Non-carbon mixed-conducting materials for PEFC electrocatalysts and electrodes

2010 DOE Hydrogen Program Fuel Cell Project Kick-Off

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Overview

Timeline

- Project start date: Sept. 1st 2010
- Project end date: Aug. 31st 2013
- Percent complete: < 5%

Budget

- Total project funding
  - DOE share: $ 1,476,230
  - Contractor share: $ 415,775
- Funding assigned to date: $ 300,000

Barriers

- Barriers addressed:
  - Fuel Cell component durability to be improved
- Targets addressed
  - < 40% ECA Loss
  - < 30% electrocatalyst support loss

Partners

- Nissan Technical Center, North America
- Project lead: Illinois Institute of Technology

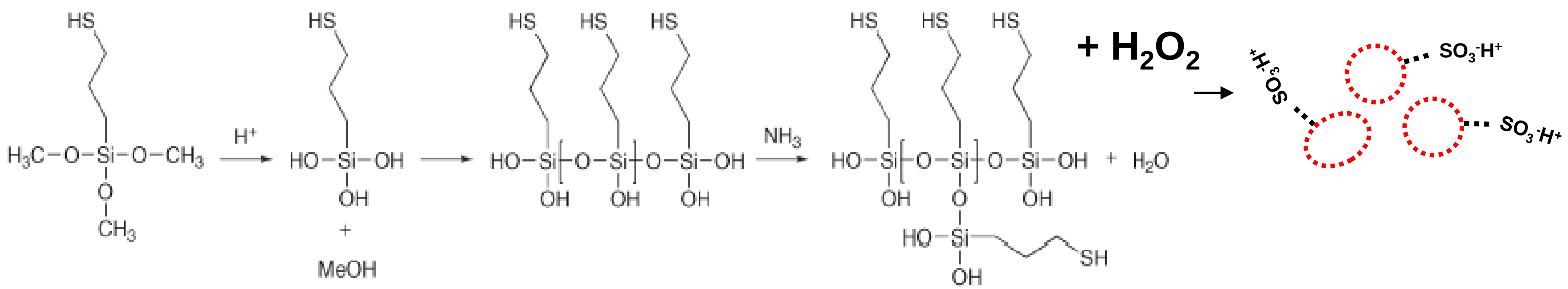
Relevance

- Objectives:
  - 1) to develop and optimize non-carbon mixed conducting materials that will serve as corrosion resistant, high surface area supports for anode and cathode electrocatalysts;
  - 2) concomitantly facilitate the lowering of ionomer loading in the electrode (by virtue of surface proton conductivity of the electrocatalyst support), thereby enhancing performance.
- 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, ECA loss and electrocatalyst support loss.

Approach

- Starting with a high surface area metal oxide
  - Silica/titania used as a model metal oxide
  - Ruthenium oxide used as model electron conducting functionality
  - Sulfonic acid groups introduced to provide proton conductivity
- Project sub-divided into 5 Tasks
  - IIT will focus on materials synthesis and characterization
  - NTCNA will focus on durability/performance testing and cost model

Approach



•Sulfonic acid functionalized silica with a multimodal pore structure will be synthesized

- TEOS/MPTMS used as precursors
- Traditional sol-gel processing

•RuO_2 introduced into micro/meso pores; macropores preserved for gas transport

•Metal – thiol interactions exploited to place platinum precursor right next to the sulfonic acid group.

Approach – List of Tasks

- **Task 1: Optimization of functionalized metal oxide**
- **Task 2: Durability of functionalized metal oxide supports under relevant stresses**
- **Task 3: Ionomer loading reduction studies**
- **Task 4: Developing MEAs with optimized structures for DOE**
- **Task 5: Developing a formal cost estimate**

Approach: Task 1

- Synthesize silica and sulfonic acid functionalized silica with a bimodal pore structure
  - Sol gel methods, with supercritical drying
- Introduce electronic conductivity by incorporating an interconnected network of ruthenium oxide wires into mesopores
- Catalyze support with Pt
- Examine evolution of mirostructure and properties at each stage as a function of processing
- Experimental methods listed on following slides

Approach: Task 1

Microstructure Characterization	
Experiment / Apparatus	**Microstructural Attribute**
N2 physisorption	Pore size distribution
N2 physisorption	Pore volume
N2 physisorption	BET surface area
CO chemisorption	Pt surface area
TEM/AFM	Pt particle size
XRD	Crystallite size
FTIR spectroscopy, XPS	Surface functionality
Transport Property Estimation	
Experiment/Apparatus	**Transport Property**
Impedance spectroscopy	Proton and electron conductivity
DC resistance	electron conductivity
Gas diffusion / permeation	Oxygen diffusion coefficient in air

Table 1.

Approach: Task 1

Ex-situ Estimation of Electrochemical Figures of Merit	
Experiment/Apparatus	**Fig. of merit (ex-situ)**
V-I polarization (RDE)	Mass/area specific catalytic activity
Cyclic voltammetry (RDE)	Electrochemically active surface area (ECA)
Potential cycling (RDE)	Support corrosion current
Potential cycling (RDE)	ECA loss due to support /catalyst corrosion
In-situ Estimation of Electrochemical Figures of Merit	
Experiment/Apparatus	**Fig. of merit (in-situ)**
Cyclic voltammetry (MEA)	Electrochemically active surface area (ECA)
Cyclic voltammetry (MEA)	ECA loss due to support /catalyst corrosion
V-I polarization (MEA)	Mass/area specific activity
V-I polarization (MEA)	Limiting current (Transport property)
V-I polarization (MEA)	Electrode ohmic resistance (Re)
V-I polarization (MEA)	Tafel slope (Kinetic property)

Table 2.

Approach: Task 2

- Study effect of accelerated durability testing on microstructure and properties of chosen multi-functional materials.
- The following questions will be addressed:
    - How does corrosion due to potential cycling affect material microstructure and hence properties?
    - How does the presence of oxygen or hydrogen in the potential cycling environment influence corrosion rate?
    - How does the presence/absence of platinum electrocatalyst influence corrosion rate?
    - How does temperature, RH and freeze-thaw cycling affect structure and properties?

Approach: Task 2

- Accelerated test protocols (both ex-situ and in-situ) will be used to test both catalyzed and uncatalyzed supports
  - Start-up and shut-down (cycling between 1V and 1.5V at 0.5V/s for up to 1000 cycles)
  - Load cycling (between 0.95 V and 0.6V under load for up to 10,000 cycles)
- In-situ tests will be performed on sub-scale MEAs prepared using catalyzed supports
  - The newly developed supports will be tested at:
    - the anode only (with traditional cathode)
    - at the cathode only (with traditional anode)
    - and at both electrodes
  - Stability and performance in reducing and oxidizing environments will be identified.

Approach: Task 2

- For the catalyzed supports:
  - the effect of platinum content on the rate of support corrosion will be monitored
  - the rate of catalyst particle dissolution during accelerated testing will be monitored.
- For both catalyzed and uncatalyzed supports:
  - materials will be subjected to detailed characterization using the experimental techniques specified earlier prior to, during and after the accelerated degradation test protocols
  - mechanism of degradation will be studied
- Results will be benchmarked against the recognized standards in the automotive industry for catalyzed and uncatalyzed supports.

Approach: Task 3

- The questions addressed in this task are:
  - How does support surface functionalization with sulfonic acid groups affect:
    - catalyst utilization, and
    - kinetic and transport properties within the electrode?
  - Does support surface functionalization with sulfonic acid permit:
    - the use of lower amounts of PCMs in the electrode?
    - more efficient electrode microstructure?

Approach: Task 3

- To address the first question:
  - MEAs will be prepared with materials that differ only in the extent of surface functionalization with sulfonic acid groups.
  - The MEAs will be tested at 80°C and 75% RH (standard fuel cell operating conditions).
  - Key kinetic and transport parameters will be ascertained through analysis of polarization data.
    - The influence of extent of sulfonic acid functionalization on utilization, kinetic, and transport properties will be ascertained.
  - The experiments will be repeated with different loadings of the PCM, starting with a binder free electrode, and progressing to high PCM loadings (~ 30 wt%).

Approach: Task 3

- To address the second question:
  - MEAs will be prepared with materials having identical extents of sulfonic acid functionalization.
  - Different PCM loading will be employed for each MEA, and the microstructure of each electrode characterized using microscopy and nitrogen desorption studies.
  - Kinetic and transport figures of merit and electrocatalyst utilization will be estimated and related to electrode microstructure.
- This task will provide insights into the interplay between surface functionalization, effective thickness of PCM binder in the electrode, and resultant kinetic and transport properties.

Approach: Task 4

- In the final year of the program, IIT, in conjunction with NTCNA, will identify the best performing and most durable catalyzed mixed-conducting supports that result from this study.
- We will provide at least 6 ~ 100 cm^2 active area MEAs and test results obtained in our laboratory to DOE for third-party testing
- The actual MEA dimensions will be decided in consultation with DOE and the testing party.

Approach: Task 5

- A formal cost estimate in terms of $/kW for the uncatalyzed and catalyzed support materials developed will be prepared.
- The estimates will be developed in conjunction with accepted economy-of-scale factors incorporated into the model.
- This cost estimate will be delivered to DOE at the end of the program.

Deliverables

- ***Project deliverables***:
  - 1) Optimized ~ 100 cm^2 MEAs (at least 6, with the optimized support/electrode at the anode only, cathode only and at both electrodes) demonstrating the best performance and durability to DOE for independent third party testing;
  - 2) Formal cost estimate for both catalyzed and uncatalyzed supports.

Milestones

- ***Phase 1 Tasks and Milestones***:
  - Substantially complete Task 1 and initiate and partially complete task 2.
  - Down-select sub-set of metal oxide based mixed-conducting supports with superior properties (aim for 0.07 S/cm proton conductivity and 2 S/cm electron conductivity; 50 m^2/g surface area) for advanced testing (both ex-situ and in-situ) at IIT and NTCNA.

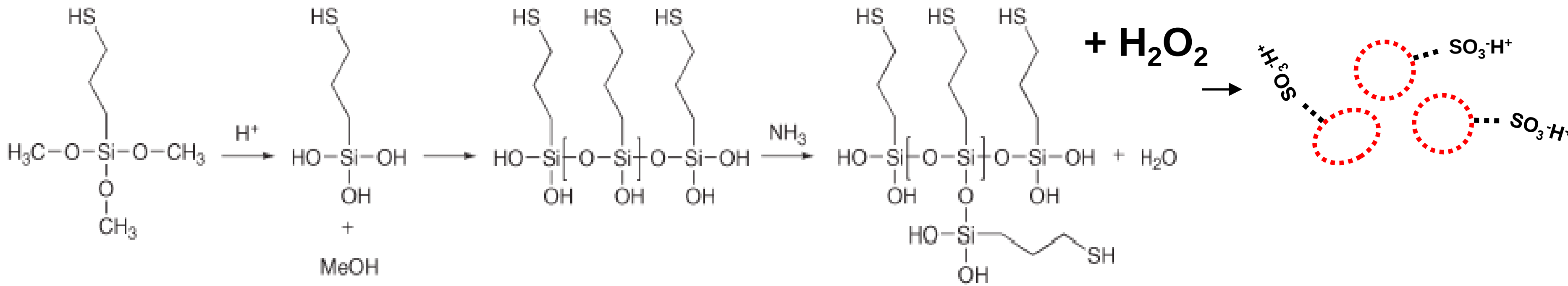
Milestones

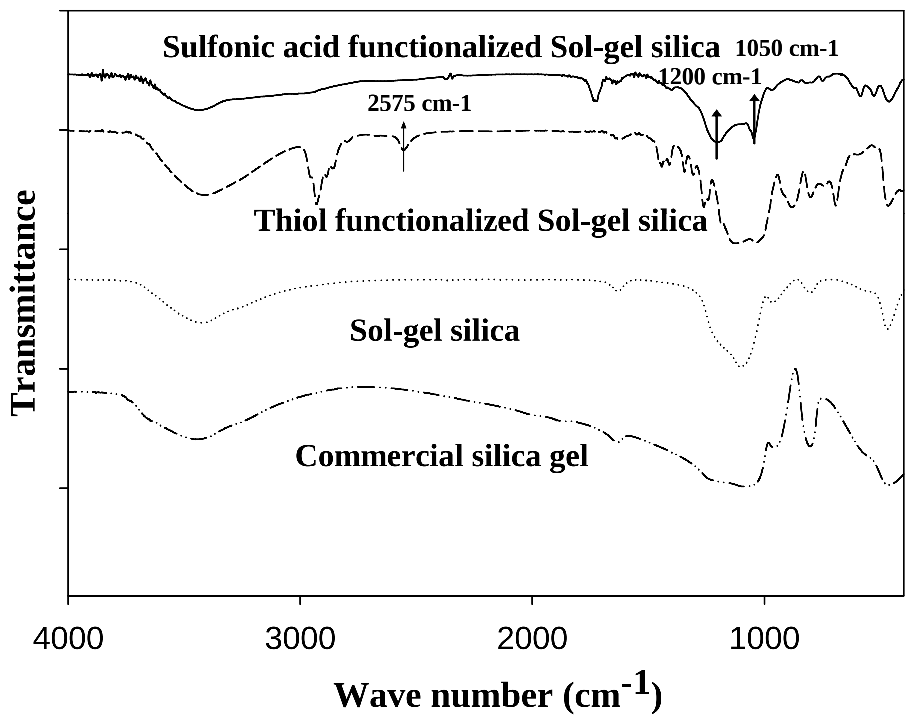
- ***Phase 2 Tasks and Milestones***:
  - Complete Tasks 1 - 3 in the first 4 quarters of period 2.
  - Further enhance proton and electron conductivity to aim for 0.1S/cm and 5 S/cm respectively.
  - Down-select 1-2 mixed-conducting supports with the best combination of performance and durability
  - Prepare and evaluate performance and durability of an MEA with the down-selected catalyzed mixed-conducting supports with a platinum loading of 0.2 mg/cm^2.
  - Prepare 6 MEAs with optimal support and ionomer formulations for delivery to DOE and also formalize cost model (tasks 4, 5).

Go/No Go Criteria

- This criterion is based on requirements in terms of conductivity and stability for an experimental non-carbon support.
- It will be applied towards the end of Phase I.
- The criterion is:
  - "At the end of Phase I, IIT and NTCNA 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".

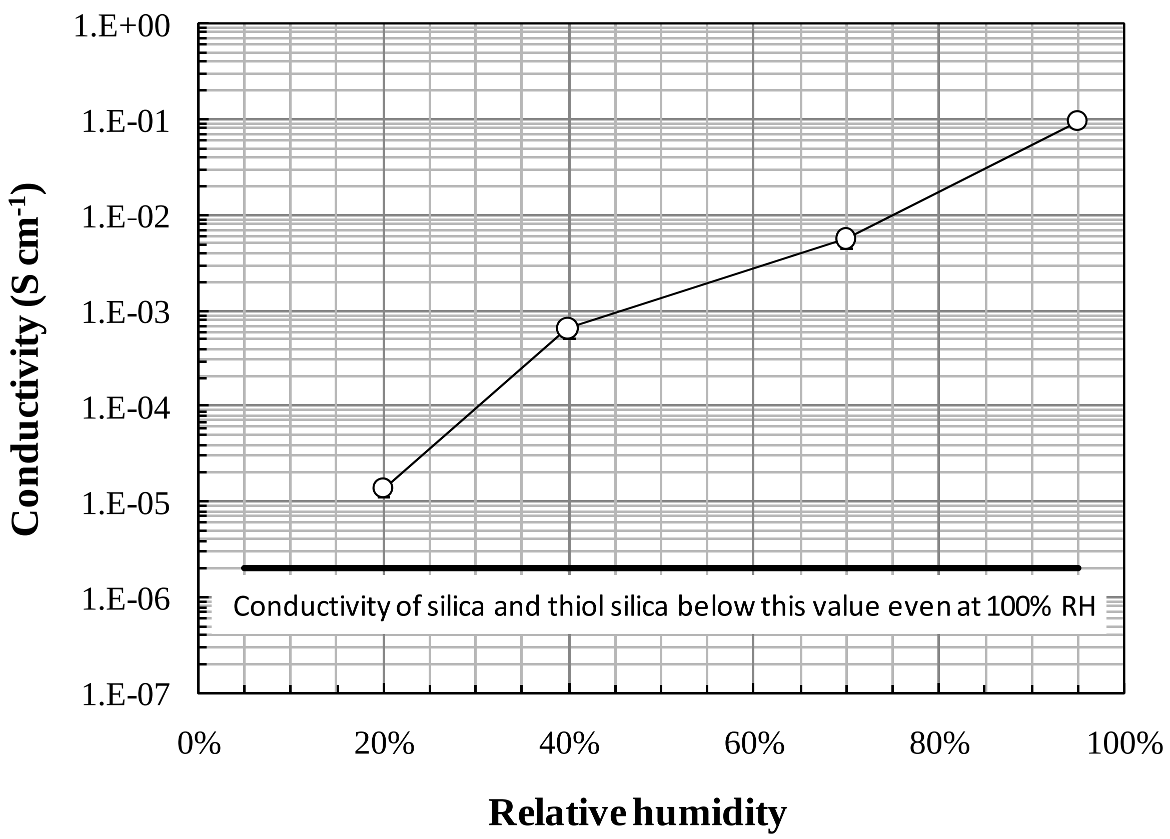
Technical Accomplishments





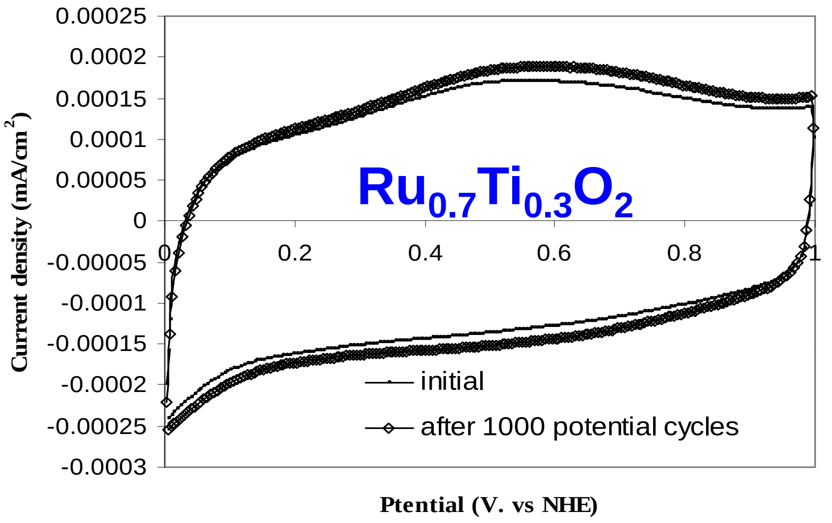
Sulfonic acid functionalized silica particles have been synthesized – detailed characterization is in progress

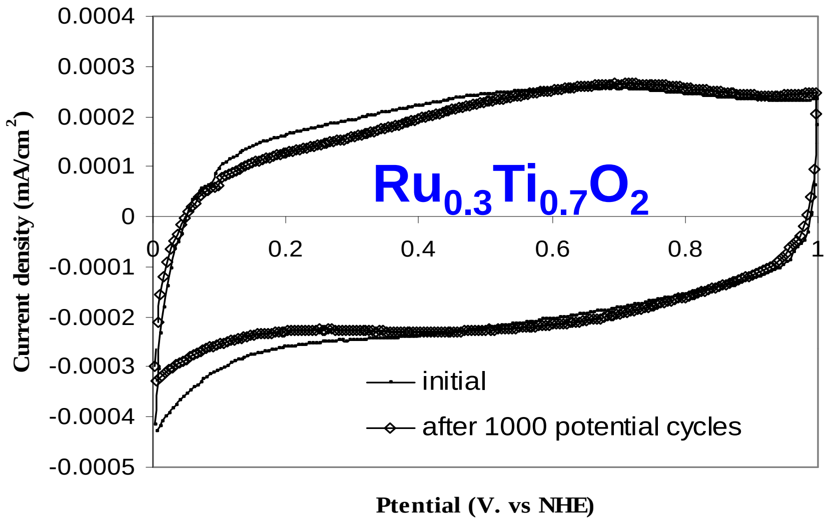
Technical Accomplishments



Sulfonic Acid functionalized silica shows respectable pellet conductivities

Technical Accomplishments





RTOs possess high stability upon cycling between 0 and 1.8 V.

Collaborations

- Project collaborations:
    - Nissan Technical Center, North America
        - PI – Dr. Kev Adjemian
- NTCNA is a sub-contractor from industry
- The collaboration is essentially on a 50-50 basis
    - 50% of federal funds are assigned to sub-contract
    - The project tasks will be performed in an integrated manner.
- Annual mutual visits are planned
    - IIT PI/Student visits to NTCNA
    - NTCNA post-doc visits to IIT
        - NTCNA PI visited in July.

Proposed future work

Period (18 months) →			1							2		
Period (Quarter) →	Q1	Q2	Q3	Q4	Q5	Q6	Q1	Q2	Q3	Q4	Q5	Q6
Task ↓												
Task 1 – optimization of support												
Task 2 – durability of support												
Task 3 – ionomer loading studies												
Task 4 – MEAs for delivery												
Task 5 – cost model for delivery												

- In FY-11, will focus largely on Task 1 – optimization of the support material
  - IIT will synthezise materials
  - IIT and NTCNA will characterize materials
  - Microstructure-property relationships obtained will guide selection of formulations for advanced durability studies (Task 2).

Summary Slide

- **Relevance**: Proposed work will lead to non-carbon supports with high durability and address support loss/ECA targets
- **Approach**: Mixed-conducting supports derived from high surface metal oxides (silica/titania functionalized with sulfonic acid groups and conducting oxides) will be synthesized and optimized. Detailed durability tests will be performed.
- **Accomplishments/Progress**:
  - sulfonic acid functionzlized silica and ruthenium oxide functionalized titania (RTO) have been synthesized
  - RTO has excellent durability on potential cycling
- **Collaborations**: IIT is lead and will work with subcontractor

- **Proposed work for FY – 11**: Substantially complete synthesis/characterization of mixed-conducting supports and initiate durability tests (Tasks 1 and 2).

Supplemental Slides