NM DOE EPSCoR Implementation Program

DOE EPSCoR Annual Meeting: July 20-23, 2008, Brookhaven National Lab

Materials for Energy Conversion

First Year Report and Program Overview

DOE/OS, EPSCoR Program Director: **Tim Fitzsimmons**

PI: **Plamen Atanassov** – UNM, Director of the Center for Emerging Energy Technologies

Co-PIs: **Kateryna Artyushkova** – UNM, Associate Director of CEET

Abhaya Datye – UNM, Director of the Center for Micro-Engineered Materials

Julia Fulghum – UNM, Vice President for Research

Corey Leclerc – NMT, Assistant Professor of Chemical Engineering

Heinz Nakotte – NMSU, Professor of Physics and LANL/LANSCE Instr. Scientists

Dimiter Petsev – UNM, Assistant Professor of Chemical & Nuclear Engineering

Tim L. Ward – UNM, Professor and Chair of Chemical & Nuclear Engineering

Juchao Yan – ENMU, Professor of Physical Sciences

Igor Sevostianov – NMSU, Associate Professor of Mechanical Engineering

Boris Kiefer – NMSU, Associate Professor of Physics (on sabbatical at UNM)

Mike Riley – NMT, Assistant Professor of Chemical Engineering

DOE EPSCoR Program in Context…

CENTER FOR EMERGING ENERGY TECHNOLOGIES

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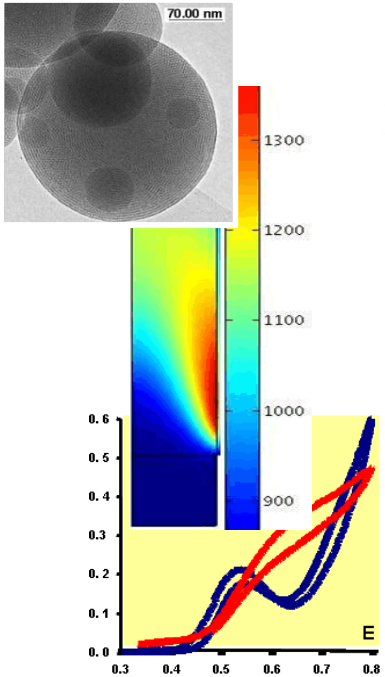


CEET FIRST NEW COLLABORATIVE INITIATIVE

DOE Experimental Program to Support Competitive Research

Materials for Energy Conversion:

Bridging Biofuel and Fuel Cell Technology through Ethanol Reforming and Direct Electro-oxidation

University of New Mexico
New Mexico Tech
New Mexico State
Eastern New Mexico University

In collaboration with:
Los Alamos National Laboratory
Sandia National Laboratories
Brookhaven National Laboratory

Leveraging on DOE-OS BES Program in Catalysis:
Methanol and Ethanol Reforming Catalysis

Office of Basic Energy Sciences · Serving the Present, Shaping the Future

Leveraging on DOE-EERE HFCTI Programs through LANL:
Los Alamos National Laboratory
Argonne National Laboratory
Brookhaven National Laboratory
Oakridge National Laboratory
University of Illinois, Urbana-Champaign
University of California, Riverside
University of New Mexico
Supported by the State of New Mexico (NMT) and UNM SOE startup for CEET

DOE Hydrogen Program

- ❑ 07 Advanced Cathode Catalysts
- ❑ 09 Increased Platinum Utilization
- ❑ 09 Nanoscale Ceramic Supports
- ❑ 09 Catalyst Layer Corrosion
- ❑ 09 PEMFC Durability

In collaboration with: GM – Fuel Cells
Cabot - SMP
Ballard Power Systems

GM

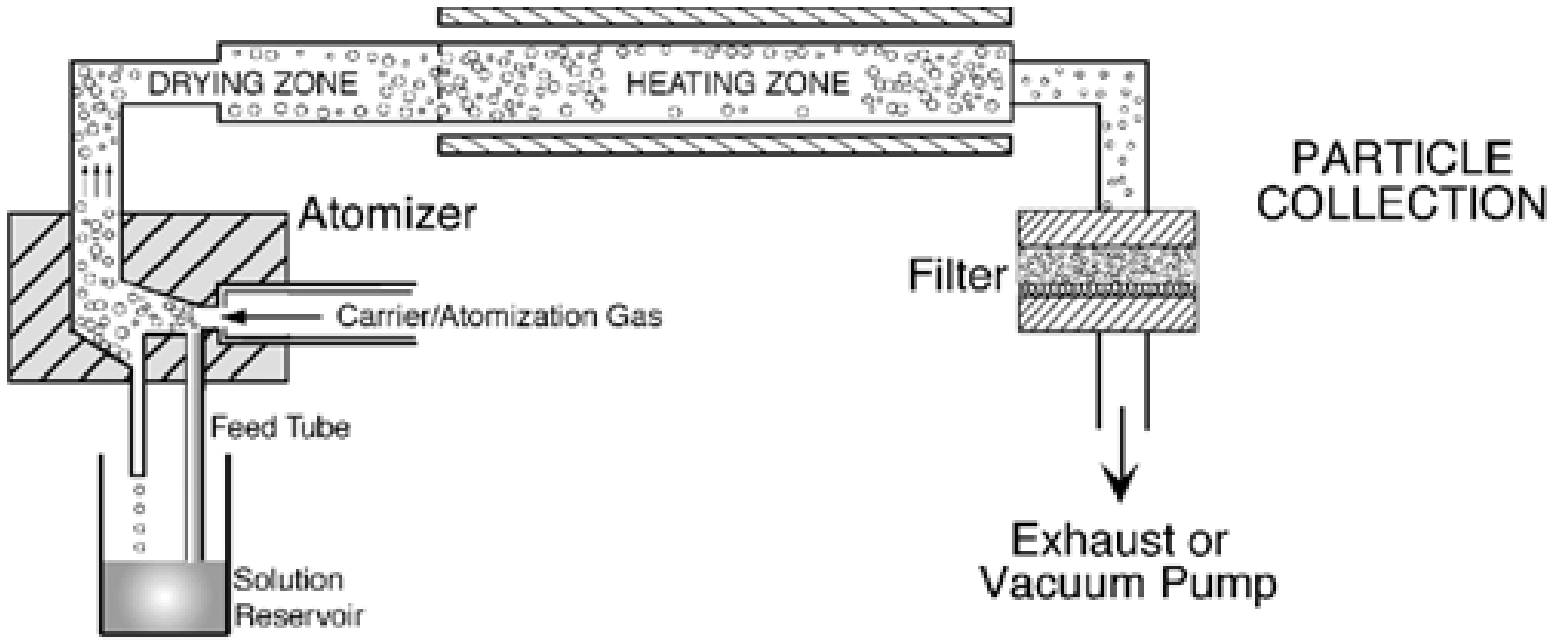
CABOT

BALLARD®

Primary Particle Synthesis Approach

Spray Pyrolysis

Lu et al, Nature 398, 223 (1999)



Features/Strengths of Spray Pyrolysis

- Spherical particles; control of particle size/distribution
- Homogeneous precursor solution – easily controlled, uniform particle composition; easy to dope
- Droplet/particle acts as container/microreactor – purity control, minimal internal diffusional resistance
- Very short process time: ~ seconds
- Scaleable/proven technology

Evaporation-Induced Self-Assembly

CENTER FOR MICRO-ENGINEERED MATERIALS

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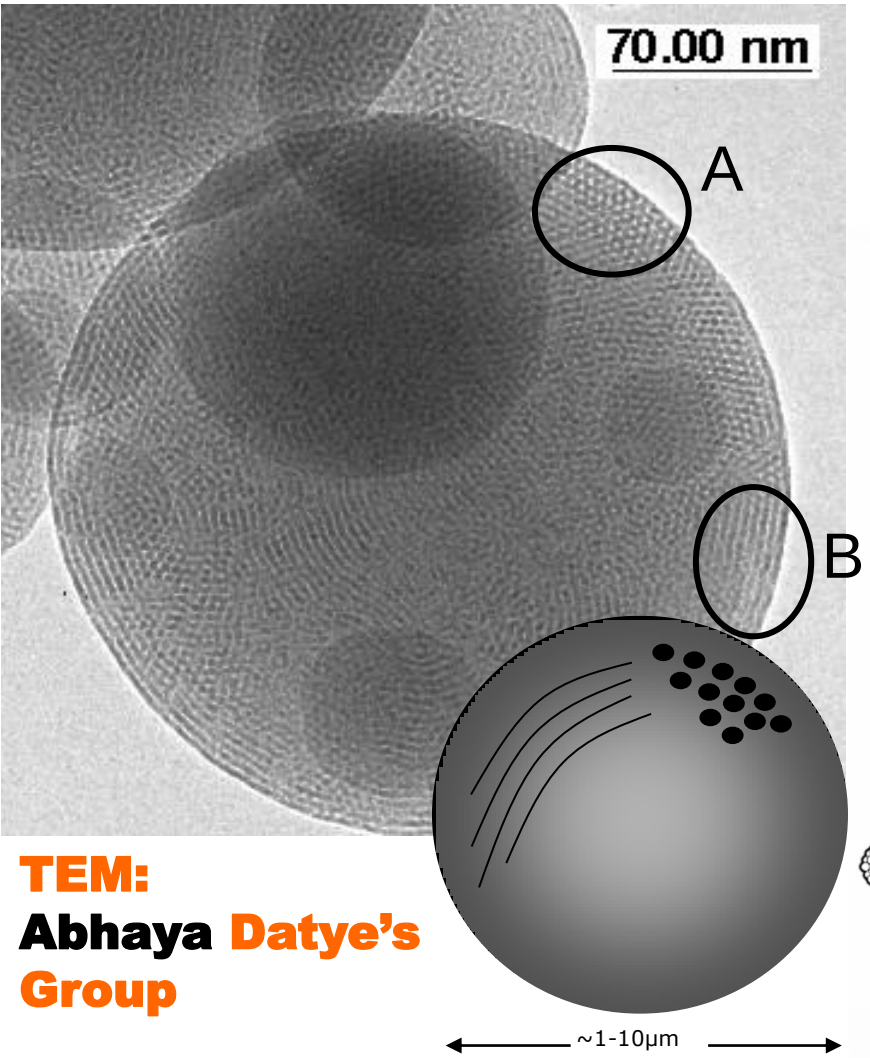
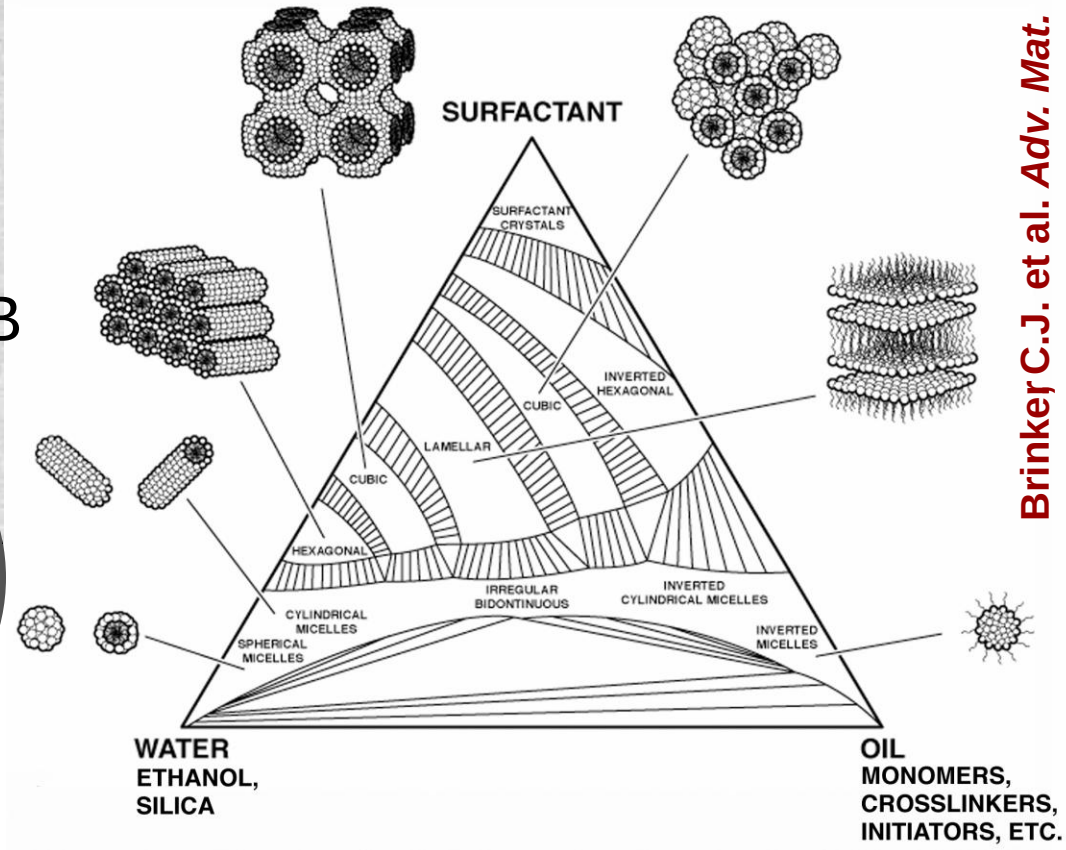


TEM:
Abhaya Datye's Group



Brinker C.J. et al. *Adv. Mat.* 11, 1999.

Structures-by-Design

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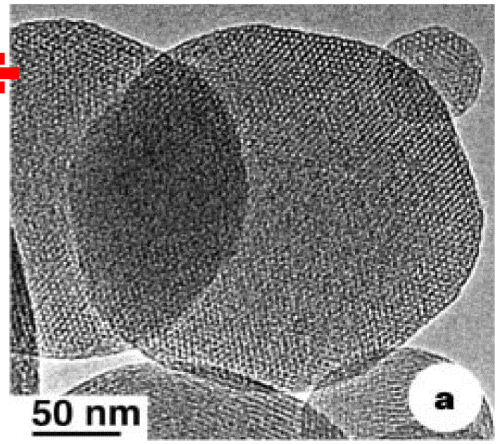
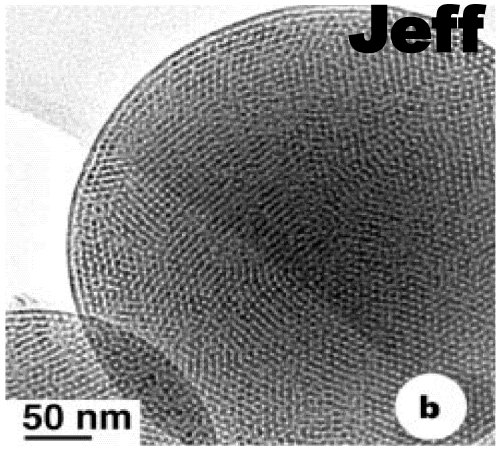
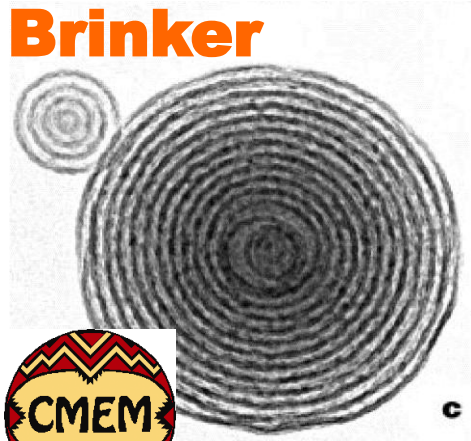
CENTER FOR MICRO-ENGINEERED MATERIALS

Gabriel Lopez

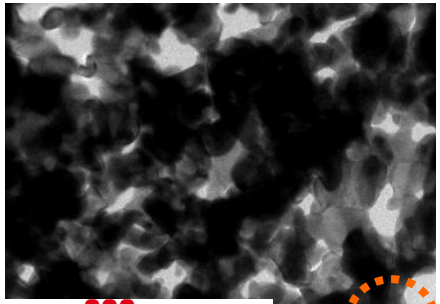


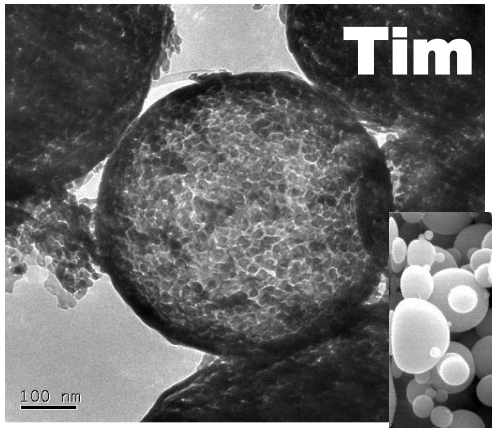
Jeff Brinker





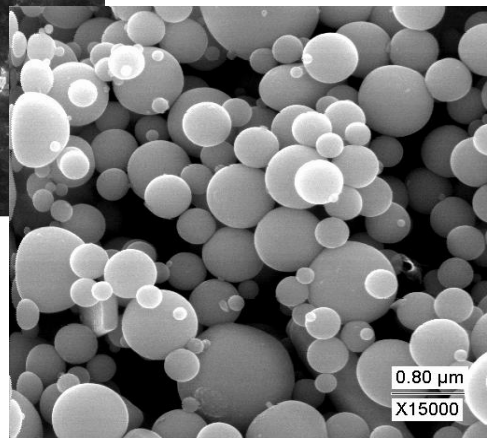
Abhaya

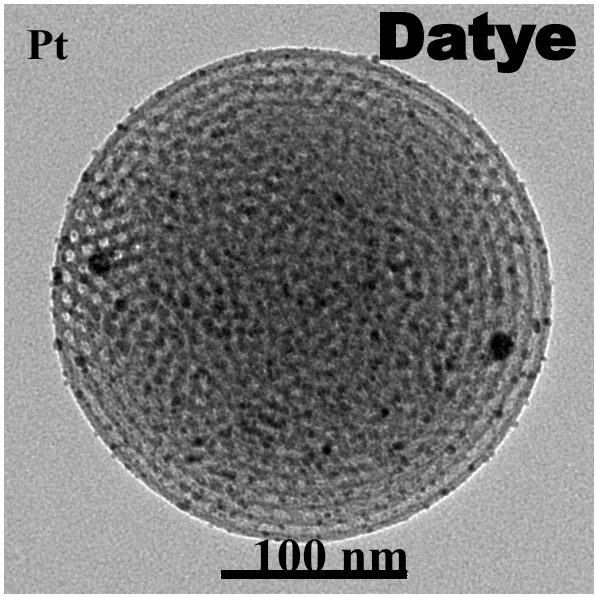




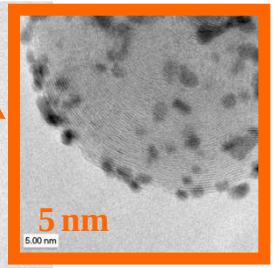
Tim Ward

department of chemical & nuclear engineering





Datye



Plamen Atanassov

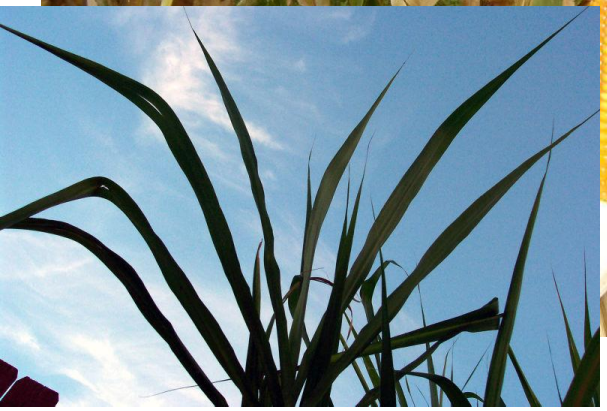
70.00 nm

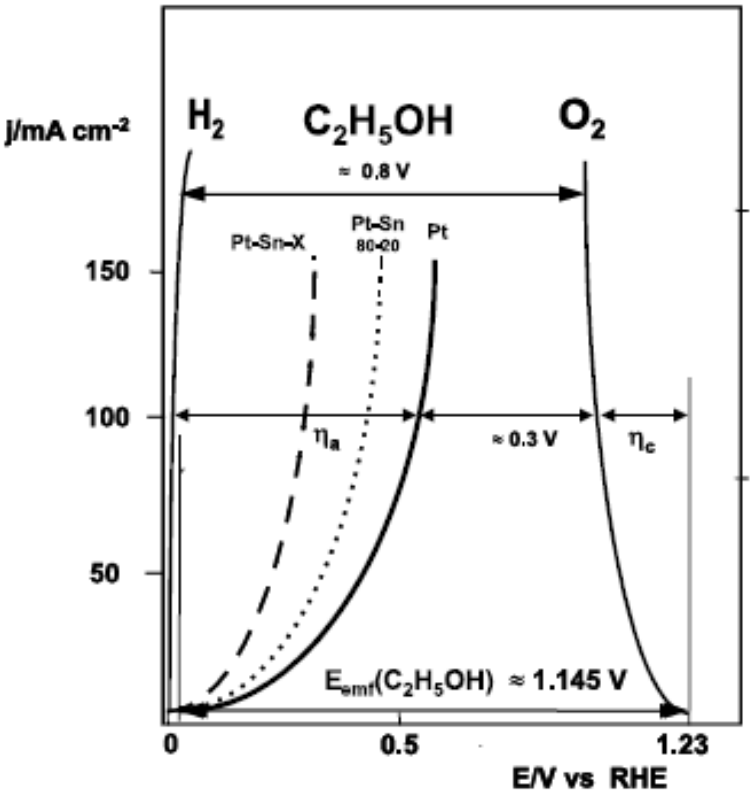
Center's Research "Hall of Fame" Program

Alcohols as a Renewable Fuels

Motivation

Ethanol can be produced from the fermentation of corn and sugar cane which makes it a truly renewable source of hydrogen.





C. Lamy, E.M.B., J.M. Leger, Journal of Applied Electrochemistry, 2001. 31: p. 799-809.

$$ANODE: C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$$

$$CATHODE: 3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$$

$$OVERALL: C_2H_5OH + 3H_2O + 3O_2 \rightarrow 2CO_2 + 6H_2O$$

Fuel	Energy Density (kWh/kg)
H_2	32.8
H_2 (Tank Storage ~1.5 wt%)	0.42
Methanol	6.1
Ethanol	8.1

Oxidation and Electro-oxidation

Chemical/Electrochemical Reaction Similarities

Chemical reaction

Step 1: Reforming $CH_3CH_2OH + H_2O \leftrightarrow 2CO + 4H_2$

Step 2: Water-Gas Shit $2CO + 2H_2O \leftrightarrow 2CO_2 + 2H_2$

Overall: $CH_3CH_2OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$

Electrochemical reaction

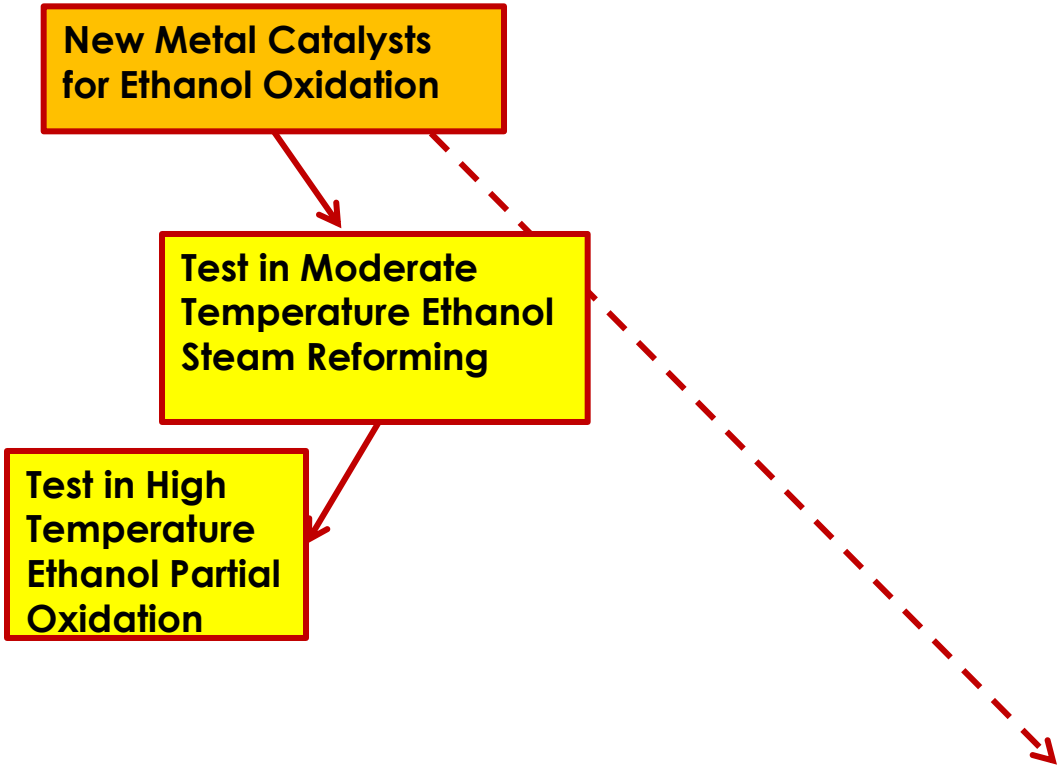
Anode: $CH_3CH_2OH + 3H_2O \leftrightarrow 2CO_2 + 12H^+ + 12e^-$

Cathode: $3O_2 + 12H^+ + 12e^- \leftrightarrow 6H_2O$

Overall: $CH_3CH_2OH + 3H_2O + 3O_2 \leftrightarrow 2CO_2 + 6H_2O$

Materials for Energy Conversion

Reforming and Oxidation of Ethanol

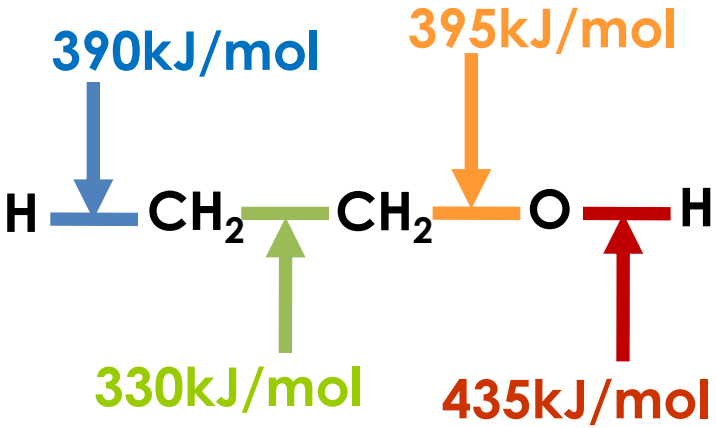


Ethanol Steam Reforming

Catalyst Requirements

THE UNIVERSITY of NEW MEXICO

Abhaya Datye



- Metal oxide catalyst, ex: ZnO, CeO_2
  - Cleave O-C bond (~395kJ/mol)
  - Cleave O-H bond (~435kJ/mol)
  - Oxidize C and CO
- Metal, ex: Rh, Pd
  - Cleave C-H bonds (~390kJ/mol)
  - Bond H
- Solution: metal supported on oxide catalyst, ex: Pd/ZnO, Rh/CeO_2
  - Cleave C-C bond (~330kJ/mol)
  - Coking is a major problem
    - ex: Ni makes carbon nanotubes.

- Need a Complex catalyst system that includes Oxide, metals, and alloys
  - Nature and importance of interactions of the catalyst system components is unclear

Ethanol Steam Reforming Catalysts

Synthesis of Phase Pure Pd-Zn Catalysts

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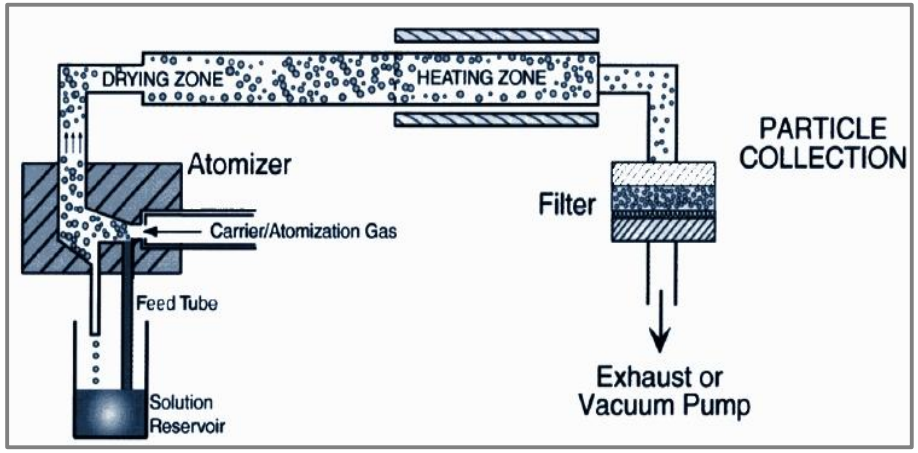
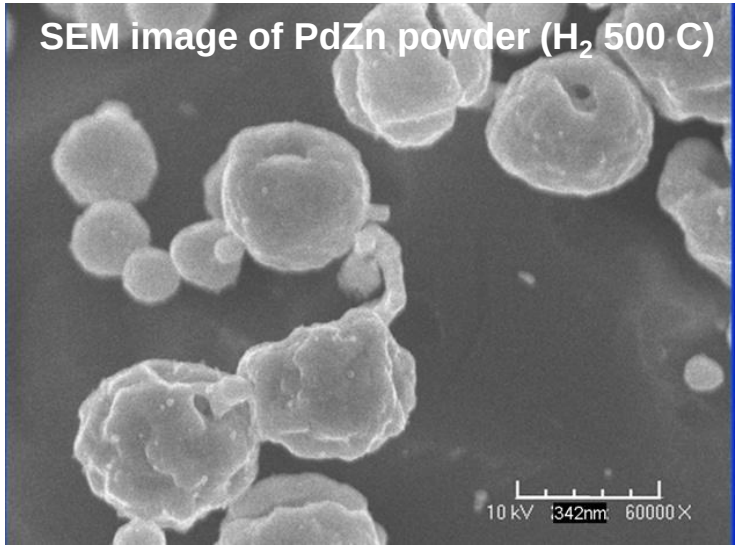
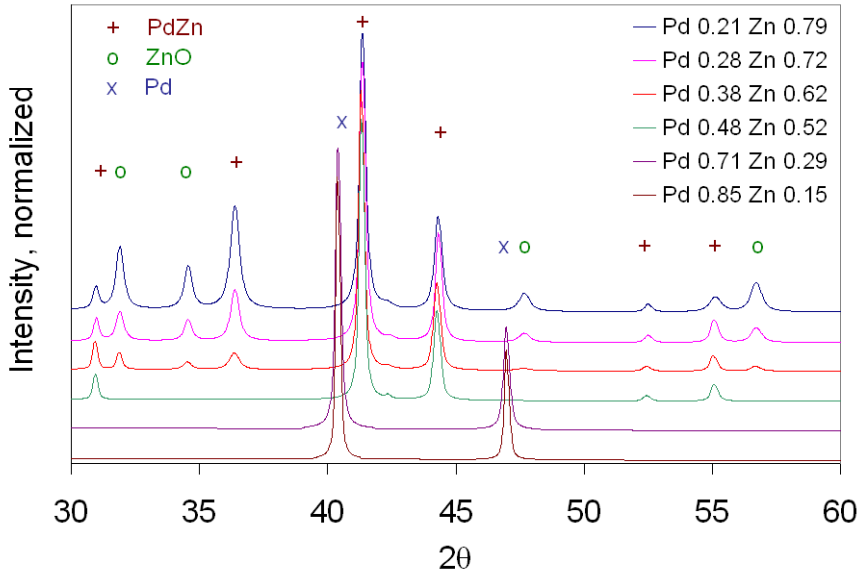
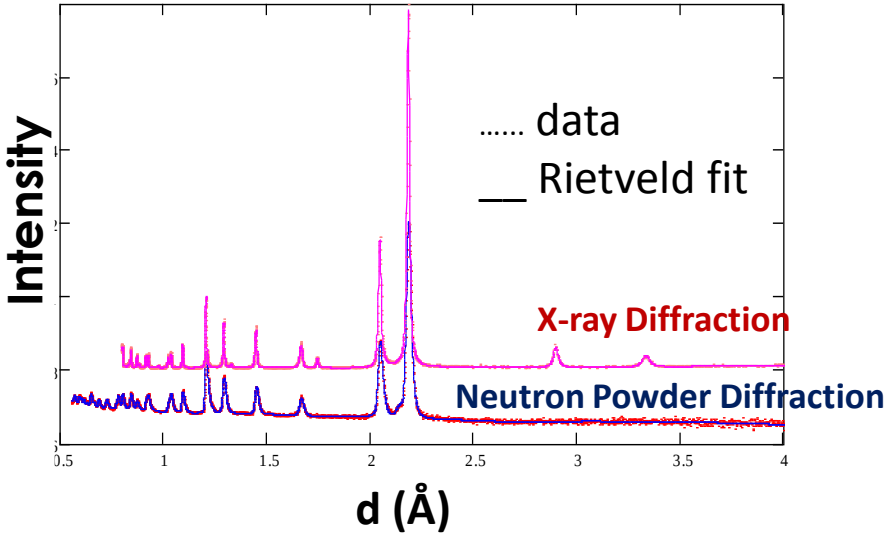


Aerosol synthesis of alloy powders





XRD shows that the PdZn phase forms at ~50%Pd



X-ray and Neutron Diffraction confirm uniformity, structure and phase purity

Ethanol Steam Reforming Catalysts

Temperature Programmed Reaction over Ordered Pd-Zn

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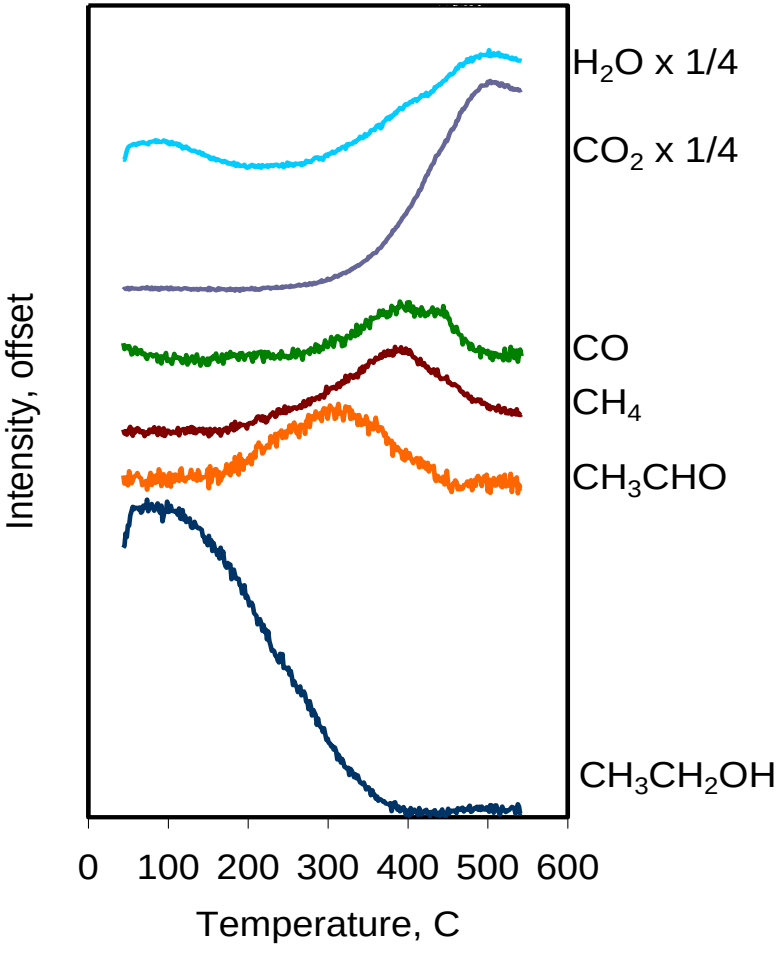
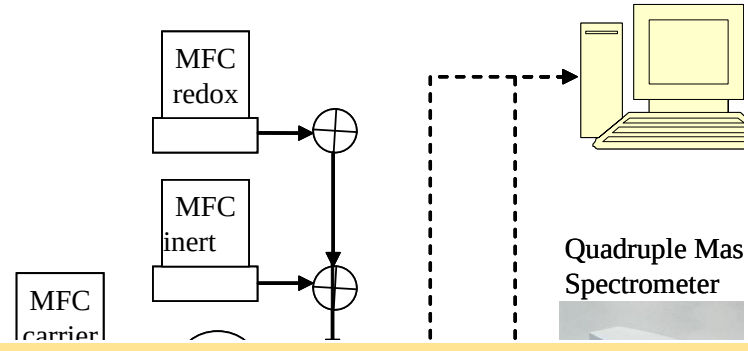
Temperature Programmed Desorption and Reaction have been used to evaluate catalyst performance and map possible reactions and reaction barriers.





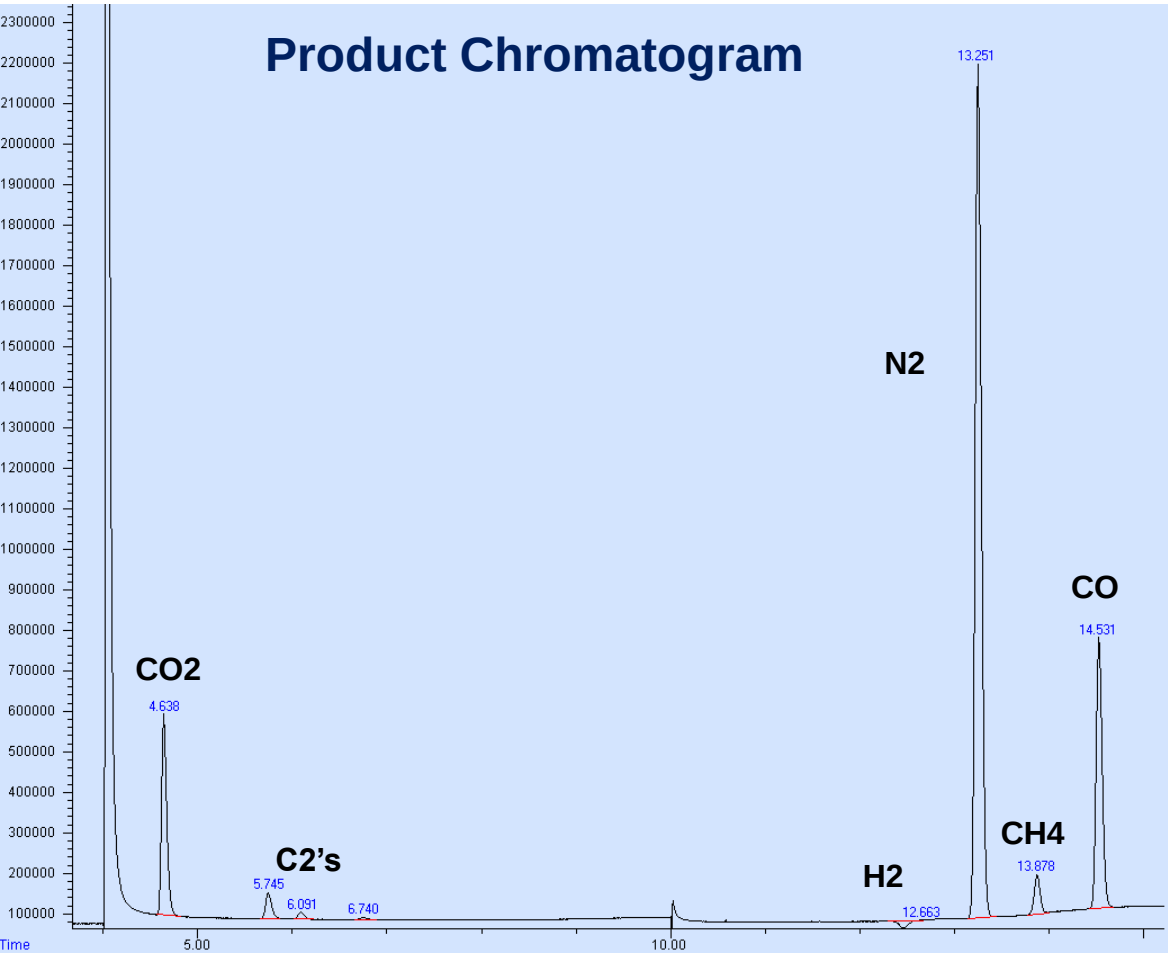
Preliminary work shows that ethanol decomposition on 1:1 bulk PdZn alloys leads to Acetaldehyde production at a lower temperature than CO and CH_4. This indicates that dehydrogenation of ethanol is energetically preferred over decomposition. Future work will be directed at detailed characterization of single phase alloy systems.

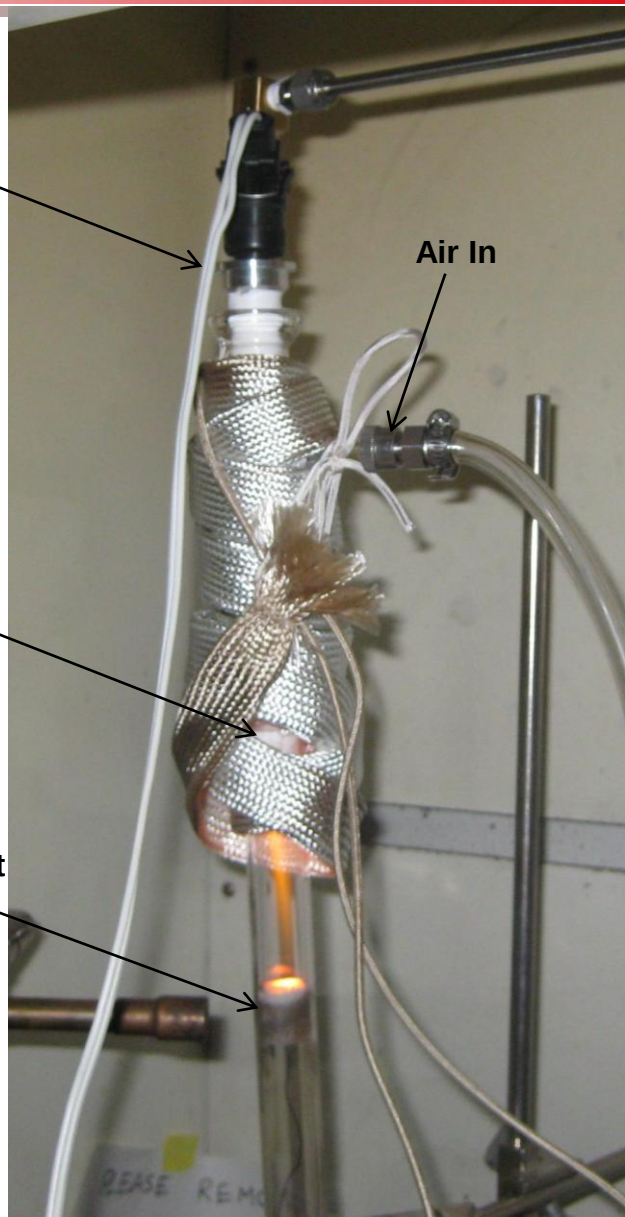
Catalytic Partial Oxidation of Ethanol

New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY

Partial Oxidation Experiments

Corey Leclerc



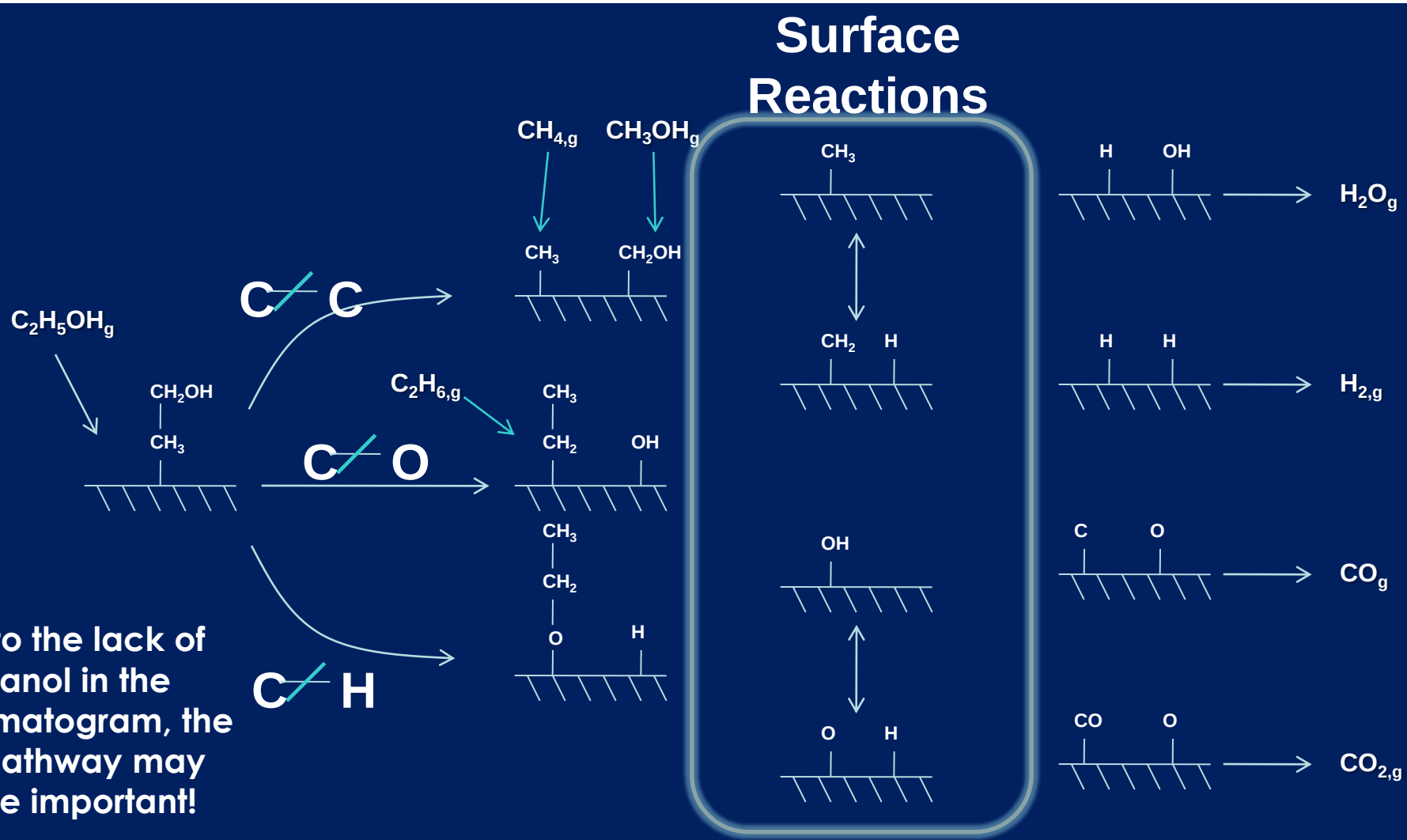


Catalytic Partial Oxidation of Ethanol

New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY

Ethanol Reaction Pathway

CO/CO2, and ethylene peaks dominate pointing to the middle and bottom paths as primary steps on Pt/Al_2O_3

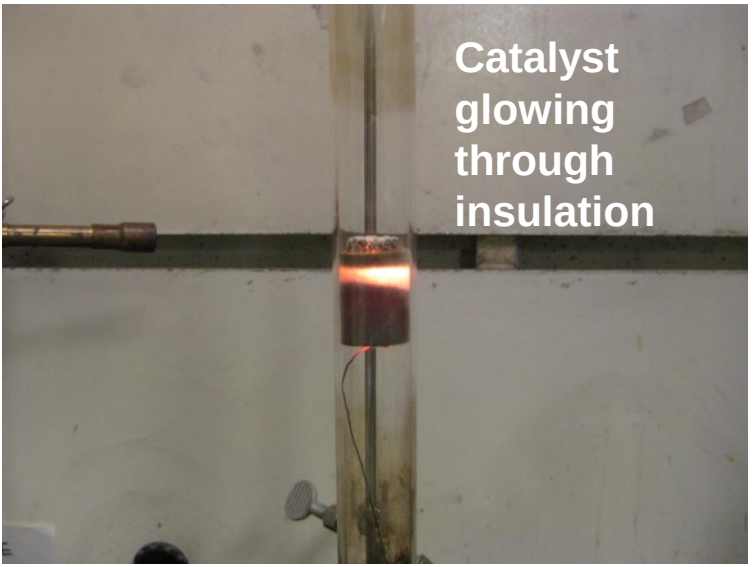


Due to the lack of methanol in the chromatogram, the top pathway may not be important!

Catalytic Partial Oxidation of Ethanol

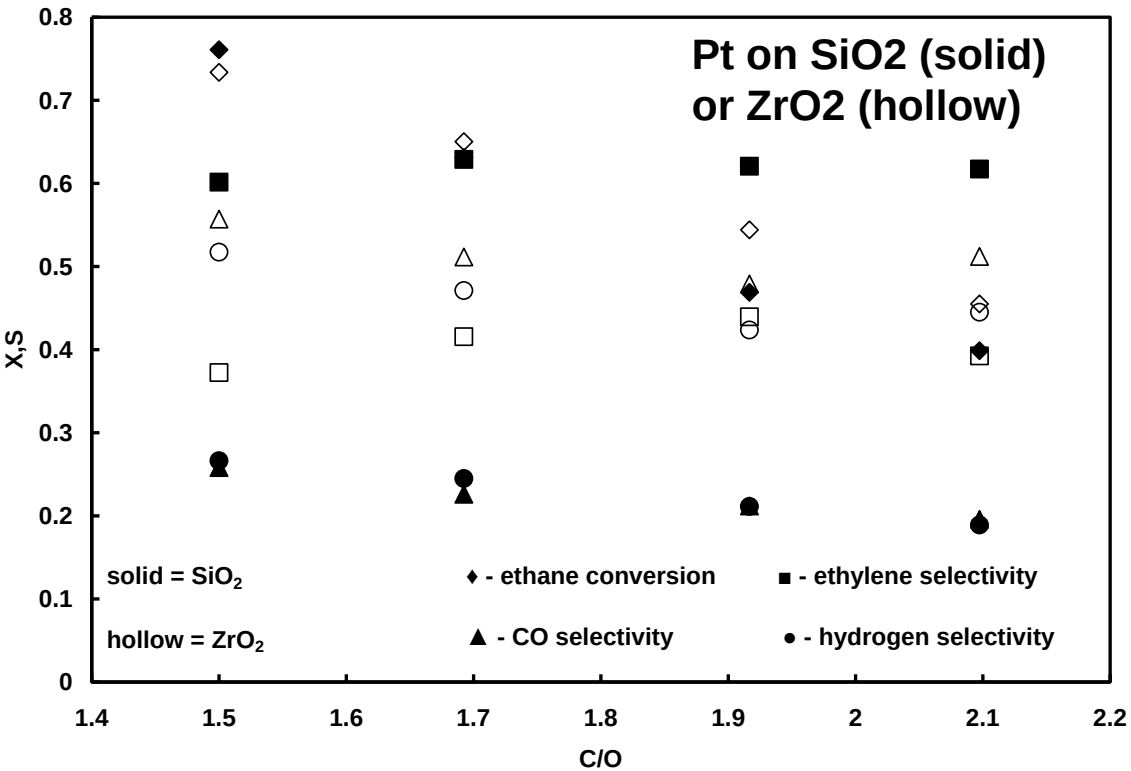
New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY

Ethane Partial Oxidation



Glowing catalyst from ethane partial oxidation experiment

At similar conversions, zirconia supported platinum produces more syngas (CO/H2 : C-C bond breakage) than silica (C2H4 : dehydrogenation)!

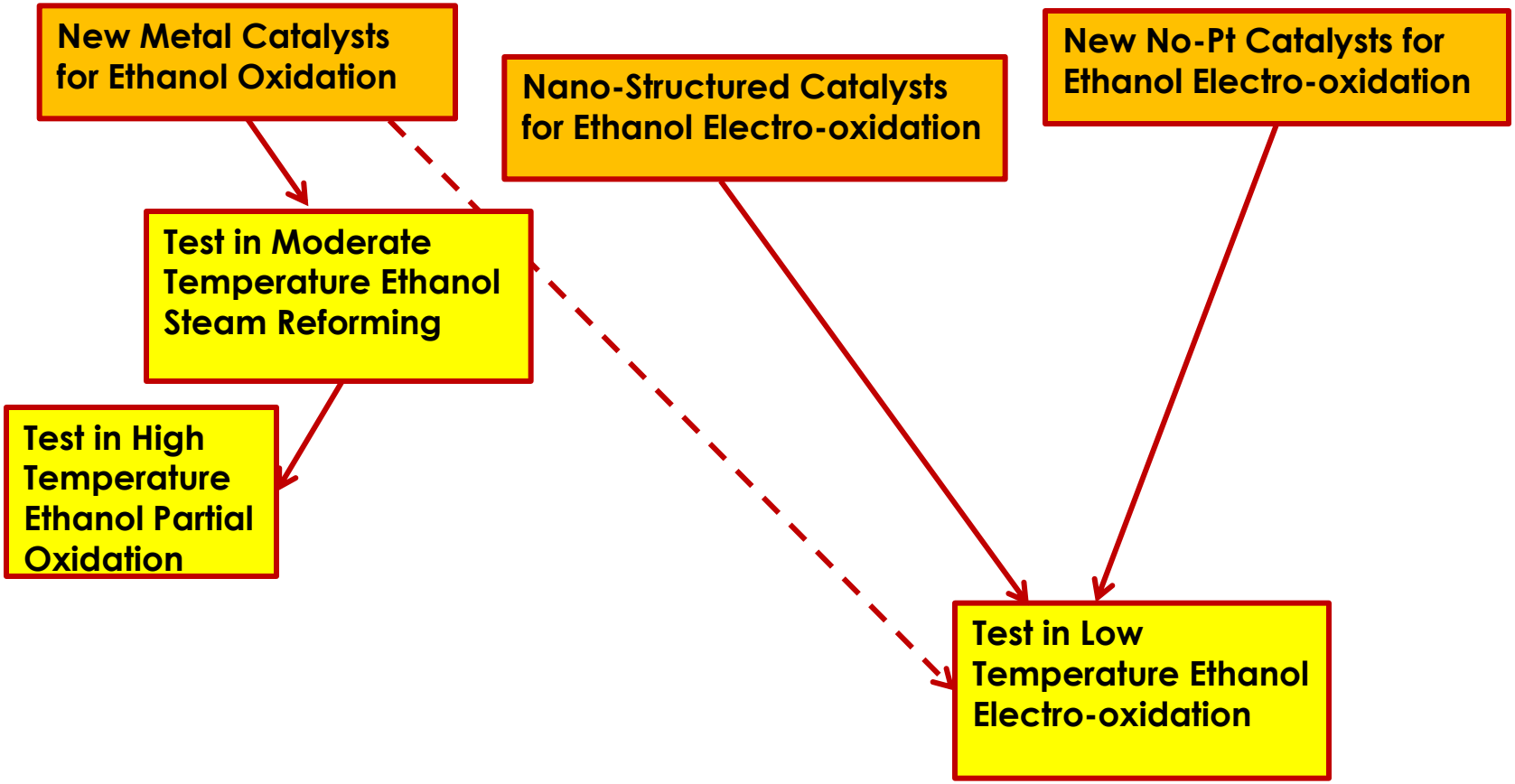


To Do:

Change pore sizes to determine importance of gas phase reactions build pathway part of mechanism for ethane POx perform temperature programmed reactions with ethane/ethanol identify aldehyde in chromatogram to identify pathway

Materials for Energy Conversion

Ethanol Electro-oxidation



Ethanol Oxidation Electrocatalysts

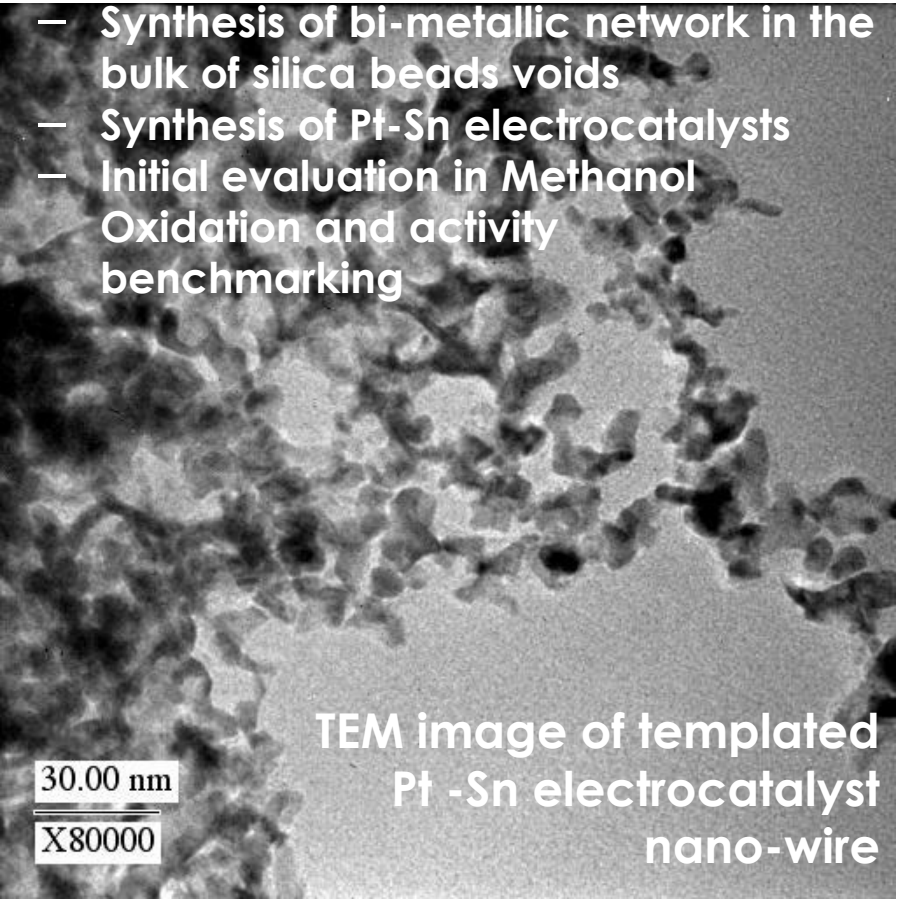
Catalysts Synthesis Approach

THE UNIVERSITY of NEW MEXICO

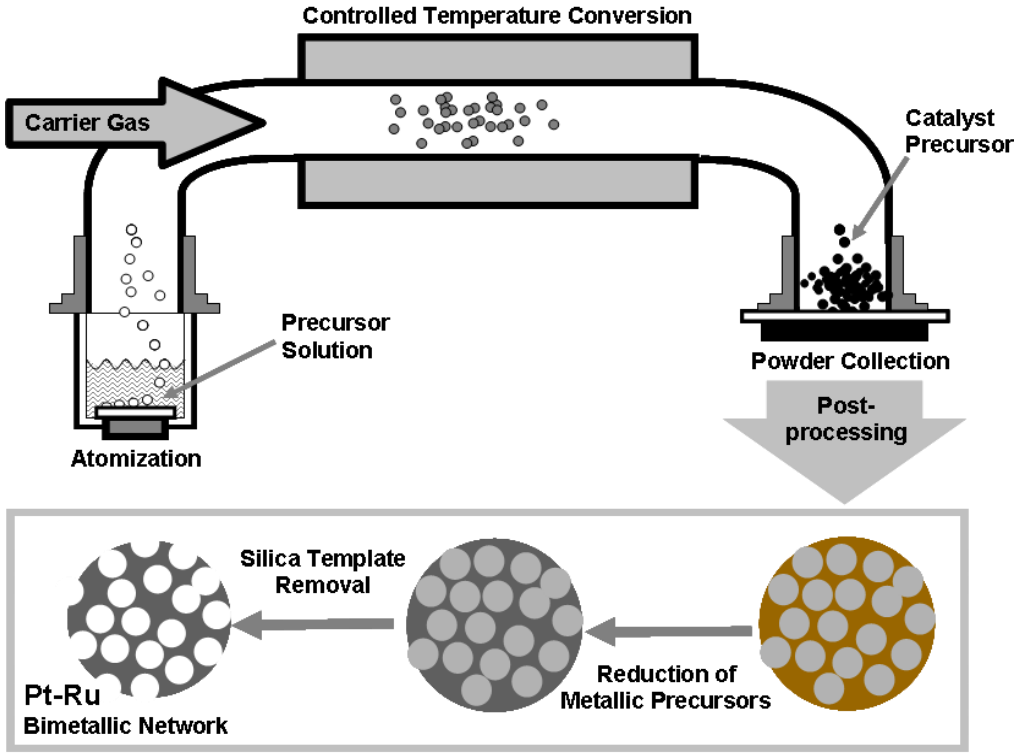
Plamen Atanassov

Results/Accomplishments:

- Templating noble metal nanowires in mesoporous silica
  - Synthesis of bi-metallic network in the bulk of silica beads voids
  - Synthesis of Pt-Sn electrocatalysts
  - Initial evaluation in Methanol Oxidation and activity benchmarking



TEM image of templated Pt -Sn electrocatalyst nano-wire



Approach:

- Templating amorphous or mesoporous silica particles in EISA during spray pyrolysis synthesis of bi-metallic allows
- Removal of the silica by etching
- Evaluation of the catalysts by RRDE

Aerosol-Templated Catalysts

Pt-Sn Ethanol Oxidation Anode Catalyst

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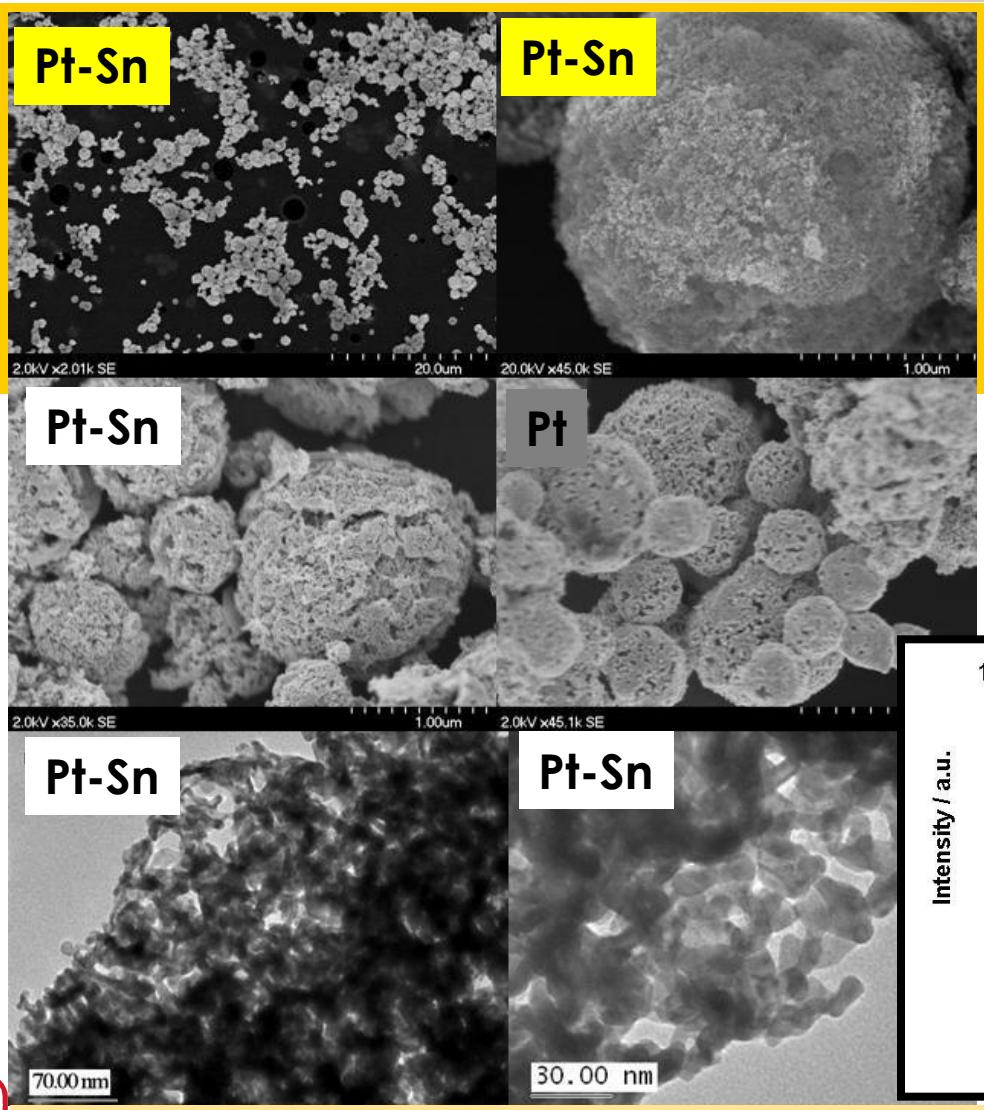
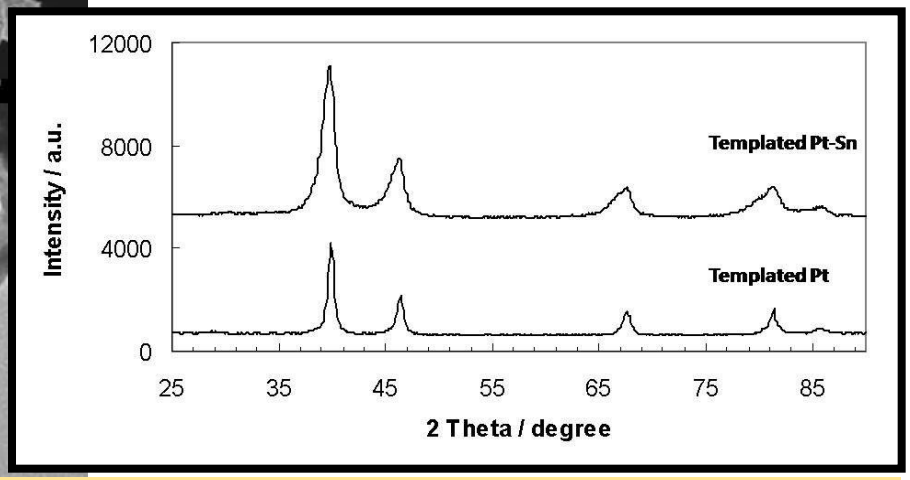
BEFORE silica template removal



Synthesis of structured electrocatalyst by templatig of the metal on silica particles and subsequently dissolving the silica template.

Materials characterization by PSD, XRD, BET, XPS, HRTEM and SEM



E. Switzer, T.S. Olson, A. K. Datye, P. Atanassov, M.R. Hibbs and C.J. Cornelius, Templated Pt-Sn Electrocatalysts for Ethanol, Methanol and CO Oxidation in Alkaline Media, *Electrochimica Acta* 54 (2009) 989-995

Non-PGM Ethanol Electrocatalysts

Ni-Zn Alloy Catalyst Materials

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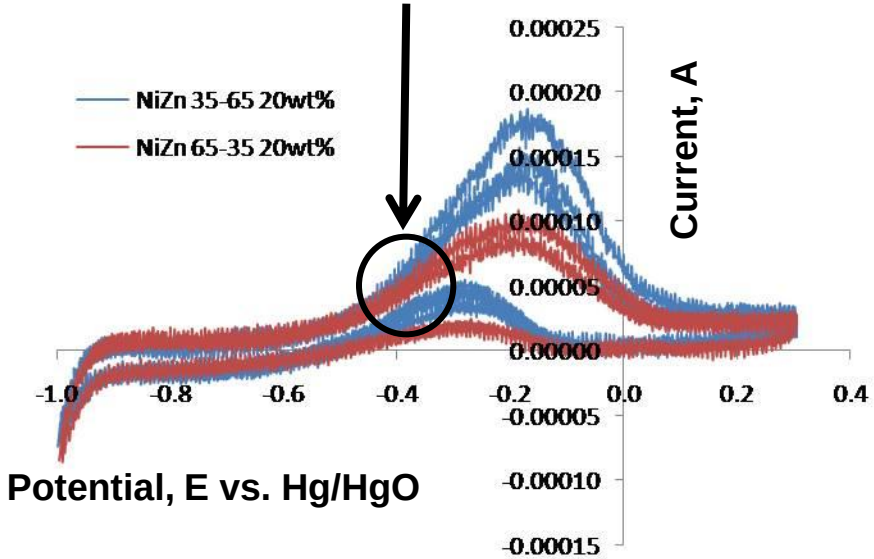
Ni-Zn/C catalyst synthesis:

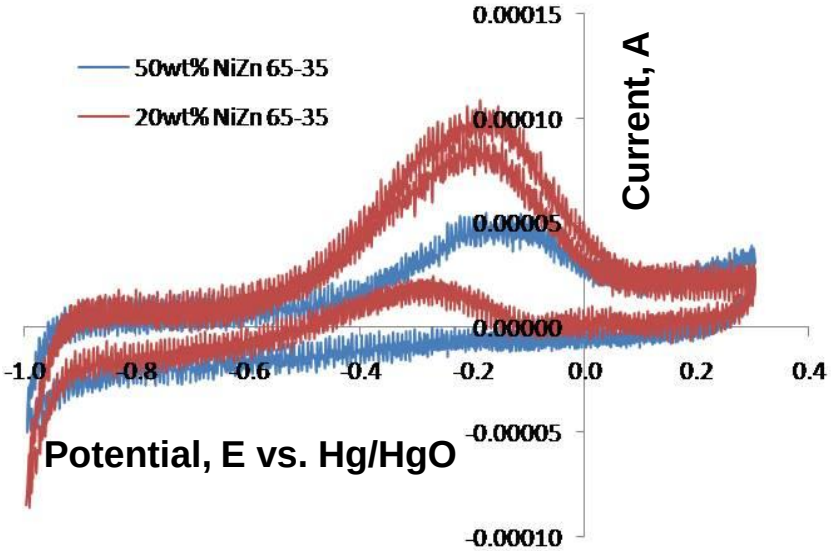
- Ni and Zn precursors were applied to XC-72 using a dry impregnation technique.
- Ni-Zn/C catalyst with different Ni:Zn wt ratios and overall metal loadings were synthesized

A highly dispersed metal phase is need for ethanol oxidation.

The Zn rich material shows better activity



20 wt% metal loading out performs 50 wt%



Non-PGM Ethanol Electrocatalysts

Highly Dispersed Ni Metal Phase

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Alcohol oxidation:

3 M KOH

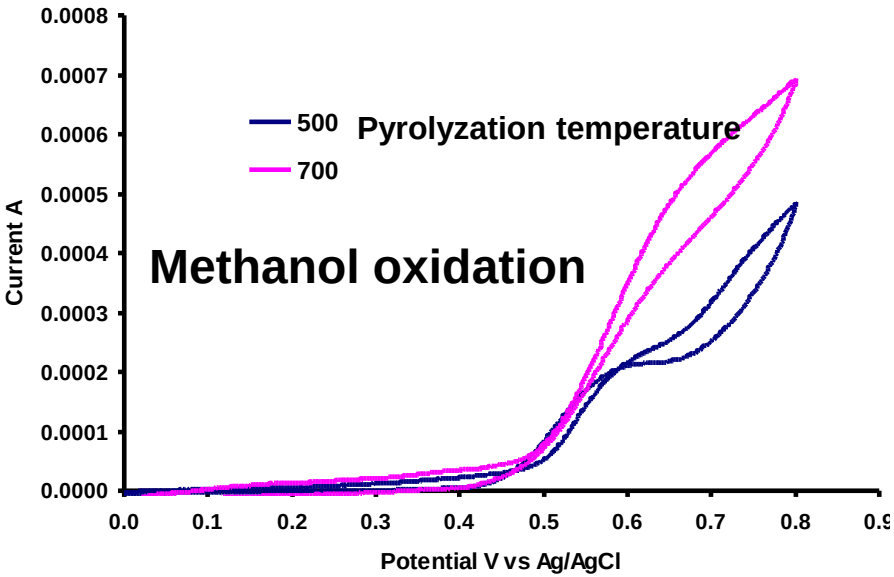
~5M alcohol concentration

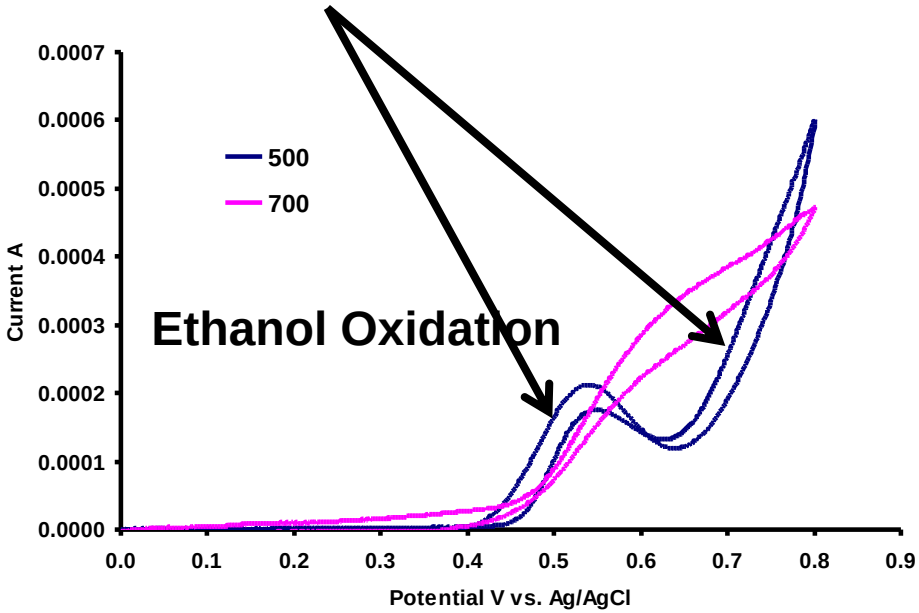
Templated Electrocatalyst Synthesis

Pyrolyzed Ni Porphyrin based catalyst material

1. Ni porphyrins templated on amorphous Si
2. Pyrolyzed at 500 C or 700 C
3. Si template removed by chemical etch

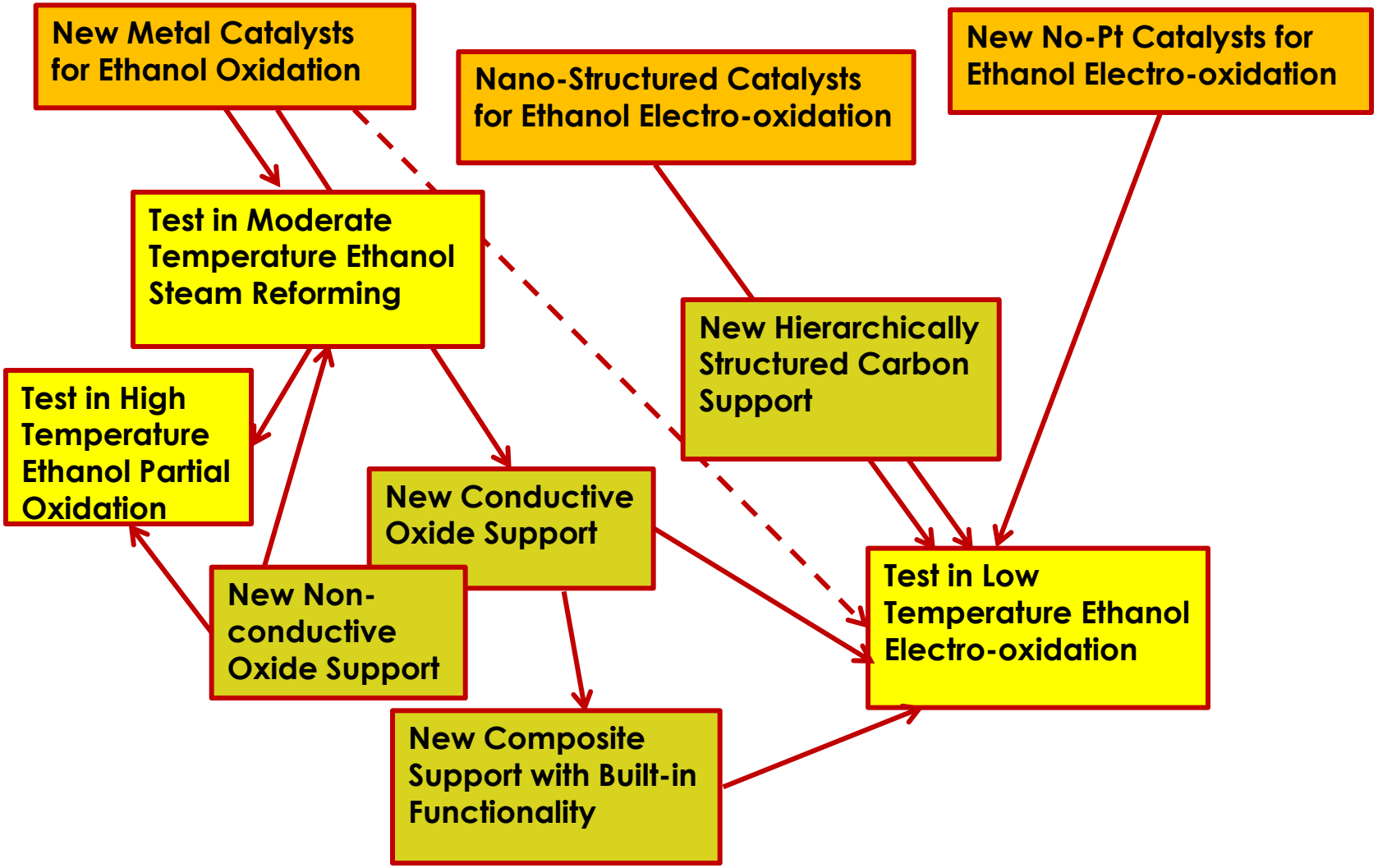
Two oxidation processes occur on the material pyrolyzed at 500 C





Materials for Energy Conversion

Catalyst Supports Design



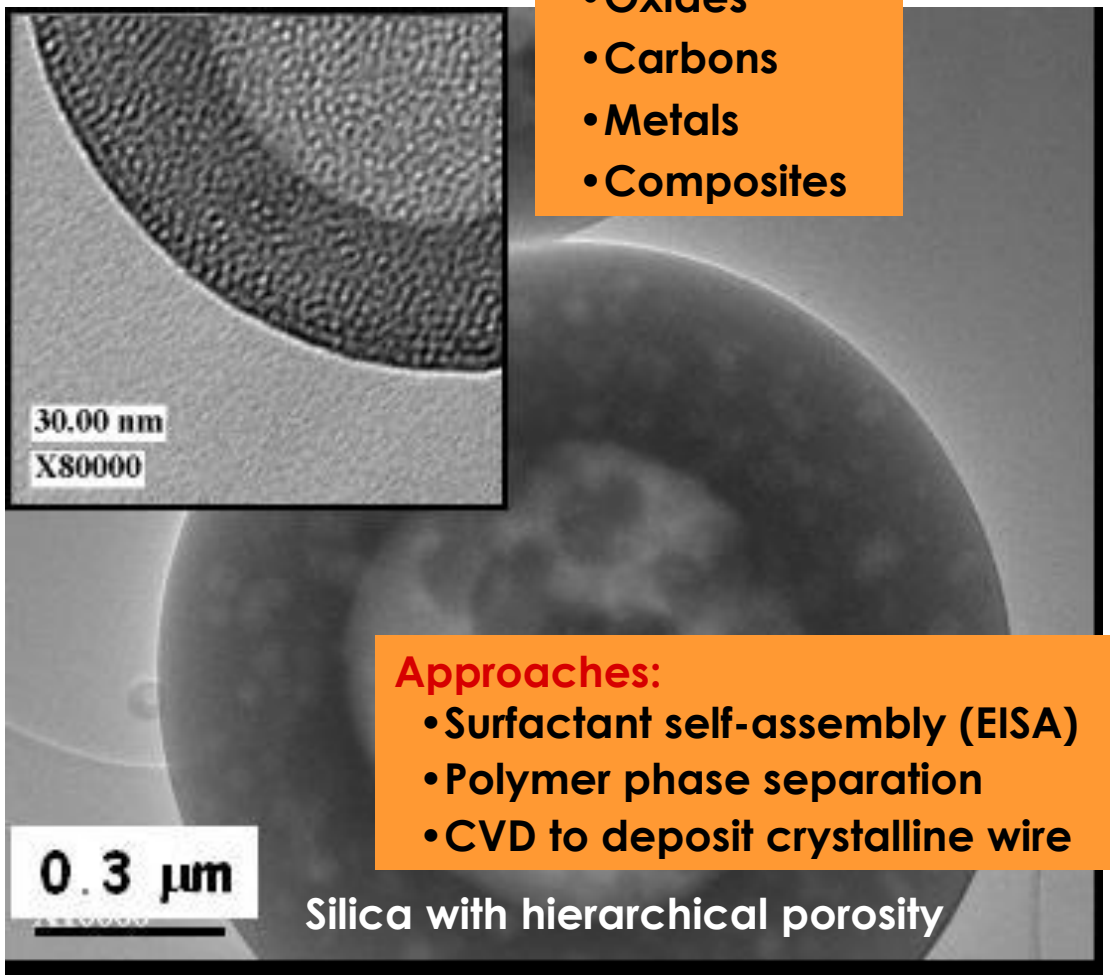
Aerosol Materials Synthesis

Meso-structured & Hierarchically Porous Particles

THE UNIVERSITY of NEW MEXICO

Tim L. Ward

Materials
- Oxides
- Carbons
- Metals
- Composites



Approaches:
- Surfactant self-assembly (EISA)
- Polymer phase separation
- CVD to deposit crystalline wire

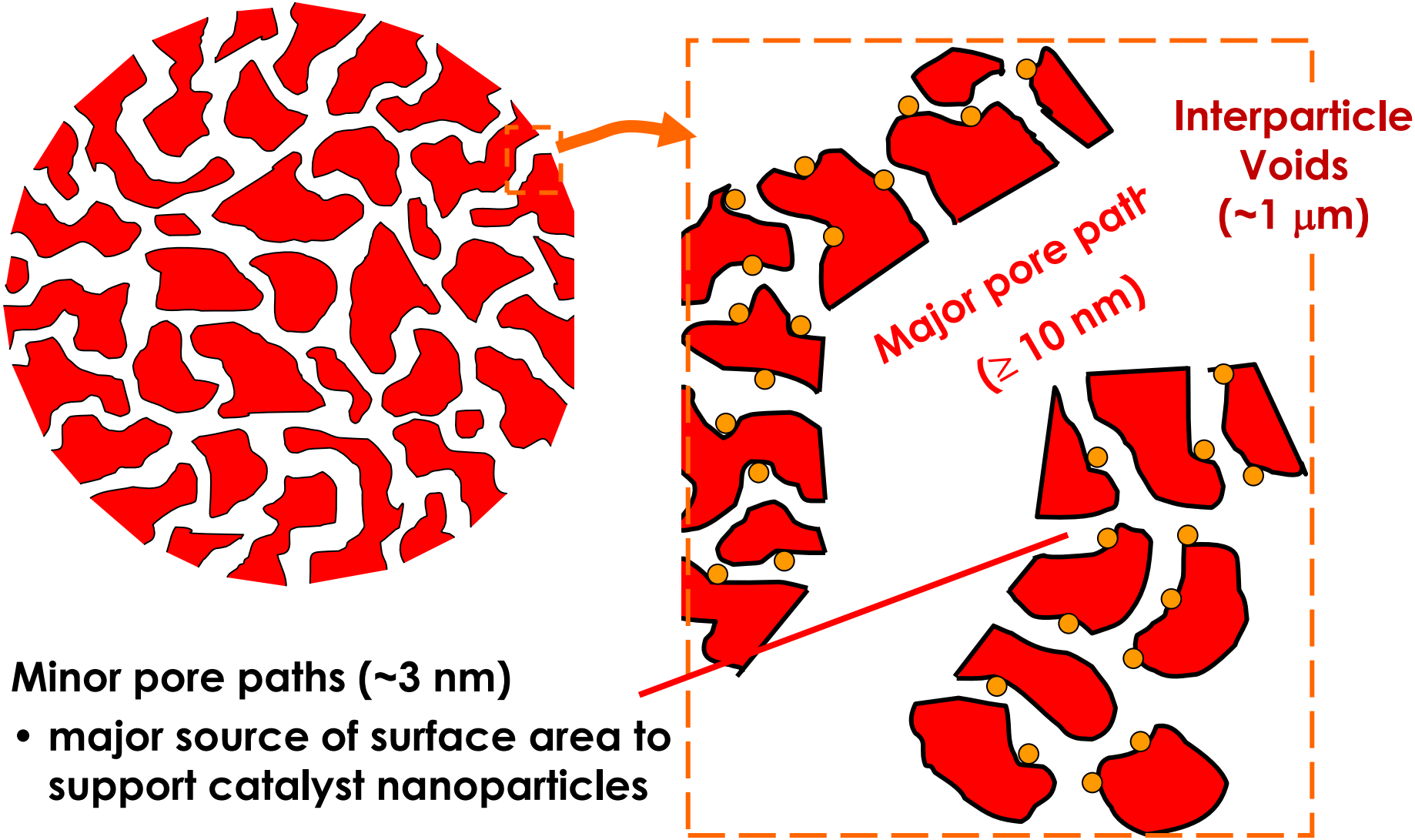
Silica with hierarchical porosity

Materials

- Electrocatalyst supports for fuel cells (conventional and ethanol oxidation)
  - Conducting oxides
  - Structured carbons
- Catalyst supports for ethanol reforming and oxidation activities (Datye and Le Clerc)
  - Structured oxides (nonconducting)

Synthetic Strategies

Hierarchical Pore Structure



Minor pore paths (~3 nm)

- **major source of surface area to support catalyst nanoparticles**

Supports Materials Systems

Conducting Metal Oxides: Nb-Ru-O

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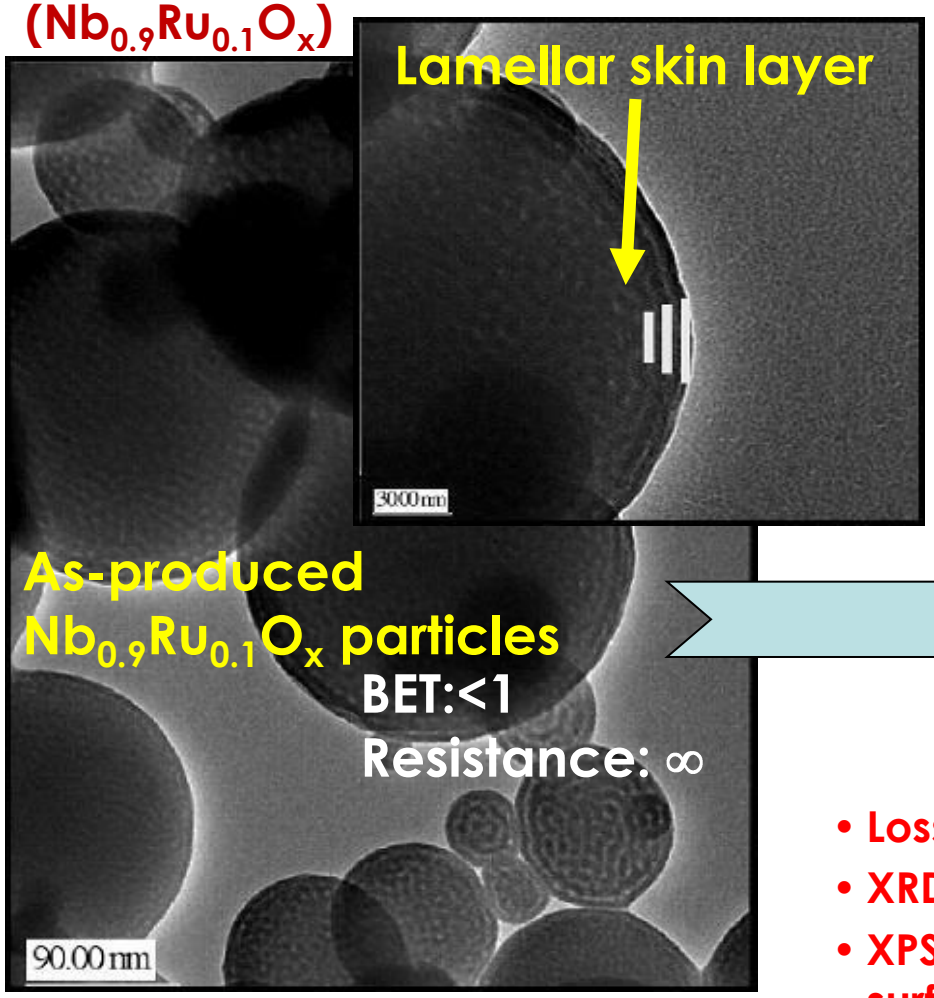
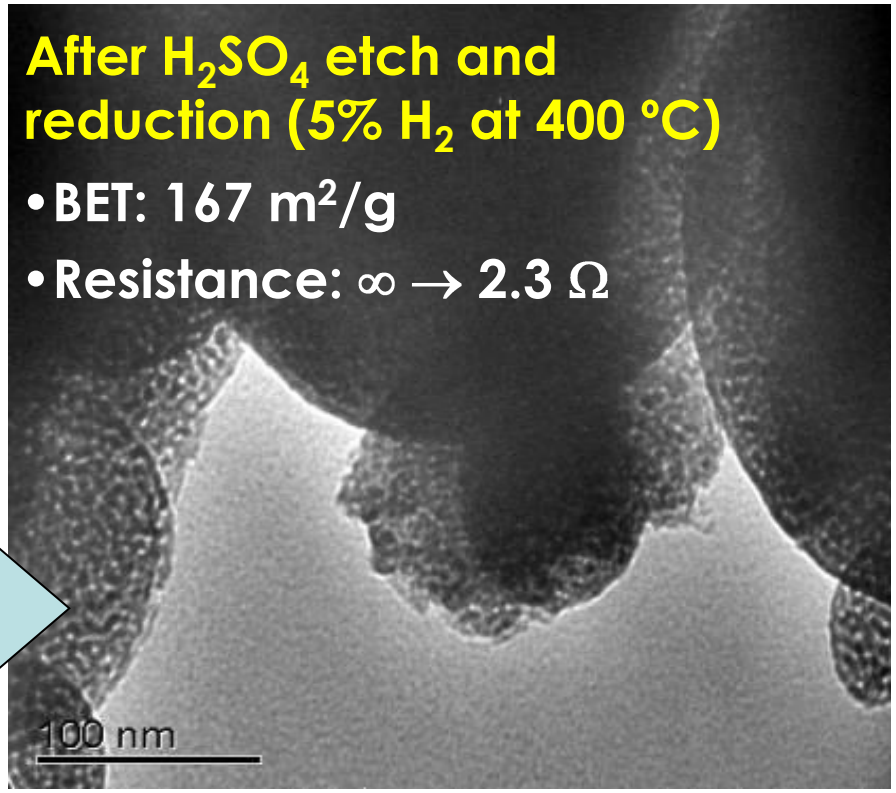
Ethanol/Water solution of $NbCl_5$, $RuCl_3$ and P123; produced at 200 °C in N_2 ($Nb_{0.9}Ru_{0.1}O_x$)





- Loss of skin layer and internal order
- XRD indicates mostly amorphous
- XPS indicates mix of Ru oxidation states at surface (& Carbon)

D. Konopka, S. Pylypenko, P. Atanassov and T. Ward, Spray Pyrolysis of Mesoporous Nb-Ru as Potential Catalytic Supports in Fuel Cells, submitted to *Applied Materials and Interfaces*

Platinum Supported on $NbRu_yO_z$

Why is Electrochemical Activity Low on Pt/$NbRu_yO_z$?

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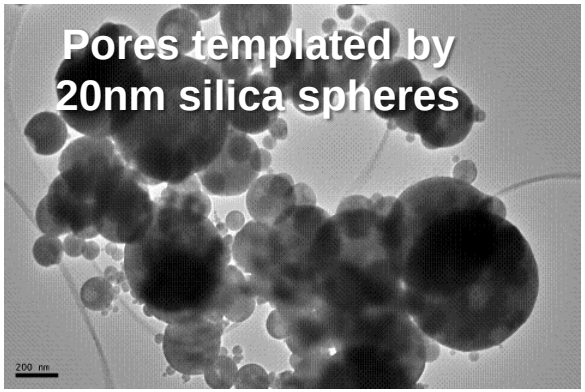
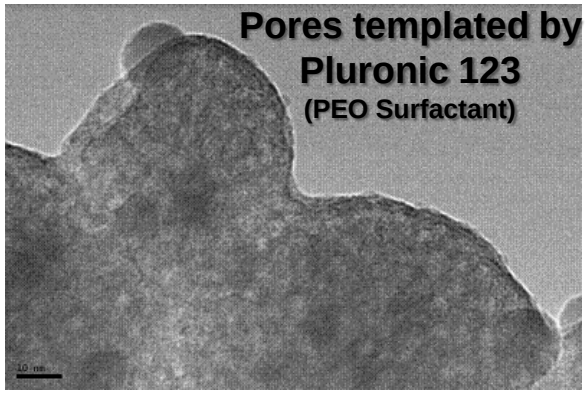
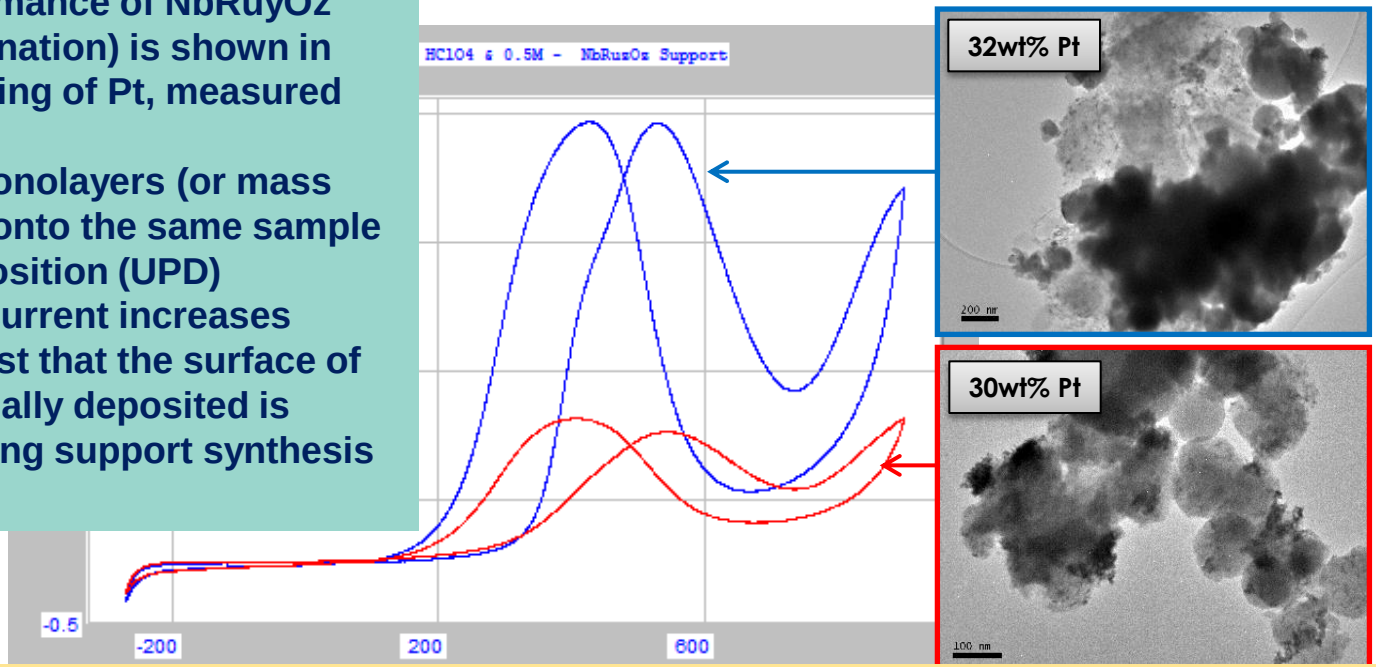
Carbon-based surfactants do not appear to be responsible for deactivation & poisoning of supported platinum

Pore templating with various, non-carbon materials all yield a material with poor electrochemical performance despite the presence of 30wt% platinum





Cyclic voltammetry performance of NbRuyOz with 30wt% Pt (dry impregnation) is shown in red. Despite the high loading of Pt, measured current is very low.
When an additional two monolayers (or mass equivalent) are deposited onto the same sample by an under-potential deposition (UPD) technique, the measured current increases greatly. This would suggest that the surface of the Pt nanoparticles originally deposited is somehow deactivated during support synthesis or post-treatment.



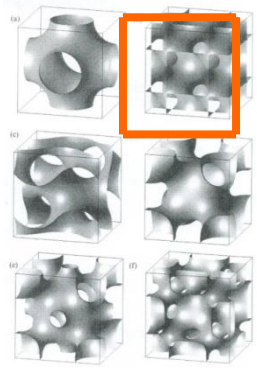
D. Konopka, S. Pylypenko, T. Ward and P. Atanassov, Nanostructured Mesoporous NbRuyOz as a Catalytic Support for Fuel Cells, submitted to *Electrochemical Society Transactions*

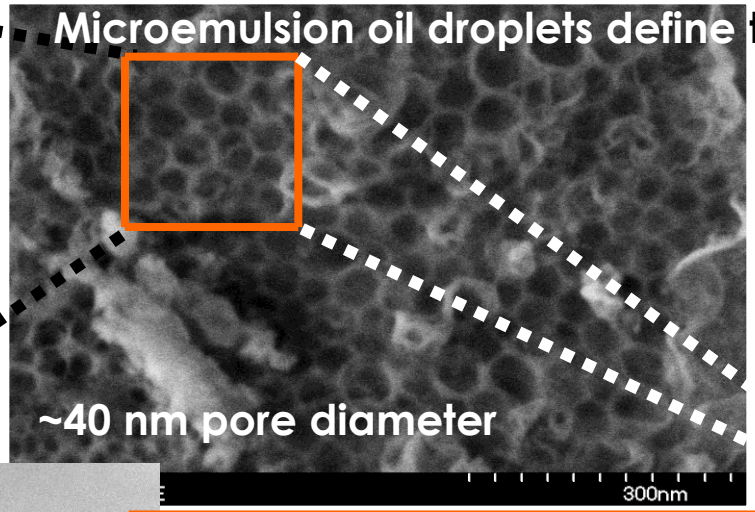
Meso-Structured Catalysts

Micro-Emulsion Templated Synthesis

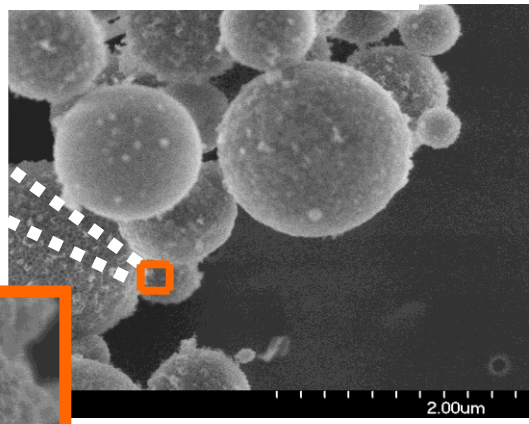
THE UNIVERSITY of NEW MEXICO

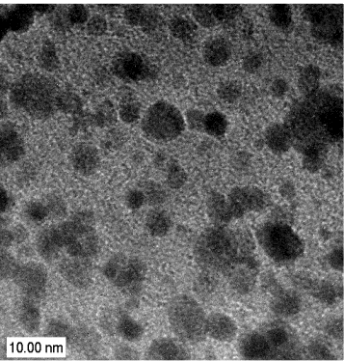
Dimiter Petsev

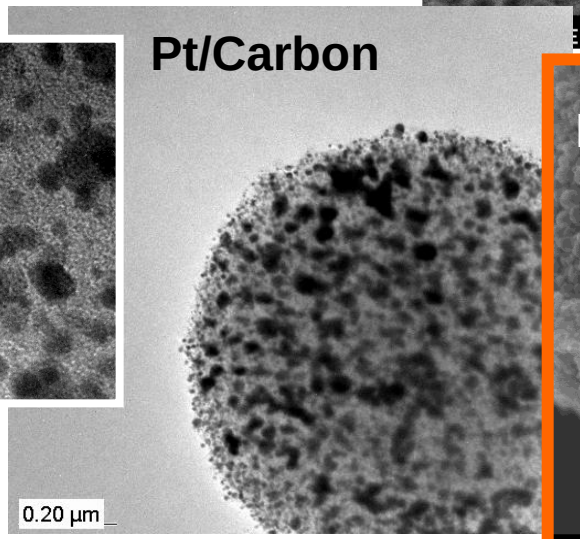


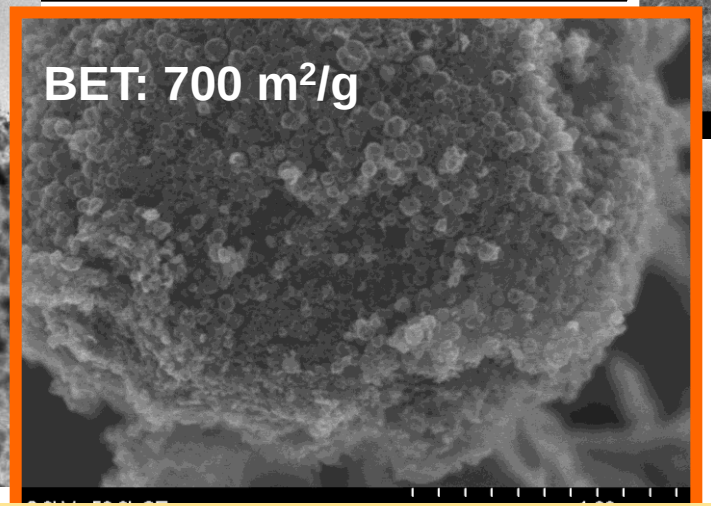


BET: 1000 m^2/g









Carbon replica after removal of silica

N. J. Carroll, S. Pylypenko, P. Atanassov and D.N. Petsev, Hierarchical Nano-Porous Microparticles Derived by Microemulsion Templating, cover-art featured article, November (2009) *Langmuir*

Templated Ethanol Catalysts

THE UNIVERSITY of NEW MEXICO

Synthesis Procedures

Heat-treatment at 120 C

Dry impregnation

Carbon precursor (sucrose)

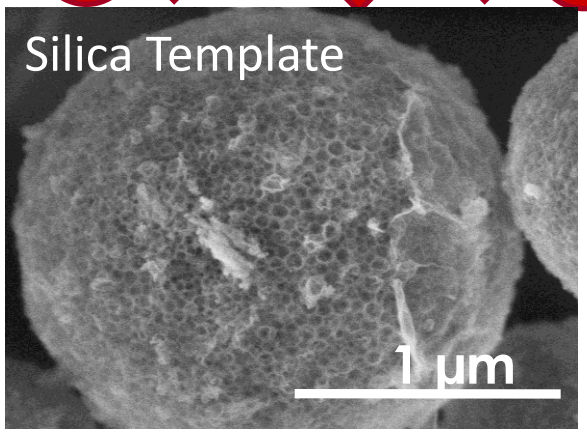
1

2

Dry impregnation

$H_2PtCl_6 + SnCl_2$;
$H_2PtCl_6 + RuCl_3$;

3

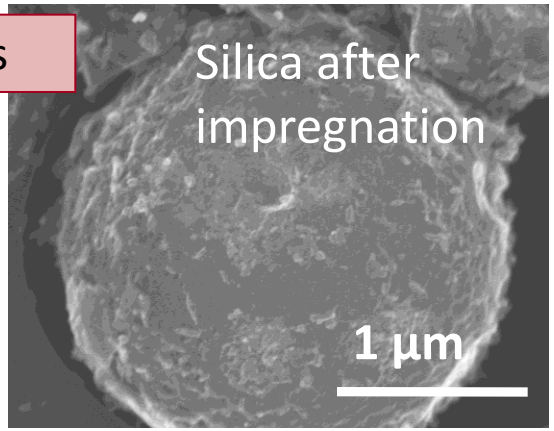


Synthesized Materials :

10% Pt/TC
10%PtSn(80:20)/TC
45%PtSn(80:20)/TC
10%PtRu(50:50)/TC
45%PtRu(50:50)/TC

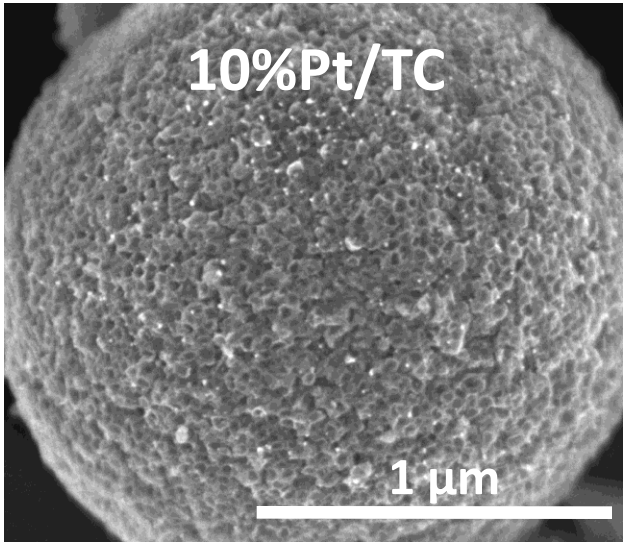
Pyrolysis

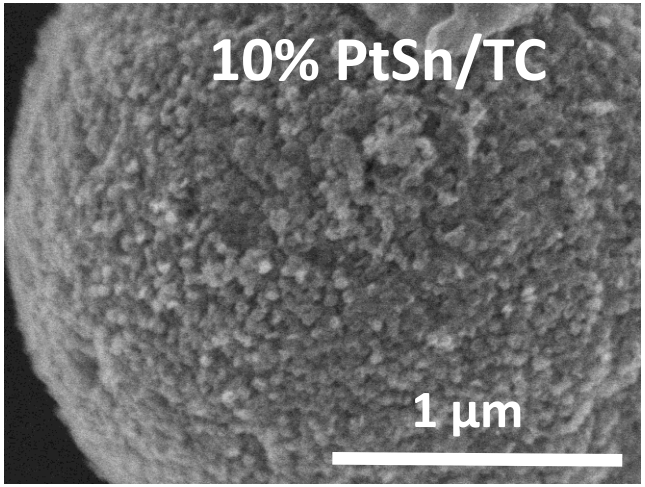
4



KOH etching

5





Templated Ethanol Catalysts

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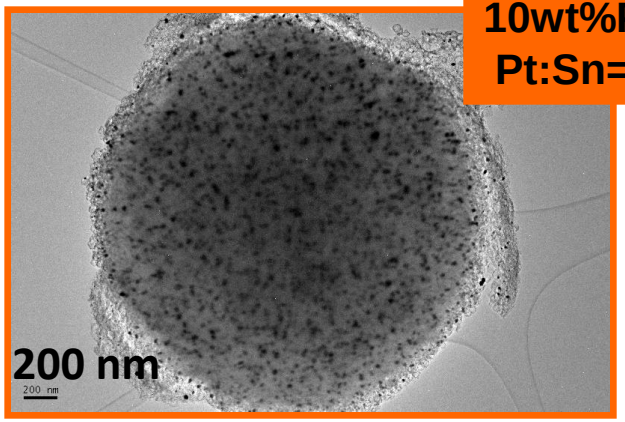
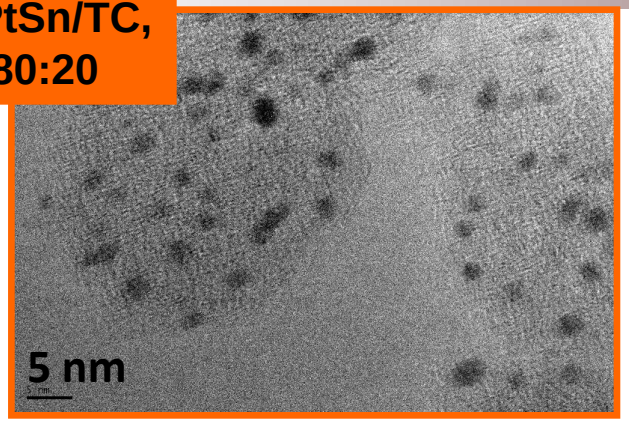
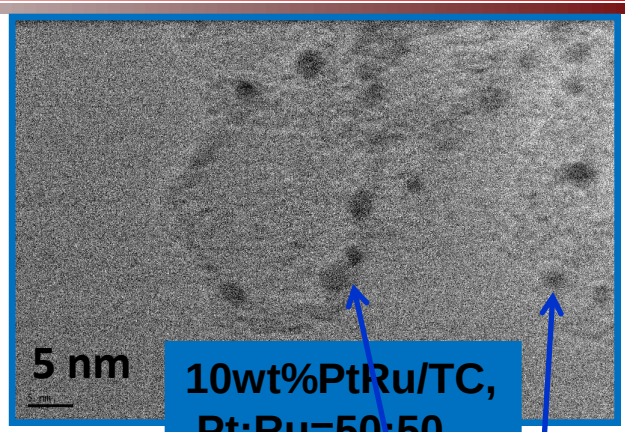
Characterization

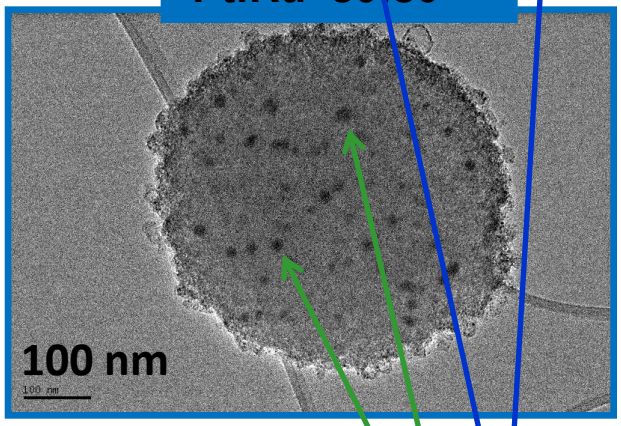
10wt%PtSn/TC, Pt:Sn=80:20



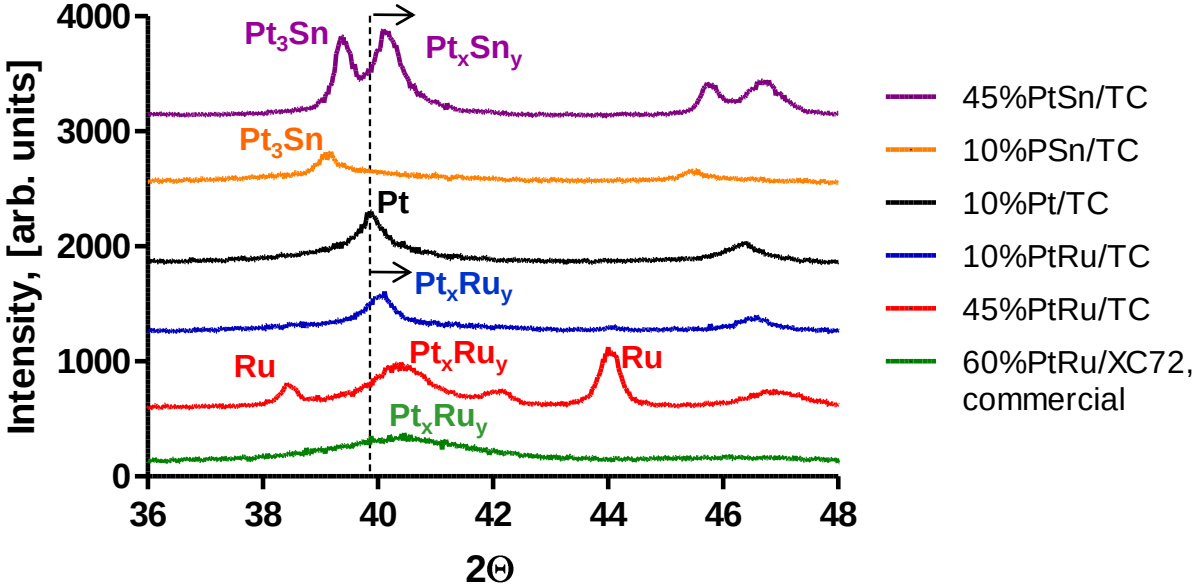




10wt%PtRu/TC, Pt:Ru=50:50



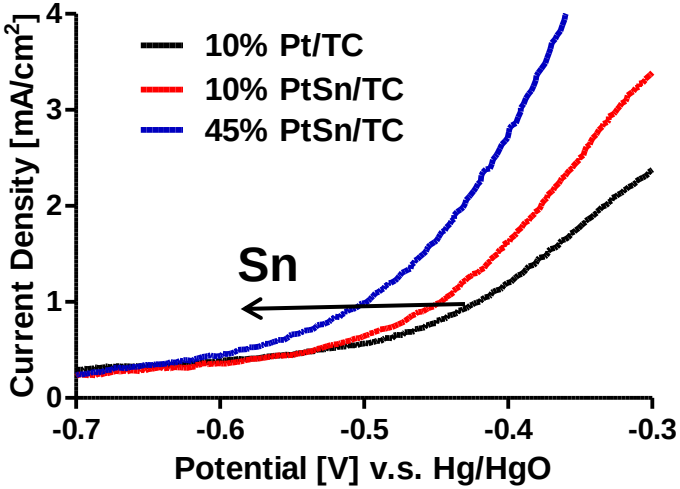
PtRu/TC: formation of Pt_xRu_y alloy that leads to contraction of the lattice parameter (based on upward shift in 2Θ); for 45 wt.% material also formation of Ru metallic phase;
PtSn/TC: formation of Pt_3Sn alloy; for 45 wt.% materials also formation of alloyed phase, that also leads to contraction of the lattice parameter, similar to Pt_xRu_y alloy



XRD indicates bimodal size distribution:
For example, for 10wt% PtRu/TC:
Small crystallite size is around 2.67 nm (fraction 0.7)
Large crystallite size is around 20 nm (fraction 0.3)

Templated Ethanol Catalysts

Ethanol oxidation. PtSn/TC



✓Onset potential shifts to more negative potentials with addition of tin;

✓ This shift becomes more pronounced as the amount of tin increases;

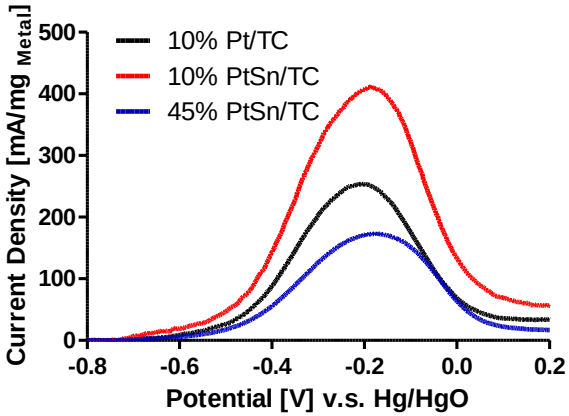
✓Area under the peak increases with the addition of the tin;

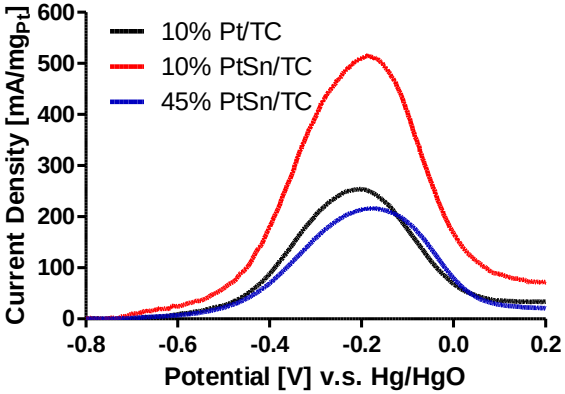
✓ Area under the peak also increases as the amount of tin increases

✓ Better utilization of metal in 10 wt.% PtSn/TC materials vs 45 wt% PtSn/TC materials

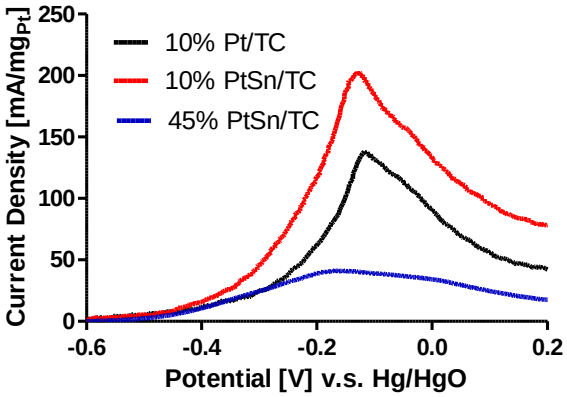
✓ Addition of tin improves ethanol electrooxidation

✓ It appears that improved ethanol oxidation for PtSn/TC materials can not be explained only by improved CO oxidation



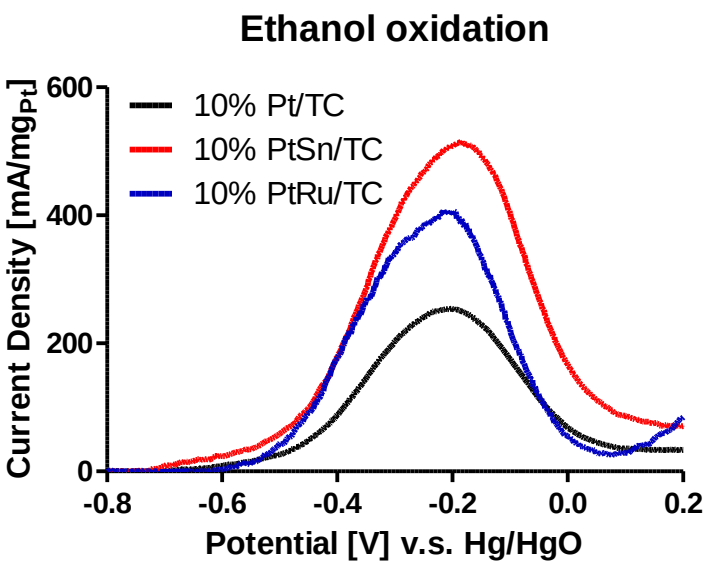


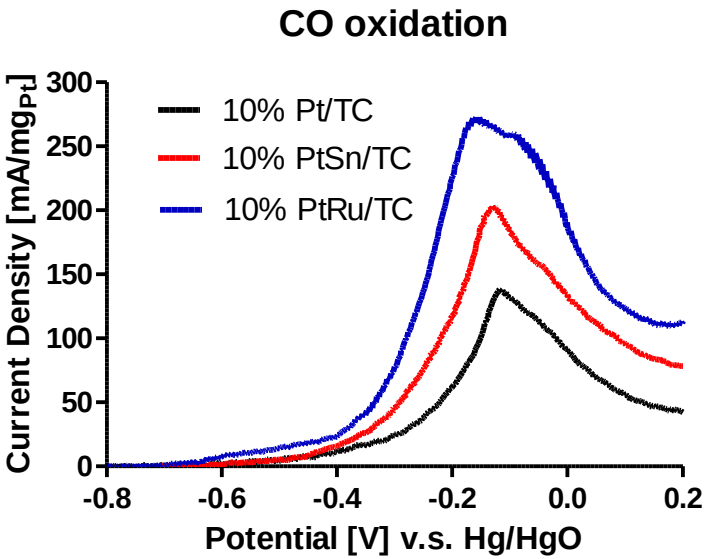
CO oxidation



Templated Ethanol Catalysts

Ethanol and CO oxidation. PtSn/TC vs PtRu/TC





- ✓ Addition of tin or ruthenium improves ethanol electrooxidation
- ✓ PtSn/TC is better for ethanol oxidation than PtRu/TC

- ✓ Addition of tin or ruthenium improves CO oxidation
- ✓ PtRu/TC is better for CO oxidation than PtSn/TC

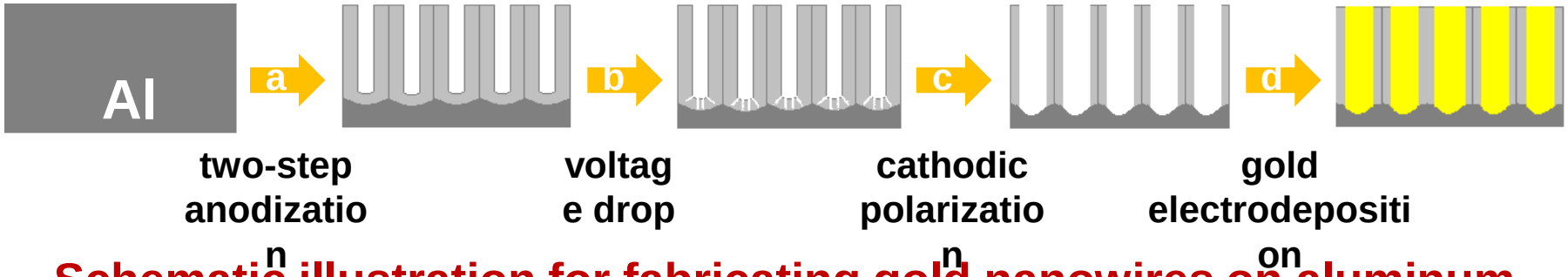
- ✓ Role of tin is not limited to the improvement of the CO oxidation
- ✓ Formation of different alloy phases observed for PtSn and PtRu materials might be the key to the differences in the performance

Gold Nanowires on Aluminum Substrates

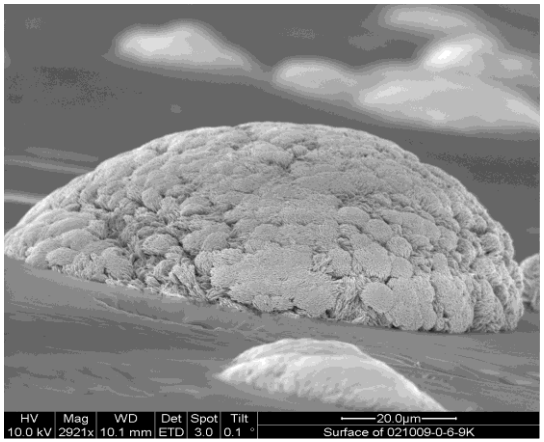
An Electrocatalyst for Ethanol Electrooxidation?

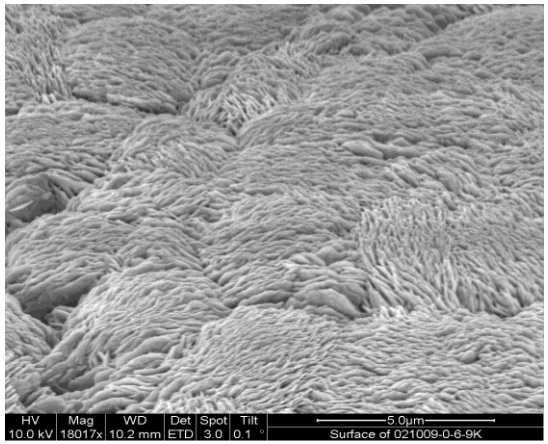
EASTERN NEW MEXICO UNIVERSITY

Juchao Yan

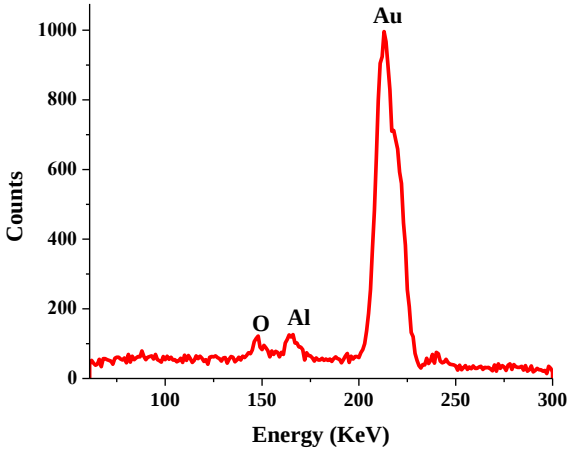


Schematic illustration for fabricating gold nanowires on aluminum substrates





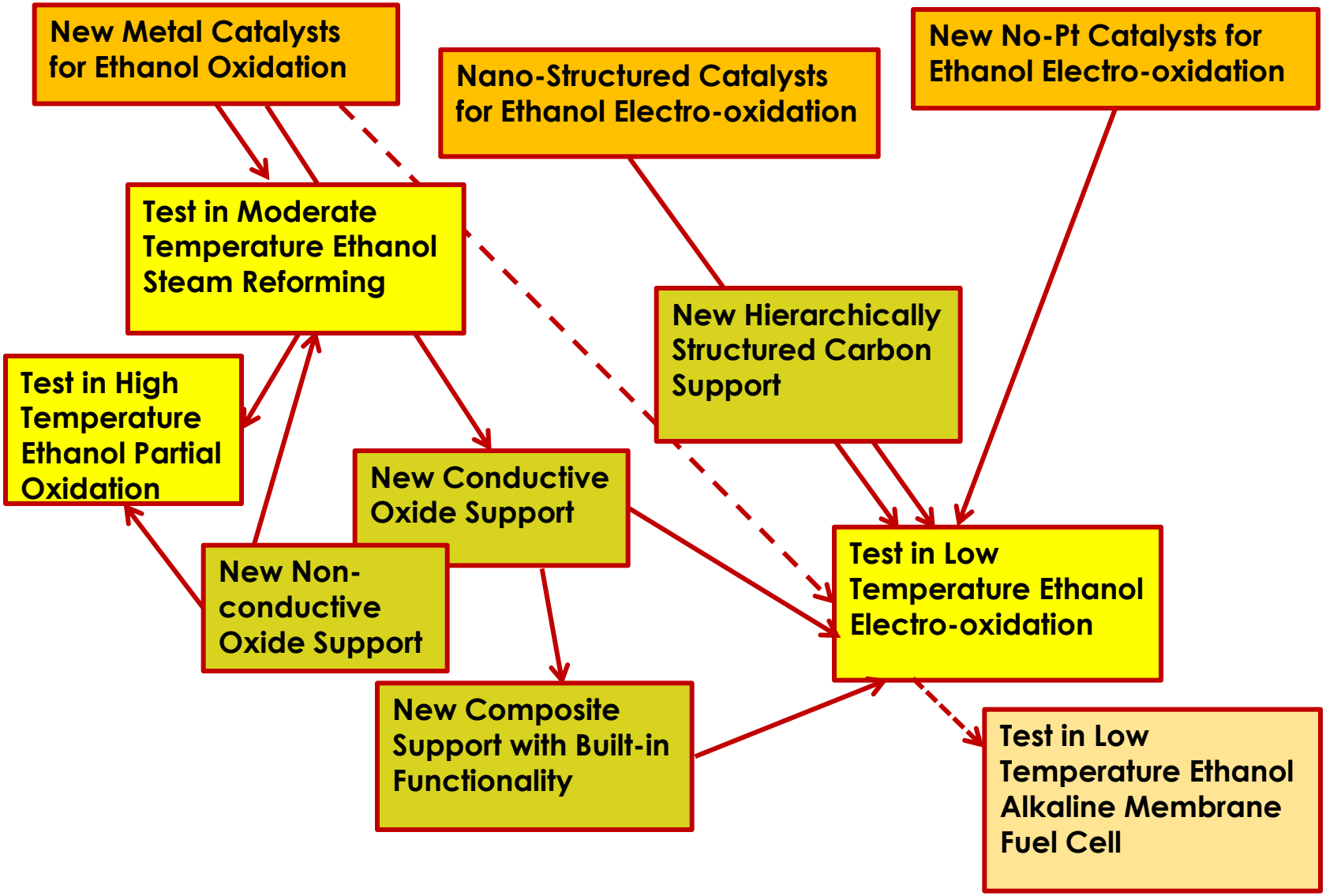
SEM plan views of a typical, cauliflower-shaped gold cap terminated gold nanowires



Energy dispersive X-ray analysis on the cap

Materials for Energy Conversion

Electrolyte Materials & Membrane-Electrode Assemblies



Alkaline Membrane Fuel Cells

Direct Ethanol Fuel Cell

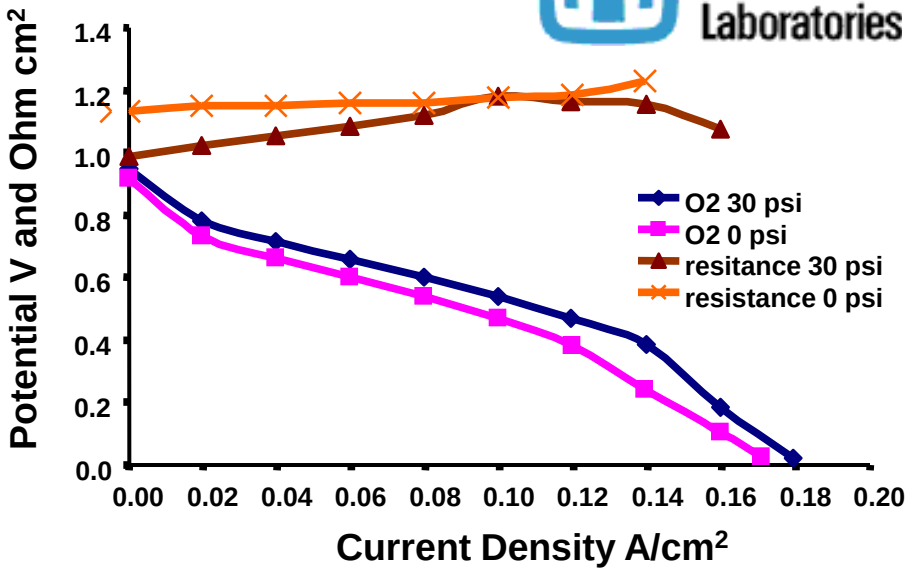
THE UNIVERSITY of NEW MEXICO

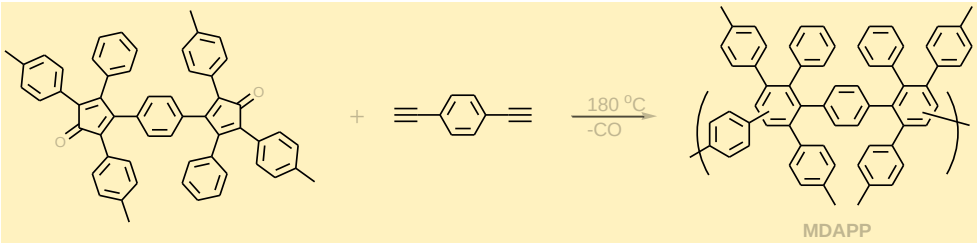
Mike Hibbs & Cy Fujimoto

Sandia National Laboratories

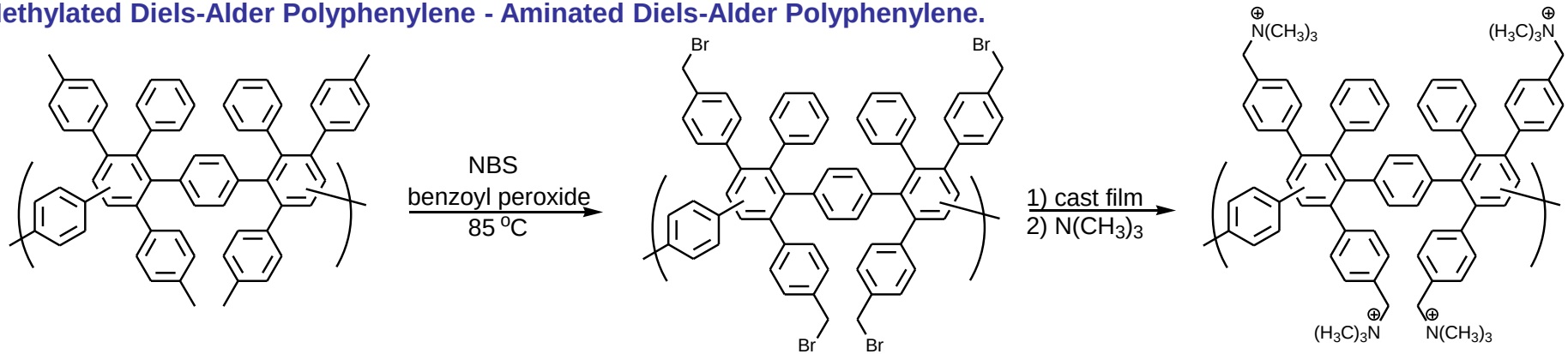
Approach:

- Stable alkaline conductive membranes
- Selective Non-Platinum cathode catalyst
- Air-breathing cathode design
- Highly effective Pt-Sn anode catalyst
- Hierarchically structured anode with a passive fuel supply





Methylated Diels-Alder Polyphenylene - Aminated Diels-Alder Polyphenylene.



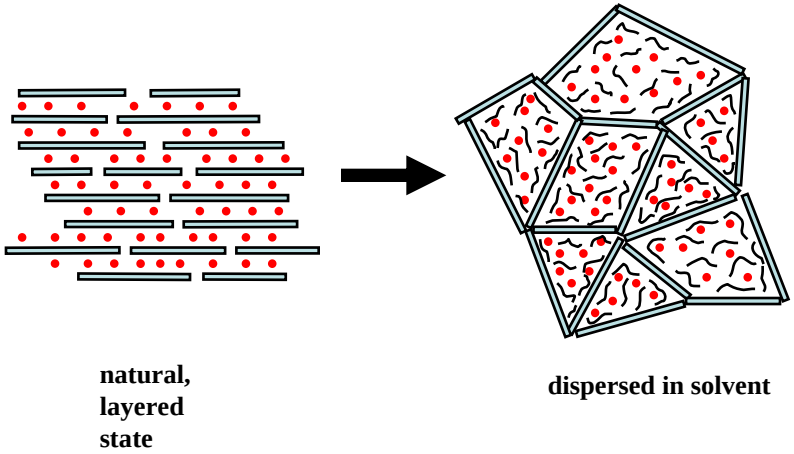
MDAPP brominated **MDAPP** aminated **DAPP**

Nanoclay Electrolytes

Approach for a Novel FC Membranes

New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY

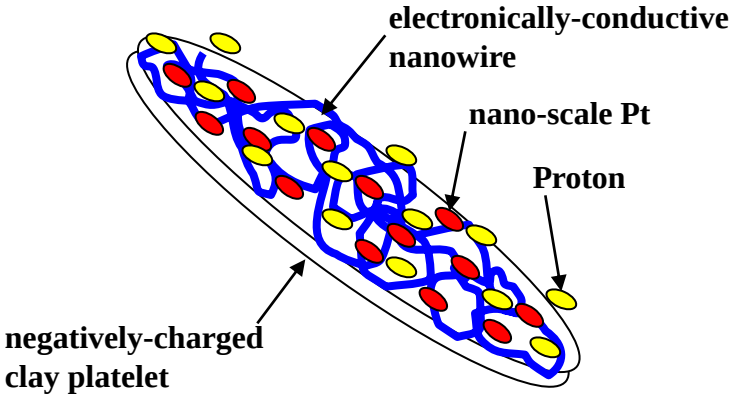
Mike Riley



Nanoclay "House-of-Cards" dispersion

Ion-conducting layered nanoclays as building blocks:

- Cationic (smectites) and anionic (layered double hydroxides)
- Ideal electrolyte: Cross-linked structure, chemically, thermally, and dimensionally stable
- Electrodes: Cross-linked structure plus catalyst and nanowire deposition



Conceptual nanoclay electrode template

Nanoclay Electrolytes

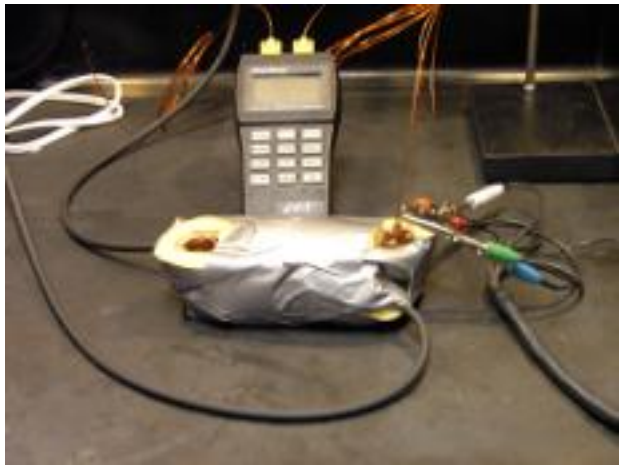
First Accomplishments

New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY

Research in Early Stages:

- Literature reviews
  - Functionalization & crosslinking
  - Catalyst deposition
  - Recent clay use in fuel cells
- Nanoclay ion exchange and dispersion
  - SEM and wet chemistry analysis
- Conductivity measurements
  - Conductivity cell designed for liquids, gels, and solids (including thin membranes)
  - Temperature control system

Molded epoxy Pt wire conductivity cell

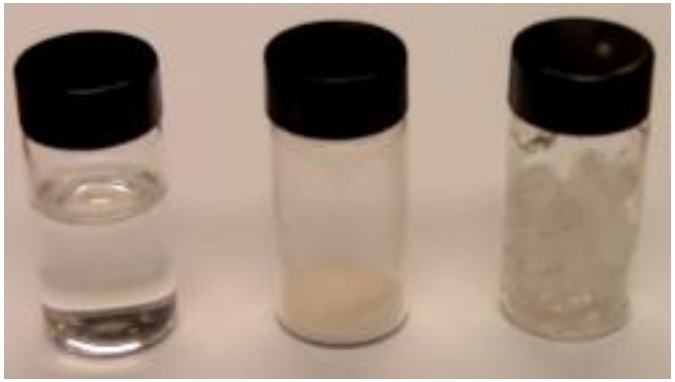


Copper coil temperature control system

Nanoclay Electrolytes

Future Directions

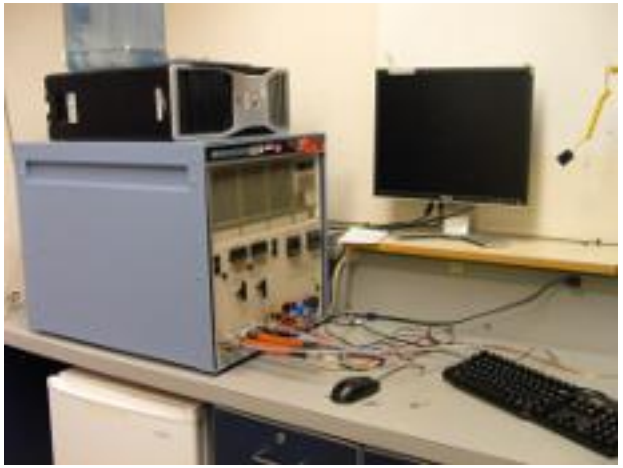
New Mexico Tech
SCIENCE-ENGINEERING-RESEARCH-UNIVERSITY



Smectite nanoclay dispersion in water (~10 wt %)

Improved Structures through Characterization:

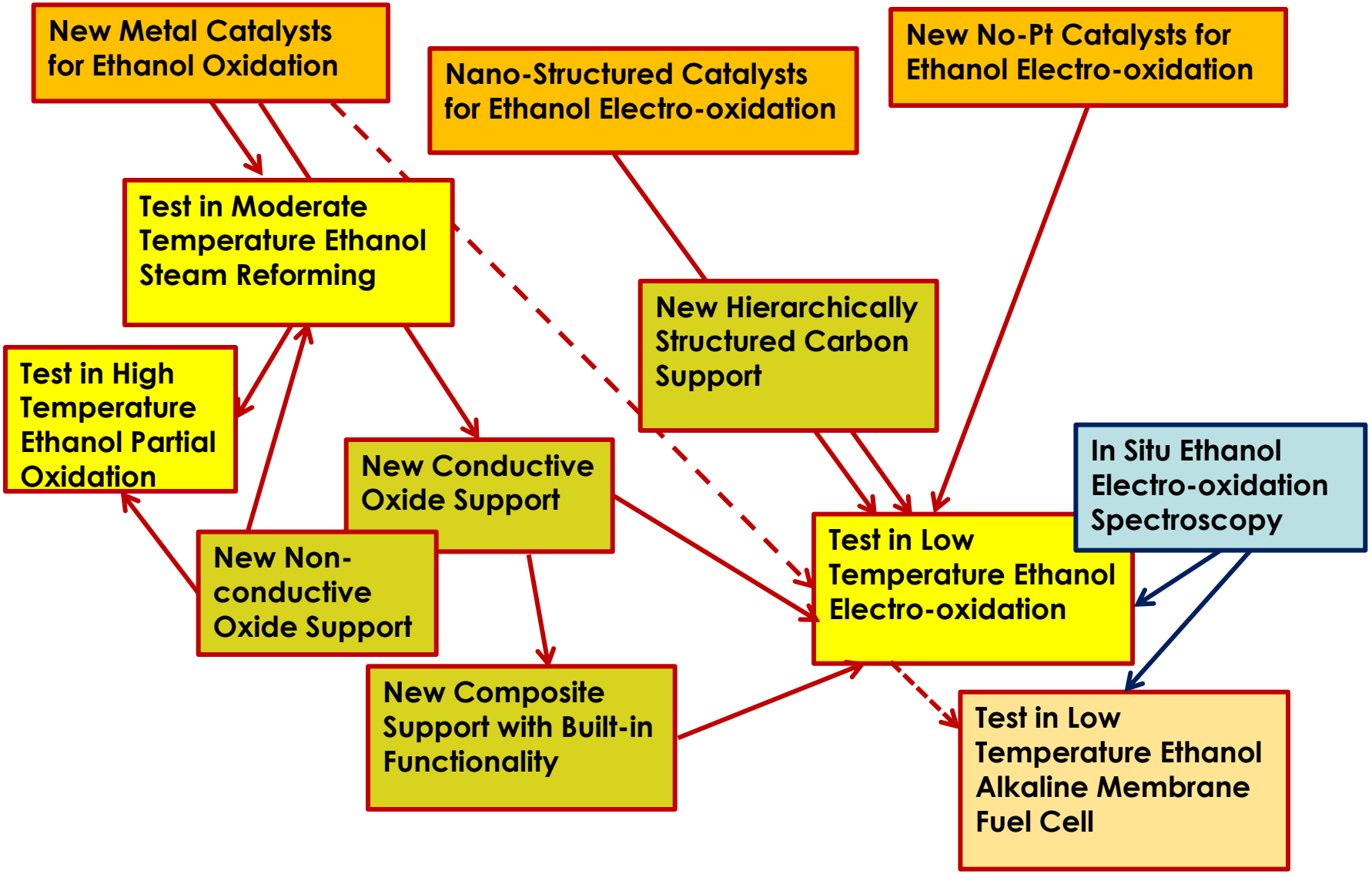
- Performance
  - Conductivity
  - Rotating disk & ring disk techniques
  - Impedance Spectroscopy
- Clay and structure characterizations:
  - SEM, TEM, XRD, AFM
  - Particle sizing & porosity
  - Zeta Potential (charge density)
- Durability:
  - TGA
  - Cyclic voltammetry
  - Fuel cell cycling



Fuel cell test station

Materials for Energy Conversion

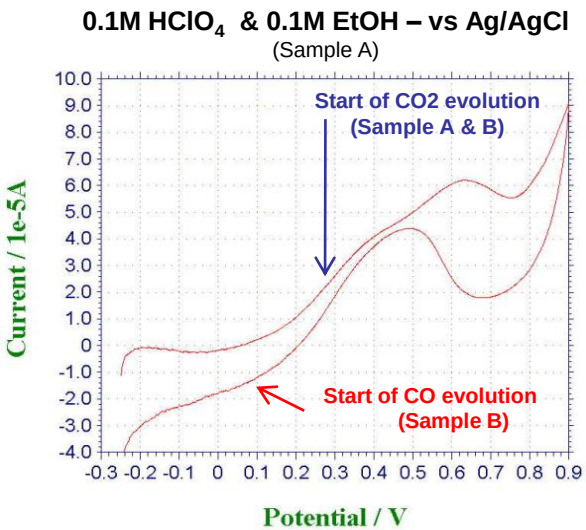
In Situ Measurements of Ethanol Oxidation

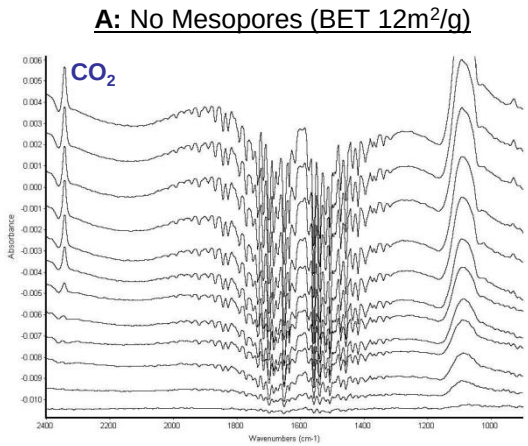


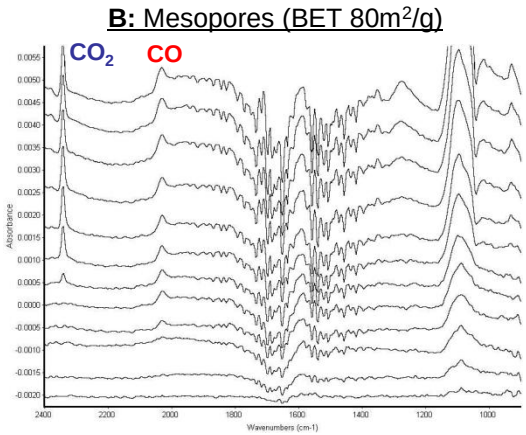
Active Supports based on $NbRu_yO_z$

Performed at Brookhaven National Laboratory

THE UNIVERSITY of NEW MEXICO

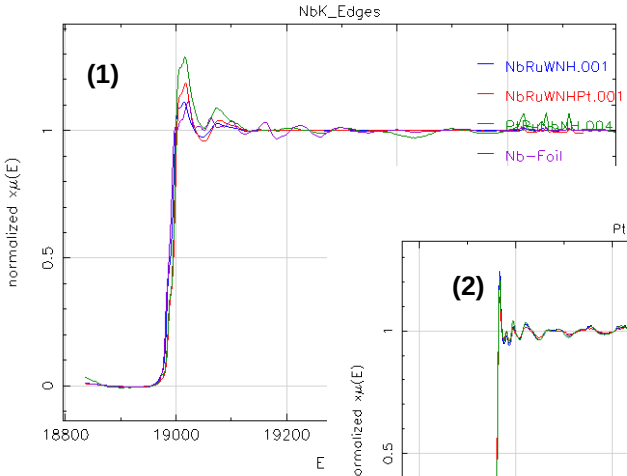


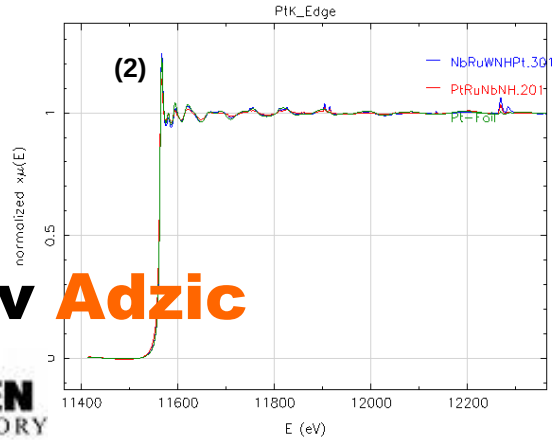




Above: InSitu-Cyclic Voltammetry using Infrared Reflection-Absorption Spectroscopy shows the evolution of CO_2 and CO on different NbRuyOz support materials. CO_2 evolution begins at a potential of 290 mV lower than platinum alone. The evolution of CO ~120mV earlier perhaps explains why Pt in sample B appears electrochemically inactive.

Right: X-ray Absorption Spectroscopy studies reveal that (1) the niobia in the most electrochemically active sample (A) is electronically different from both inactive samples of similar composition as well as metallic Nb.
(2) The platinum deposited onto Sample B appears identical to metallic Pt, while that of the active sample is chemical altered by the support, perhaps via surface/particle interactions, or in an inter-metallic Nb-Pt or Ru-Pt phase.





Radoslav Adzic

BROOKHAVEN NATIONAL LABORATORY

Future Studies

Higher Performance Support Materials

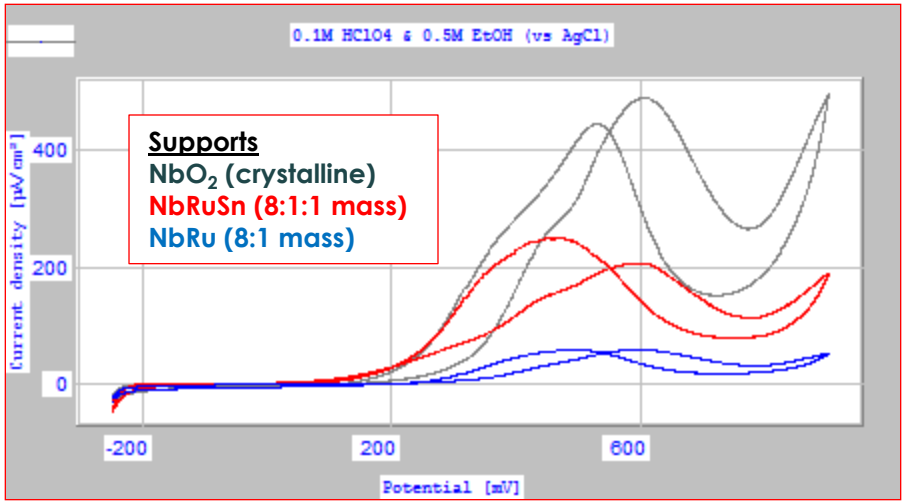
THE UNIVERSITY of NEW MEXICO

Literature studies have reported benefits of various metal-oxides, when incorporated into the catalyst or support, towards complete oxidation of ethanol to CO_2.

Future materials synthesized via spray pyrolysis will study some of these oxides which have shown promising results in early electrochemical testing. These support materials will also be more compatible with the processing necessary for UPD deposition of monolayer amounts of precious metal catalyst, increasing the overall ratio of surface to interior catalyst atoms.

As shown to the left, ruthenium is typically used to reduce poisoning of Pt catalyst by adsorbed CO. In this case, it also provides electrical conductivity to the niobia support. The presence of SnO_x has shown to increase measured current and, with precious metals, has also been shown to evolve moderate amounts of CO_2. Early studies have also shown NbO_2 to provide larger currents than NbRu (8:1), perhaps by further reducing the electrical resistivity of the support, or through some other surface effect yet to be determined.

These materials have shown lesser performance, though proportional performance gains, in alkaline media. Initial studies in acid continue to provide information for synthesizing more stable catalyst supports. The improved materials mentioned above will be tested in alkaline electrolyte for performance and stability. PeriodicTEM studies of various supports during different stages of electrochemical testing will be used to study catalyst stability, and will be compared to similar studies available for commercial Pt/C.



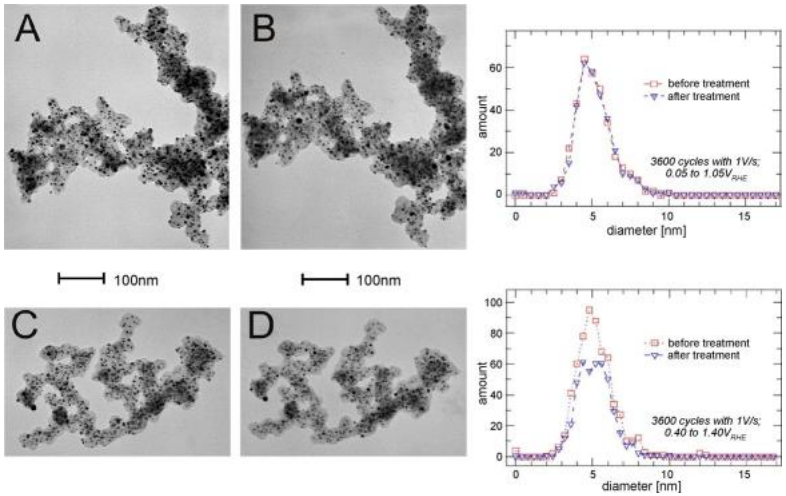


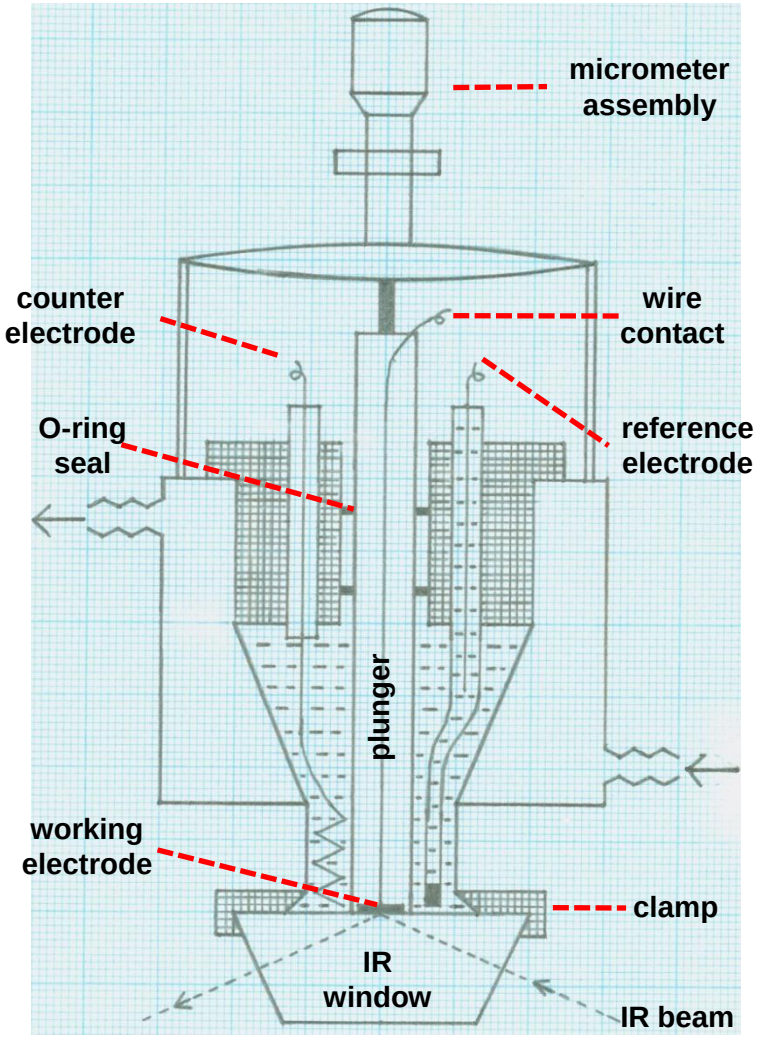
Fig. 2. IL-TEM micrographs recorded with a magnification of 100 k of the catalyst before (A+C) and after electrochemical treatment (B+D) in 0.1 mol L−1 HClO4. The electrochemical treatment between A and B was 3600 cycles with 1.0Vs−1 in the potential region of 0.05 and 1.05VRHE, between C and D in the potential region of 0.40 and 1.4VRHE.
The according Pt particle size distributions are depicted next to the corresponding images
K.J.J. Mayrhofer et al. / Journal of Power Sources 185 (2008) 734–739

In-situ Infrared Reflectance Spectroscopy

Design of A Thin-Layer Spectroelectrochemical Cell for IRS

EASTERN NEW MEXICO UNIVERSITY

Juchao Yan

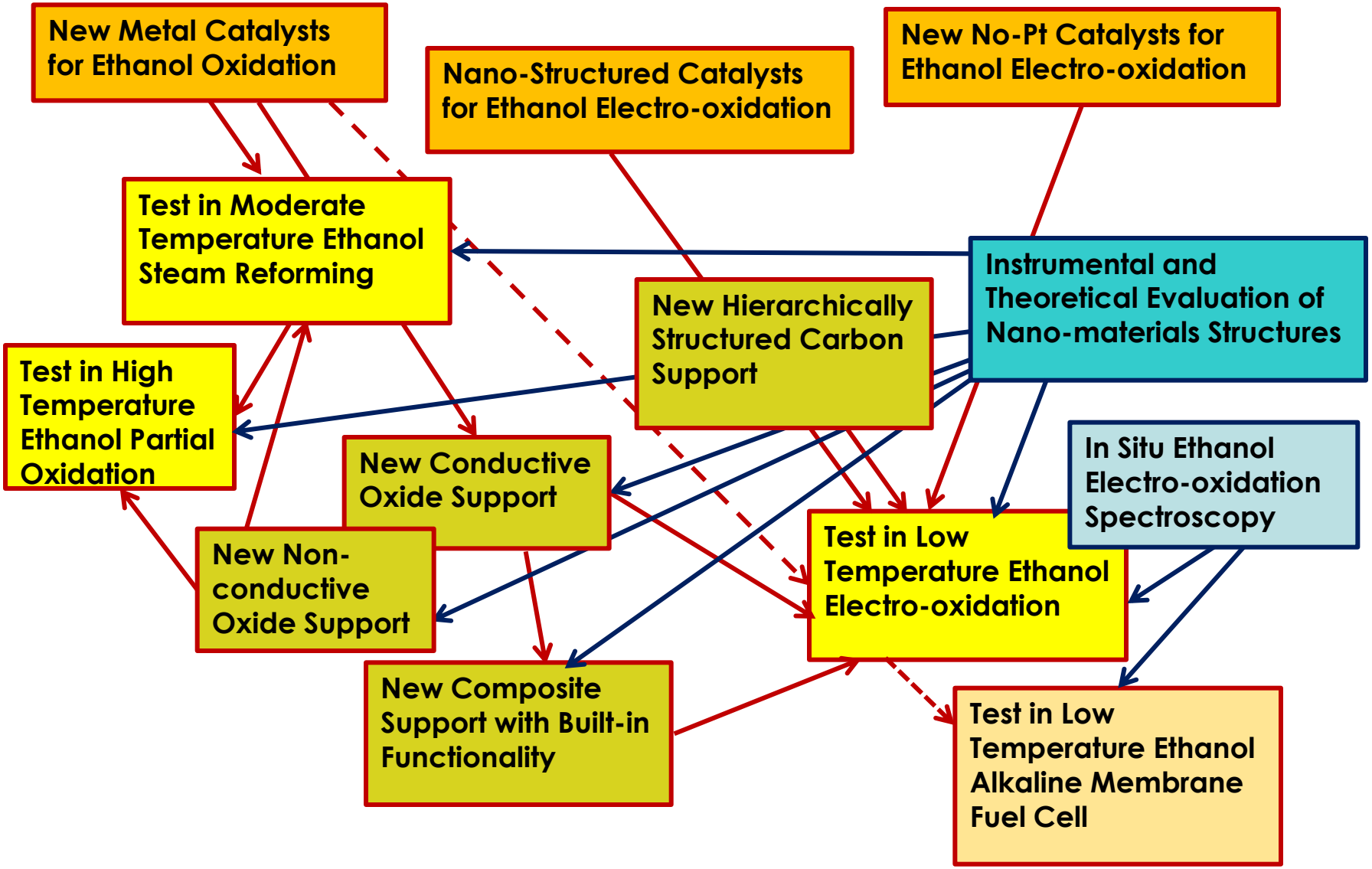


Schematic diagram of the cell for IRS *via* external reflection sampling

- The trapezoidal IR window promises to improve the limit of detection.
- The micrometer assembly attached to the plunger enables the precise control of the thickness of the thin-layer (favorably 1 - 5 μm), enhancing the signal-to-noise ratio of the IR spectra of the adsorbed molecules.
- The water-jacketed glass cell allows the accurate control of the electrolyte temperatures (20 - 80 °C). Measurements at temperatures above ambient could improve mass transport and charge distribution in the thin-layer.

Materials for Energy Conversion

Structural Characterization

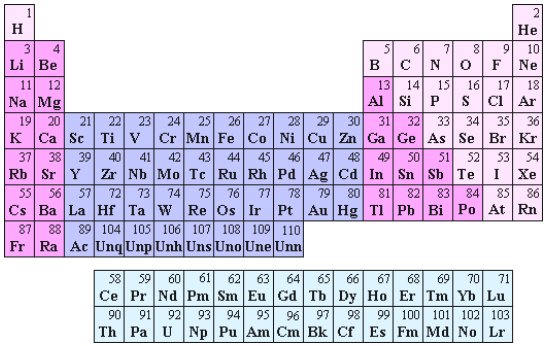


Theoretical Evaluation of Nanomaterials

Computational Exploration of Catalytic Materials

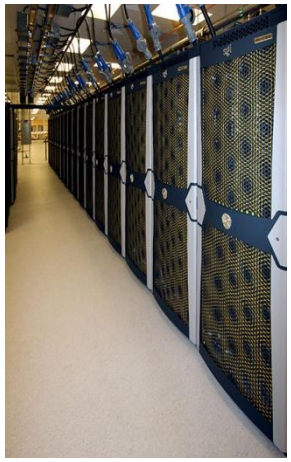
Boris Kiefer

Materials:
- Oxides.
- Transition metals and alloys.
- Carbon based structures.



First-principle Calculations
- provide versatile toolkit and predictive power

Density-Functional-Theory (DFT)



Deliverables:
- Bulk properties.
- Surfaces:
  - Morphology.
  - Adsorption.
  - Binding sites.
- Reaction path.
- Reaction mechanisms.
- Activation Barriers.
- Diffusion.
- Electrochemistry.

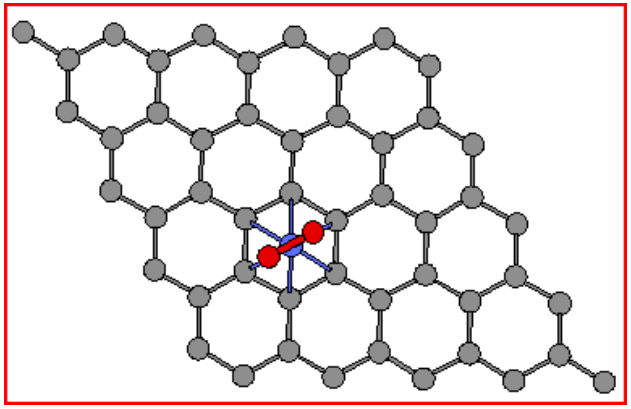
Impact:
- Rational materials design.
- Materials optimization.
- Complementary to experiment.

Theoretical Evaluation of Nanomaterials

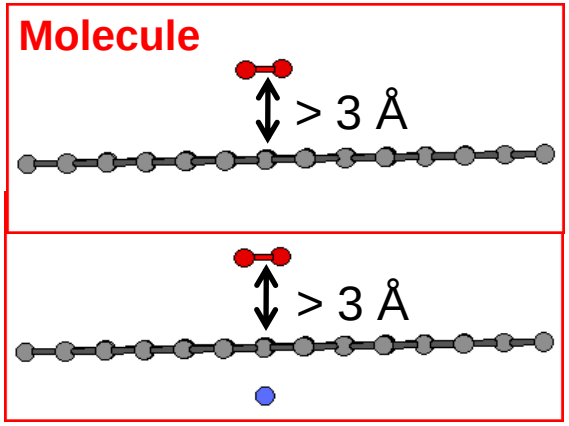
Carbon Based Catalysts

Carbon based catalysts

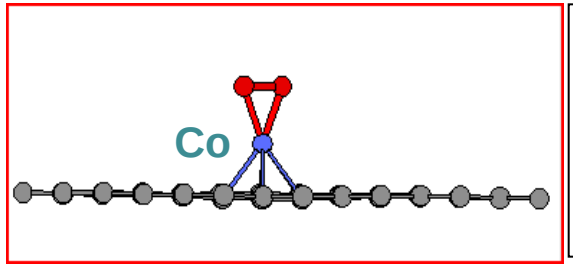
NMSU-UNM: Sam Kattel (NMSU, graduate student), Boris Kiefer, Tim Olson, Plamen Atanassov.



Graphene + Co:
- **Hollow site.**
- **E_B ~ 1.2 eV.**
- **π-electrons.**



- ***No* binding.**



- **Binding.**
- **E_B ~ 2.7 eV**
- **d(O=O) ~ +12 %**
- **d(C-O) ~ +5.6 %**

Projects:

- **Carbon does not directly enhance catalysis.**
- **Bond weakening.**

Future direction:
- **Peroxide adsorption.**
- **Nitrogen defects in graphene.**

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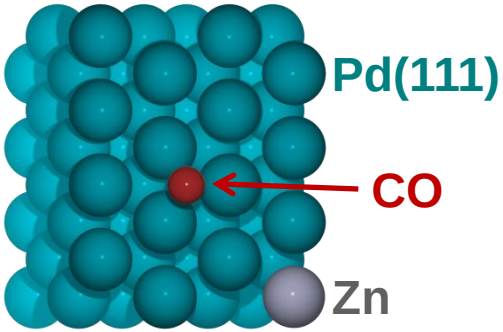
Theoretical Evaluation of Nanomaterials

Other Grant Related Research Activities

$Pd_{1-x}Zn_x$: CO poisoning?

Patrick Burton (UNM, graduate student), Boris Kiefer, Abhaya Datye, Felix Studt, Frank Abild-Pedersen (CAMD).

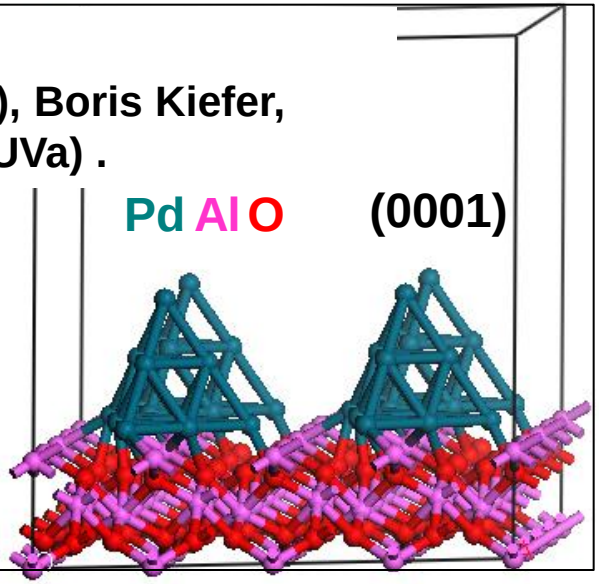


Sintering: Pd/α-Al_2O_3

Levi Houk (UNM, graduate student), Boris Kiefer, Abhaya Datye, and Matt Neurock (UVa) .

Objective:

- **Diffusion ➔ aging.**
- **Effects of hydration?**

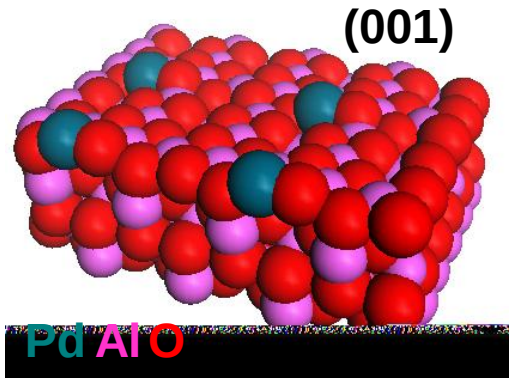


Site-blocking: γ-Al_2O_3: Pd, Zn, Mg, Ba.

Eric Peterson (UNM, graduate student), Boris Kiefer, Abhaya Datye, and Matt Neurock (UVa) .

Objective:

- **Material synthesis and catalytic site accessibility.**



Project Objectives:

- **Catalyst aging.**
- **CO poisioning.**
- **Site blocking.**

Structural Evaluation of Nanomaterials

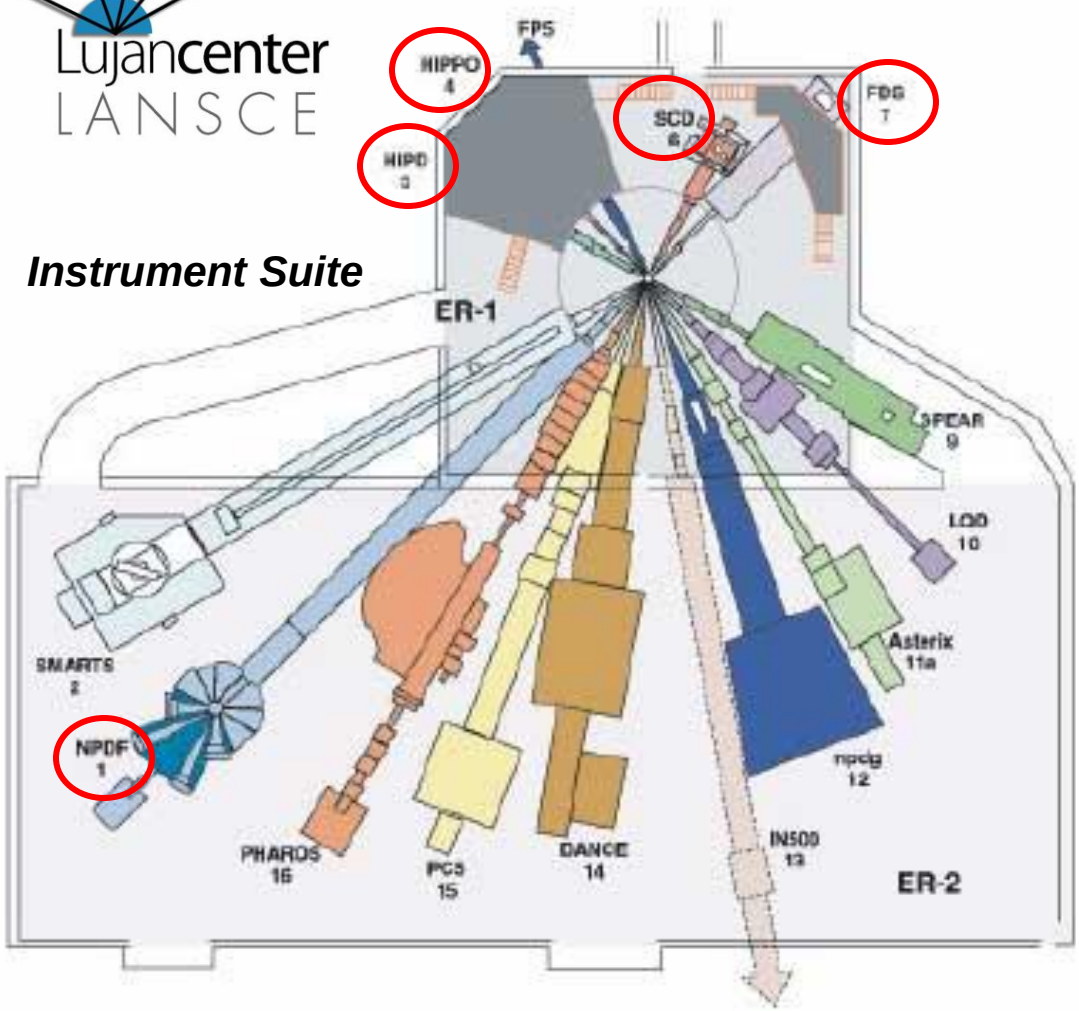
Structure Determination of Catalytic Materials

Heinz Nakotte

Los Alamos NATIONAL LABORATORY

Lujancenter LANSCE

Instrument Suite



- ❑ Catalyst Materials of Interest
  - ✓ Pd-containing catalyst
  - ✓ Non Pd/Pt containing catalyst

- ❑ Instruments
  - ✓ HIPD
  - ✓ HIPPO
  - ✓ NPDF
  - ✓ SCD

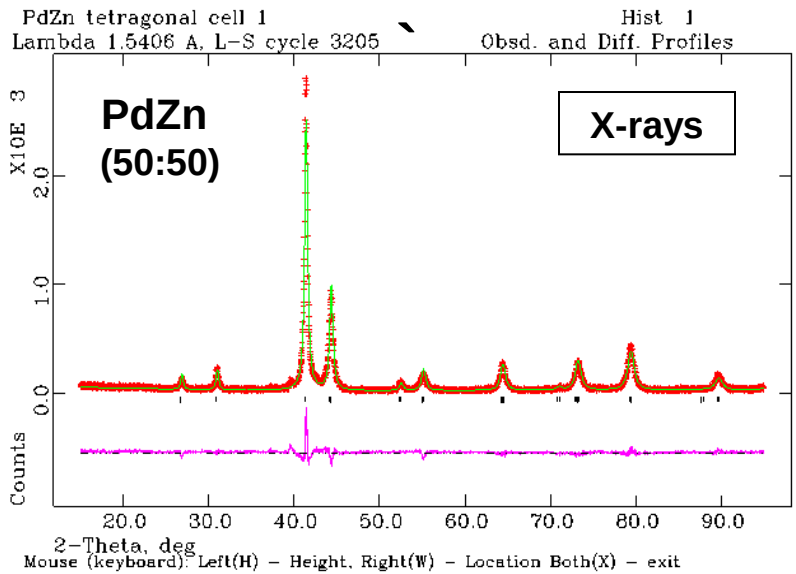
  } Neutron diffraction, Structure - Bulk
  - ✓ FDS – Inelastic scattering Dynamical Properties
  - ✓ XRD – X-ray diffraction Structure - Surface

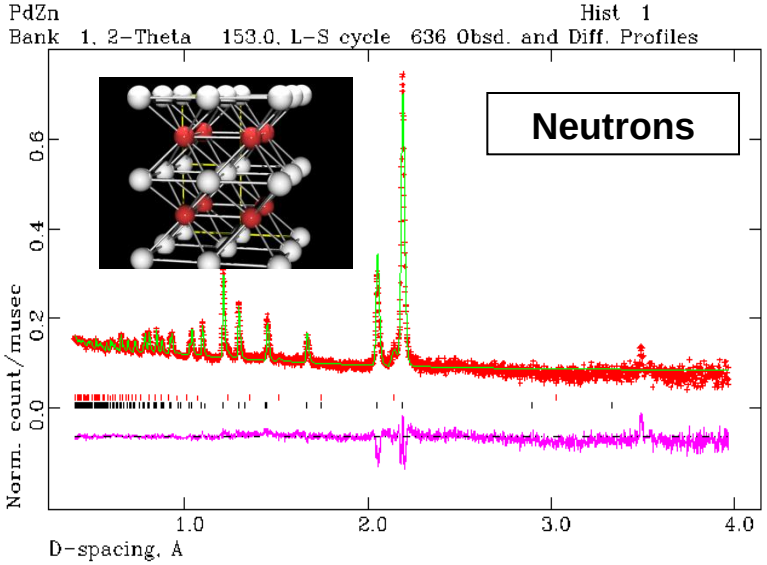
- ❑ Analysis Software
  - ✓ Rietveld refinement – GSAS
  - ✓ SCD data analysis – ISAW
  - ✓ Pair Distribution Function (PDF) analysis – PDFgetN
  - ✓ INS data analysis – Gaussian, a-climax, HyperChem …

Structural Evaluation of Nanomaterials

Pd-containing Catalysts

Research Team: Joe Peterson (NMSU, grad student), Eric Peterson (UNM, grad student), Boris Kiefer (NMSU), Abhaya Datye (UNM), Anna Llobet (LANL)





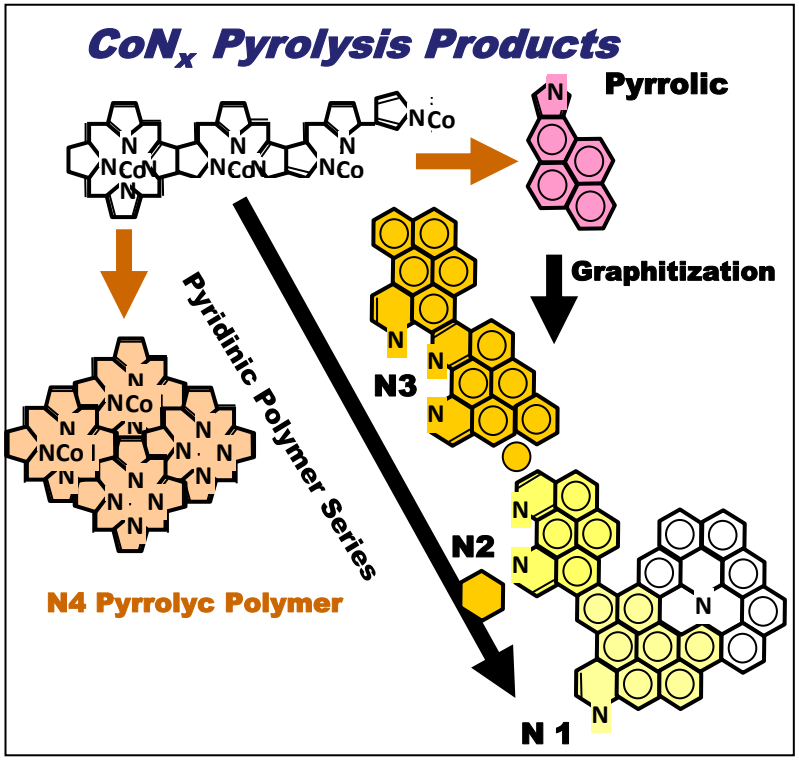
- **X-ray experiments yield**
  - ✓ predominantly tetragonal phase in bulk
  - ✓ possible monoclinic phase at surface
- **Neutron experiments yield**
  - ✓ tetragonal phase in bulk
  - ✓ possible nanocrystalline cubic Zn inclusions

❑ **Future Work on PdZn Catalysts**

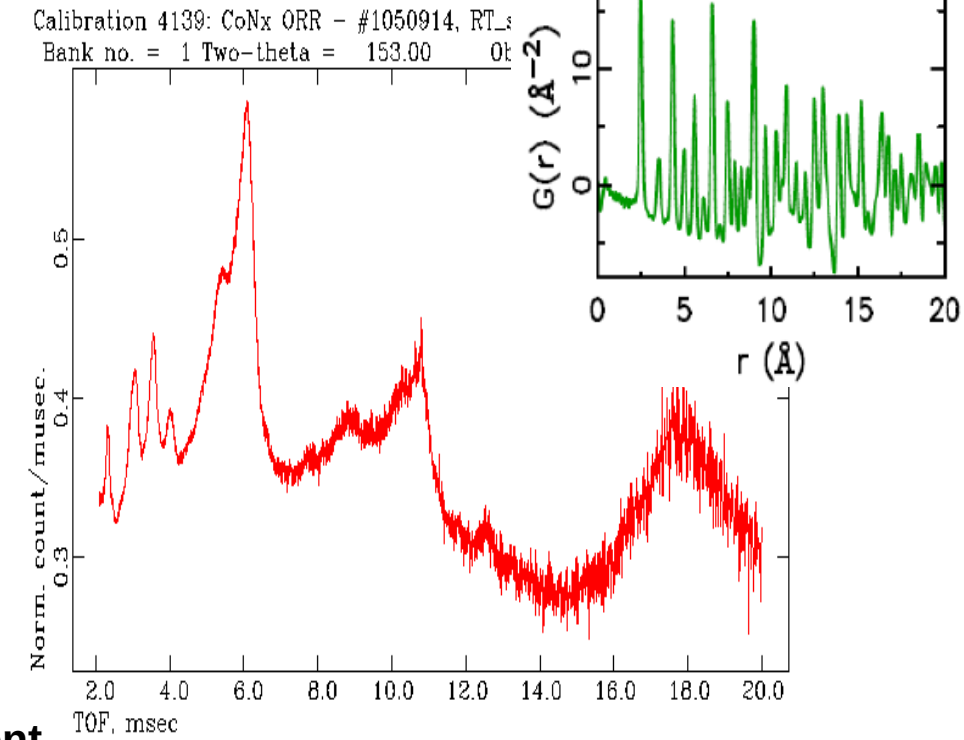
- **X-ray and neutron experiments as function of temperature, composition and pressure**
- **complementary TEM studies**

Structural Evaluation of Nanomaterials

Non-Pd/Pt Catalysts



Research Team: Joe Peterson (NMSU, grad student), Tim Olson (UNM, post doc), Plamen Atanassov (UNM), Thomas Proffen (LANL)



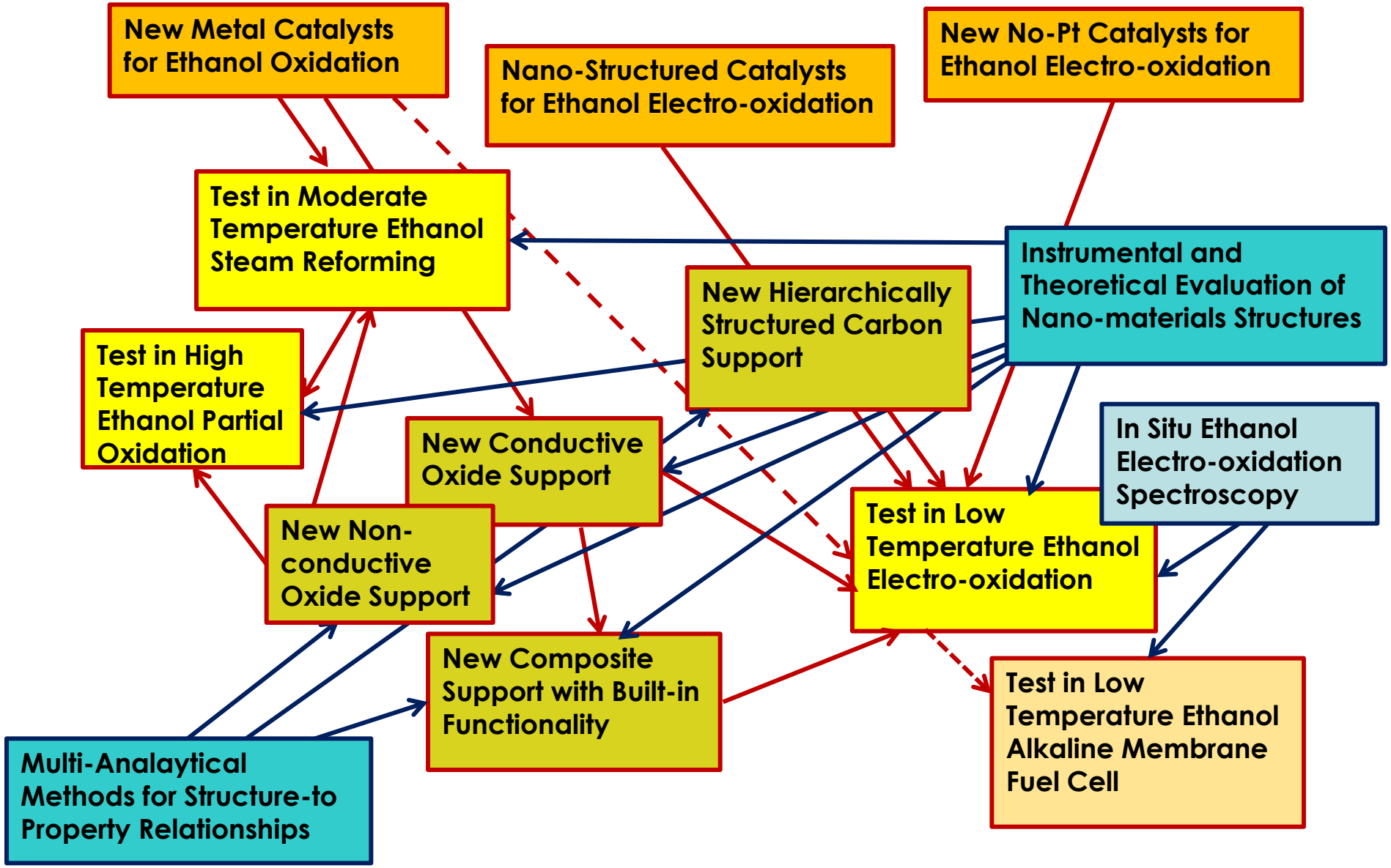
- ➢ Neutron experiments show
- ✓ standard Rietveld refinement is insufficient
- ✓ short-range pair-distribution function (PDF) analysis to determine G(r) is needed

❑ Future Work on CoN$_x$ Catalysts

- ➢ extended PDF studies using NPDF
- ➢ additional temperature, compositional and pressure studies

Materials for Energy Conversion

Flow Chart of the Program



Characterization and modeling approach

Composition, Structure, Morphology and Electrochemistry

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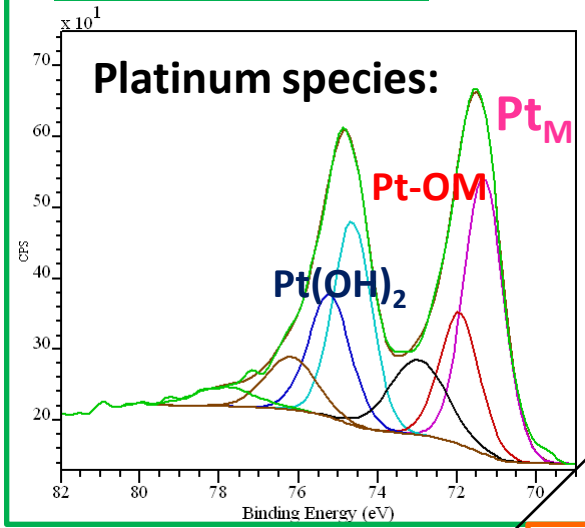
XPS analysis

- Elemental composition:
- Chemical speciation



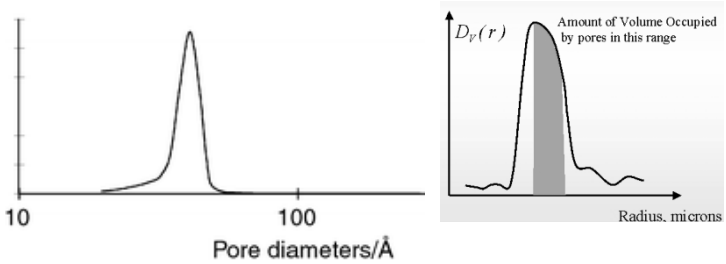
Model based on statistical correlation among all variables /parameters

Adsorption analysis:

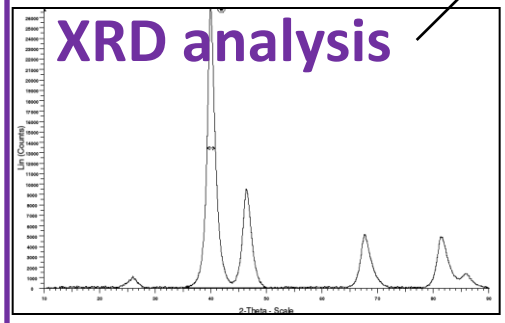
BET surface area

Pore size of the support

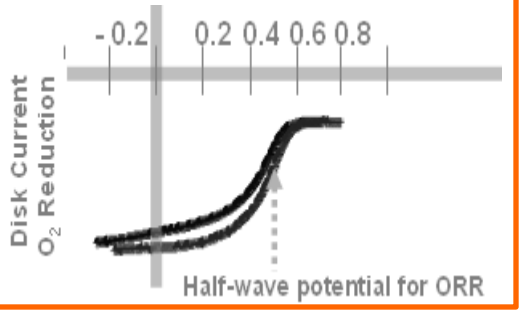
Pore Volume of the support



XRD analysis



Electrochemical characterization

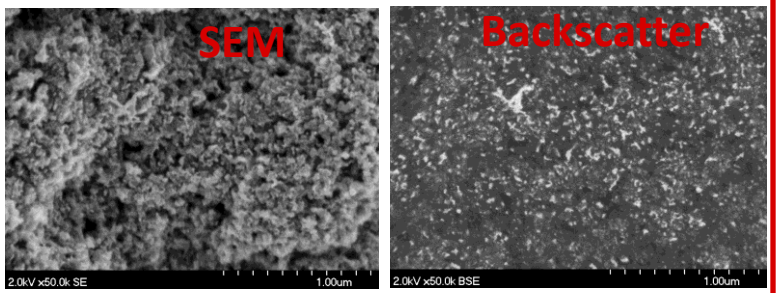


SEM analysis:

Roughness:

Ra, Rsk;

Pt particle distribution



ACCOMPLISHMENTS

SEM CHARACTERIZATION. SCALES OF SURFACE ROUGHNESS

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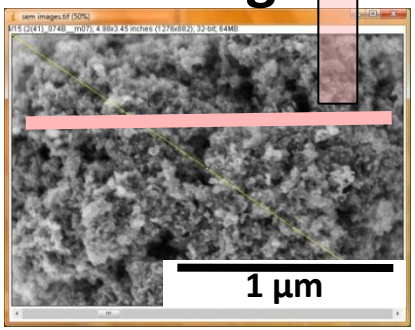
Usefull parameters:

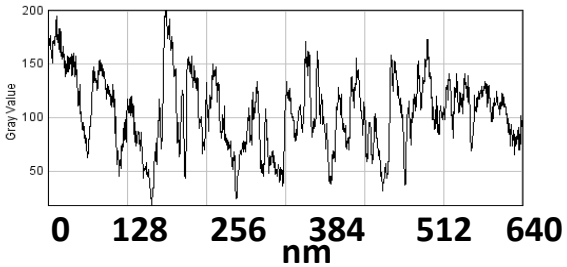
Ra- Roughness average; ***average of the absolute*** **distance from the baseline with no indication of the algebraic position of the deviation.**

Rsk – Skewness: domination of peaks (particles) or valleys (pores)

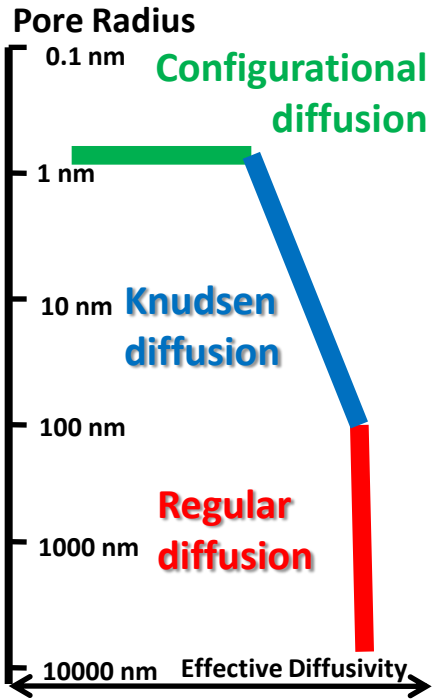
Total image

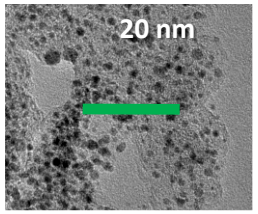


Roughness Profile

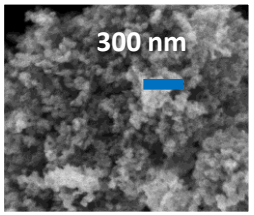


Applied high- and low-pass filtering to separate micro and meso-roghnesses

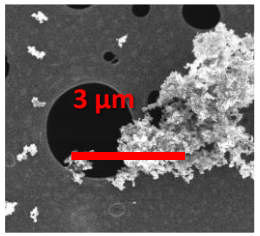




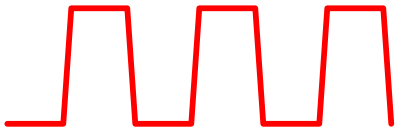
Roughness due to microporosity



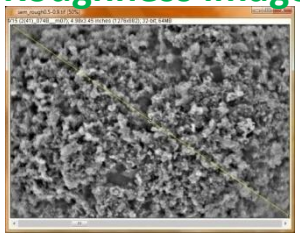
Roughness due to mesoporosity



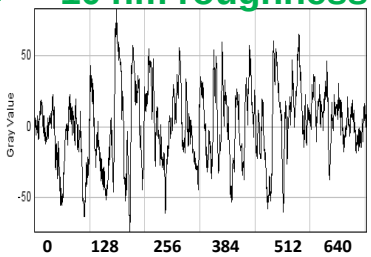
Roughness due to macroporosity



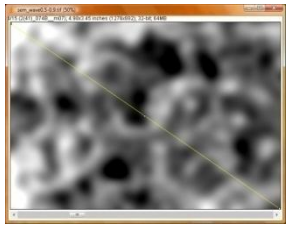
Roughness image



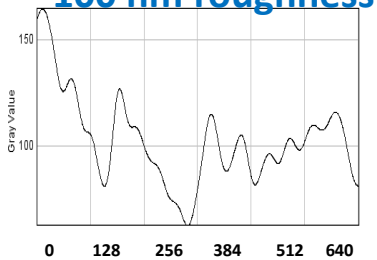
~10 nm roughness



Waveness image



~100 nm roughness



Analytical modeling

Microstructure-property relationships

Igor Sevostianov

The main goal: to develop a quantitative micromechanical model that interrelates physical properties of interest – electron and ion transport through the solid, porous media fluid permeability, specific catalyst area, and mechanical properties – to the porous space geometry.

Current activity: Cross-property connections between conductivity and fluid permeability of the electrodes in fuel cells

Tortuosity of the porous space is the microstructural parameter controlling fluid permeability.
Tortuosity of the solid phase is the microstructural parameter controlling conductance of ions and electrons across the solid phase.

Analytical modeling

Microstructure-property relationships

Variational bound has been developed:

For a porous material with arbitrary microstructure

$$\tau_p^2 \geq \frac{(1-p)(\tau_s^2-1)+p}{2(\tau_s^2-1)+p}$$

τ_s **tortuosity of the solid phase**

τ_p **tortuosity of the porous space**

p **porosity**

It yields

$$\frac{L^2}{8k} \leq 1+\frac{(1-p)^2}{p^2}\frac{(\sigma_s-\sigma_{eff})}{\sigma_{eff}}$$

σ_s **conductivity of the solid phase**

σ_s **effective conductivity**

k **permeability**

L **Length parameter**

Analytical modeling

Microstructure-property relationships

Work in progress: quantitative characterization of microstructures of fuel cells electrodes with respect to three groups of problems listed below and possible connections between them

- **Modeling of effective electronic/ionic conductivities and their dependence on relevant geometrical features (to be identified)**
- **Modeling of the permeability of porous media**
- **3-PB areas and their dependence on the model parameters**

DOE-EPSCoR Materials for Energy Conversion

46 Researchers Involved

9 University Co-PIs and
9 Natl. Lab Collaborators + 3 NEW collaborators

3 Research Faculty / Senior Researchers
2 Postdoctoral Fellows
11 Graduate Students
8 Undergraduate Students and
1 High School Student

9 Female
28 Male

5 Hispanics

1 Native American

E. Switzer, T.S. Olson, A. K. Datye, P. Atanassov, M.R. Hibbs and C.J. Cornelius, Templated Pt-Sn Electrocatalysts for Ethanol, Methanol and CO Oxidation in Alkaline Media, *Electrochimica Acta* 54 (2009) 989-995

N. J. Carroll, S. Pylypenko, P. Atanassov and D.N. Petsev, Hierarchical Nano-Porous Microparticles Derived by Microemulsion Templating, cover-art featured article, November (2009) *Langmuir*

D. Konopka, S. Pylypenko, T. Ward and P. Atanassov, Nanostructured Mesoporous NbRuyOz as a Catalytic Support for Fuel Cells, submitted to *Electrochemical Society Transactions*

D. Konopka, S. Pylypenko, P. Atanassov and T. Ward, Spray Pyrolysis of Mesoporous Nb-Ru as Potential Catalytic Supports in Fuel Cells, submitted to *Applied Materials and Interfaces*

E. Switzer, T.S. Olson, A. K. Datye, P. Atanassov, M. R. Hibbs, C.Fujimoto, and C. J. Cornelius, Novel KOH-free Anion Exchange Membrane Fuel Cell: Performance Comparison of Alternative Anion Exchange Ionomers in Catalyst Ink, *J. Electrochemical Society*, submitted after revision 2009

Electrocatalysis Mechanisms

INSTITUTE OF ADVANCED STUDIES SPONSORED WORKSHOP

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3rd Workshop on Materials for Energy Conversion:

Radoslav Adzic, BNL
Jen-Pol Dodelet, INRS
Edward Solomon, Stanford
Jens Norskov, DTU

Los Alamos NATIONAL LABORATORY

September 9-11, 2009

Santa Fe, NM – just outside of town

DOE-EPSCoR Materials for Energy Conversion

Answering Tim's Questions

a) ***Does the proposer have a plan to or has the awardee made competitive faculty hires and retained outstanding faculty within the scope of the implementation award?***

YES: Critical LANL technical lead hire – joint as Distinguished National Laboratory Professor
Retaining of the CEET Director actually worked all the way around – it resulted in EPSCoR IA ☺

b) ***Does the proposer have a plan to attract or has the awardee hired outstanding graduate students and post docs?***

YES: Barr Halevi (U Penn); 2 NSF-IGERT fellows; 6 NSF REU undergraduates

c) ***Does the proposer have plans to develop or have they developed as part of the implementation award unique infrastructure capabilities that are critical to the advancement of science or technology? Alternatively, are they planning to or making unique contributions to DOE oriented capabilities (e.g., building or developing unique capabilities for a DOE experiment or facility)?***

YES: UNM Pioneers multi-analytical methods in analysis of catalysts and electrocatalysts

d) ***Does the proposer have plans to be or are the grantees on track to a sustained leadership position in their discipline(s)?***

YES: Publications, reviews, ACS and ECS symposia organizing, industrial collaborations

e) ***Does the proposer have plans to or are the grantees effectively leveraging DOE funding and capabilities with local and regional resources?***

YES: Working with state, universities and private companies

How has the jurisdiction's EPSCoR Committee planned to and what actions have they taken to maximize the long-term impact of the award?

DOE EPSCoR Program in Context…

CENTER FOR EMERGING ENERGY TECHNOLOGIES

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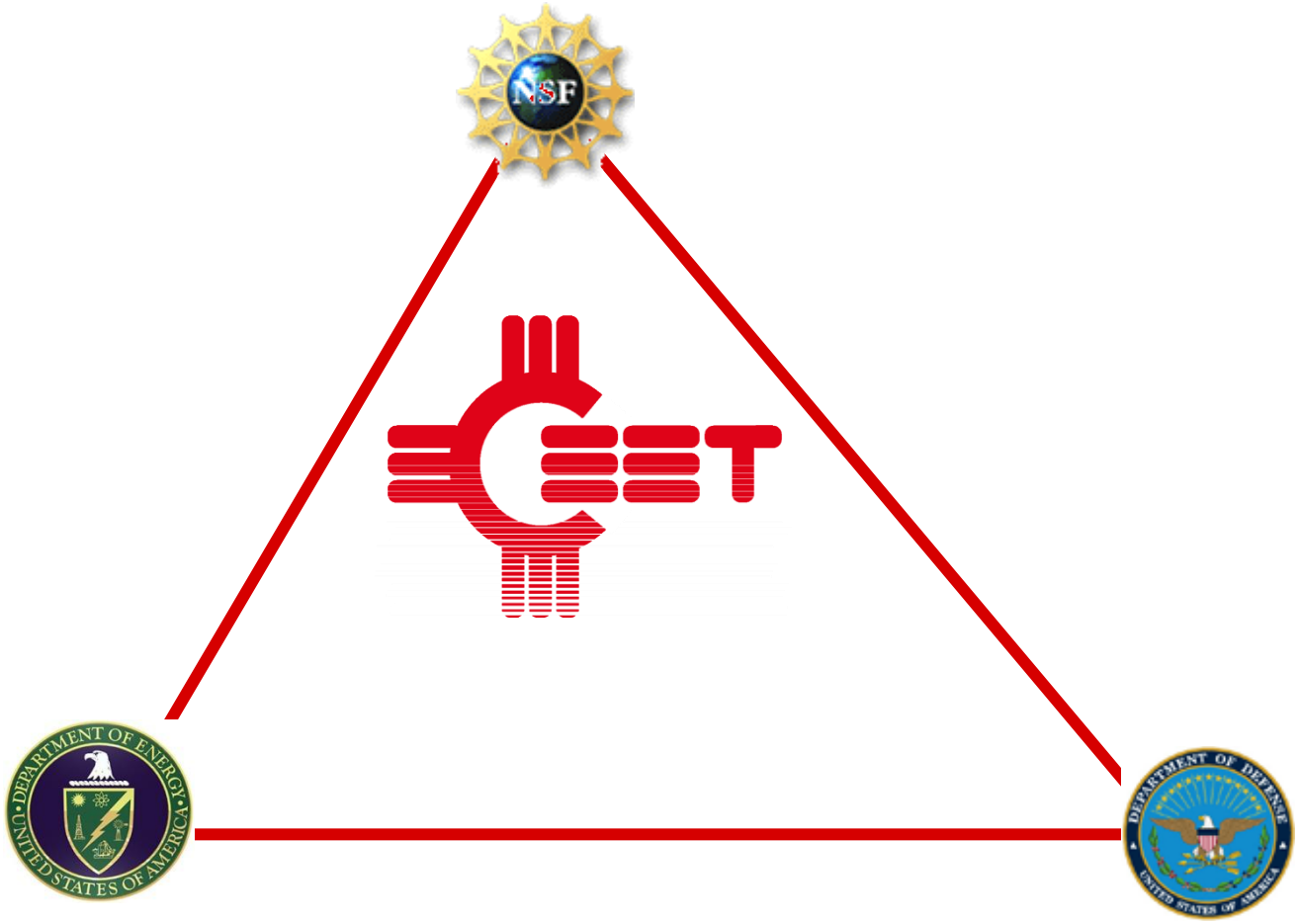

DOE EPSCoR Program in Context…

CENTER FOR EMERGING ENERGY TECHNOLOGIES

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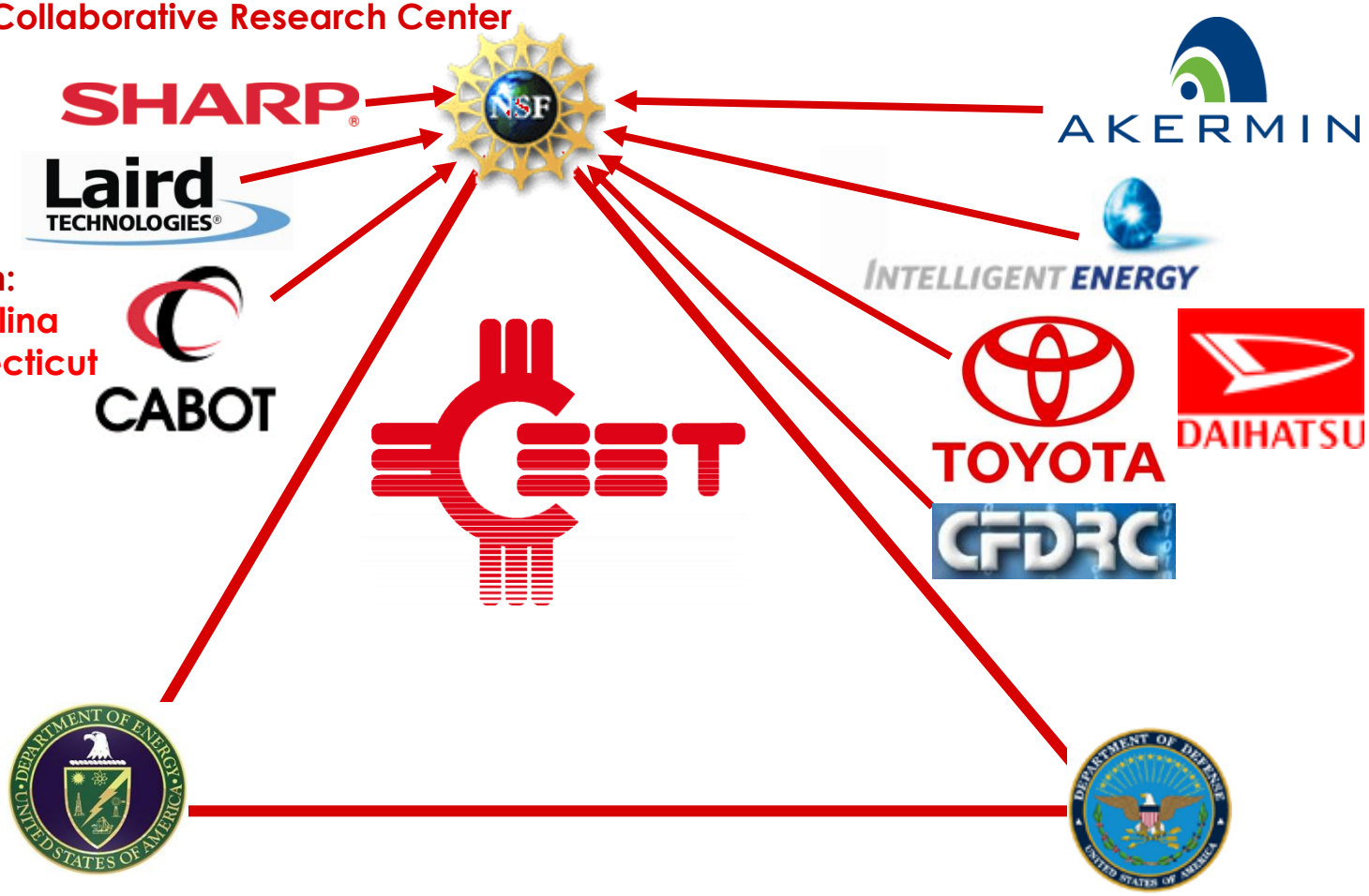
NSF Industry/University Collaborative Research Center

Materials solutions for energy technologies:
Rutgers University
Penn State

Currently engaging with:
University of South Carolina and University of Connecticut



DOE EPSCoR Program in Context…

THE UNIVERSITY of NEW MEXICO

CENTER FOR EMERGING ENERGY TECHNOLOGIES

NSF Industry/University Collaborative Research Center

Materials solutions for energy technologies:
Rutgers University
Penn State

Currently engaging with:
University of South Carolina and University of Connecticut

SHARP

Laird TECHNOLOGIES

CABOT

NSF

AKERMIN

INTELLIGENT ENERGY

TOYOTA

DAIHATSU

CFDRC

CEET

Micro-fabricated power devices:

Sandia National Laboratories

DOD AFOSR MURI
Enzymatic Biofuel Cells:
Columbia University
St. Louis University
University of Hawaii – Manoa
Michigan State
Northeastern University

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DOE EERE HIFCT Program
Novel Electrocatalysts Program:
LANL (prime), ONR, BNL and
University of Illinois – Urbana
University of California – Riverside
Cabot SMP

- ❑ 09 1A
- ❑ 09 2A
- ❑ 09 3A
- ❑ 09 3A

DOE EPSCoR New Mexico Implementation Program in Biofuels in Fuel Cells
New Mexico Tech
New Mexico State
Eastern New Mexico

Micro-fabricated power devices:

DOD AFOSR MURI
Enzymatic Biofuel Cells:
Columbia University
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