ composites (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 (Task 1,3)

Back-up Slides

Acronyms Used in Presentation

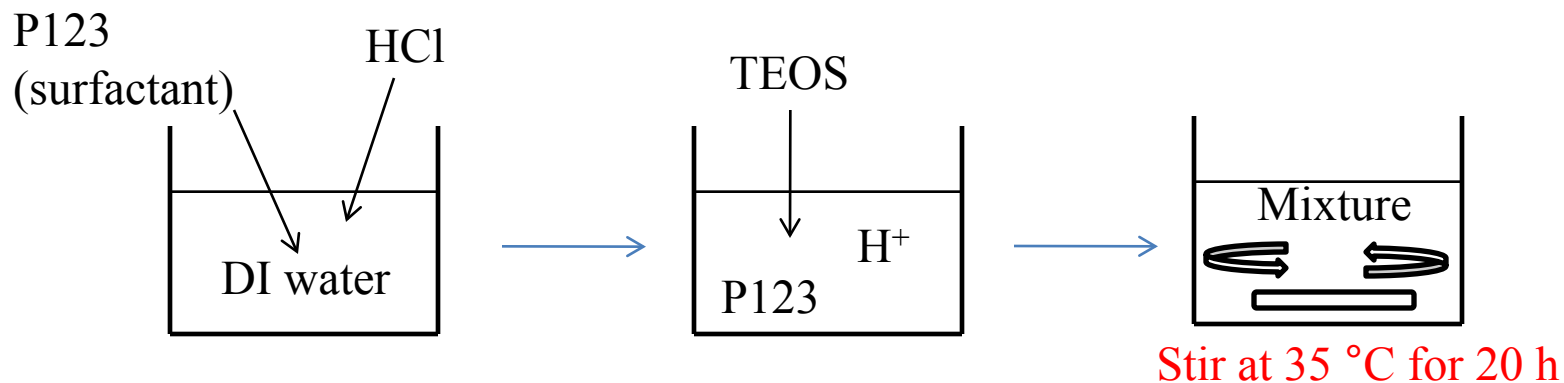
TEOS	Tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$
TMOS	Tetramethyl orthosilicate, $\text{Si}(\text{OCH}_3)_4$
MPTMS	3-mercaptopropyl trimethoxysilane, $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
SBA-15	Santa Barbara Amorphous type SiO_2
P123	Pluronic P [®] -123, a triblock copolymer
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
RuO ₂ -SiO ₂ (x:1)	RuO ₂ deposited on SiO ₂ . The mole ratio of RuO ₂ :SiO ₂ is x:1	RuO ₂ -SiO ₂ (x: 1), Where x=0, 0.24, 0.3, 0.33, 0.5 or 0.6
Pt/ RuO ₂ -SiO ₂ (x:1)	Pt deposited on RuO ₂ -SiO ₂ .	Pt/ RuO ₂ -SiO ₂ (x:1) Where x=0.33
X % sulfonic acid functionalized SiO ₂ -1	Sulfonic acid functionalized silica. The mol % of the functionalized domain is X. The material was prepared by method 1.	X% HSO ₃ -SiO ₂ -1, where X= 20, 30, or 40
X % sulfonic acid functionalized SiO ₂ -2	Sulfonic acid functionalized silica. The mol % of the functionalized domain is X. The material is prepared by method 2.	X% HSO ₃ -SiO ₂ -2, where X=0, 25, 50, or 75

Approach: Synthesis of SBA-15

SBA-15 was synthesized as follows

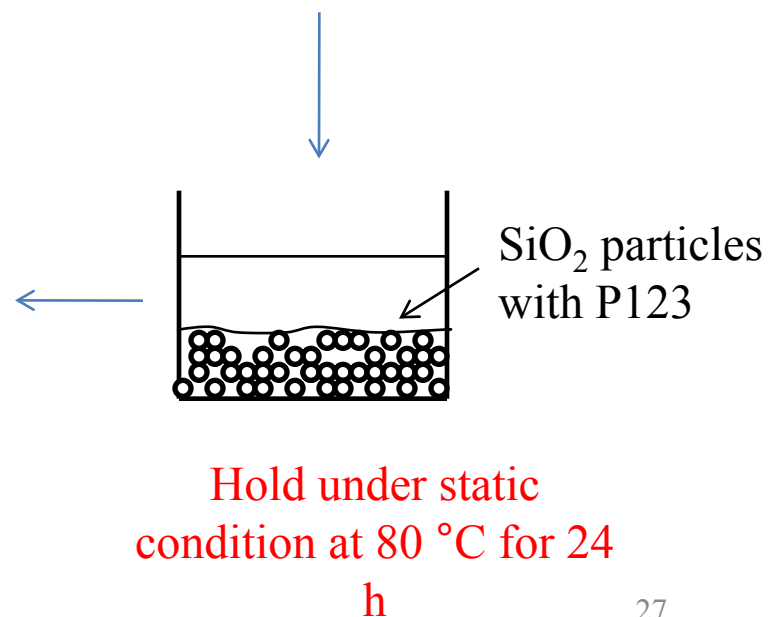


The molar composition of SiO₂ for 18 g P123 was:
0.19mols TEOS : 1.01mols HCl : 31.12mols H₂O



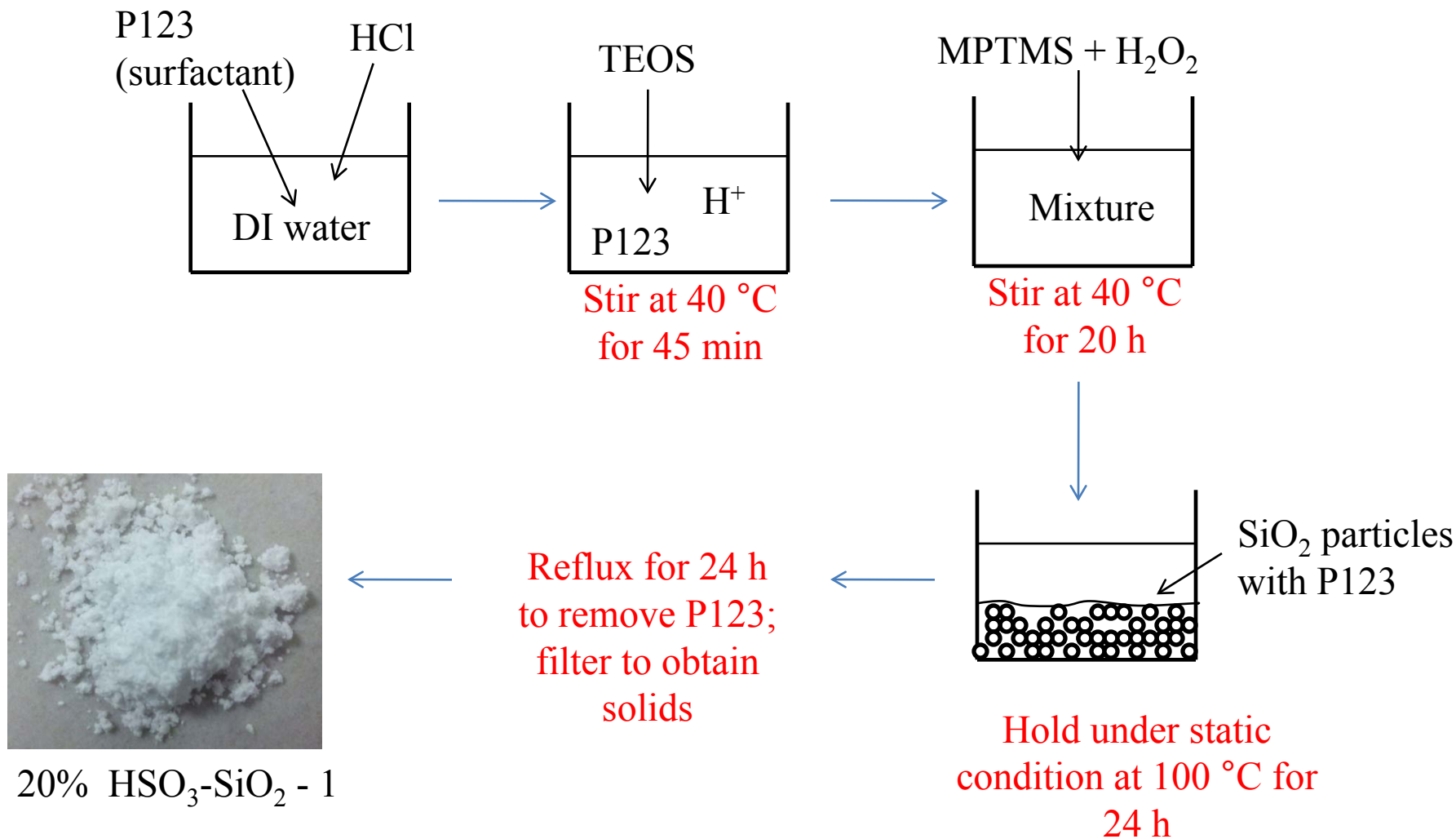
SBA-15 SiO₂

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

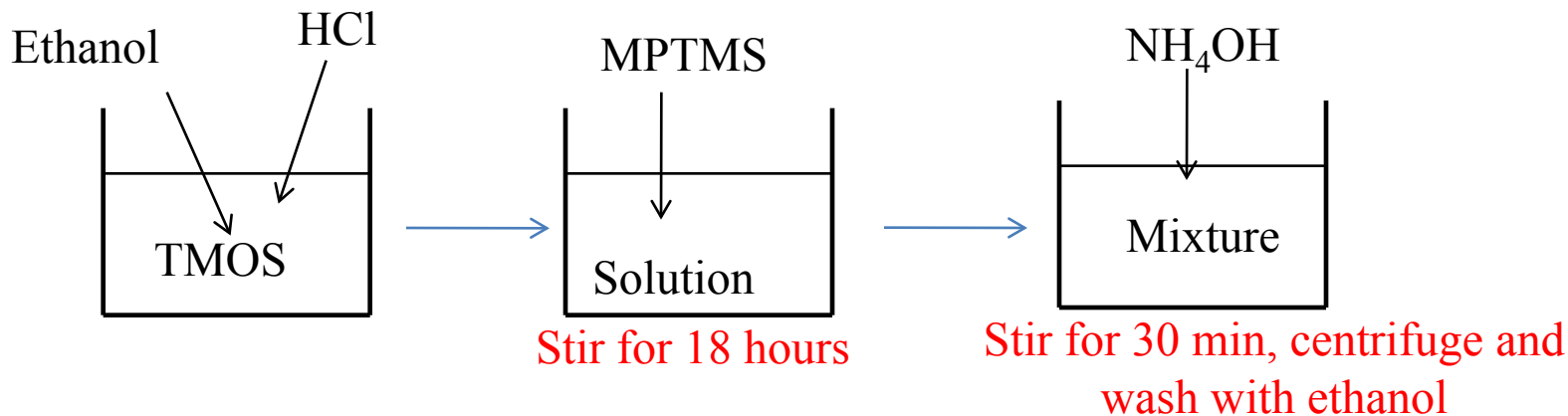


Approach: Synthesis of Sulfonic Acid Functionalized SiO₂ – Method 1

The molar composition used to prepare 20% functionalized SiO₂ with 4 g P123 was:
0.0328 mols TEOS : 0.0082 mols MPTMS: 0.0369 mols H₂O₂ : 0.24 mols HCl : ~6.67 mols H₂O



Approach: Synthesis of Sulfonic Acid Functionalized SiO₂ – Method 2



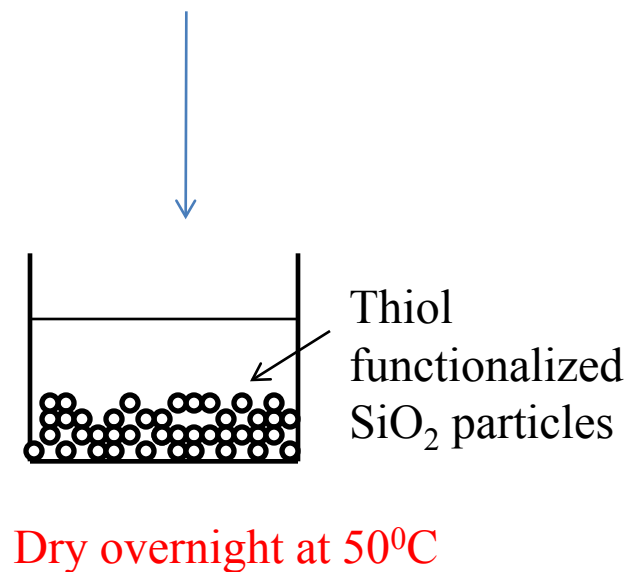
Ratio of starting materials is:
(TMOS+MPTMS):H₂O:C₂H₅OH:HCl= 1:30:10:6
For 25% HSO₃-SiO₂-2, ratio of TMOS:MPTMS=0.25:0.75

X%HSO₃-SiO₂-2



25%HSO₃-SiO₂-2

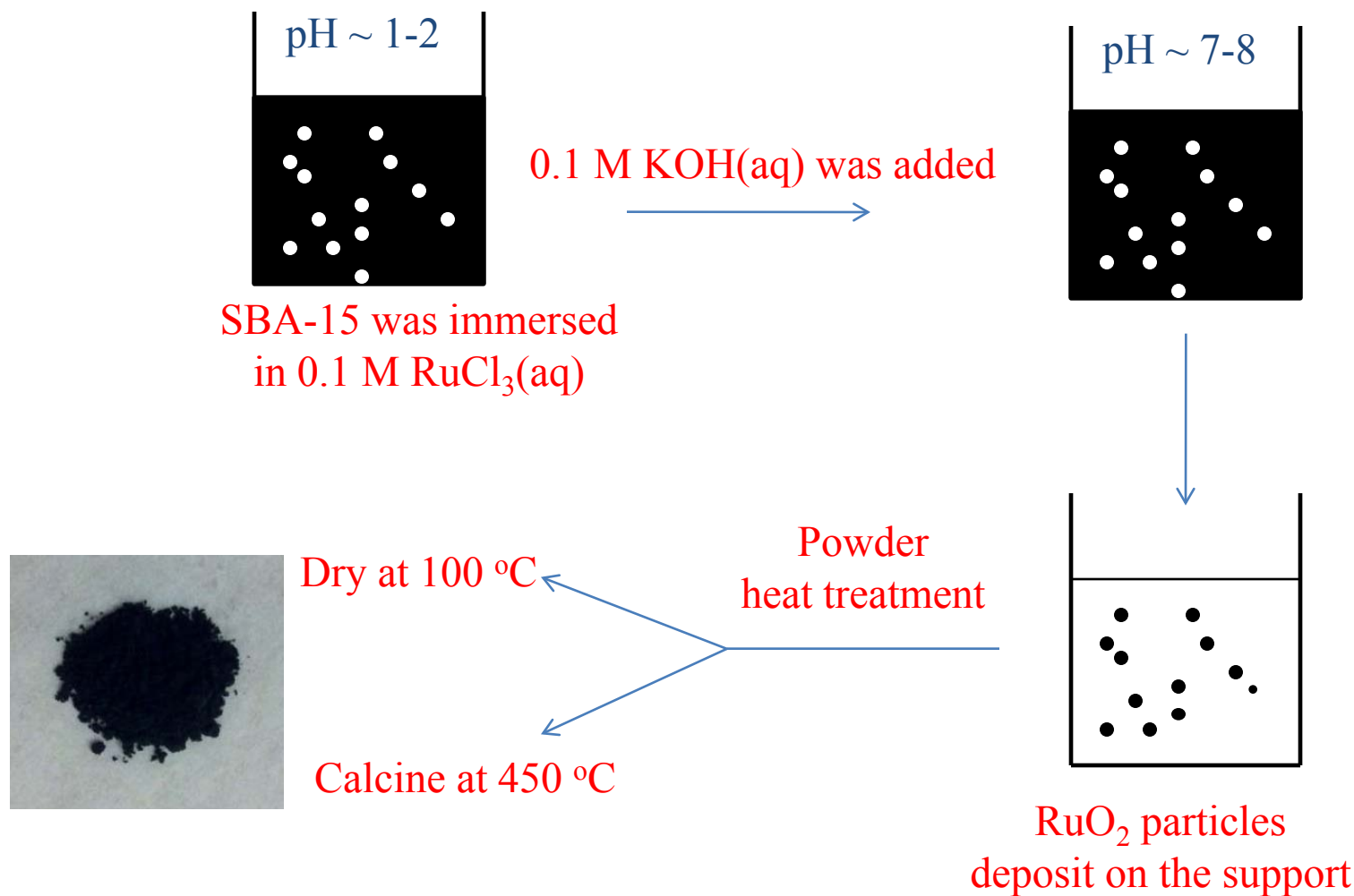
Oxidize the thiol group to sulfonic acid using 35% H₂O₂



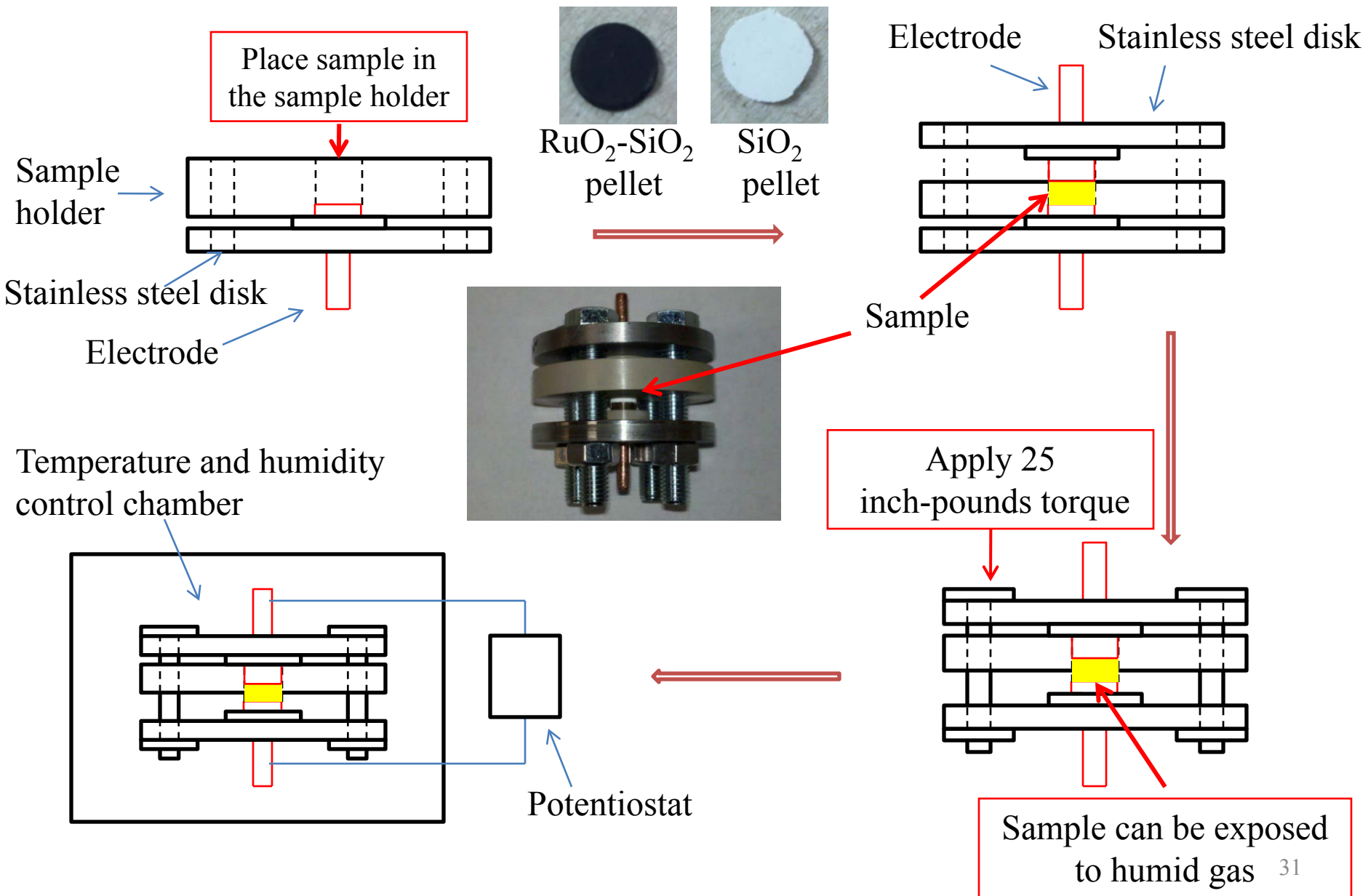
Approach: Synthesis of RuO₂-SiO₂ Composites: RuO₂ deposition

RuO₂-SiO₂ composites were prepared by depositing RuO₂ on SBA-15.

The mole ratio of RuO₂:SiO₂ was: 0~0.6 :1



Approach: Conductivity Measurements



Approach: Potential Cycling to Estimate Support Stability

- Three Electrode Cell with Rotating Disk Electrode
 - Working Electrode : Glassy carbon 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.: $200 \mu\text{g}/\text{cm}^2_{\text{geo}}$
- Pt loading: $50 \mu\text{g}/\text{cm}^2_{\text{geo}}$
- Potential cycling protocol
 - Range: 0 V to 1.8 V back to 0V (vs. RHE)
 - Perform 1000 cycles at 1 V/s
 - Record CV (at 10 mV/s) every 200-250 cycles

