Improving Fuel Cell Durability and Reliability

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Center for Clean Energy Engineering
University of Connecticut
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Overview

Timeline Data:
- ✓ Start date: August 1, 2010
- ✓ End date: July 31, 2012
- ✓ Percent complete: 35%

Barriers Addressed:
- ✓Durability
- ✓Cost
- ✓Performance

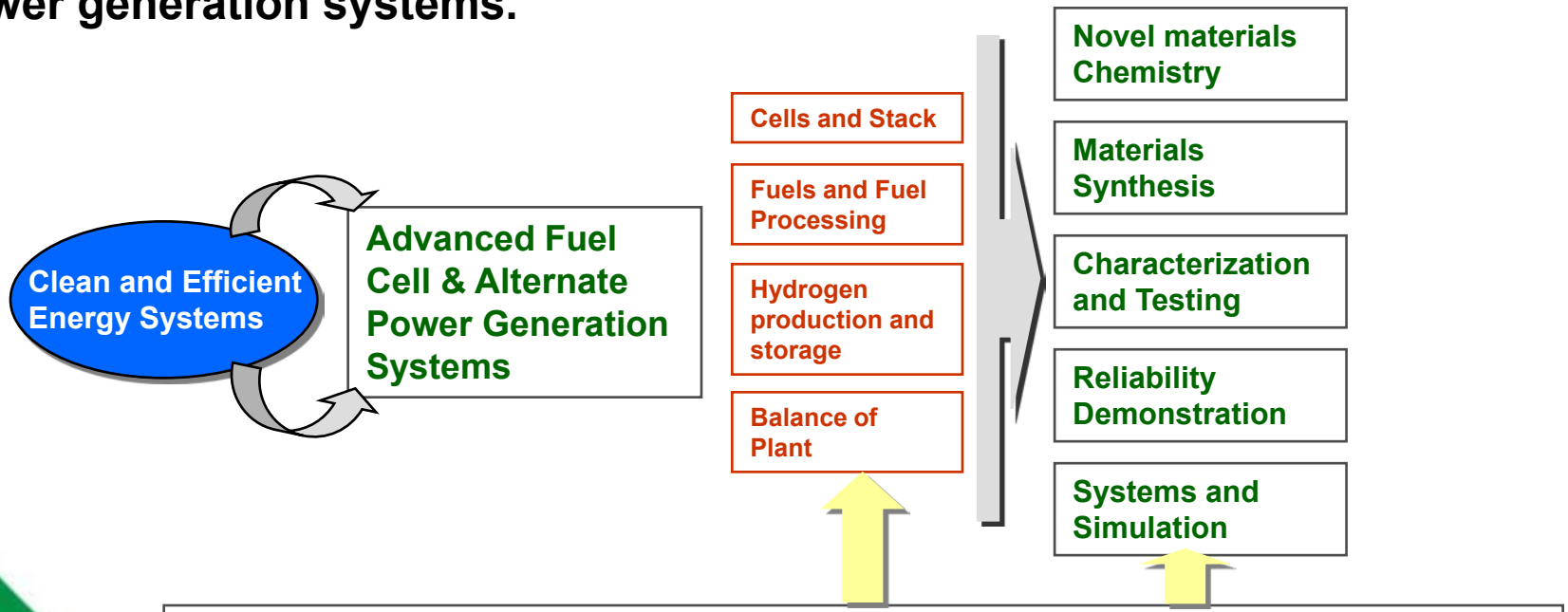
Budget:
- ✓ Total project funding
  - ➢ DOE share: $2,500,000
  - ➢ Contractor share: $ 625,000
- ✓ Funding received in FY10: $ 2,500,000
- ✓ Funding for FY11: $ 0

Partners:
- ✓ Interactions/ collaborations
- ✓ Project lead

Relevance

Objectives:

- Develop an understanding of the degradation processes in advanced electrochemical energy conversion systems.
- Develop collaborative research programs with industries to improve the performance stability and long term reliability of advanced fuel cells and other power generation systems.



Relevance (continued)

Technology Objectives:

- ✓ Advance fuel cell based power generation systems architecture, including renewable hybridized energy conversion and storage (Barriers: B-Cost, C-Performance)
- ✓ Develop novel cell and stack structural and functional materials and validate their performance under the nominal and transient operational conditions for the evaluation of long-term bulk, interfacial and surface stability (Barriers: A-Durability, B-Cost, C-Performance)
- ✓ Gain fundamental understanding of chemical, mechanical, electrochemical and electrical processes related to:
  - Utilization of fuels ranging from bio-derived fuels to liquid petroleum to hydrogen,
  - The role of fuel impurities on degradation and processes for their removal from feedstock
  - Surface and interface phenomena related to surface adsorption, interfacial compound formation, and electron/ion generation and transport,
  - Electrodics and Electrochemistry
  - Novel membranes, heterogeneous catalyst materials and structures will be developed and subsequently validated.

Address Barriers ⇨ A-Durability, B-Cost, C-Performance

Approach

The overall scope of the energy systems and technology research and development initiative, at UConn Center for Clean Energy Engineering, will focus on the development and validation of the mechanistic understanding and subsequent creation of novel cost effective materials to mitigate degradation processes.

- **The performance stability and reliability of the power generation systems will be improved through the implementation of advanced materials and fabrication processes.**

- **Specific technical areas of interest, to be addressed by the industry/university collaborations will include:**
  - **Performance stability and reliability of fuel cell systems.**
  - **Fuels, fuel processing and catalysis**
  - **Advanced functional and structural materials, processes and systems**
  - **Hydrogen storage and power management**
  - **Renewable energy and resources**

Approach

- Develop Collaborative Programs with Industry that Identify and Solve Technology Gaps through Joint Industry / University Research Programs. These relationships will accelerate the development and deployment of clean and efficient multi-fuel power generation systems.

- The scope of research programs will include identification and prioritization of the technology gaps and research needs along with the development of enabling technologies that meet the overall stack and balance of plant improvements from a Durability, Cost and Performance perspective.

Collaborations

First Year Industrial partners for the collaborative energy systems research and development program at UConn include:

- ✓FuelCell Energy
- ✓UTC Power
- ✓UTC Research Center
- ✓nzymSys
- ✓NanoCell
- ✓APSI
- ✓Oasys Water
- ✓W.R. Grace and Co.

Proposed Future Work

- Advanced functional and structural materials R&D will continue to address long term surface , interface and bulk instabilities at engineered systems level. Research will continue in areas related to solid- liquid – gas interactions as they relate to surface corrosion, electrochemical poisoning, agglomeration and coarsening of porous aggregates, and catalytic degradation.
- UConn and its partners will continue to develop advanced fuel cleanup and processing technologies to enable multi-fuel capabilities of advanced fuel cell systems. Cost effective technologies for the removal of contaminants from gas phase will be developed and validated.
- Developed technologies will be transferred to industries to accelerate the development and deployment of advanced fuel cell systems.
- Research findings will be presented and published in technical meetings and peer reviewed journals.

Summary Slide

- University of Connecticut Center for Clean energy Engineering (C2E2) is leveraging USDOE funds with industrial funds to accelerate the development of advanced clean and efficient energy systems. UConn has partnered with 10 industries to address the systems issues from advanced cell and stack to fuels cleanup and processing to thermal management and balance of plant materials.
- C2E2 and its industrial partners have successfully identified technology gaps and research needs for accelerating the development and deployment of advanced fuel cell systems.
- Research efforts will examine long term electrical performance degradation related to cell component materials stability (bulk and interfacial), electrodics, fuel impurities and nominal/transient operation. Mechanisms will be developed and validated.
- Technologies related to materials, processing, gas cleanup systems, balance of plant will be transferred to industries for implementation in manufacturing.

Technical Approach & Accomplishments

Technical and programmatic tasks for year one:

- **Task 1: Performance stability and reliability of fuel cell systems**
  - 1.1 Modeling of Resin Flow in the Manufacture of PAFC GDLs
    Industry Partner: UTC Power, PI: Prof. Rajeswari Kasi, Co-PI: Prof. Prabhakar Singh
  - 1.2 Develop Mechanistic Understanding of long term MCFC Matrix Stability
    Industry Partner: FuelCell Energy, PI: Prof. Prabhakar Singh
- **Task 2: Fuels, fuel processing and catalysis**
  - 2.1 Biomass Cleanup (Desulfurization) for Energy Conversion,
    Industry Partner: FuelCell Energy, PI: Prof. Steve Suib
  - 2.2 Fuel Reforming Catalysts for Efficient Energy Usage
    Industry Partner: Advanced Power Systems Inc., PI: Prof. Steve Suib
  - 2.3 Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup
    Industry Partner: nzymSys, PI: Prof. Ashish Mhadeshwar
- **Task 3: Advanced functional and structural materials, processes and systems**
  - 3.1 Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization
    Industry Partner: UTC Research Center, PI: Prof. Pu-Xian Gao
  - 3.2 Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components
    Industry Partner: W.R. Grace and Co., PI: Prof. George Bollas
  - 3.2 Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture
    Industry Partner: NanoCell Systems Inc., PI: Prof. Radenka Maric

Task 1.1: Modeling of Resin Flow in the Manufacture of PAFC GDLs

Background and Objectives

- Resin flow into carbon fiber based substrates blocks open pore structure of these fibers impacting properties like mass transport of L and G to catalyst layers as well as thermal and electrical conductivity of the final GDL.
- To address this problem the goals of this project – (1) understand the properties of the GDL preparation at each step, (2) relate if possible material properties with processing conditions, and (3) improve substrate manufacturing efficiency of GDL.
- Increase efficiency/life of power plant – lowering cost in keeping with EERE goals.

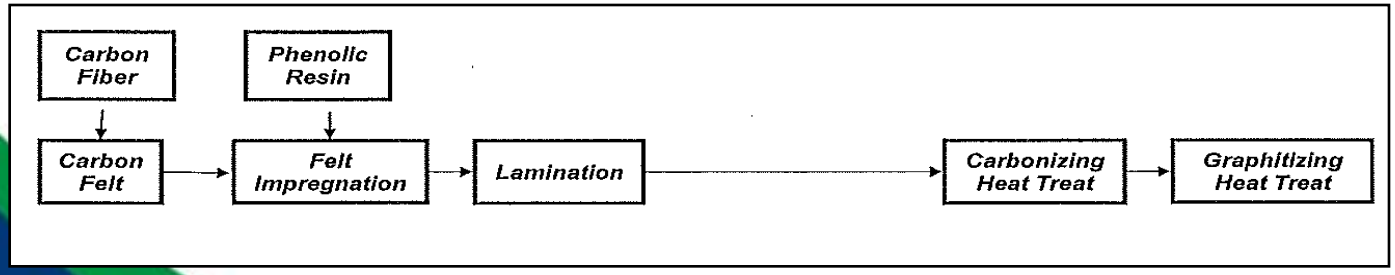
Technical Approach

INFORMATION SUPPLIED BY UTCPower

- Predefined specs of carbon fibers, carbon felt, phenolic resin composition, impregnated felt, lamination process, and GDL processing parameters
- Images of fibers – idea of surface of fibers as well as pore size (distribution), overall morphology of fibers at various levels of thickness
- Processing conditions, flow properties of the resin.

EXPERIMENTAL METHODOLOGY & TECHNIQUES THAT WILL BE USED

- Surface and cross-sectional analysis of the fibers will be investigated using optical methods as well as scanning electron microscopy for samples prepared under various processing conditions.

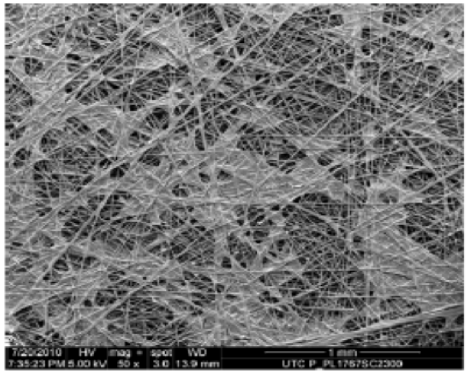


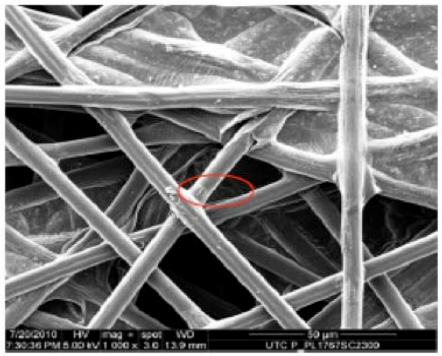
Task 1.1: Modeling of Resin Flow in the Manufacture of PAFC GDLs

Work Accomplished

TASK 1: The morphology (surface and cross-section) of the fibers in the graphitized state were investigated to understand where the resin is localized. This included randomly selected areas of these samples to understand structural variations and to evaluate macro and micro features. SEM and optical microscopy were used.

Result: Our observations show that the carbonized graphite felt remains highly non uniform in structure with the localized presence / buildup of graphite around carbon felt.





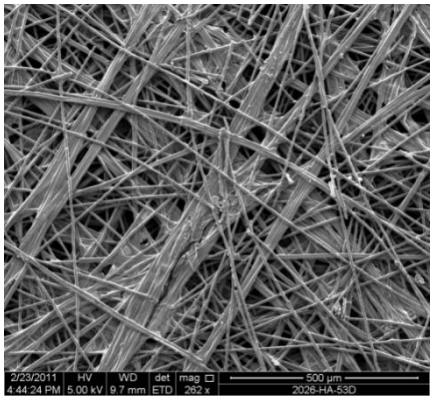
Morphology of the GDL produced from carbon felt at low paper speed, 14% melt flow, 2300 lb graphitization load during heat treatment was analyzed to understand localized carbon (from resin heat treatment) deposition as well as structural variations and features. Morphological analysis of the cross-sectional area also showed the presence of fiber/graphite agglomerations.

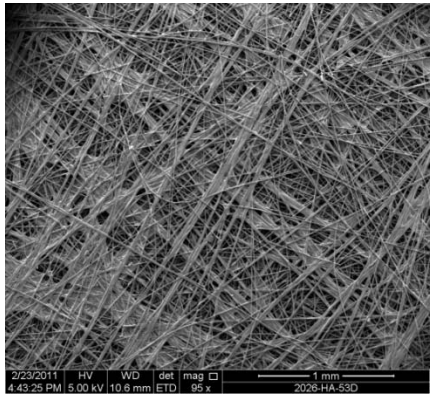
Task 1.1: Modeling of Resin Flow in the Manufacture of PAFC GDLs

Work Accomplished & Future Work

TASK 2: The surface and cross-sectional morphology of GDL prepared with (1) different amounts of resin in the feed (53 and 45%), (2) different felt paper speed (slow and fast) and (3) different resin melt flow (3.5, 7 and 14%) were investigated.

Result: Our observation shows that the graphitized felt remains highly non uniform. Dense blotches of organic material was found attached to the fiber. These were better observed when cross-section of these samples were investigated.





GDLs prepared using different amounts of resin in the feed were used in the following surface morphology. Cm by cm strips were cut from the main fiber mat and the surface was directly imaged by optical methods and SEM. Morphological analysis of the cross-sectional area of the sample prepared from 53 wt% resin showed the presence of fiber/graphite agglomerations.

Future Work: Develop a mechanistic understanding of the micro-structural development during the processing of GDL. Correlate the microstructure with the electrical performance.

Task 1.2: Develop Mechanistic Understanding of Long Term MCFC Matrix Stability

Objectives

- Develop an understanding of degradation processes related to matrix coarsening and interconnect degradation,
- Develop advanced cost effective materials that improve the system life and reduce overall cost,
- Validate the materials in operating cells,
- Transfer technology to industrial partner.

Accomplishments

- ✓ Developed matrix coarsening hypothesis related to oxide dissolution in the molten salt
- ✓ Developed an experimental setup to measure solubility of select matrix materials under cell operating conditions
- ✓ Developed experimental test setup to measure the accelerated interconnects corrosion under bi-polar conditions

Mechanistic understanding and validation

$LiAlO_2$ dissolution – Oxide Fluxing

Acidic dissolution

$$LiAlO_{2(s)} + \frac{3}{2}CO_{2(g)} \leftrightarrow \frac{1}{2}Li_2CO_{3(l)} + Al^{3+}{}_{(l)} + CO^{2-}{}_{3\,(l)} + \frac{1}{4}O_{2\,(g)}$$

$$[Al^{3+}] \; \alpha \; P_{CO_2}$$

Basic dissolution

$$LiAlO_{2(s)} + CO^{2-}{}_{3\,(l)} + \frac{1}{4}O_{2(g)} \rightarrow \frac{1}{2}Li_2CO_{3(l)} + AlO^{2-}{}_{2\,(l)} + \frac{1}{2}CO_{2(g)}$$

$$[AlO_2^{2-}] \; \alpha \; P_{CO_2}^{-1}$$

Dissociation constant:

$$\frac{[Al^{3+}].P_{CO_2}^{1/4}}{P_{CO_2}^{3/2}} = K_a \rightarrow [Al^{3+}] = K_a.P_{CO_2}^{3/2}.P_{O_2}^{-1/4}$$

and

$$\frac{[AlO_2^{2-}].P_{CO_2}^{1/2}}{P_{O_2}^{1/4}} = K_b \rightarrow [AlO_2^{2-}] = K_b.P_{CO_2}^{-1/2}.P_{O_2}^{1/4}$$

For the acidic dissolution

$$\log K_a = \frac{\Delta G^O}{2.303RT} = (a_{Al^{3+}}).P_{CO_2}^{3/2}.P_{O_2}^{-1/4}$$

$$\log a_{(Al^{3+})} = \exp\frac{\Delta G^O}{2.303RT} - \log P_{CO_2}^{3/2}.\log P_{O_2}^{-1/4}$$

For the basic dissolution

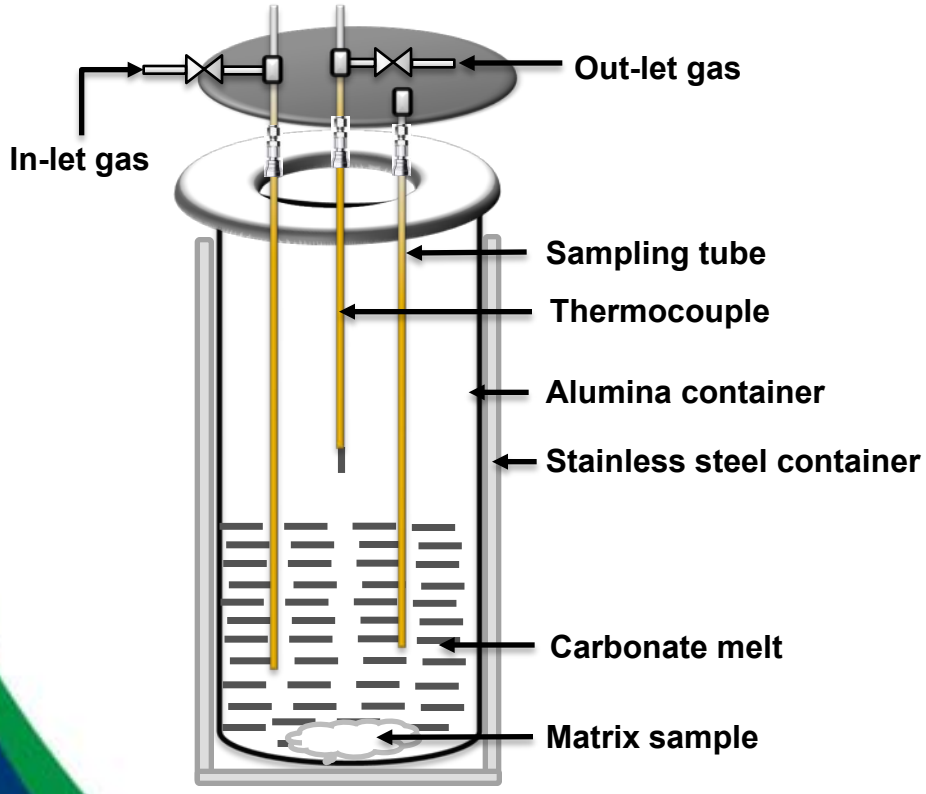
$$\log K_b = \frac{\Delta G^O}{2.303RT} = (a_{AlO_2^{2-}}).P_{CO_2}^{-1/2}.P_{O_2}^{1/4}$$

$$\log a_{(AlO_2^{2-})} = \exp\frac{\Delta G^O}{2.303RT} - \log P_{CO_2}^{-1/2}.\log P_{O_2}^{1/4}$$

The effect of the lithium fraction on the equilibrium solubility:

$$\log(X) = [\log(pCO_2) - \log(K_d)]$$

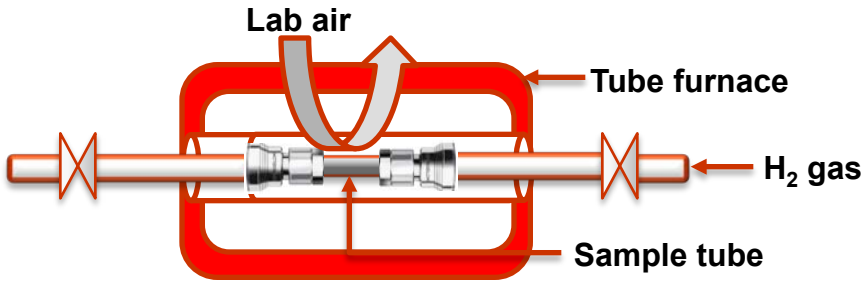
Mechanistic understanding and validation



Versatile test set up has the capability to measure select matrix component stability under oxidizing, reducing and transient cell operating conditions. Analytical techniques used for the materials stability study includes:

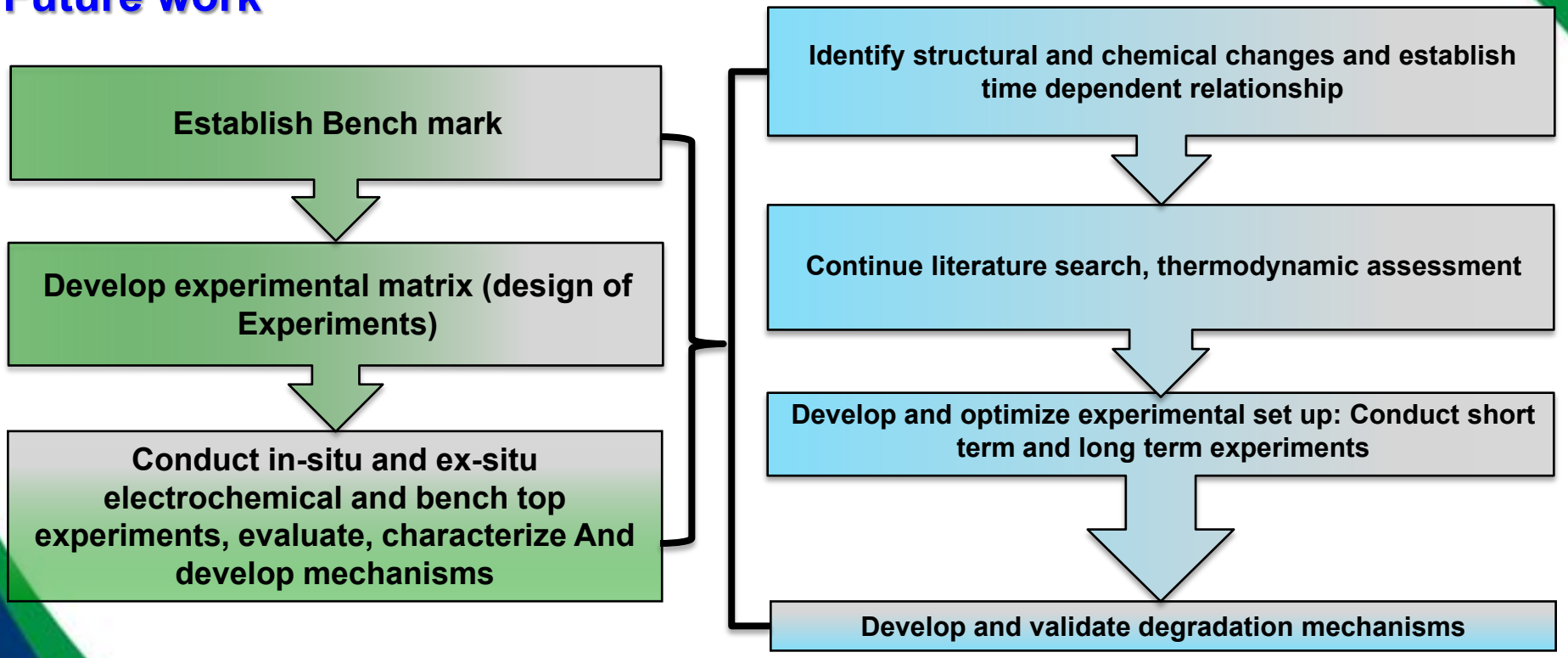
- **High temperature XRD**
- **MS-ICP**
- **FIB-FESEM and TEM**

Corrosion of select IC and BOP component materials will be studied under simultaneous exposure to an oxidizing and reducing gas streams representative of MCFC operating conditions.



Task 1.2: Develop Mechanistic Understanding of Long Term MCFC Matrix Stability

Future work



Task 2.1: Biomass Cleanup (Desulfurization) for Energy Conversion

OBJECTIVES

- Synthesis of Novel Adsorbents & Catalysts for Trace Sulfur Species from Anaerobic Digested Gas.
- Characterization of Adsorbents, Catalysts, Breakthrough Curves.
- Study Effects of Co-adsorbed Species, Temperature, Pressure.
- Studies of Mixed Adsorbents & Catalysts.
- Licensing and Technology Transfer to FCE of Next Generation Adsorbents for Cleanup of Anaerobic Digester Gas (ADG).

APPROACH

- ✓ Synthesis of Adsorbent and Catalysts for Desulfurization.
- ✓ Focus on Desulfurization of Carbon Sulfur Species.
- ✓ Understanding Effects of Water, Breakthrough, All Important Parameters.
- ✓ Developing Mechanistic Studies of Desulfurization.
- ✓ Close Collaboration with FCE with Testing done at Both FCE and UCONN.

Partner: FuelCell Energy
PI: Prof. Steven Suib

Task 2.1: Biomass Cleanup (Desulfurization) for Energy Conversion

ACCOMPLISHMENTS

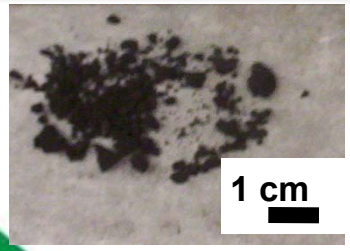
Procedure

1. Prepare Solutions A, B and C.
   Sol. A: 19.8 g $MnSO_4$ in 67.5 mL DDW + 6.8 mL HNO_3
   Sol. B: 13.3 g $KMnO_4$ in 225 mL DDW
   Sol. C: 10 wt.% $Fe(NO_3)_3$ in 50 mL
   (or 10 wt.% $Co(Ac)_2$ or 10 wt.% $Cu(Ac)_2$)
2. Add Sol. B and C drop-wise to Sol. A while stirring vigorously.
3. Reflux at 100 °C for 24 h.
4. Wash and filter with 4 L DDW.
5. Dry overnight at 80 °C.
6. Prepare granules (as shown below).

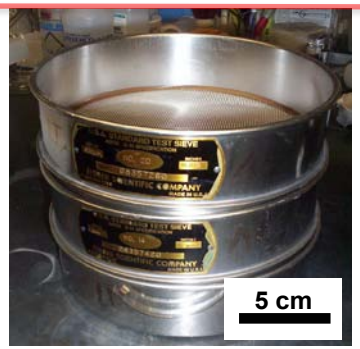
Synthesized Materials

1. Fe-OMS2
2. Fe-OMS2_PDMS
3. AMO
4. AMO_PDMS

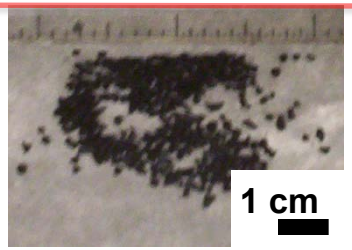
Co-KOMS2



Sieves 14-20 mesh
(1.4 mm - 850 μm)



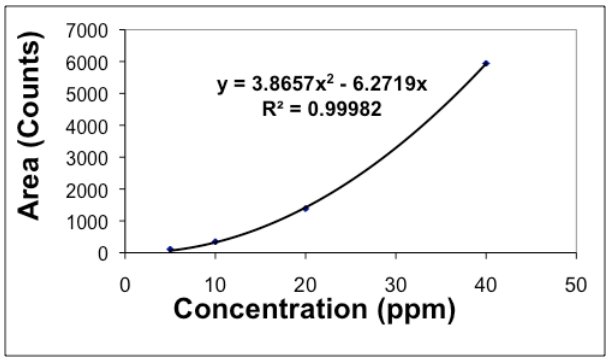
Co-KOMS2 granules



Partner: FuelCell Energy
PI: Prof. Steven Suib

Task 2.1: Biomass Cleanup (Desulfurization) for Energy Conversion

Calibration Curve



Sulfur Capacity (SC)

$$SC\left(\frac{g\cdot sulfur}{100g\cdot sorbent}\right)=(WHSV)\times\left[\frac{M}{V_{mol}}\times\int_0^t(C_{in}-C_{out})dt\right]\cdot 1x10^{-4}$$

WHSV	Weight hourly space velocity, $Lh^{-1}g^{-1}$
M	Atomic weight of sulfur, 32 $g.mol^{-1}$
V	Molar volume, 24.5 $L.mol^{-1}$
C_{in}, C_{out}	Inlet and outlet concentrations, ppm
T	Breakthrough time, h

Tested Catalysts and Future Experiments

Material	Mass (g)	Breakthrough (h)	Sulfur Capacity (g-sulfur per 100 g sorb.)	RH (%)	CO_2 (SCCM)	Cont./CH_4 (SCCM)	CH_4 (SCCM)	Total Flow (SCCM)
Fe-OMS2	0.1	**8.97**	**1.9**	**0**	30	15	30	75
	0.1	**3.24**	**0.7**	**20**	30	15	30	75
	0.1	**1.67**	**0.4**	**40**	30	15	30	75
Fe-OMS2_PDMS	0.1	**5.14**	**1.1**	**0**	30	15	30	75
	0.1	**0.46**	**0.1**	**20**	30	15	30	75
	0.1	**0.41**	**0.1**	**40**	30	15	30	75
AMO	0.1	**9.30**	**2**	**0**	30	15	30	75
	0.1	**9.56**	**2.1**	**20**	30	15	30	75
	0.1	tbd	tbd	**40**	30	15	30	75
AMO_PDMS	0.1	**4.02**	**0.9**	**0**	30	15	30	75
	0.1	tbd	tbd	**20**	30	15	30	75
	0.1	tbd	tbd	**40**	30	15	30	75

Task 2.1: Biomass Cleanup (Desulfurization) for Energy Conversion

FUTURE WORK

- Siloxane strategy
- CO_2 and Moisture impacts to medias
  - Cost, capacity, literature data on equilibrium.
- Market and cost issues:
  - Benefits of proposed idea on efficiency, cost, and environments, etc.
  - Need capacity and price data
- Commercial strategy
  - Skid provider or fabricator as a partner?

Task 2.2: Fuel Reforming Catalysts For Efficient Energy Usage

OBJECTIVES

- Preparation of Next Generation Fuel Reforming Catalysts.
- Characterization and Modeling of Catalysts and Reactions.
- Catalytic Testing of Fuel Reforming Catalysts with Biodiesel and Lignin Feeds.
- Measure the Effects of Fitch Fuel Catalysts on Emissions and Burner Efficiency.
- Licensing and Technology Transfer to APSI, Inc. from UCONN of Next Generation Fuel Reforming Catalysts.

APPROACH

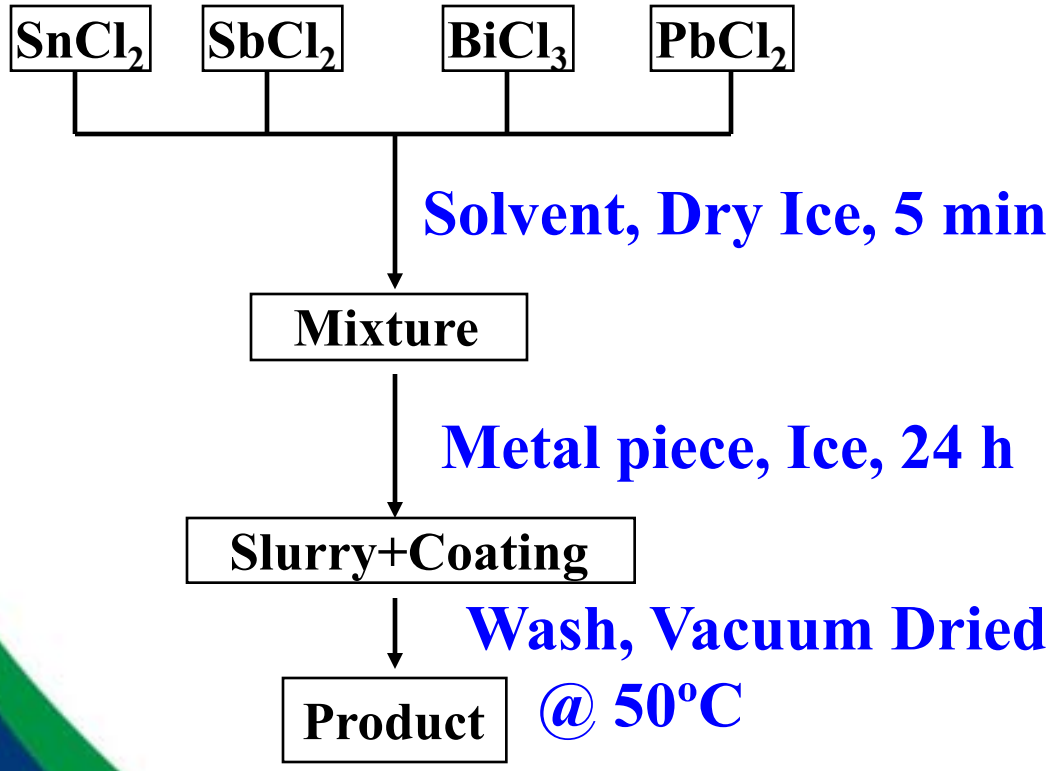
- Synthesis – Use of Thin Films to Decrease Material Costs.
- Use of Sol gel, Dip Coating Methods.
- Mechanistic Studies Including Modeling Studies.
- Characterization Using Surface, Mass Spec, Diffraction Methods.
- Next Generation Alloy Catalysts.
- Catalytic Testing Using Fuel Reforming and Biomass Reactors.

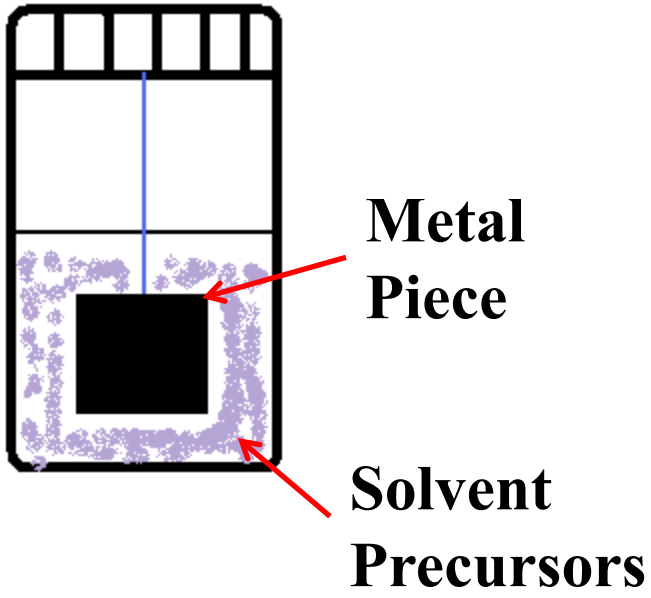
ACCOMPLISHMENTS and HIGHLIGHTS

1. Generation of A Mechanism of Reaction of the Fitch Fuel Catalyst.
2. Synthesis of Next Generation Fitch Fuel Catalysts.
3. Characterization of Next Generation Catalysts.
4. Catalytic Testing in Biomass Conversion Studies.

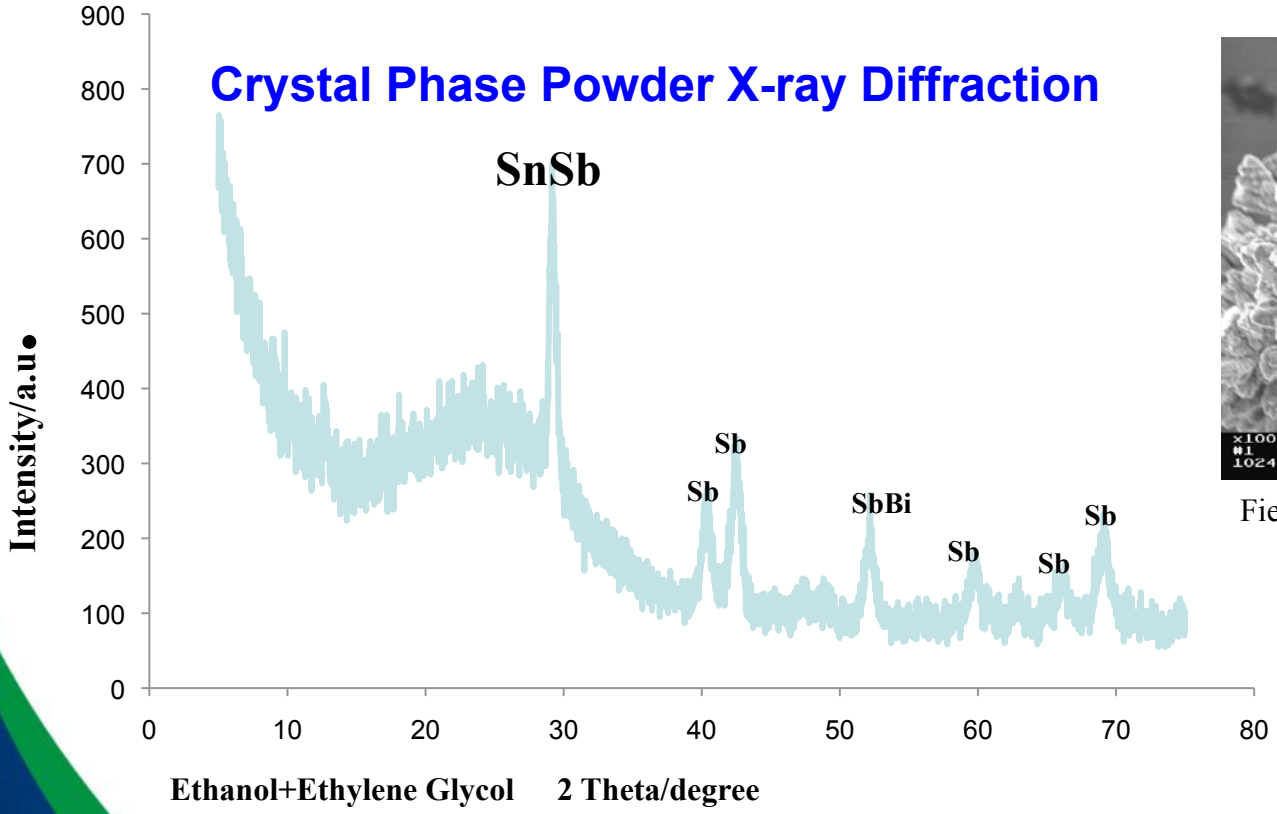
Task 2.2: Fuel Reforming Catalysts For Efficient Energy Usage

Synthesis of SnSbBiPb Alloy

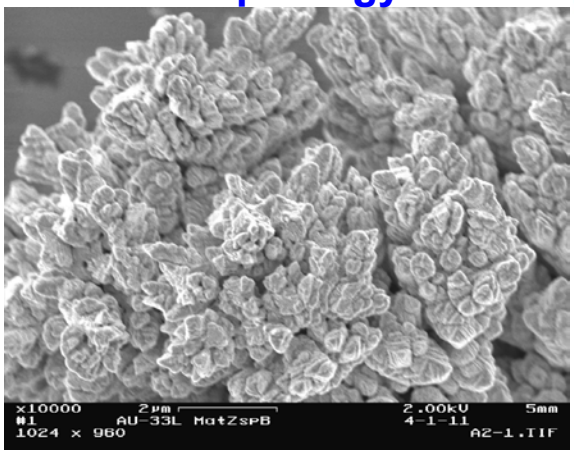




Task 2.2: Fuel Reforming Catalysts For Efficient Energy Usage



Morphology



Field Emission Scanning Electron Microscopy

Zn, Ethylene Glycol @ R.T.

Future Work: 1) Continue synthesis of Thin Film Fitch Fuel Catalysts, 2) Test catalysts in Fuel Reformer, 3) Test catalysts for Biomass Conversion, 4) Perform characterization analysis and mechanistic studies

Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

Goals and Objectives:

- Generate fundamental understanding of enzyme-based desulfurization of biogas and landfill gas.
- Evaluate the effect of operating conditions on removal efficiency of sulfur containing species.
- Understand the effect of impurities on separation performance.
- Develop desulfurization kinetics for scale-up.
- Conduct economic analysis of desulfurization technologies for commercialization feasibility.

Program Plan

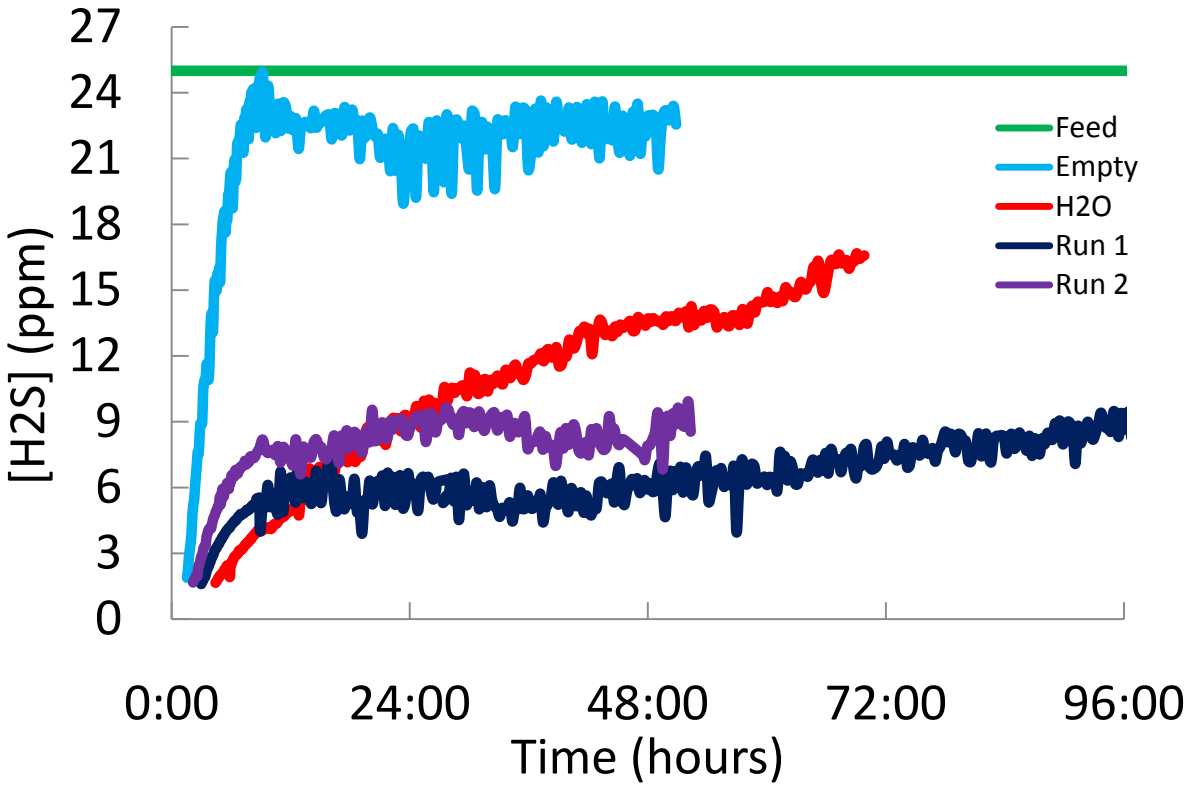
- **Task : Reactor design, setup, and operation.**
  - Gas-liquid scrubber system.
  - Analysis of gas and liquid streams.
  - Testing of enzyme-containing liquid with simulated gas (CH4, CO_2, and H_2S).
- **Task 2: Evaluation of reaction kinetics and effect of operating parameters.**
  - Effect of temperature, flow rate, S-concentration in the gas, impurity concentration in the gas, and extent of liquid dilution.
  - Model for enzyme-based reaction kinetics and parameter estimation.
- **Task 3: Economic analysis and commercialization feasibility.**
  - Economics at larger scales.
  - Comparison with competing S-removal technologies.
  - Commercialization feasibility to specific emerging markets.

Industry Partner: nzymSys
PI: Prof. Ashish Mhadswhar

Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

Tests with 25 ppm H_2S/He

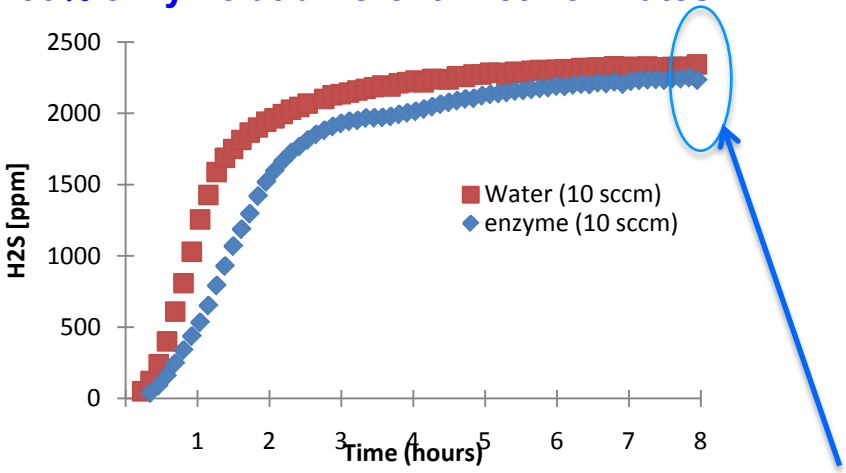
10 sccm of H_2S/He flowing through 60 mL of 100% concentrated enzyme

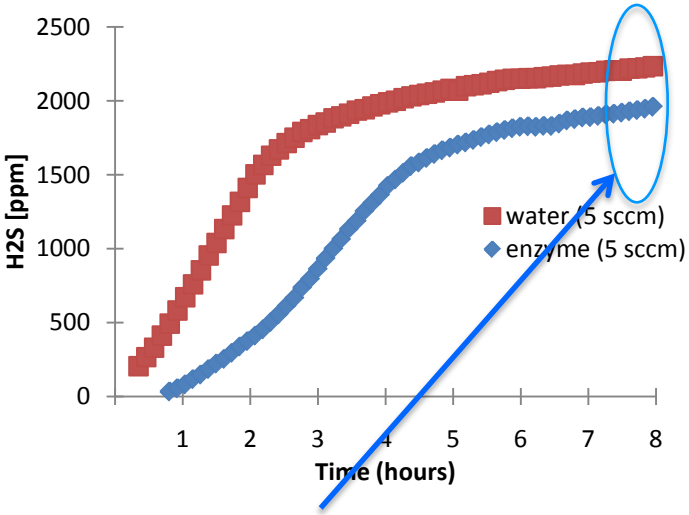


Demonstrated promising enzyme effect on removal of hydrogen sulfide from Helium gas

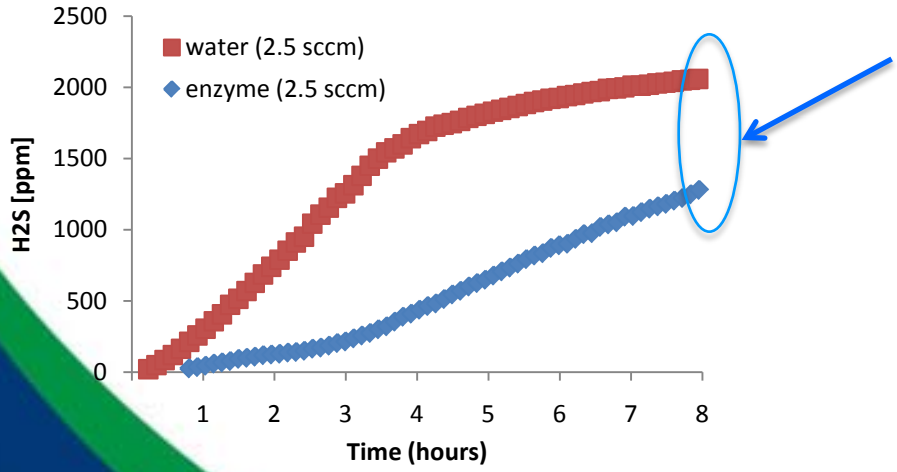
Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

100% enzyme at different inlet flow rates

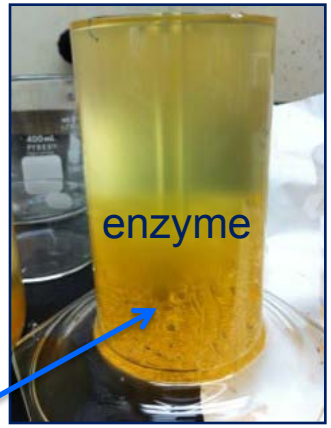


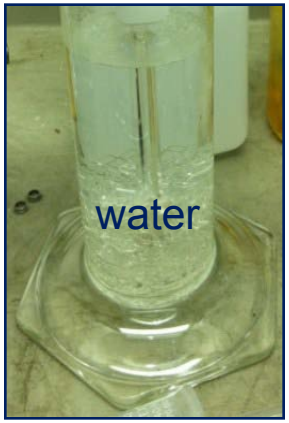


Significant effect of flow rate on enzymatic removal of H_2S



Tests with 3000 ppm H_2S





S_2 precipitate

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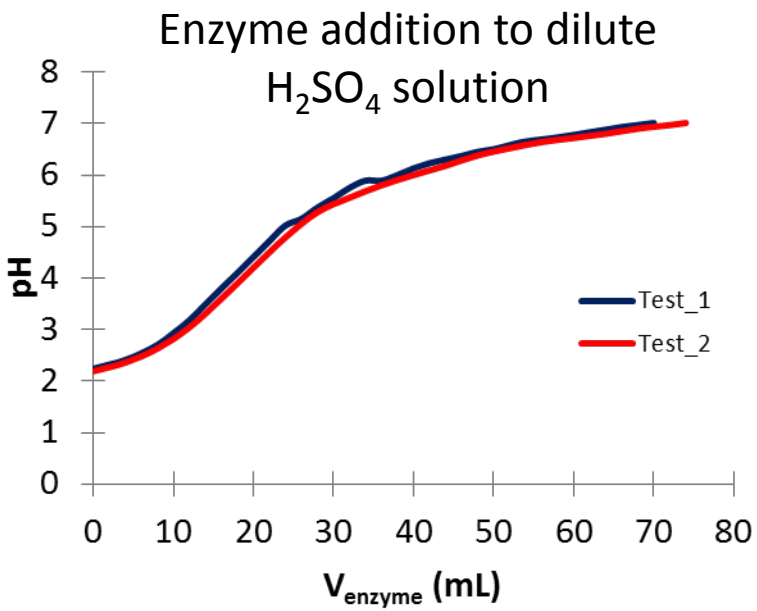
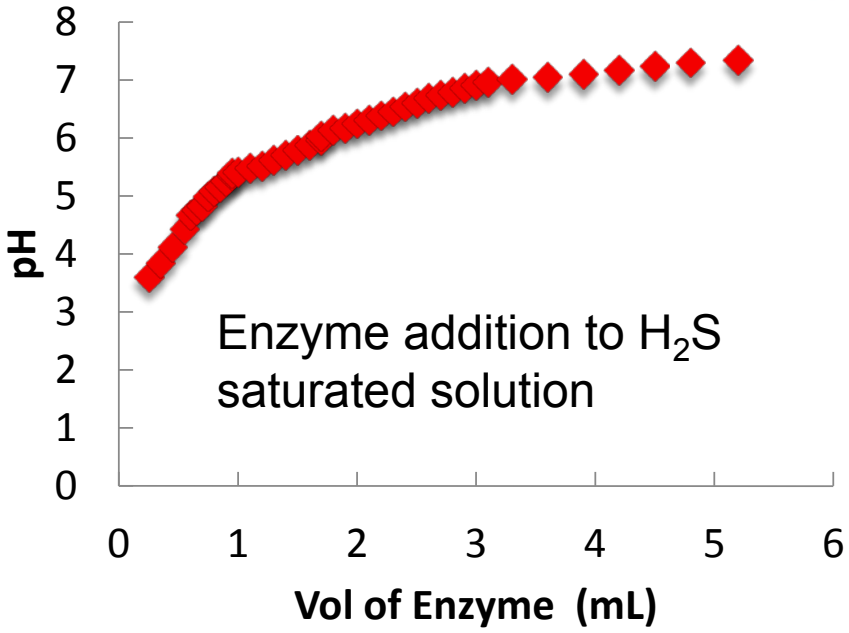
Industry Partner: nzymSys
PI: Prof. Ashish Mhadswhar

Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

pH effect





- **Effect of enzyme addition:**
  - **Enzyme is reactive to sulfates and H_2S.**
  - **pH testing could be effective for large scale monitoring of sulfur removal.**

Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

Accomplishments

- Reactor setup with GC is completed. Appropriate safety measures are taken while testing H_2S.
- GC is calibrated and analysis method is developed for the measurement of H_2S, CO_2, and CH_4.
- Enzyme performance is demonstrated with 25 ppm H_2S. Effect of higher H_2S concentration (3000 ppm) is investigated. Additional variables include effect of enzyme concentration, liquid volume, presence/absence of other gases (CO_2 and CH_4), and residence time.
- Enzyme performance is demonstrated with sulfates and H_2S saturated water using pH tests.

Future Work

- ✓ Determine optimal operating conditions (residence time, enzyme concentration, packing material) for the enzymatic removal of H_2S from a synthetic biogas sample containing 3000 ppm of H_2S.
- ✓ Study the effect of CO_2 on the enzyme performance.
- ✓ Evaluate the scale-up effect on enzymatic desulfurization of biogas.
- ✓ Study the effect of temperature on enzymatic desulfurization of biogas.
- ✓ Conduct economic feasibility analysis.

Task 3.1: Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization

Research Objectives

- Control the growth of zinc hydroxylstannate (ZHS) cubes films onto polycrystalline metals or transparent conductive oxides, such as fluorine doped ZnO (FZO) or indium tin oxide (ITO) using hydrothermal synthetic method;
- Unravel chemical and physical structure evolution during the thermal decomposition of ZHS cube films at different temperature, gradients and treatment durations using a variety of microscopy and spectroscopy techniques;
- Investigate the electronic and optical properties evolution in the ZHS cubes, and thermally graded cubes.
- Investigate the solar cell efficiency and optimize device performance by adjusting fabrication parameters

Main Achievements

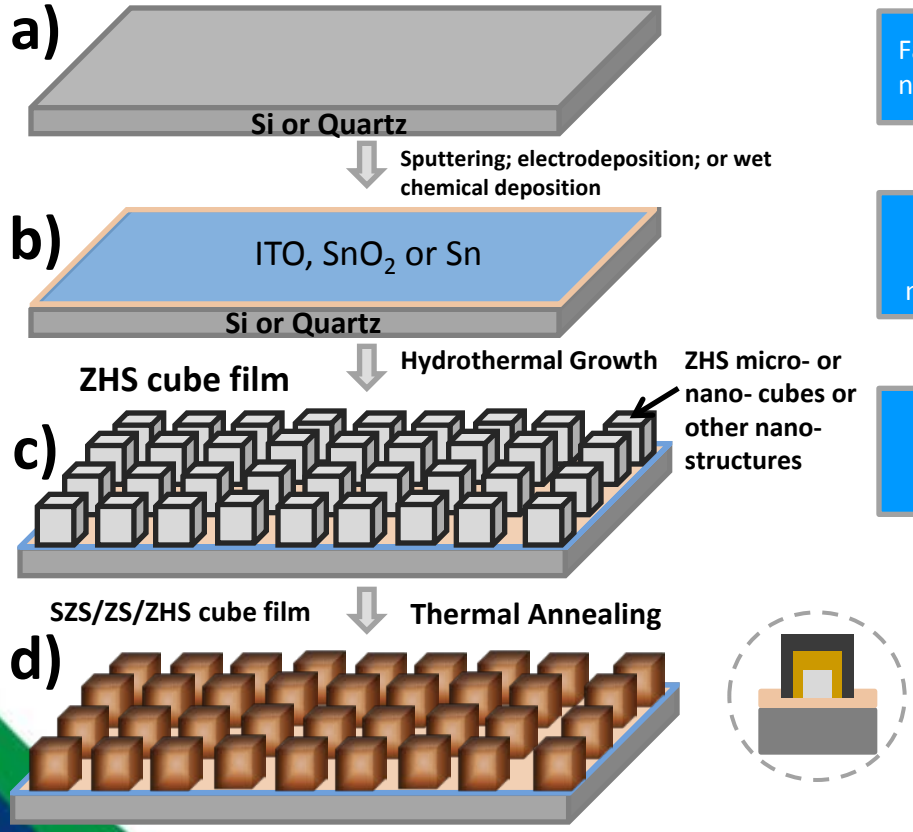
- Crystalline ZHS micro and nanocubes have been successfully grown on different substrate, including tin foil, Quartz, indium tin oxide (ITO)/Quartz, and SnO_2 /Quartz.
- Moreover, large sized and uniform ZHS cube film with high aerial density on transparent substrates have been achieved.
- The size of ZHS cube is controllable and tunable in the range of 100 nm to10 µm based on the precursor concentrations, growth temperature, and duration time.
- The chemical and physical structure evolution during the thermal decomposition of ZHS cube films at different temperature have been explored by using microscopy and spectroscopy techniques.
- A decomposition pathway of Zinc hydroxystannate (ZHS) $^{200\sim 400^{\circ}C}$ Amorphous Zinc stannate (ZS) $^{400\sim 600^{\circ}C}$ crystalline ZS $^{800^{\circ}C}$ Spinel zinc stannate (SZS) has been found.

Industry Partner: UTC Research Center
PI: Prof. PuXian Gao

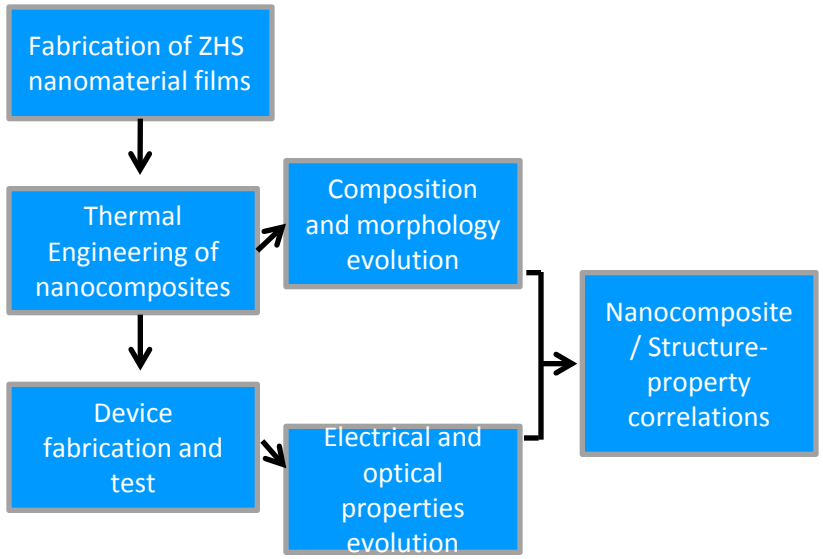
Task 3.1: Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization

Our Approach

Fabrication procedures



Research Flow Chart

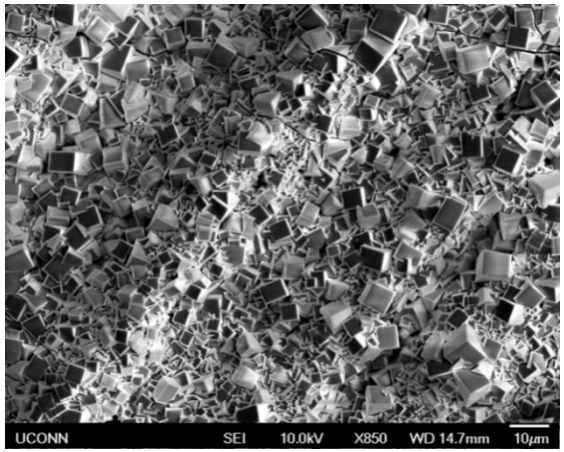


Task 3.1: Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization

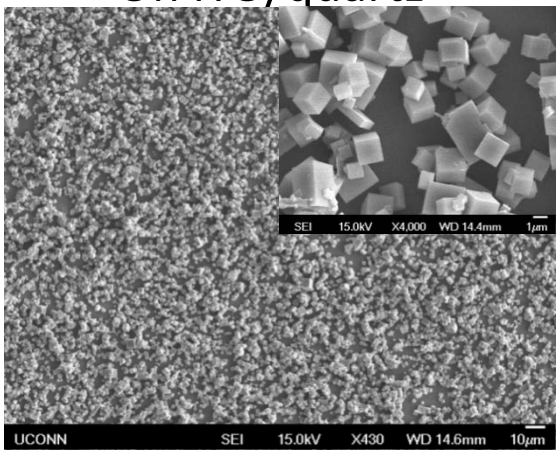
Achievement

1. Controlled growth of different sized ZHS cubes on various substrates

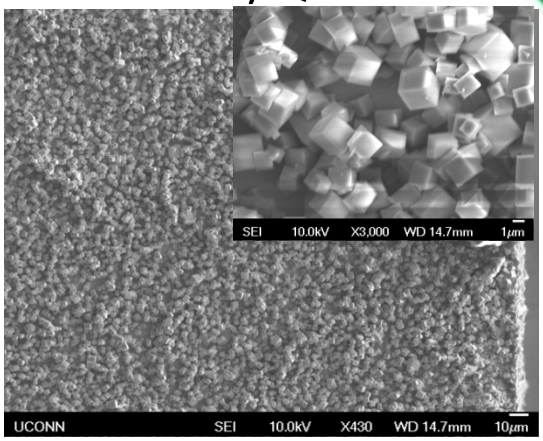
SEM images On tin foil



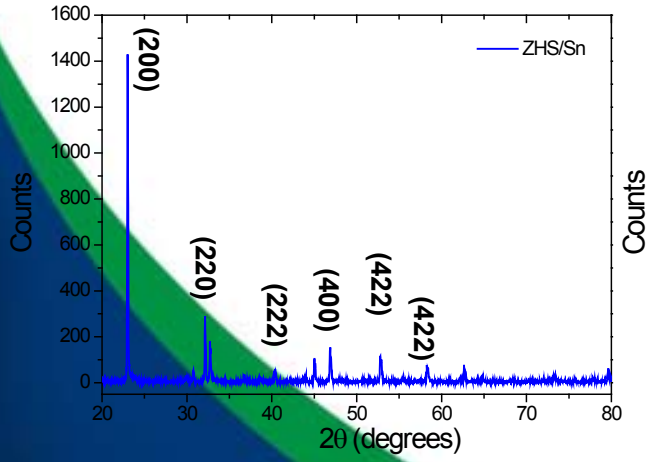
On ITO/quartz

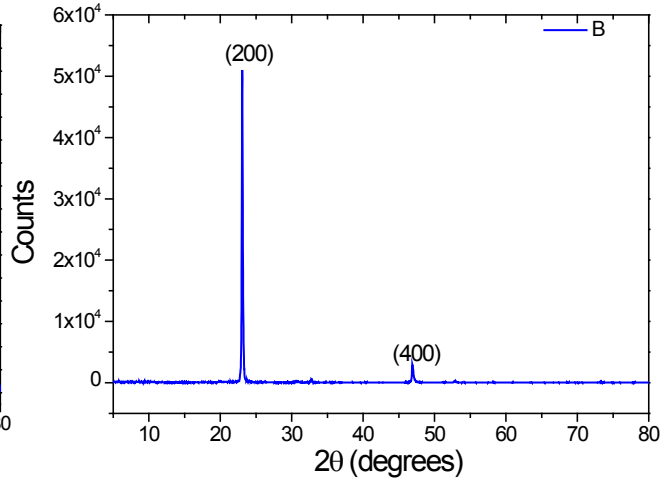


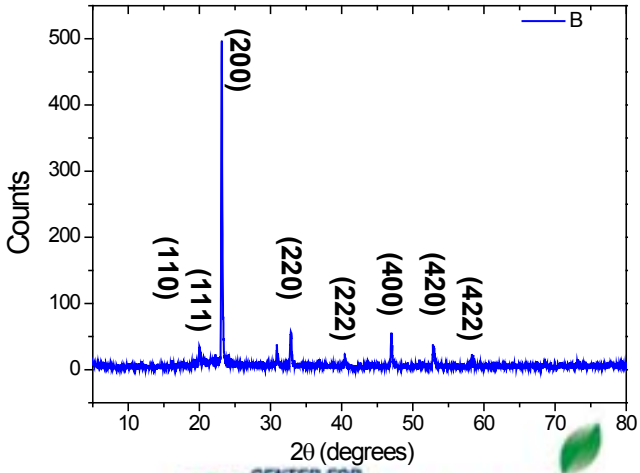
On SnO2/Quartz



XRD Spectra







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PI: Prof. PuXian Gao

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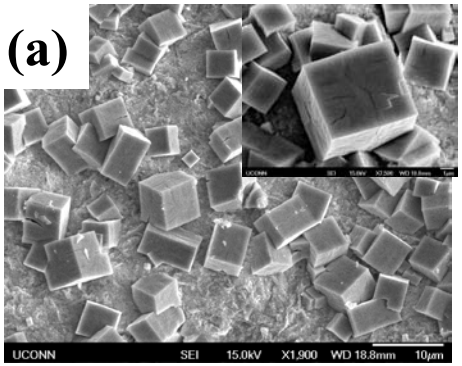
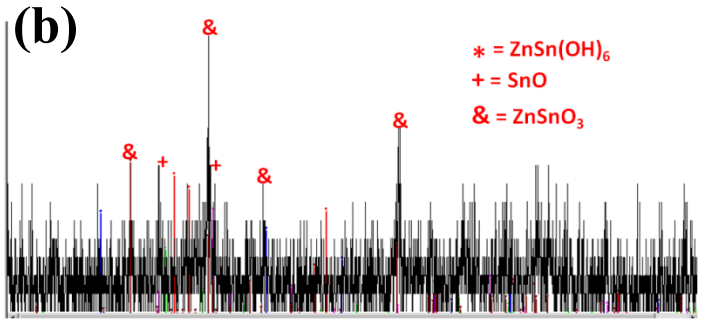
Achievement

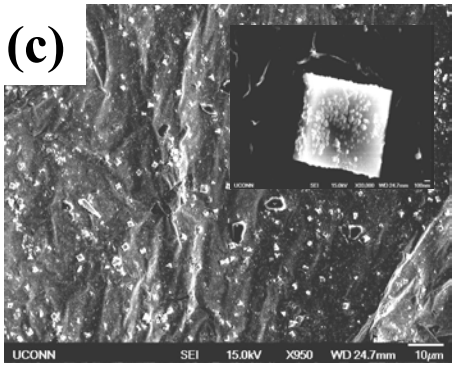
2. Thermal engineering of ZHS:

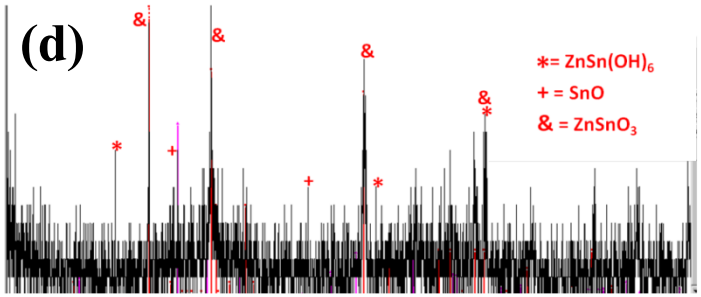




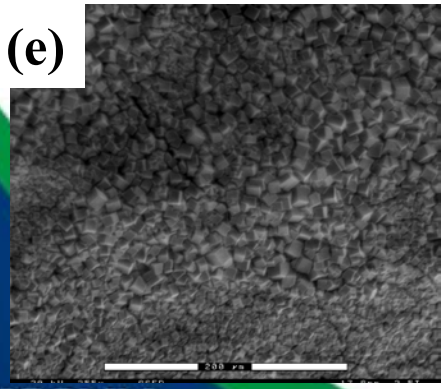
1hr @ 400°C in air

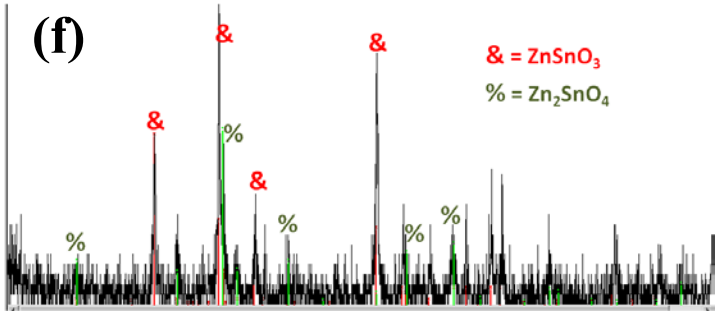
$ZnSn(OH)_6 \xrightarrow{400\sim600°C} ZnSnO_3$





1hr @ 600°C in air





1hr @ 800°C in air

$ZnSnO_3 \xrightarrow{800°C} Zn_2SnO_4 + SnO_2$

Industry Partner: UTC Research Center
PI: Prof. PuXian Gao

Task 3.1: Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization

Future Work

- Thermal engineering for fabricating gradient structures;
- Identification of the band gaps of zinc hydroxylstannate ($ZnSn(OH)_6$), zinc stannate ($ZnSnO_3$);
- Electrical and optical characterization of ZHS, ZS, SZS, and the gradient composites;
- Fabrication of solar cells and testing of device performance;
- Structure-property correlations.

Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

Goal and Research Objectives

Develop detailed models of state-of-the-art catalyst evaluation procedures for different types of reactors.

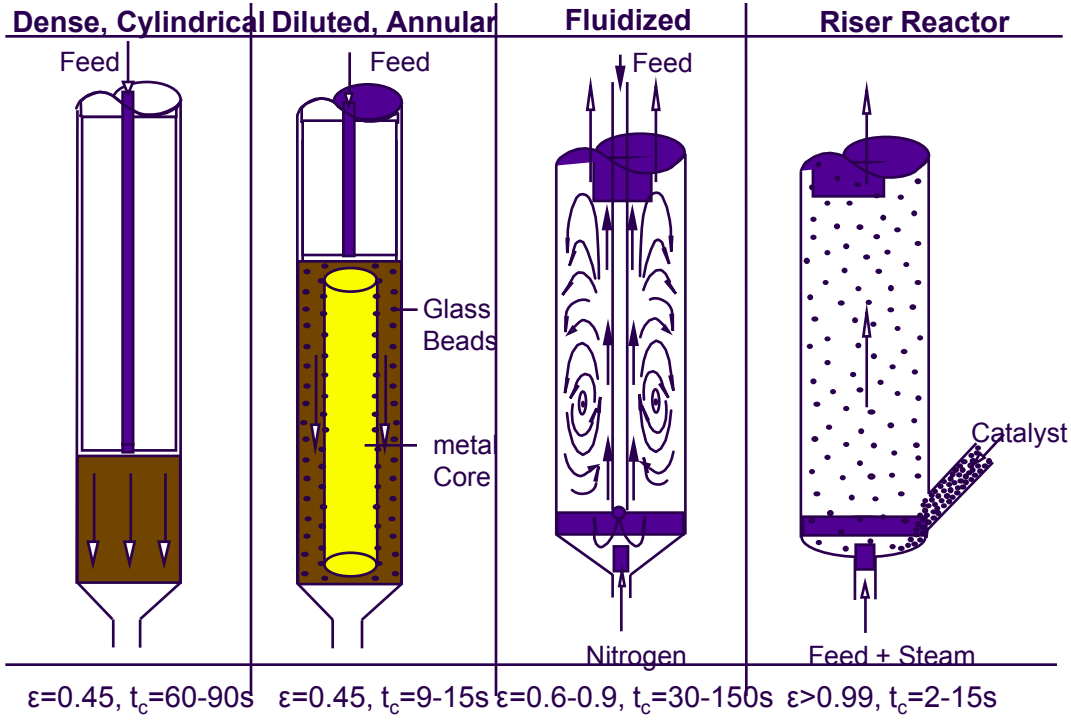
Research Objectives:

- Develop models for different catalyst evaluation reactors.
- Develop detailed reaction kinetics network.
- Decouple reaction kinetics and catalyst deactivation from reactor design.
- Separate the effects of zeolite and matrix on catalyst activity and selectivity.
- Achieve model-based optimization of catalyst testing.
- Achieve model-based optimization of catalyst formulation.
- Improve refinery efficiency.

Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

Technical Approach

Modeling of different catalyst testing reactors using the same reaction kinetics network and the same catalyst deactivation function will provide metrics for the comparison of the performance of different catalysts and insight to decoupling the effects of reactor hydrodynamics and reaction kinetics on product selectivity.

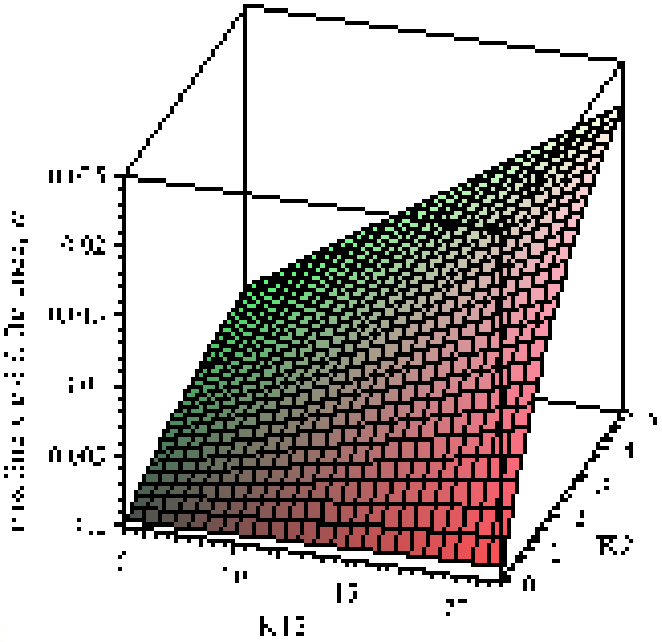


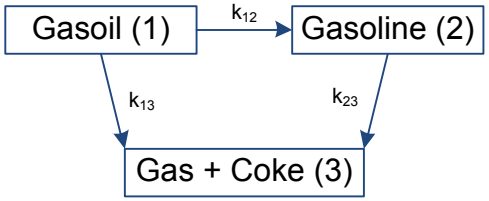
Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

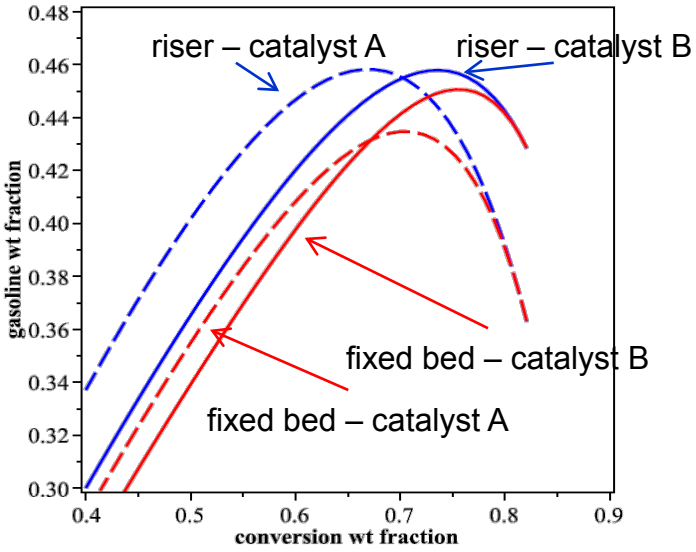
Proof of Concept

Using the three-lump model of Weekman

- Catalyst performance is significantly different.
- Catalyst ranking depends on reactor design.
- Inverse catalyst ranking cannot be obtained.







Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

Process Model Fixed Bed Reactor

$$\varepsilon \frac{\partial C_i}{\partial t} + u_o \frac{\partial C_i}{\partial z} = R_{ij}$$

Process Model Bubbling Bed Reactor

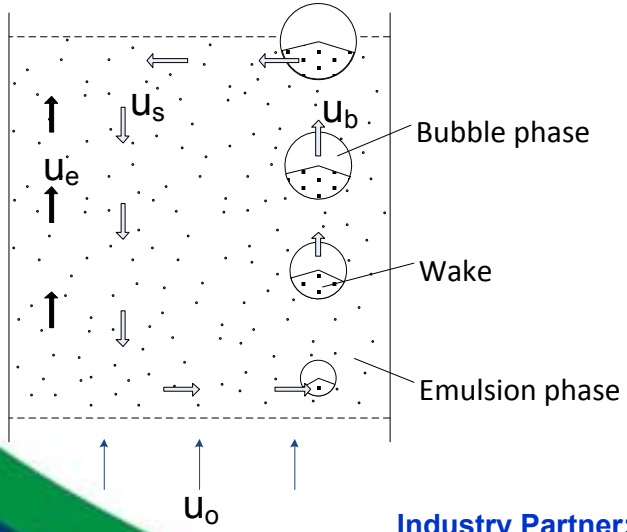
Gas in bubble+wake phase

$$(\delta + \alpha\delta\varepsilon_{mf})\frac{\partial C_{j,b}}{\partial t} + \frac{\partial}{\partial z}\left[u_b(\delta + \alpha\delta\varepsilon_{mf})C_{j,b}\right] = K_{j,be}(C_{j,e} - C_{j,b})(\delta + \alpha\delta\varepsilon_{mf}) + (\lambda_1 C_{j,b} + \lambda_2 C_{j,e})\frac{\partial}{\partial z}\left[u_b(\delta + \alpha\delta\varepsilon_{mf})\right] + R_{j,b}\rho\alpha\delta(1 - \varepsilon_{mf})$$

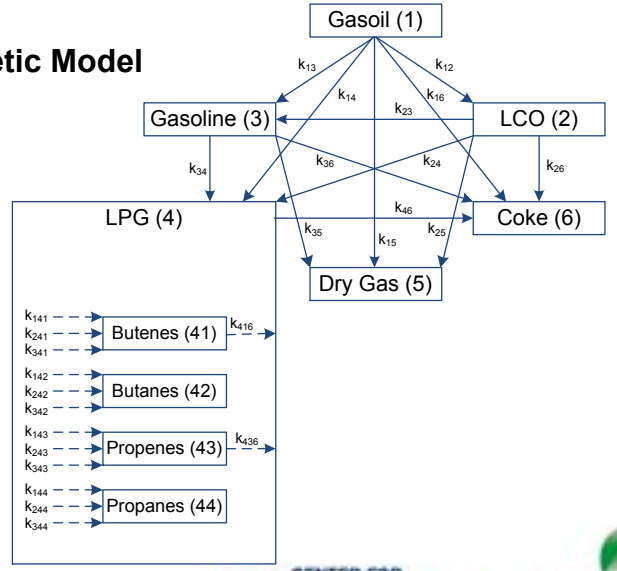
Solid in wake phase

$$\alpha\delta(1 - \varepsilon_{mf})\rho\frac{\partial C_{j,w}}{\partial t} + \frac{\partial}{\partial z}\left[u_b\alpha\delta(1 - \varepsilon_{mf})\rho C_{j,w}\right] = K_{j,we}(C_{j,e} - C_{j,w})\rho\alpha\delta(1 - \varepsilon_{mf}) + (\lambda_1 C_{j,w} + \lambda_2 C_{j,e})\frac{\partial}{\partial z}\left[u_b\alpha\delta(1 - \varepsilon_{mf})\rho\right] + R_{j,w}M_j\rho\alpha\delta(1 - \varepsilon_{mf})$$

Physical Model Bubbling Bed Reactor



Preliminary Kinetic Model



Industry Partner: W.R. Grace & Co.
PI: Prof. George Bollas

Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

Milestone / Task Description	Planned Completion	Completion Date
Modeling catalyst testing reactors		
Identify key characteristics of catalyst testing reactors	01/01/11	01/01/11
Survey existing models	01/01/11	01/01/11
Develop and validate models with available data	04/01/11	In progress
Reaction network and catalyst deactivation		
Examine performance of catalyst decay functions	01/01/11	01/01/11
Survey existing kinetic networks	04/01/11	In progress
Develop kinetic network and par. estimation algorithm	06/01/11	In progress
Integrate all models into a user friendly interface	09/01/11	In progress
Validate model with experimental results	10/01/11	
Effect of catalyst properties (zeolite and matrix)		
Literature survey of the reactions occurring on matrix	12/01/11	
Develop separate kinetic networks for matrix and zeolite	12/01/11	
Incorporate effectiveness factors	03/01/12	
Integrate all models	06/31/12	
Validate model with experimental data	07/31/12	
Streamline the process of improving models with new experimental data and understanding	09/31/12	

Publications from this project

- **ACS Annual Meeting, August 2010, Boston MA USA. *FCC selectivity studied in lab-scale units and pilot plants.* George M. Bollas, Dariusz Orlicki, Hongbo Ma**
- **AIChE Annual Meeting, November 2010, Salt Lake City UT USA. *Some uses and misuses of FCC catalyst testing experimental data.* George M. Bollas, Dariusz Orlicki, Hongbo Ma**

Task 3.2: Optimization of FCC selectivity through detailed modeling of catalyst evaluation experiments and the contributions of catalyst components

Future Work

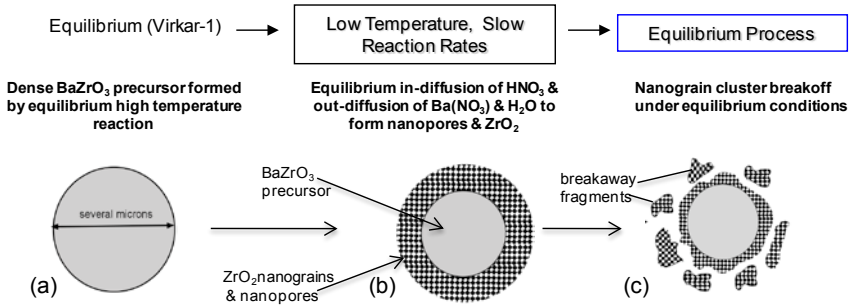
- Modeling catalyst testing reactors
  - Validate process models with available data
  - Validate kinetic network and parameter estimation algorithm
- Reaction network and catalyst deactivation
  - Examine performance of catalyst decay functions
  - Survey existing kinetic networks
  - Integrate all models into a user friendly interface
  - Validate kinetic model with experimental results.
- Effect of catalyst properties (zeolite and matrix)
  - Literature survey of the reactions occurring on matrix.
  - Develop separate kinetic networks for matrix and zeolite
  - Incorporate effectiveness factors
  - Integrate all models
  - Validate model with experimental data
  - Streamline the process of improving models with new experimental data and understanding.

Task 3.3: Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture

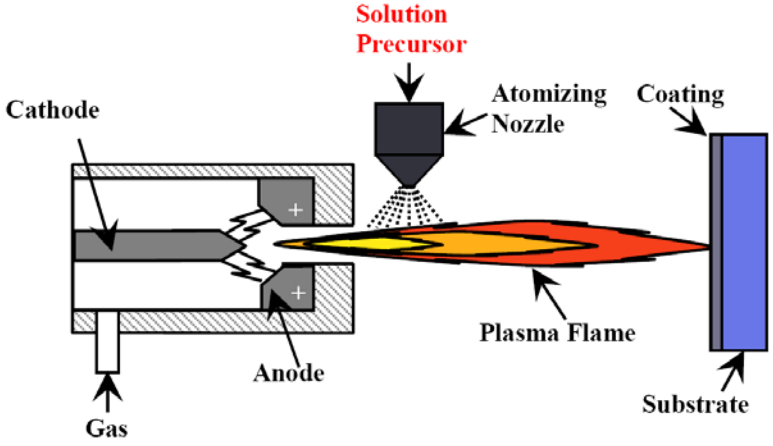
Synthesis routes for 8 mol% YSZ

8 mol% YSZ was fabricated by three different methods to examine the effect of quenching on the conductivity of the material

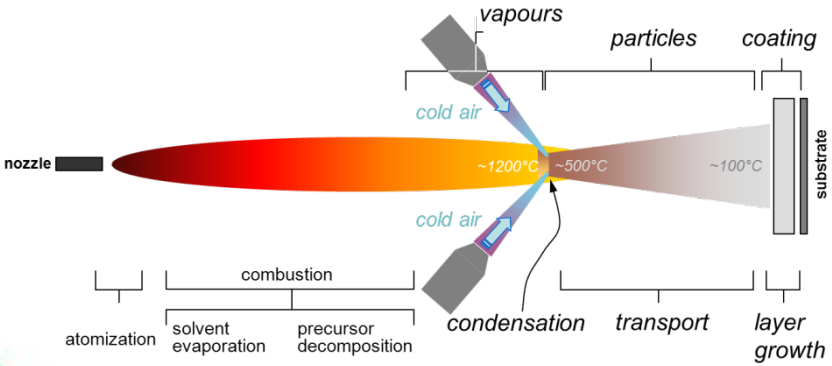
Method 1: Molecular decomposition



Method 2: Solution precursor plasma spray



Method 3: Reactive spray deposition technology



Industry Partner: NanoCell Systems
PI: Prof. Radenka Maric

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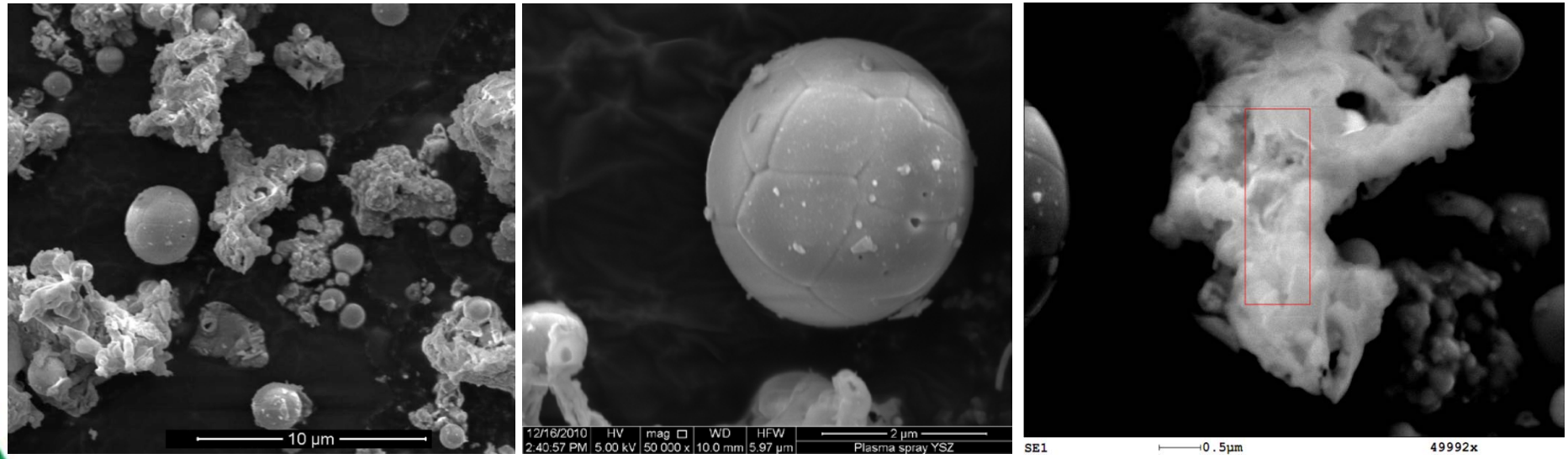
Task 3.3: Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture

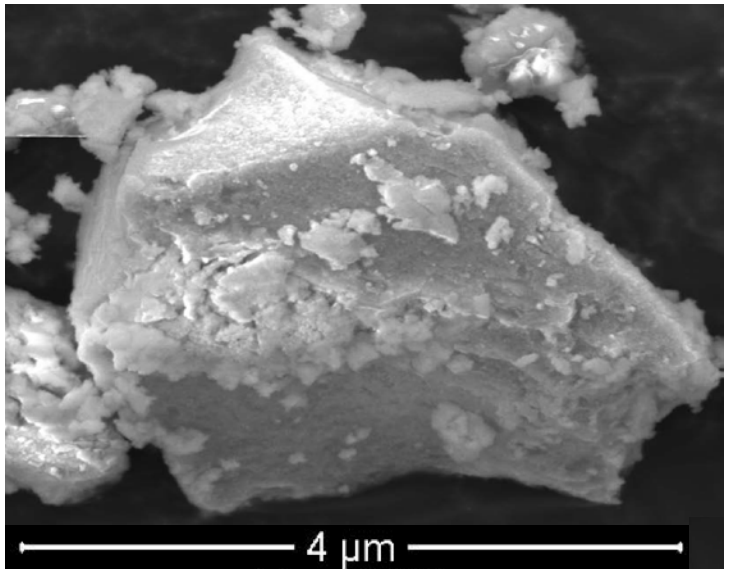
Solution Precursor Plasma Spray Process (SPPS)



- solidified micron size particles as well as agglomerated vapor-quenched particles

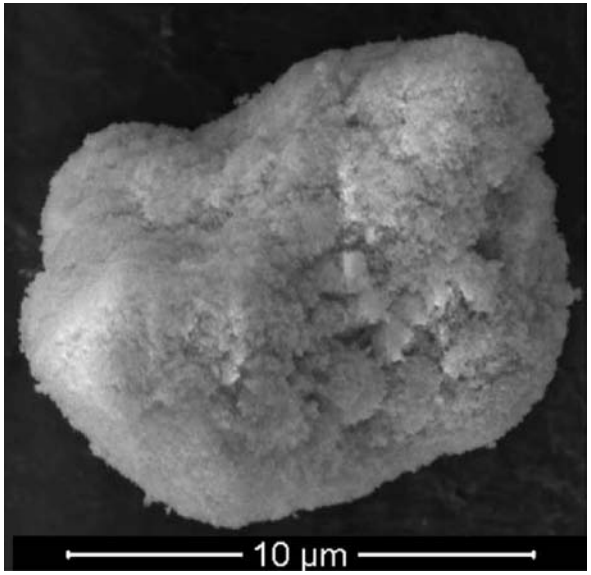
Task 3.3: Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture

Molecular Decomposition



- Fragmentation of a large mass of chemically reacted material
- Broad XRD pattern suggests very small crystallite size and non-crystalline product

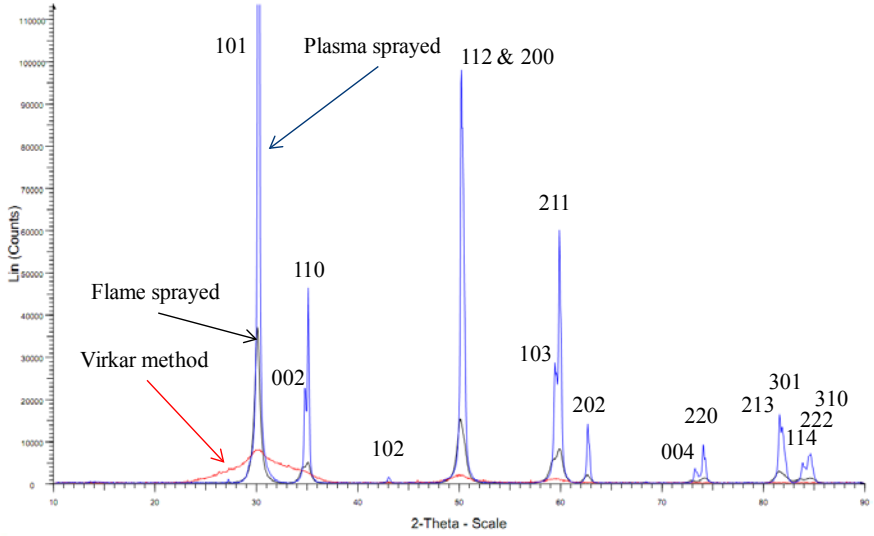
Reactive Spray Deposition Technology

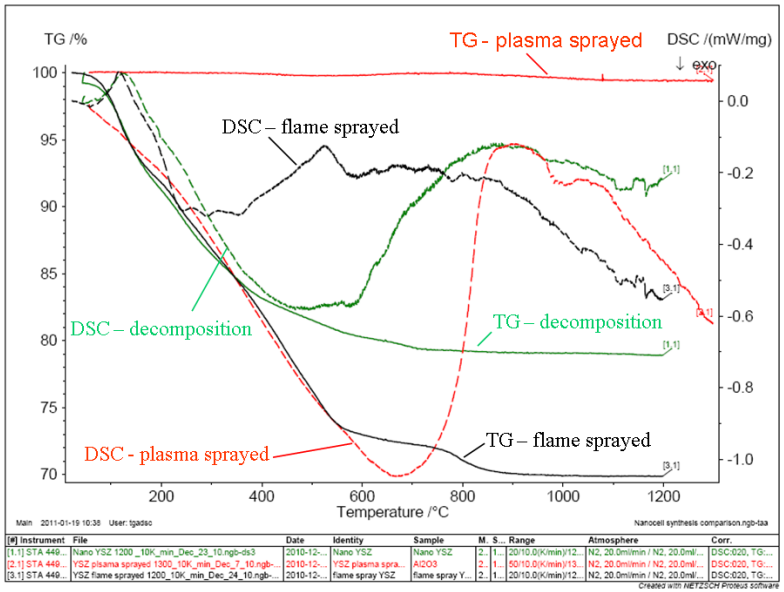


- Individual nanoparticles exist within a loosely agglomerated micron-size particulate
- By ultrasonication, the nanoparticles within such agglomerate may be dispersed to form a slurry or colloidal suspension

Task 3.3: Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture

Material Characterization





- The pattern of all three powders nominally matches that for PDF card: 00-048-0224 corresponding to $Zr_{0.92}Y_{0.08}O_{1.96}$ with a tetragonal lattice and space group #137 (P42/nmc) with a= 3.61100 and b = 5.16750 Å.
- Endothermic peaks of the DSC trace for the decomposition and flame sprayed peaks located at 120°C are attributed to desorption of the adsorbed water
- Plasma sprayed powder does not exhibit water desorption due to the fact that the powder was heat treated at 160°C for 2 days after filtration

Task 3.3: Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture

Future Work

- Powders will be synthesized by three separate synthesis methods and characterized.
- Batch powder synthesis techniques to produce large batches of given formulations will be developed.
- Electrical and structural properties of the synthesized powders will be measured. Mechanisms for modifications in electrical and structural properties will be developed and validated.