Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

PI: Vijay K. Ramani

Department of Chemical and Biological Engineering

Illinois Institute of Technology

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Project ID #

FC085

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Overview

Timeline

- Project start date: 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 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 **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 mV after 100 hrs at 1.2 V, per GM protocol).

Approach: Material Studied and Desired Properties

We are investigating mixed metal oxides (SiO_2-RuO_2) 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 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
  - > 5-10 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
- **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 cm^2 MEAs
    - Development of cost model.

Approach: Milestones and GNG Criterion; Current Status

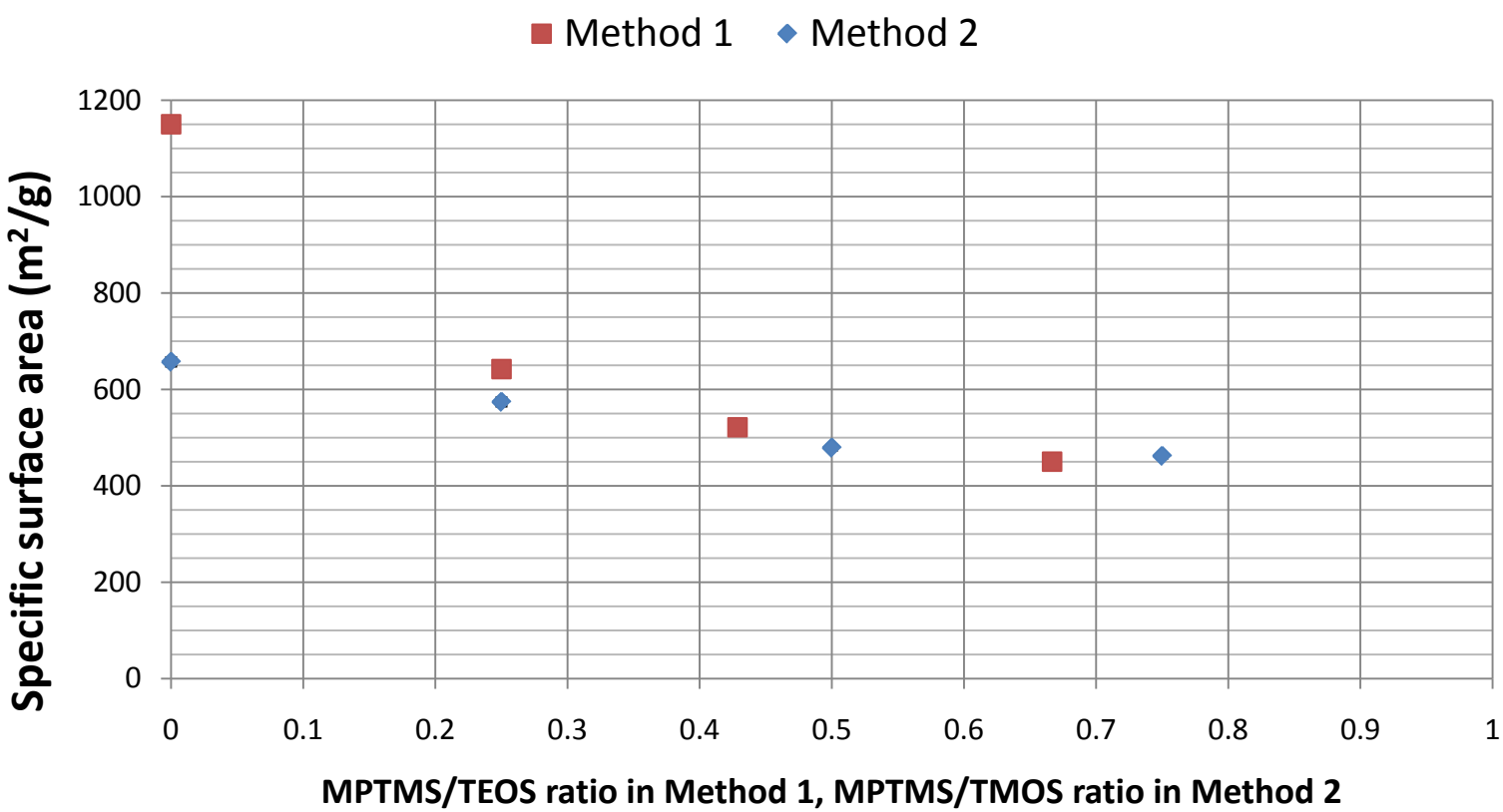
- Milestone 1 (End of Phase 1; Q1; 2012 [calender year])
  - Synthesize a support that demonstrates at least:
    - 70 mS/cm proton conductivity [Current status ~ 40 mS/cm; stand-alone]
    - 2 S/cm electron conductivity [Current status ~ 10 S/cm; stand-alone]
    - 50 m^2/g BET surface area [Current status > 250m^2/g]
    - Durability* in acidic electrolyte [Current status - 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 ~ 40 -50 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 - ongoing]
  - Prepare Pt-catalyzed supports [Current Status: Not yet started]
  - 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*"

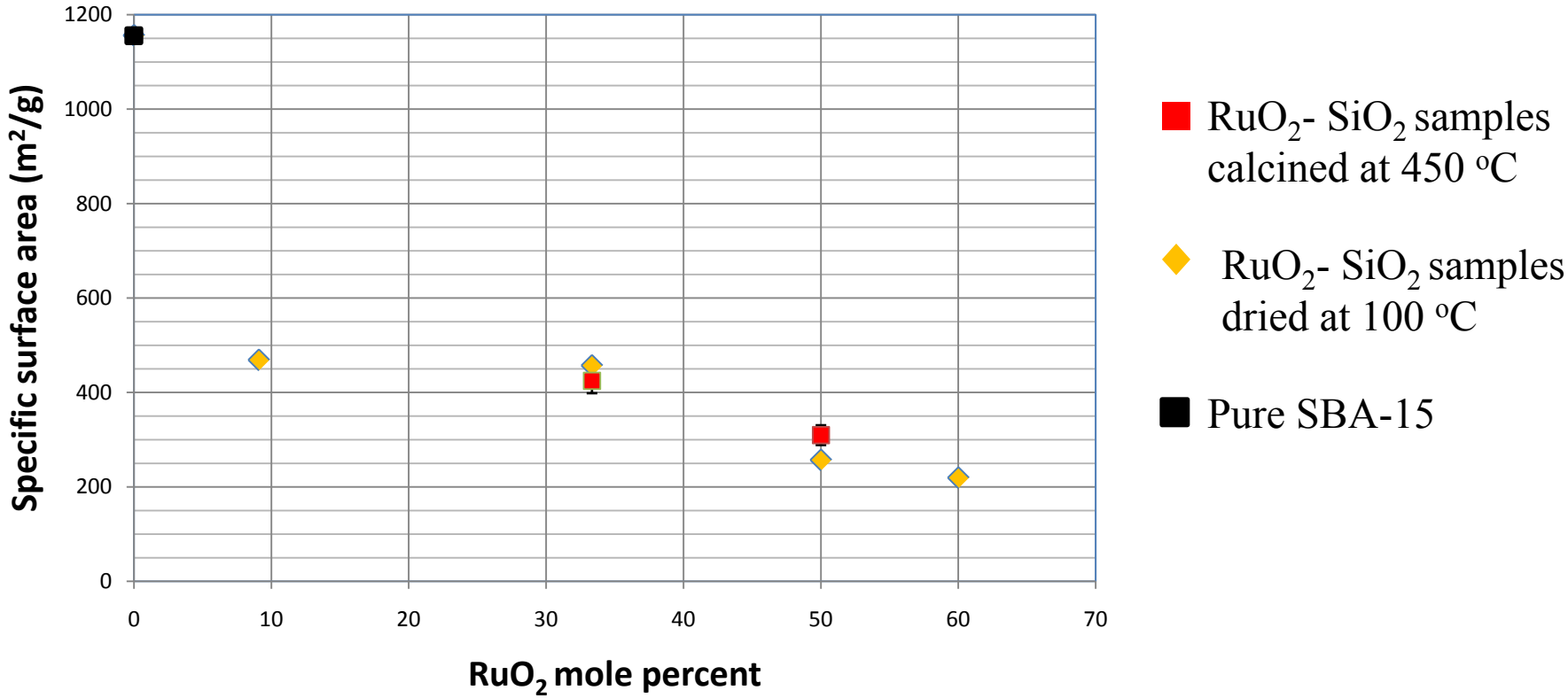
Technical Accomplishments: BET Surface Area of Sulfonic Acid Functionalized SiO_2



- 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

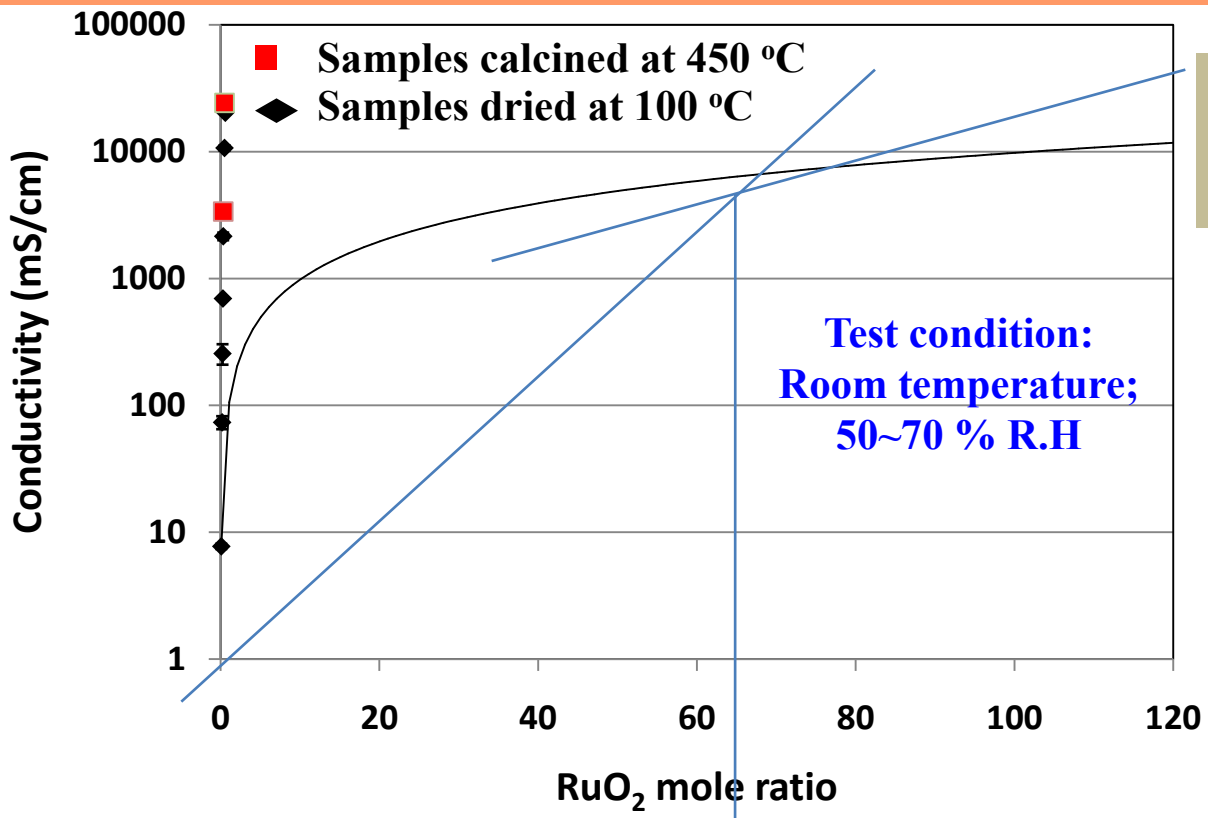
*Marschall *et al.*, Small, 5 (2009) 854

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



- 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

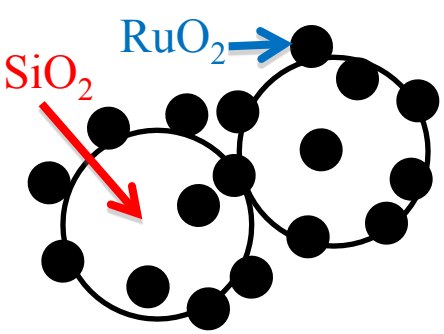
Technical Accomplishments: Electrical Conductivity of RuO_2 -SiO_2



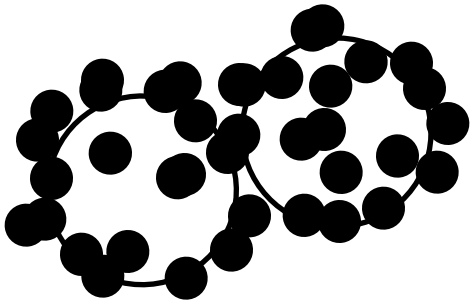
•Samples calcined at 450 °C have higher conductivity.

RuO_2 particles are dispersed without contacting each other.

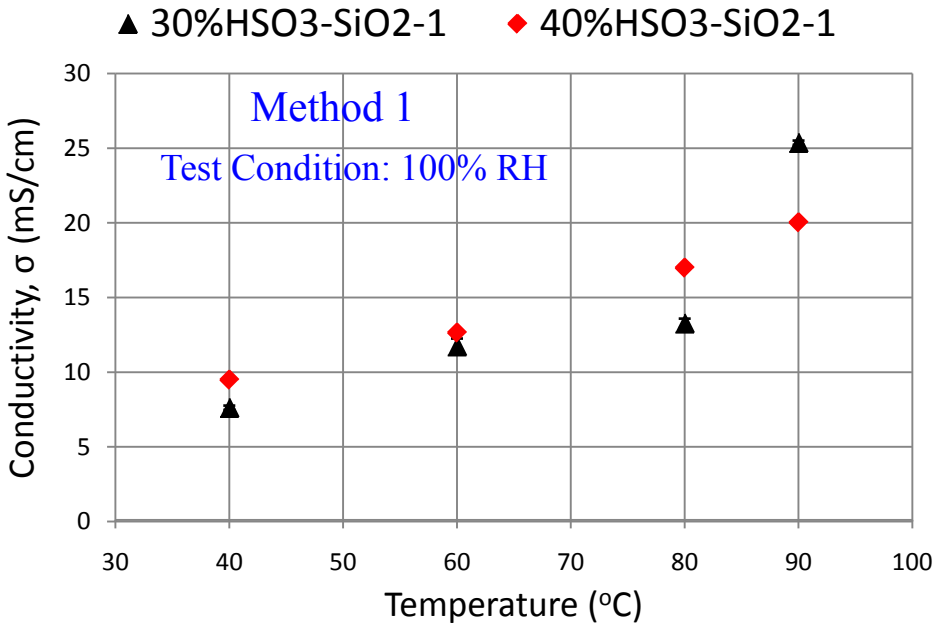
RuO_2 particles are in good contact with each other.

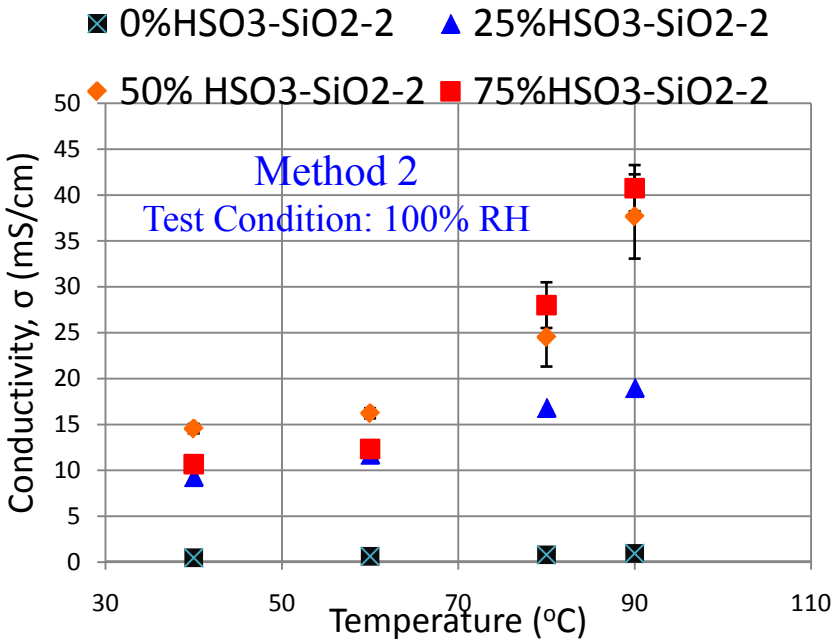


- The stand-alone electrical conductivity already exceeds milestones.
- The next step is to impregnate RuO_2 onto supports with sulfonic acid functionalization



Technical Accomplishments: Proton Conductivity of Sulfonic Acid Functionalized SiO_2 Prepared by Methods 1 and 2





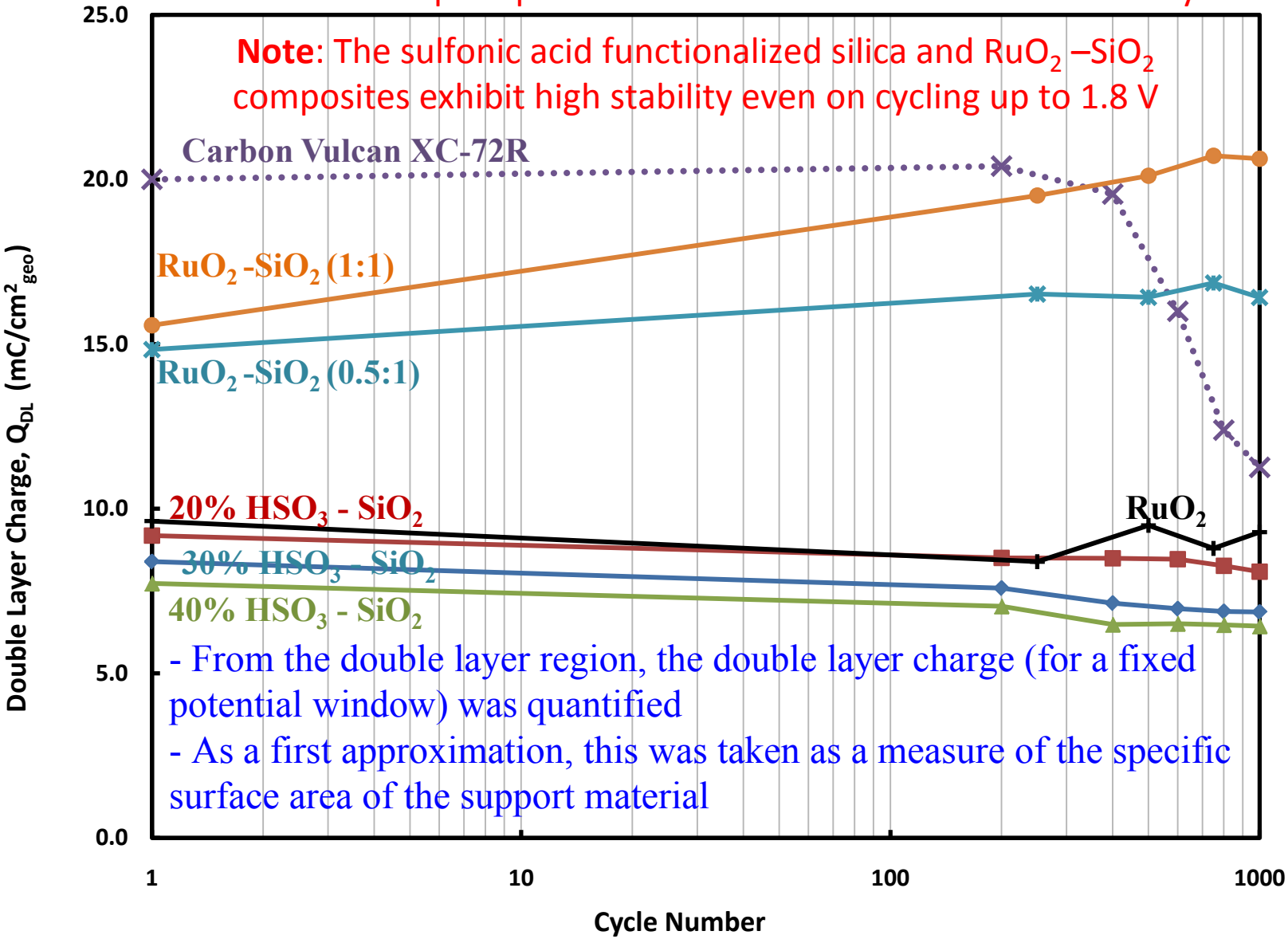
-The stand-alone proton conductivity currently tops out at 40 mS/cm at 90C and 100% RH (Method 2)

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

-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

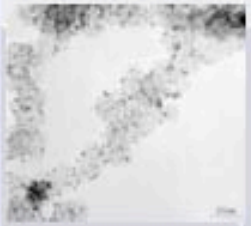
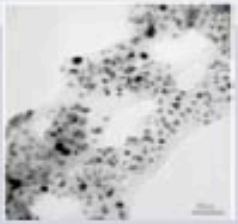
- Proton and electron conducting metal oxides have been synthesized in support of project objectives with
  - Stand-alone proton conductivities > 40 mS/cm
    (100 mS/cm overall target)
  - Stand-alone electron conductivities of > 10 S/cm
    (5 S/cm overall target)
  - BET surface areas of > 250 m^2/g
    (50 m_2/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

Collaboration with Nissan, North America - Benchmarking

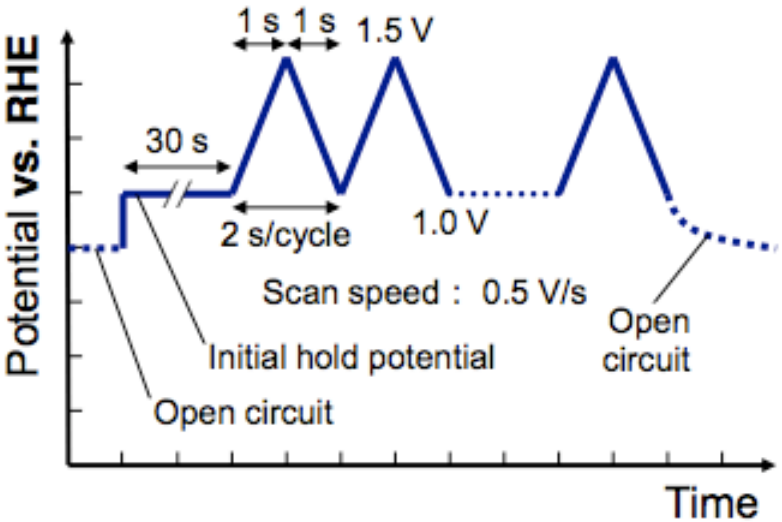
Catalyst Information

	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

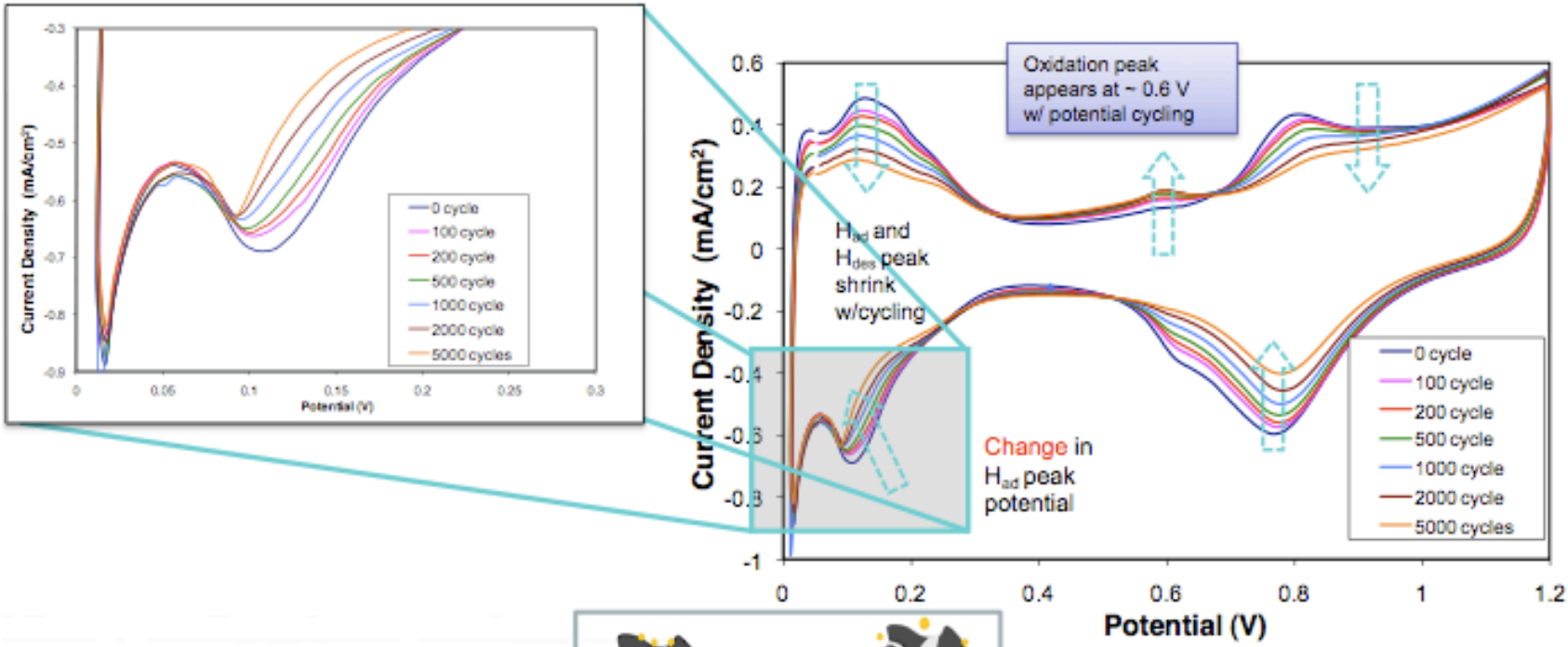
Diagnosis: CV at 0, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000 cycles

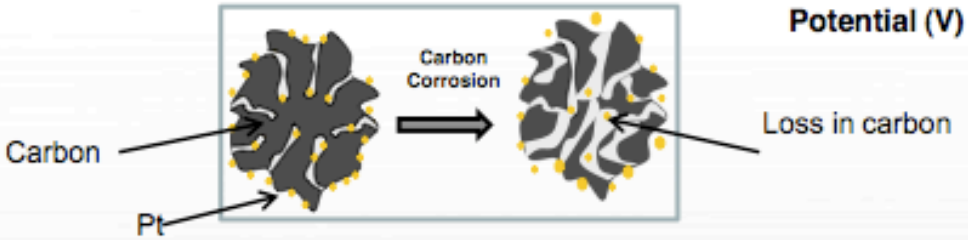
(Indispensable item: Electrochemical area)

Collaboration with Nissan, North America - Benchmarking

Catalyst Support Durability Evaluation

Example RDE: Vulcan Support

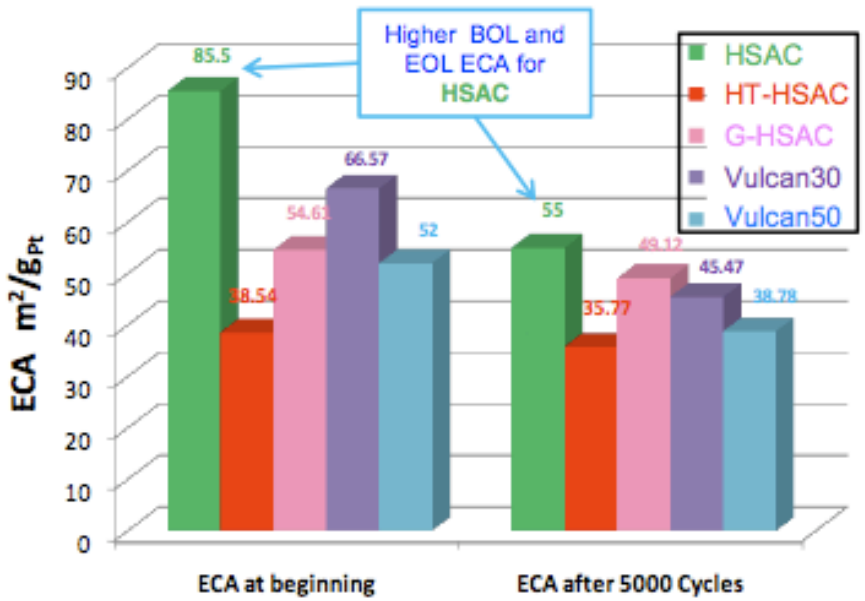


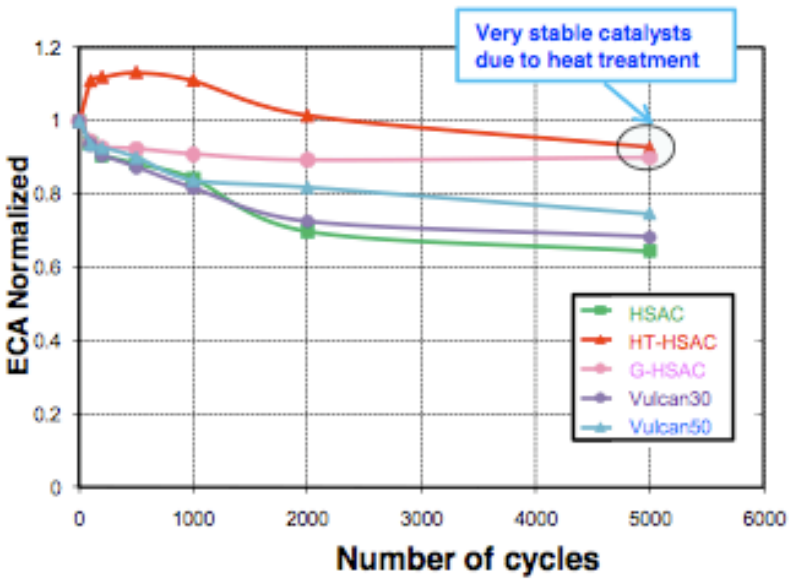


- H_{ads} peaks and oxidation peaks decreased with potential cycling.
- Double layer increased slightly with more potential cycling, as opposed to other catalyst

Collaboration with Nissan, North America - Benchmarking

Carbon Support Corrosion Evaluation
Comparison RDE



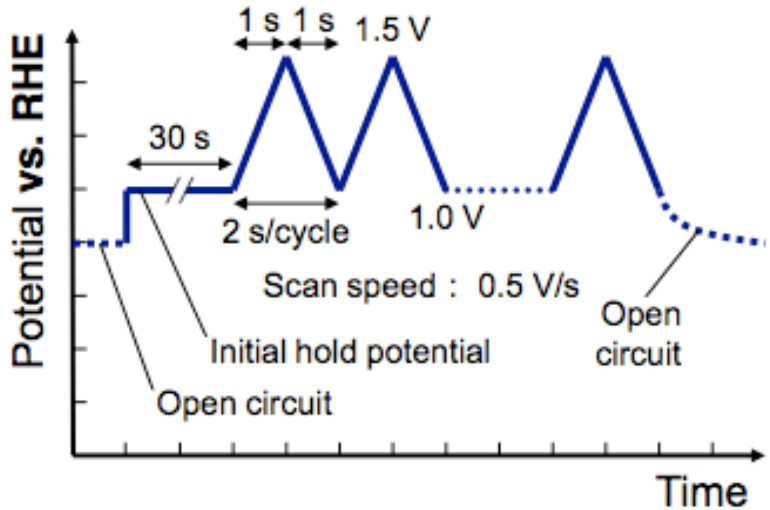


Catalyst	% ECA Loss
HSAC	~ 38%
HT-HSAC	~ 7%
G-HSAC	~ 10%
Vulcan30	~ 32%
Vulcan50	~ 25%

- 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)

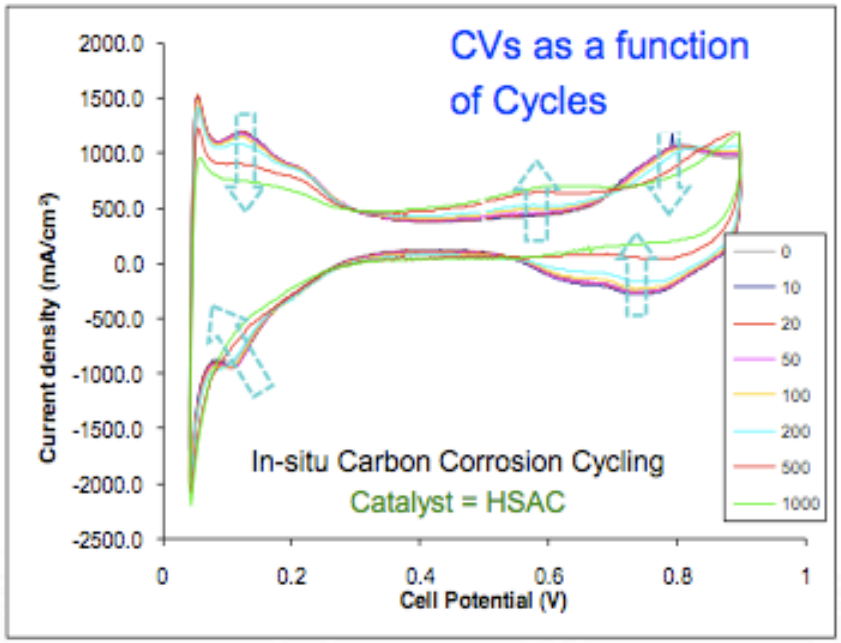
At high voltage, carbon oxidation reaction (carbon corrosion) accompanies the H_2O consumption. To prevent drying of cathode, the dew point should be set slightly above 80 °C.

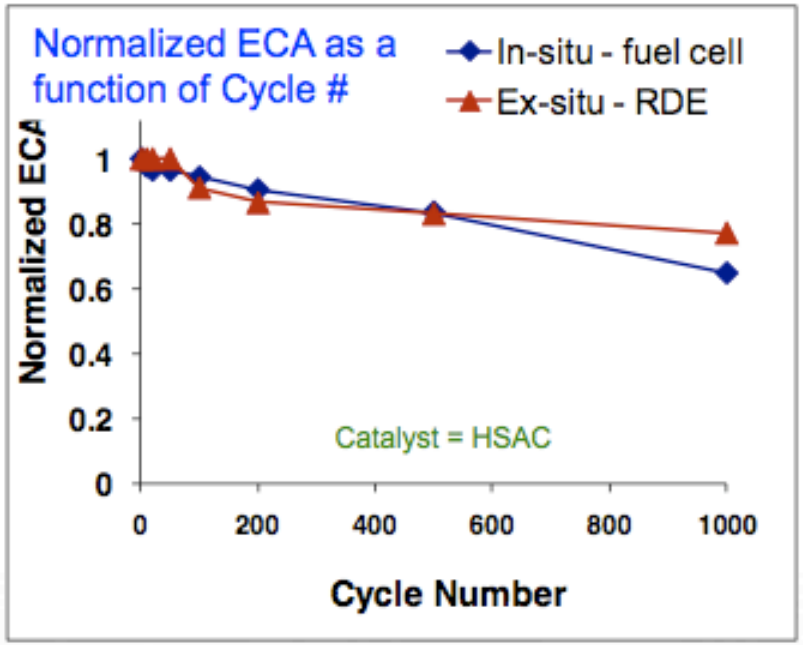
Collaboration with Nissan, North America - Benchmarking

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

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 SiO_2:SO_3H-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 m^2/g (50 m_2/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 SiO_2:SO_3H-RuO_2 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

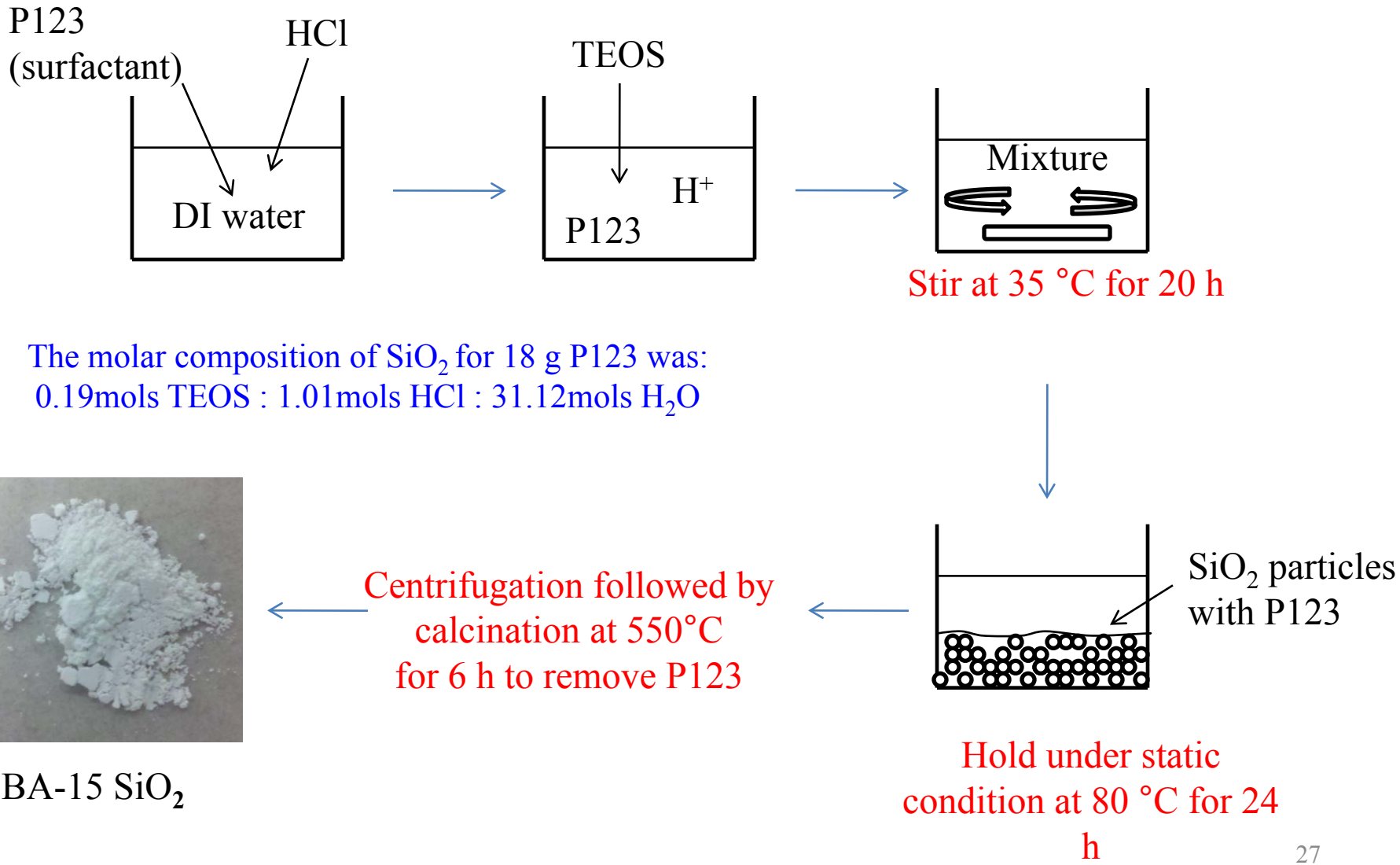
TEOS	Tetraethyl orthosilicate, $Si(OC_2H_5)_4$
TMOS	Tetramethyl orthosilicate, $Si(OCH_3)_4$
MPTMS	3-mercaptopropyl trimethoxysilane, $HS(CH_2)_3Si(OCH_3)_3$
SBA-15	Santa Barbara Amorphous type SiO_2
P123	Pluronic P®-123, a triblock copolymer
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
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
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

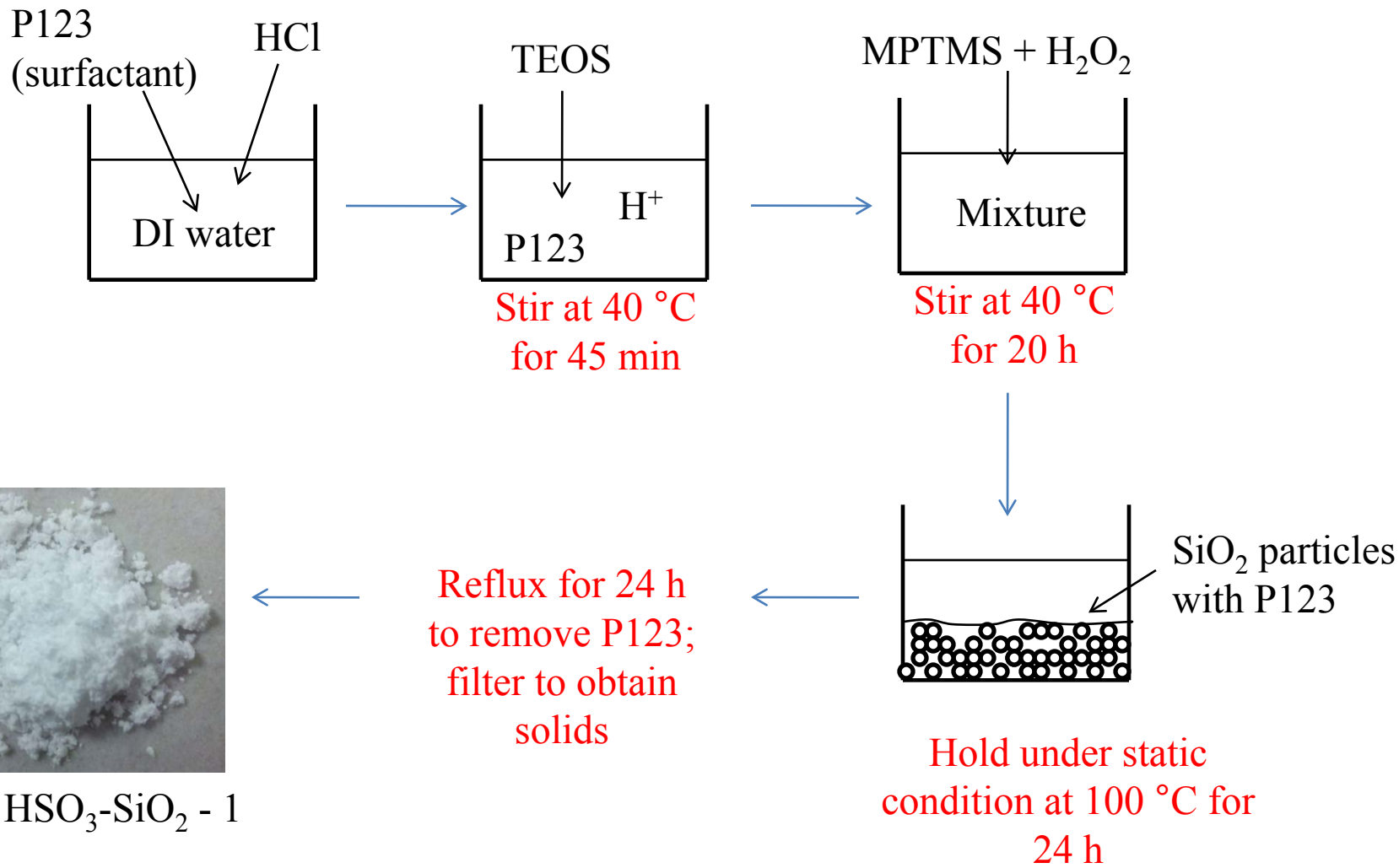


The molar composition of SiO_2 for 18 g P123 was:
0.19mols TEOS : 1.01mols HCl : 31.12mols H_2O

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

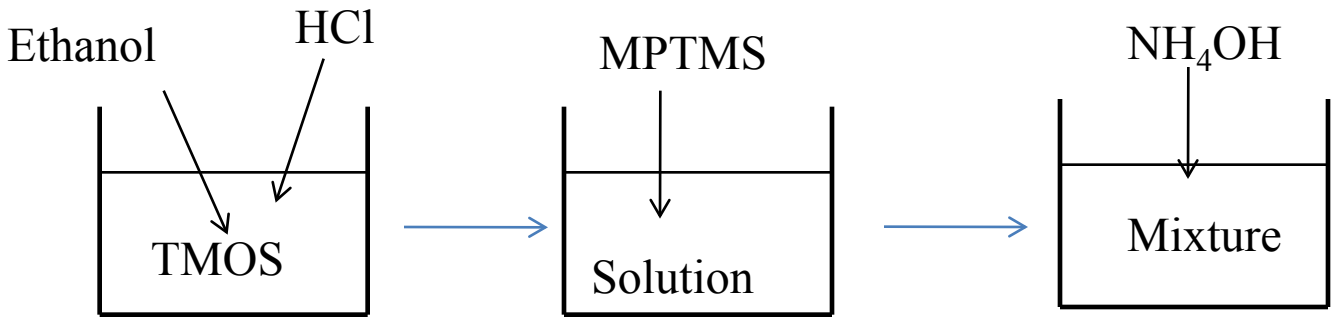
Approach: Synthesis of Sulfonic Acid Functionalized SiO_2 – Method 1

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

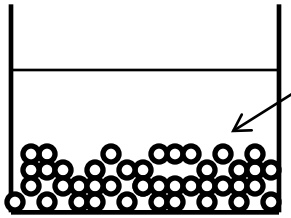
Approach: Synthesis of Sulfonic Acid Functionalized SiO_2 – Method 2



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

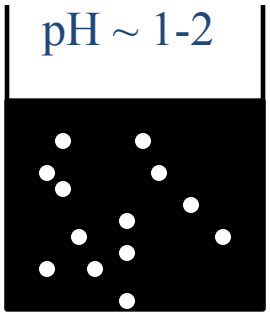
25%HSO_3-SiO_2-2

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

Approach: Synthesis of RuO_2-SiO_2 Composites: RuO_2 deposition

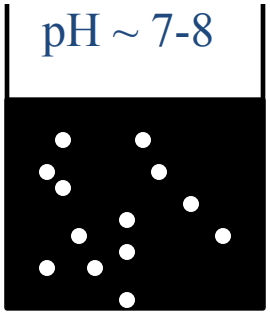
RuO_2-SiO_2 composites were prepared by depositing RuO_2 on SBA-15.

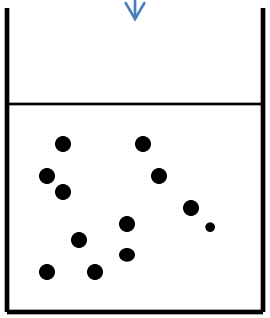
The mole ratio of RuO_2:SiO_2 was: 0~0.6 :1



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

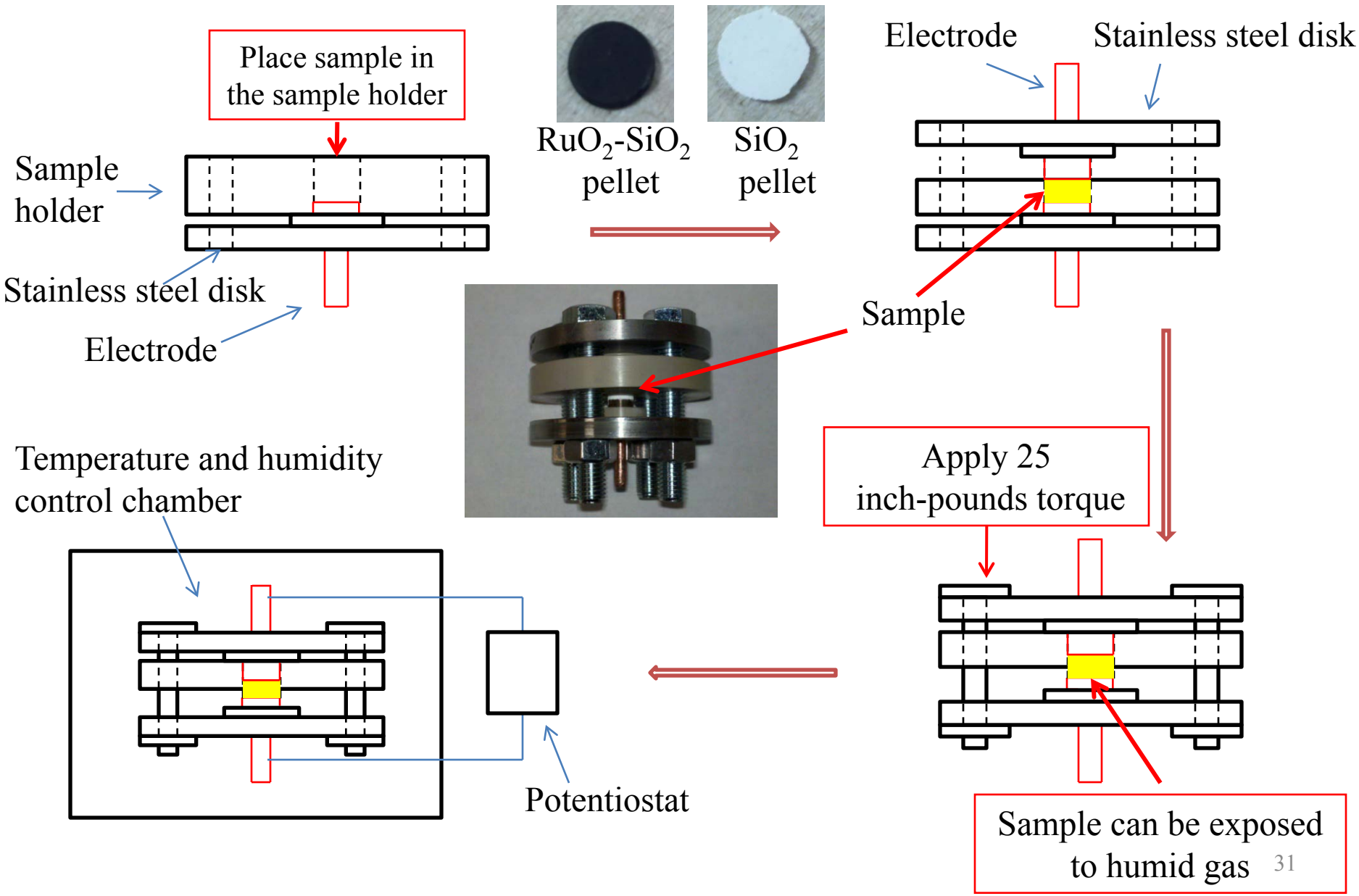
Powder heat treatment

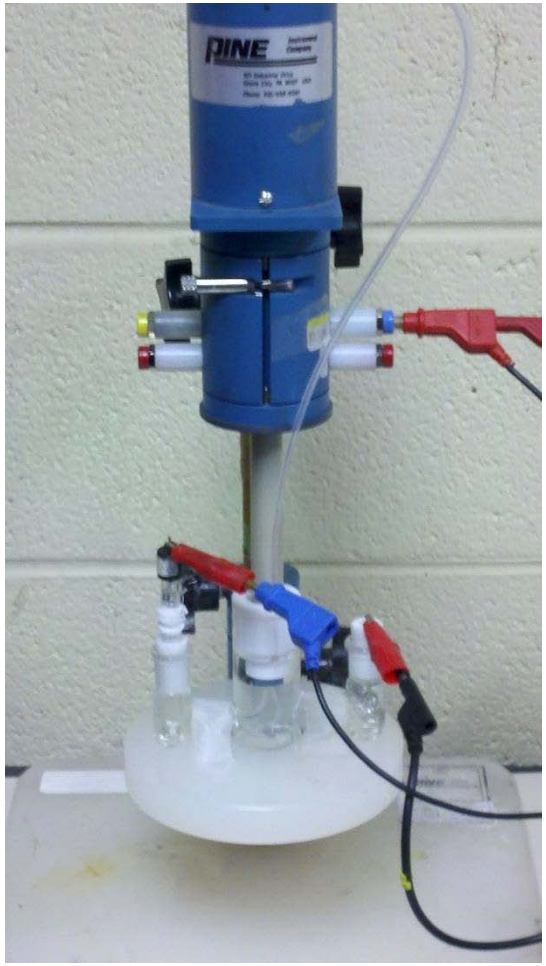
Dry at 100 °C

Calcine at 450 °C

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

Approach: 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 $\mu g/cm^2_{geo}$
- Pt loading: 50 $\mu g/cm^2_{geo}$
- 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