LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

SD2: Energy Materials

Ramu Ramachandran

The goal of this SD is to study materials for the generation, conversion, and storage of energy using experimentally validated computational methods.

FOCUS 1

Electrochemical Capacitors Based on Nanotube Forests

FOCUS 2

~~Hydrogen Storage Materials~~

Lithium ion batteries and electrochemical sensors

FOCUS 3

Catalyst Materials

SD2: Energy Materials

Electrochemical Supercapacitors

Tulane, UNO

- CNT forest-based supercapacitors

Lithium Ion Batteries and electrochemical sensors

LA Tech, Xavier

- Stable and high-capacity electrode materials.
- YSZ-based exhaust gas sensors.

Energy Materials

yttria-stabilized zirconia

Catalysts for Energy Applications

LSU, LA Tech, SUBR, Grambling

- DFT studies of Fischer-Tropsch catalysis
- Nitrogen-doped fullerenes as Pt-substitutes in hydrogen fuel cells.

Electrochemical Supercapacitors

Tulane, UNO

Focus 1: CNT-based supercapacitors

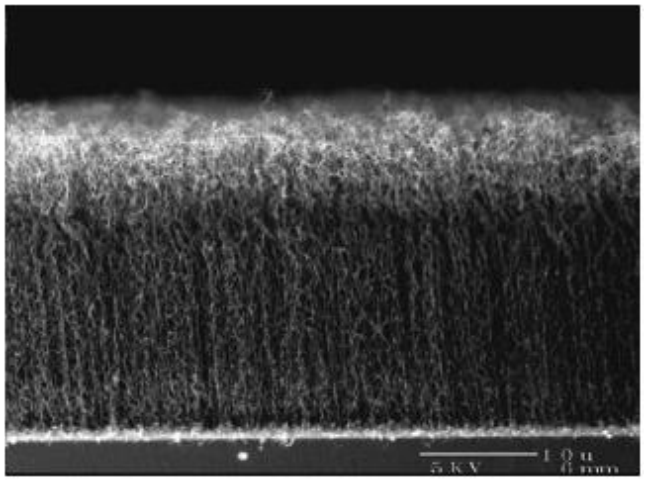
Lawrence Pratt

Noshir Pesika

Steve Rick

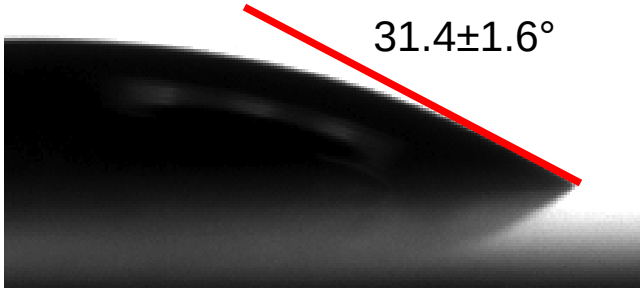
Tulane University

THE UNIVERSITY of NEW ORLEANS

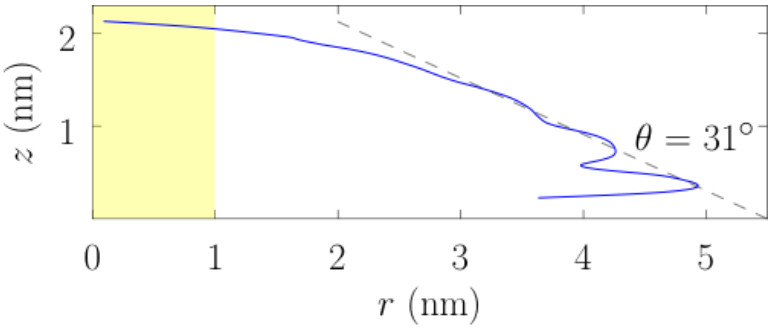


http://mitei.mit.edu/news/novel-ultracapacitor

- Electrochemical capacitors based on carbon nanotube forests show great potential.
- A molecular level understanding of the interaction of CNT's with the electrolyte is needed.



Propylene carbonate droplet contact angle with graphite - experiment

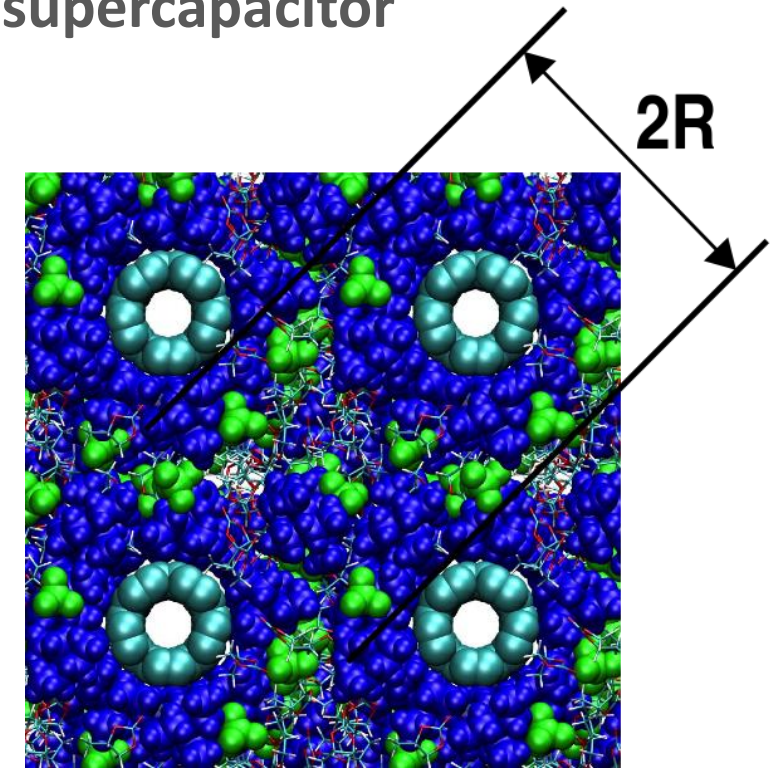


Propylene carbonate droplet contact angle with graphite - simulation.

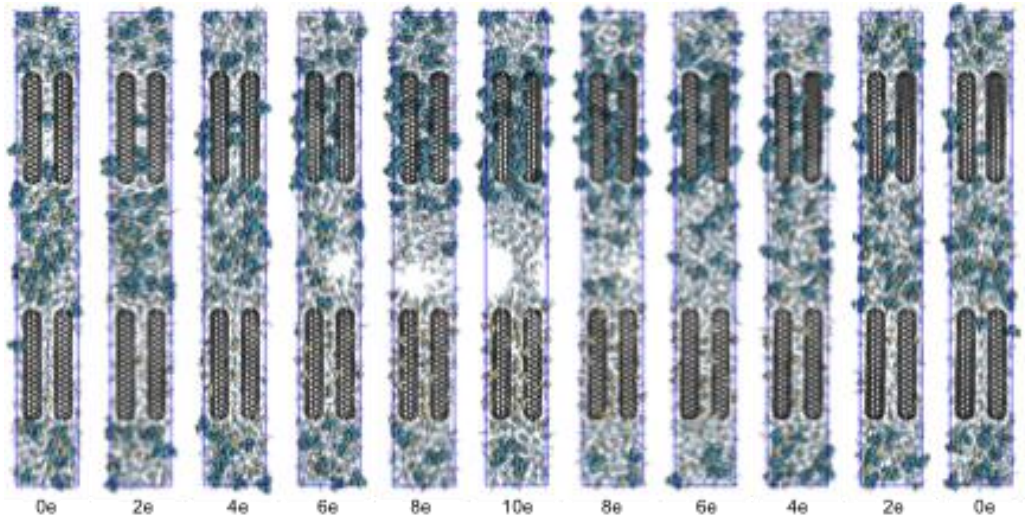
X. You, M. I. Chaudhari, L. R. Pratt, N. Pesika, K. M. Aritakula, and S. W. Rick, "Interfaces of propylene carbonate, " *J. Chem. Phys.* **138**, 114708 (2013).

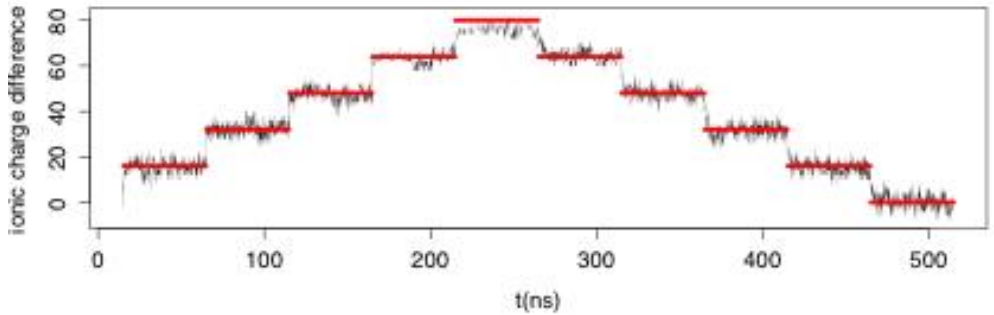
Focus 1: CNT-based supercapacitors

The first direct simulation of pore-filling in a CNT supercapacitor



Computer model: $(C_2H_5)_4N^+..BF_4^-$ in propylene carbonate interacting with a carbon nanotube forest.

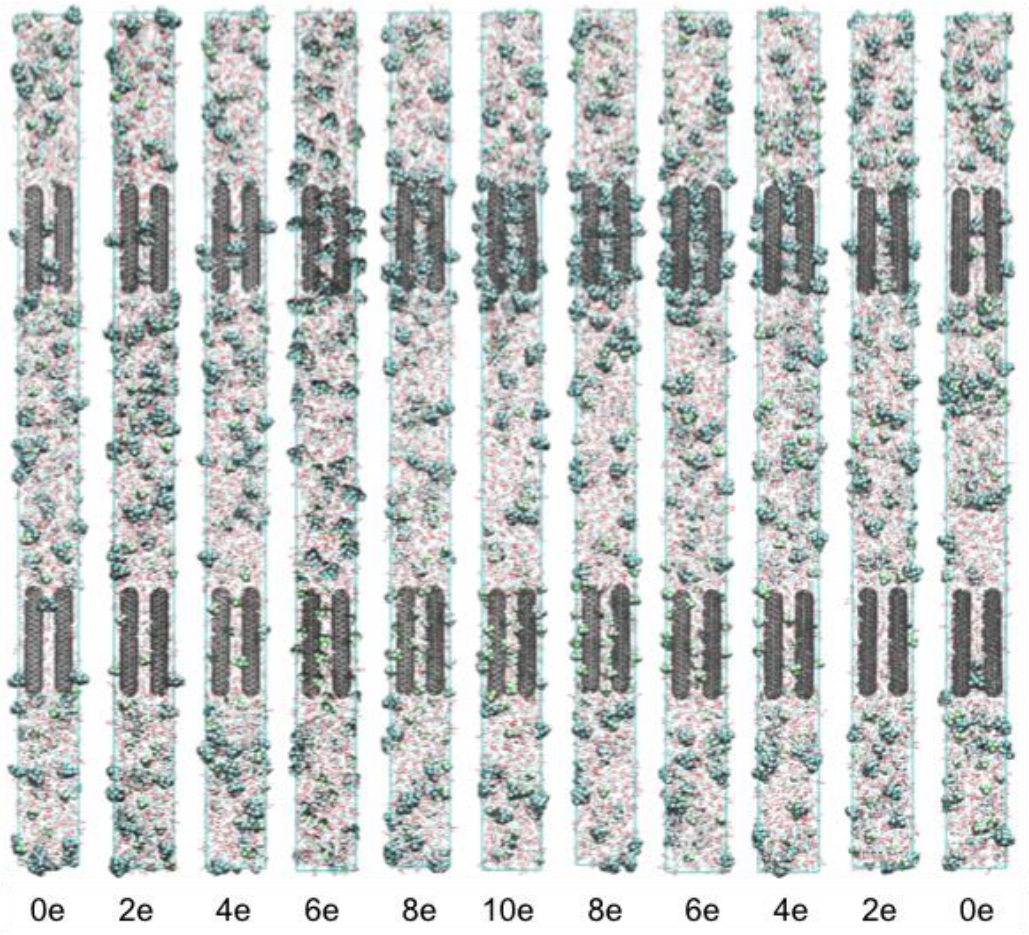




Direct numerical simulation: filling of CNT forest with electrolyte solution

A molecular level understanding of the distribution of ions in the CNT forest and the charge transfer during charge-discharge cycles has been obtained.

Direct simulation of filling: twice the reservoir size



X. You and L. R. Pratt, preliminary results

See posters (p. 5, 33, 81)

SD2 Focus 1 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Simulation of pore filling in nanowire capacitors .	X	X	X			*On Track*
Study chemical damage at elevated electric potentials.	X	X	X			*On Track*
Optimize computational efficiency of ab initio MD techniques.	X	✓				*Done*
Study role of quantum capacitance in electrochemical capacitance.		X	X	X		*Ahead*
Explore additional nanoforest-based capacitor systems.			X	X	X	*On Track*

Lithium Ion Batteries

LA Tech, Xavier

Focus 2(a): Li Ion Batteries

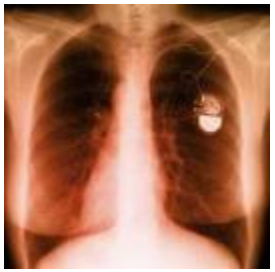
Lamar Meda

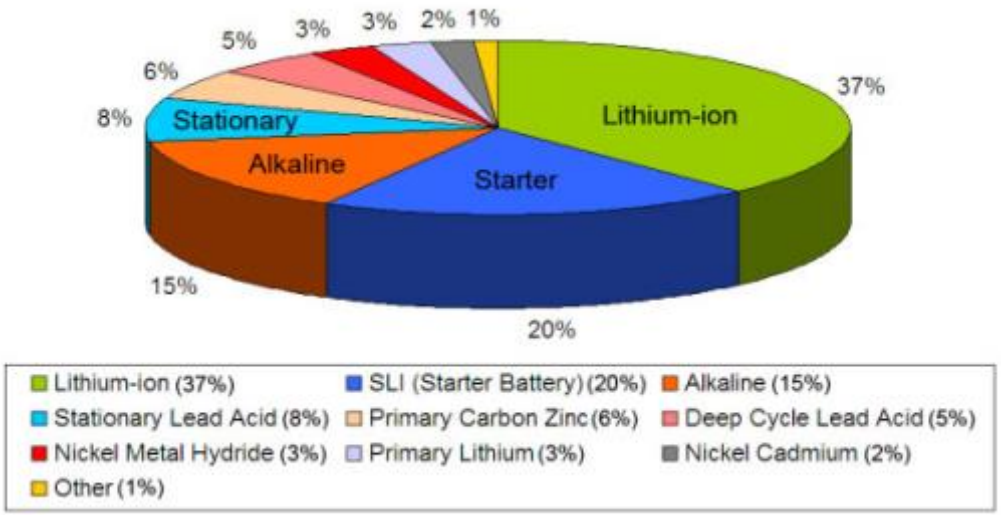
Ramu Ramachandran

Collin Wick

GENERAL INTRODUCTION/MOTIVATION FOR THIS WORK



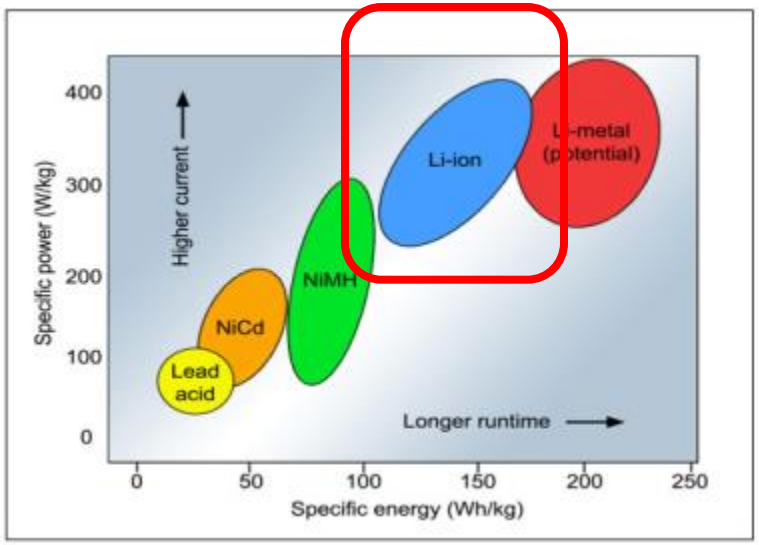


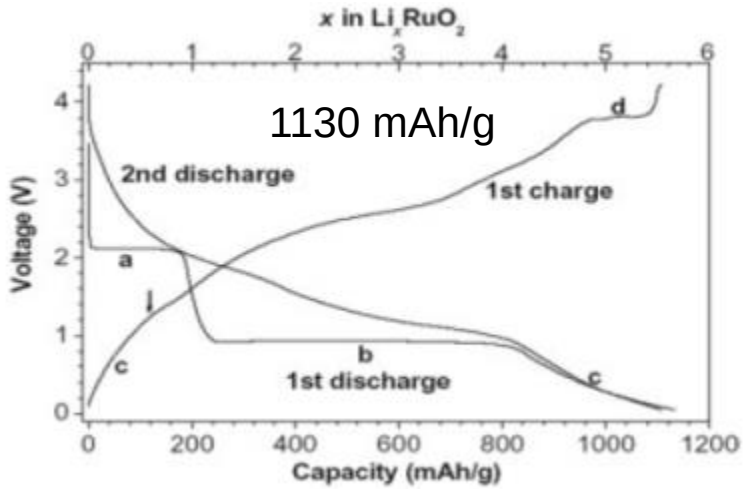
Figure 1*: Revenue contributions by different battery chemistries

Need for :

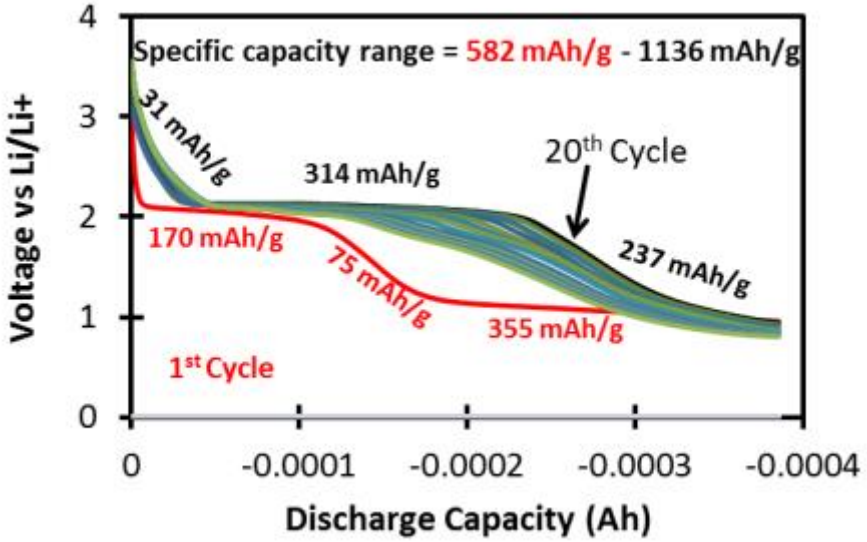
- ❑ Highly reactive materials with much higher energy and power density
- ❑ High cyclability- electrodes maintain structural integrity upon multiple charge-discharge cycles

Focus 2(a): Li Ion Batteries

Experimental motivation for this work



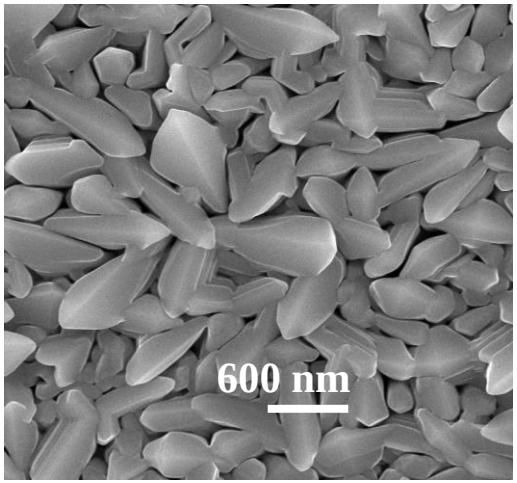
Balaya et al. Adv. Funct. Mater. ***2003****, 13, 621-625*



- Experimental studies on RuO_2 nanoparticles reported by Balaya et al.:
  - With "deep discharge," electrodes cycle only twice before losing capacity.
- Experimental studies on RuO_2 "nanoplates" by Prof. Meda, Xavier University:
  - Stopping short of deep discharge, can cycle many times without loss of capacity.
- In both cases, the first discharge curve looks significantly different from subsequent discharges, suggesting that some permanent changes occur in the electrode in the first cycle.

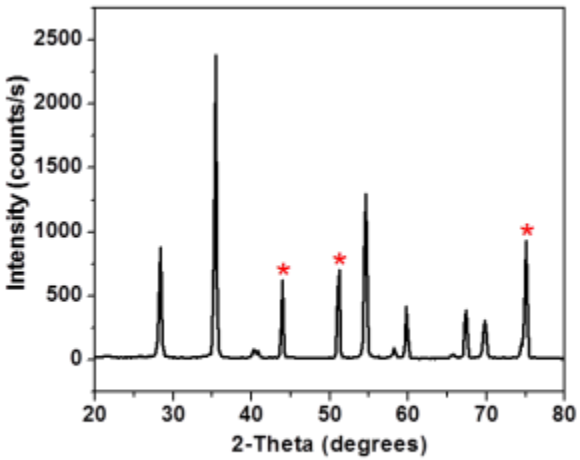
RuO_2 Nanoplates Grown by Chemical Vapor Deposition

L. Meda, Xavier University

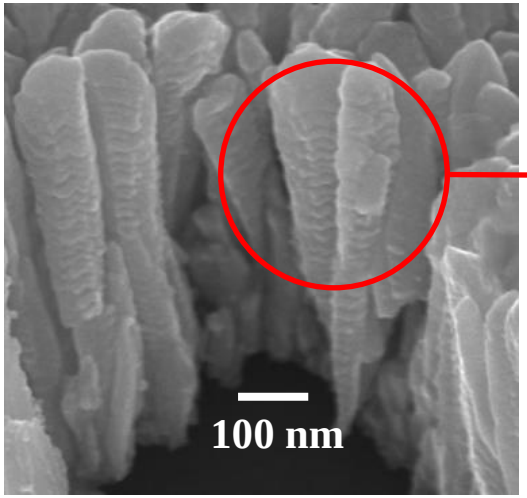


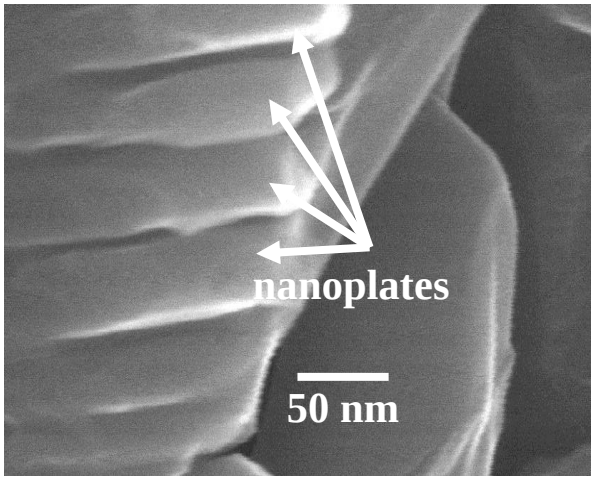
Field Emission SEM images of RuO_2 nanoplates deposited on stainless 304L substrates.

Rutile structure



PXRD patterns of RuO_2 thin films (*stainless steel patterns)





Focus 2(a): Li Ion Batteries

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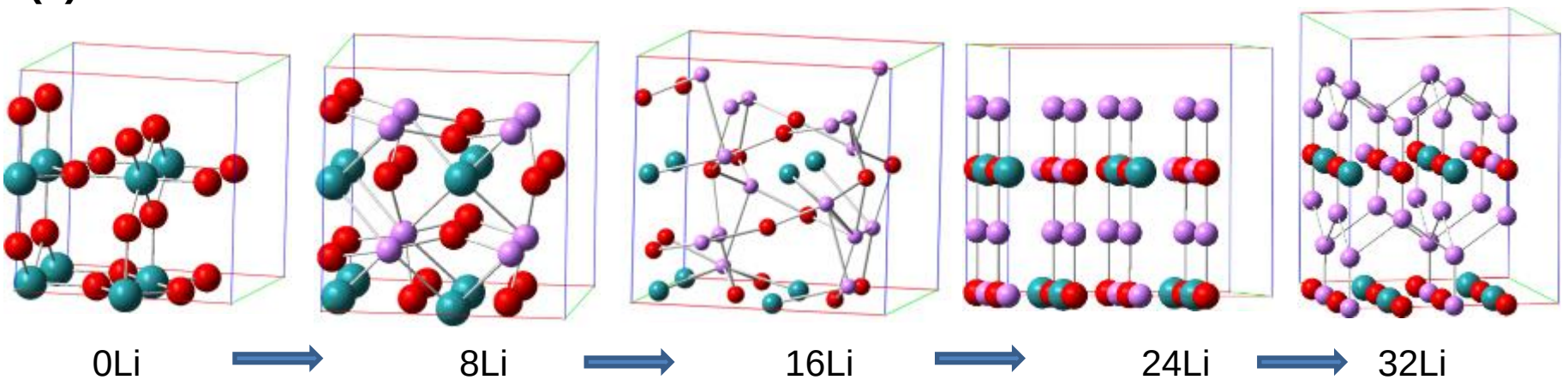
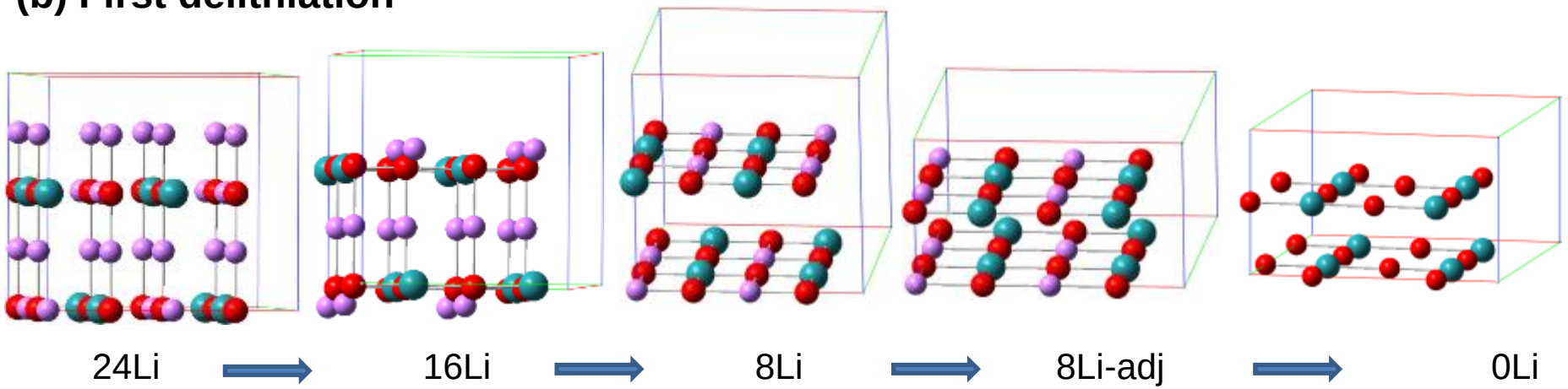
The starting RuO_2 structures for the first and subsequent discharges are different!

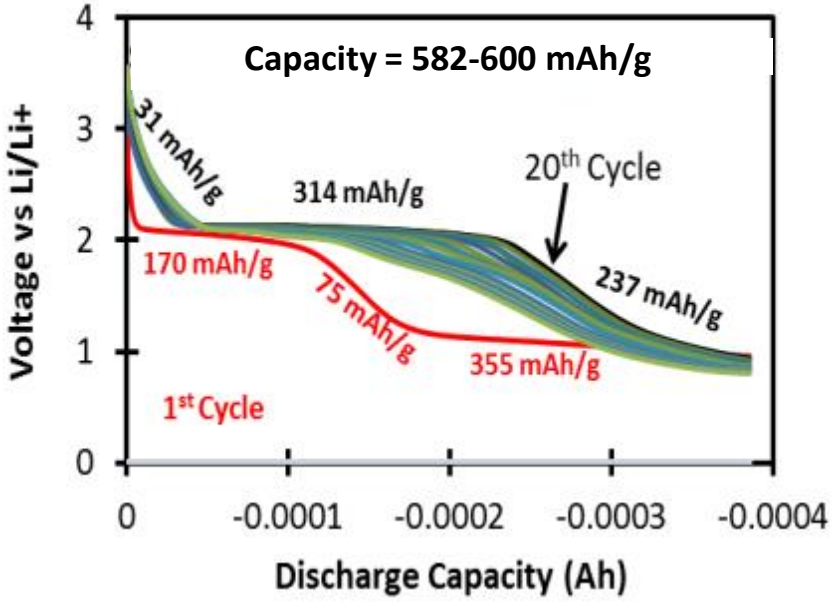
(a) First lithiation

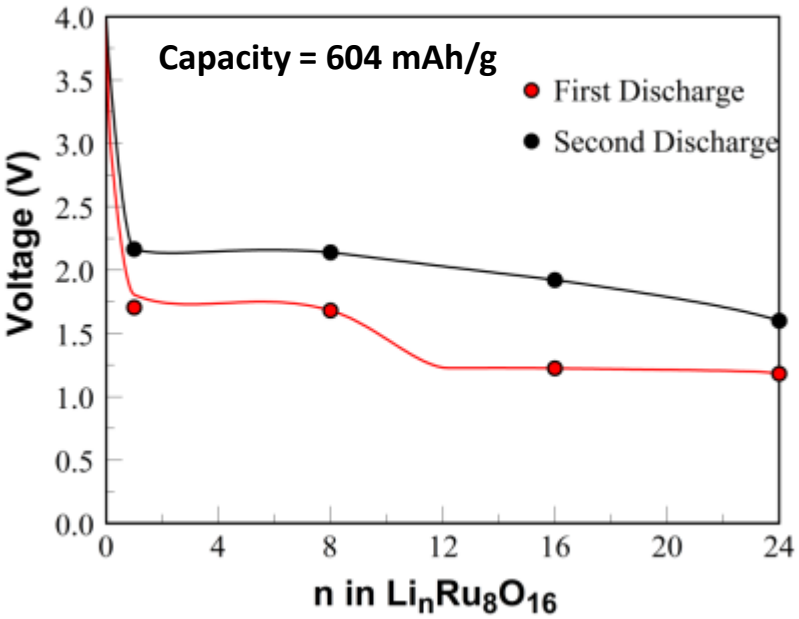


(b) First delithiation



Simulations provide nearly quantitative agreement with experimental observations!





- Posters:
- Metal oxide nanoparticles as electrode materials (p. 85)
- RuO_2 and other crystalline metal oxides (p. 89)

Electrochemical sensors

LA Tech

Focus 2(b): Electrochemical Sensors

Erica Murray

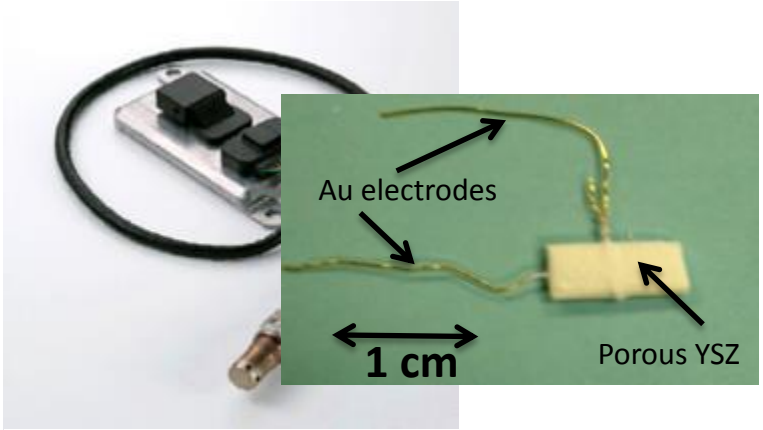
Daniela Mainardi

Weizhong Dai

Automotive NO_x Sensors

Murray Research Group

- Commercial NO_x exhaust gas sensor systems can detect up to 10 ppm.
- New emission standards require greater sensitivity.
- **Conventional NO_x Sensor Design:**
  - Dense electrolyte and porous electrodes architecture
    - NO_x sensitivity capable down to 10 ppm
- **Novel NO_x Sensor Design:**
  - Porous electrolyte microstructure with dense electrodes
    - *Potential for NO_x sensitivity down to 1 ppm*
  - Novel porous microstructure is promising for satisfying future emission standards



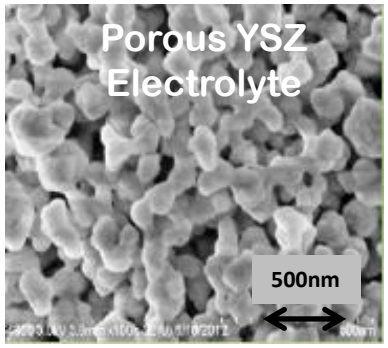
NGK commercial NO_x Sensor

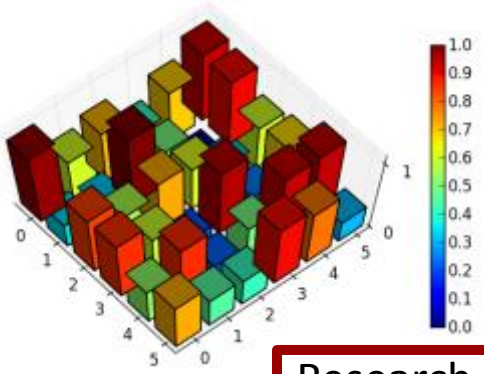
- Research Challenges:
  - Achieving ideal porosity
    - Excess porosity lowers sensitivity
    - Insufficient porosity limits gas diffusion
  - Identifying reaction mechanisms impacting sensing

Focus 2(b): Electrochemical sensors

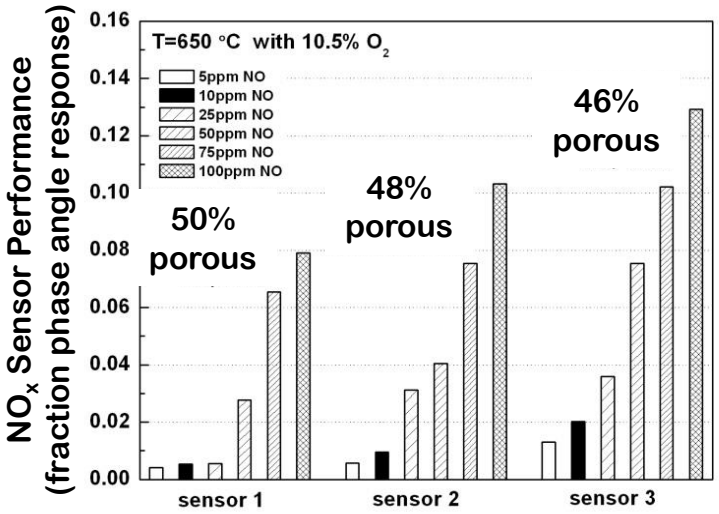
NO_x Sensor Research

- Research Aim:
  - Correlate YSZ synthesis methods to porosity.
  - Determine sensitivity of various synthesized YSZ.





Sensor Response to NO Gas



Typical performance for sensors with 3 different porous microstructures.

- Image analysis algorithms analyze SEM images,
- Provide input to mathematical models that estimate porosity.

Research Highlights:

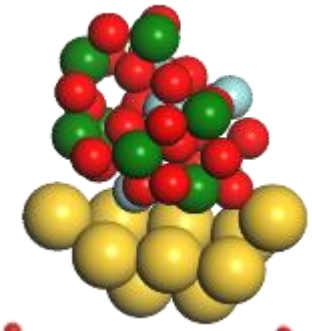
- ***Greater NO_x sensitivity and stability achieved, particularly for NO_x concentrations down to 5 ppm*** as the porosity decreased to 46%.
- ***Dissociative adsorption of O_2 appeared to be the dominant rate limiting reaction***, based on impedance spectroscopy and modeling results.
- The porous YSZ based NO_x sensor could be tuned to give a more rapid response.

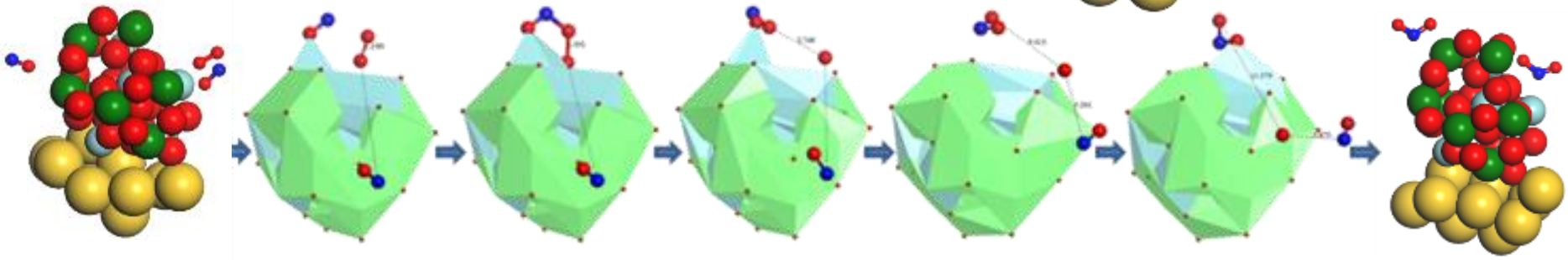
Kinetics of Nitric Oxide and Oxygen Gases on Porous Y-stabilized ZrO_2 based Sensors

Sajin Killa and Daniela Mainardi, Louisiana Tech University

$$2NO + O_2 \leftrightarrow 2NO_2$$

Tested on a 56-atom YSZ/Au model cluster (62% YSZ porosity)





Reaction path: oxygen surface reactions

NO association with adsorbed O_2 on a Zr surface site, followed by O_2 dissociative adsorption, atomic oxygen diffusion, and further NO_2 formation.

Extrapolated data at 62% YSZ porosity (~126 kJ/mol) indicates the calculated barriers are in reasonable agreement with experiments, especially when the RPBE functional is used.

Eqn. 3	Theory Level			
	PWC	PW91*	PBE*	RPBE*
ΔU (kJ/mol)	156.2	137.7	133.5	123.6
ΔG(650°C) (kJ/mol)	181.7	163.2	159.0	149.1

Focus 2(b): Electrochemical sensors

SD2 Focus 2 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Computational study of lithiumion adsorption on metal oxide nanoparticles.			✓			*Done*
Computational study of lithium ion adsorption on metal oxide thin films and other promising electrode materials.			X	X	X	*On Track*
Experimental study of nanostructured metal oxides as potential electrode materials for lithium ion batteries.		X	X	X	X	*On Track*
Multi-scale computational modeling of the kinetics and thermodynamics of NOx and O_2 reactions on YSZ sensors for vehicle exhaust applications.			X	X	X	*On Track*
Fabrication and testing of YSZ sensors for NOx and O_2 in diesel exhaust streams.			X	X	X	*On Track*
Update VisTrails so that it can be used for workflow of lithium-ion battery tomography studies.			X	X	X	*On Track*

Catalysts for Energy Applications

LSU, LA Tech, Southern Grambling

Focus 3: Catalysis


Les Butler


Bin Chen


Barry Dellinger


Daniela Mainardi


Ramu Ramachandran

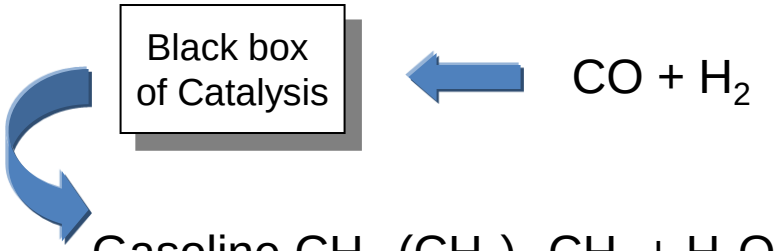

Collin Wick

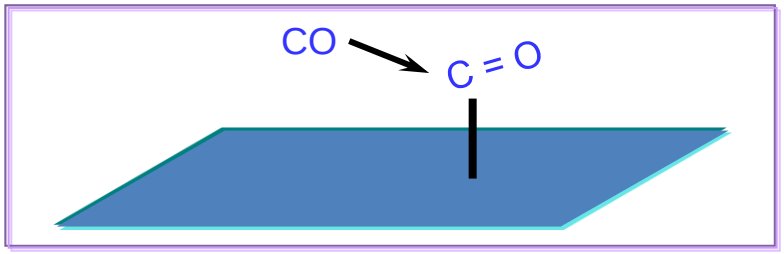

Guanglin Zhao


Naidu Seetala

Towards rapid computational evaluation of Fischer-Tropsch catalysts

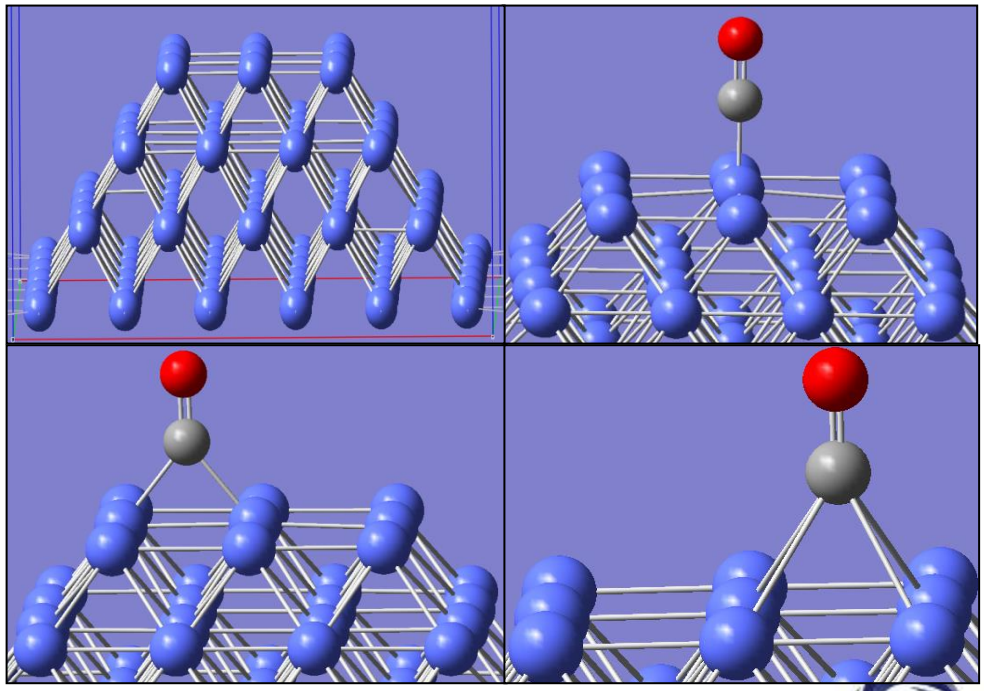
Shuo Yao, Oneka Cummings, Josh Riggs, Collin Wick and R. Ramachandran





- CO binding energies - very difficult to get agreement with experiments.
- Developing computational protocols using DFT functionals developed by Perdew – with some success!
- Collaborating with a North Louisiana start-up – Jupiter Fuels (> $3M in venture capital).
- Modeling CO binding on catalyst nanowire tips.

http://www.asi20.com/page9/index.html



CO adsorption on Cobalt nanowire tips

Focus 3: Catalysis

Louisiana EPSCoR

Fischer-Tropsch Synthesis

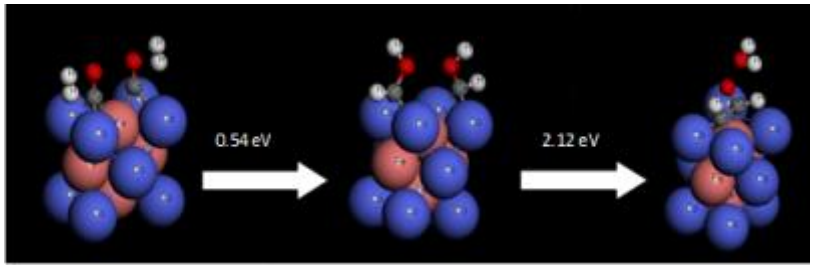
Fernando Soto, Purnima Kharidehal, Suraj Gyawali and Daniela Mainardi Louisiana Tech University



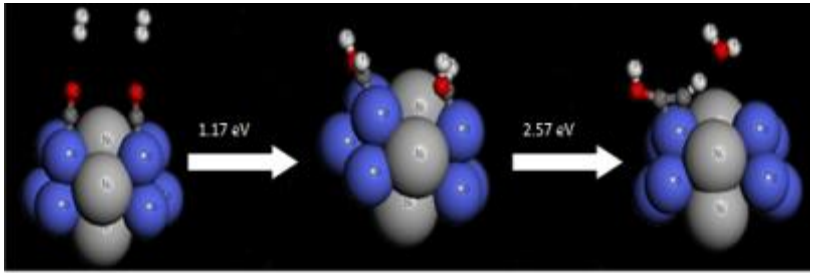
Core-shell nanoparticles investigated in the context of FTS mechanism

- CO bonds strongly to **Co top sites** in pure **Co** and in **CoNi** systems
- CO bonds strongly to **mixed CoFe hollow sites** in **CoFe** systems

$Co_{10}(Fe_4)$



$Co_{10}(Ni_4)$



- The **energy cost to hydrogenate** CO varies as the **composition** of the nanocluster is tweaked
- **Co-shell (Fe)-core at a 1:1 ratio** shows the most promising result with an energy cost as low as 0.1 eV for the initiation step

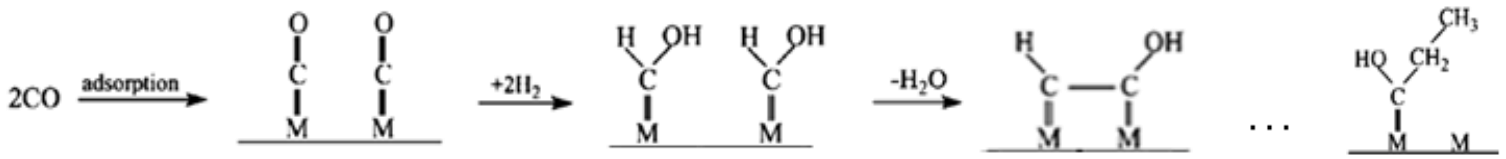
Fe is preferred over Ni when used as core element in a Co core-shell catalysts.

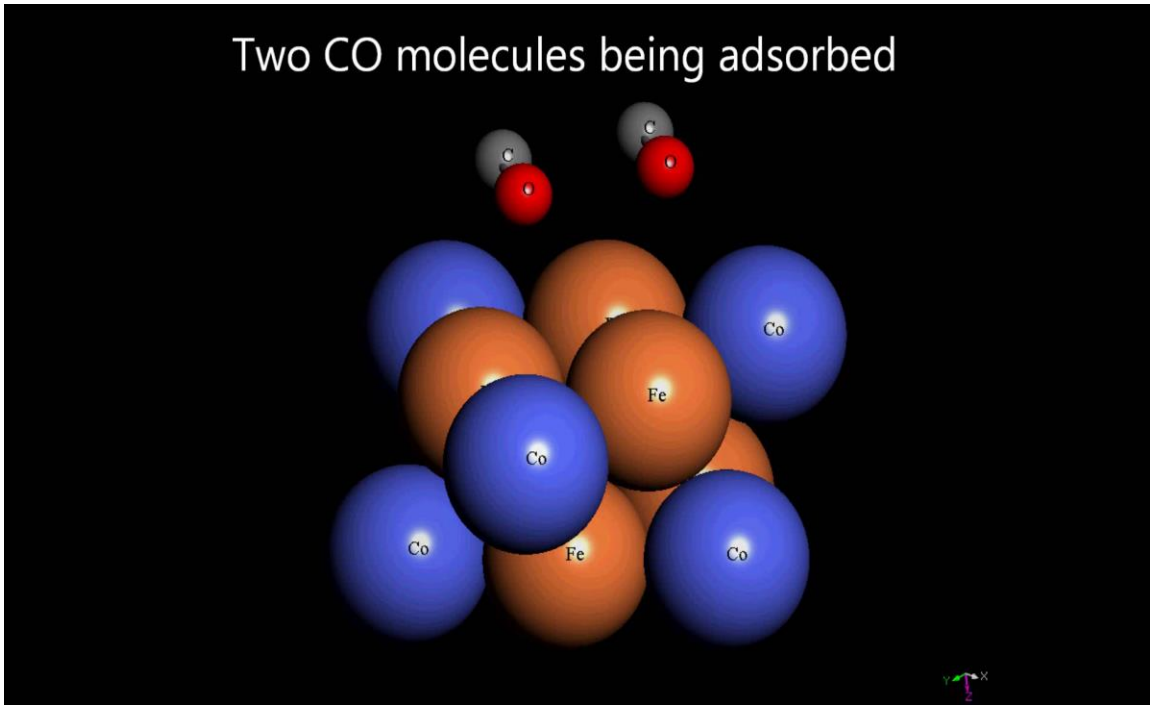
Focus 3: Catalysis

Fischer-Tropsch Synthesis

Fernando Soto, Purnima Kharidehal, Suraj Gyawali and Daniela Mainardi Louisiana Tech University







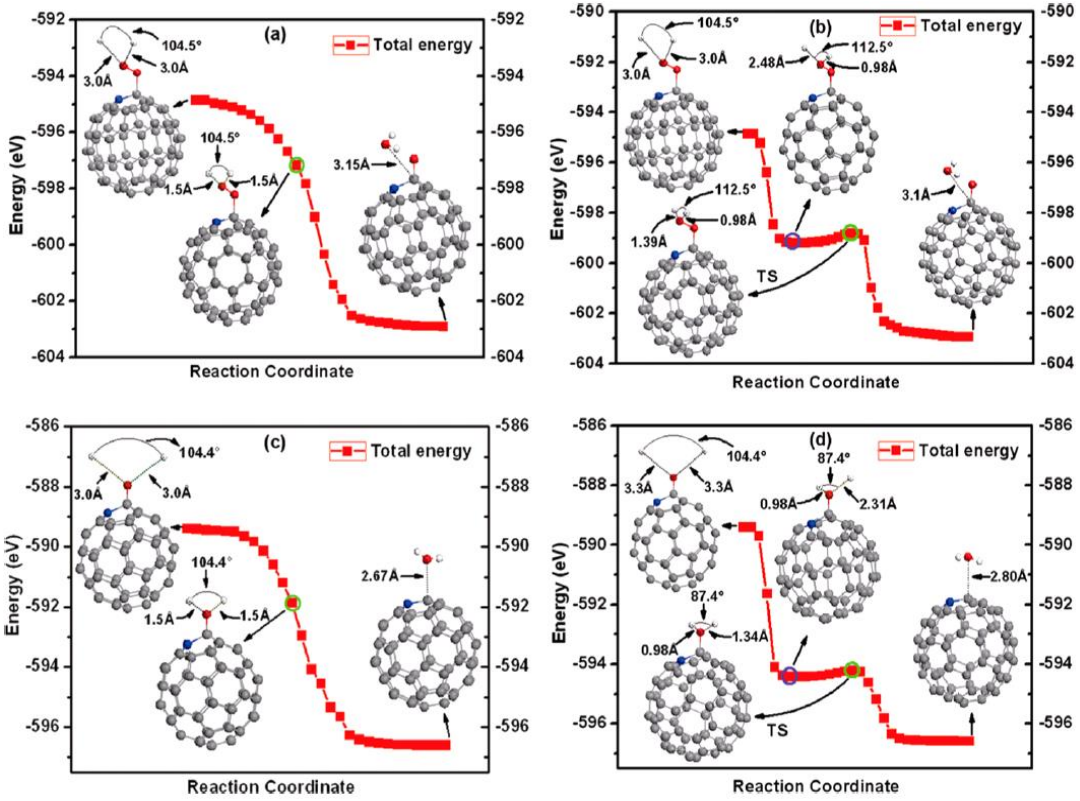
See poster (p. 141)

Focus 3: Catalysis

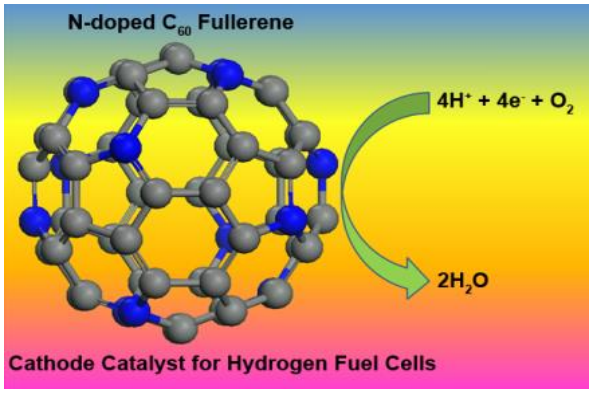
Nitrogen-doped fullerenes as fuel cell catalysts

Can N-doped C60 replace Pt in hydrogen fuel cells?

Spin-polarized DFT calculations of nitrogen-doped C_{60} fullerene (N-C_{60}) as a cathode catalyst for hydrogen fuel cells.



Minimum energy path for H_2O formation process on O(1) through (a) direct pathway and (b) indirect pathway; and H_2O formation process on O(2) through (c) direct pathway and (d) indirect pathway, on HH Pauling site of N-C_{60} fullerene. Embedded images show the atomic structures of the initial, intermediate, and final states of the reaction process, respectively.



F. Gao, G.L. Zhao, S. Yang, J. J. Spivey, "Nitrogen-Doped Fullerene as a Potential Catalyst for Hydrogen Fuel Cells", *Journal of the American Chemical Society*, 2013, **135**, 3315-3318.

Collaboration between LA-SiGMA and DoE EFRC.

Focus 3: Catalysis

SD2 Focus 3 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Develop force fields with environment-dependent charges for one metal oxide system.	X	✓				*Done*
Use DFT-based ab initio MD and kinetic Monte Carlo methods to study Fischer-Tropsch and related reactions on metal/metal oxide catalytic systems.			X	X	X	*On Track*
Exploration of spin-state dependent structure and energetics of metal oxide clusters, especially $(FeO)_n$.			X	X	X	*On Track*
Perform computational modeling of PCDD/PCDF production on metal oxide clusters.		X	X	X		*On Track*
Develop computational methods for evaluating catalytic sites in carbon nanotubes for hydrogen fuel cells.		X	✓			*Done*
Computational evaluation of nitrogen doped CNT's and fullerenes as alternatives for platinum in hydrogen fuel cells.			X	X	X	*On Track*

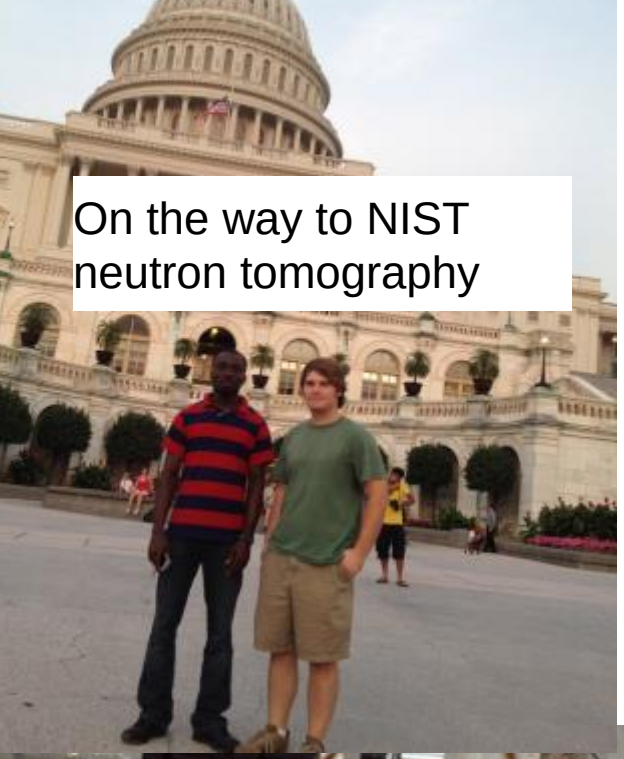
Other notable SD2 accomplishments

Shawn Cole, PhD student at LA Tech received an Indo-US Science and Technology Forum fellowship to visit and work at IIT-Delhi (ethanol fuel cells).

Steve Rick, UNO, received a $450,000 grant from NSF: “The Effects of Charge Transfer on Aqueous and Ionic Systems.”

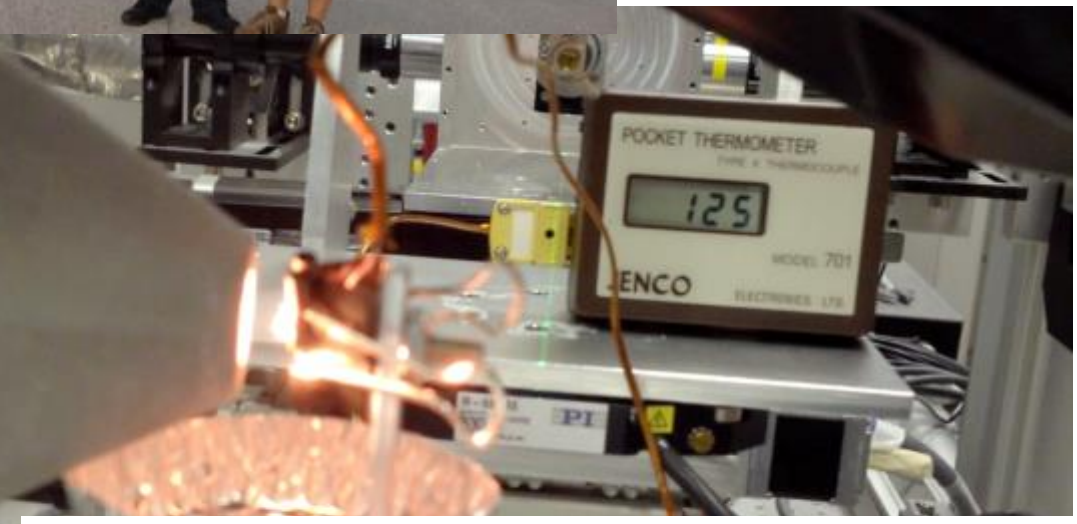
Daniela Mainardi, LA Tech, receives AIChE Excellence and Service Award; partner in North Carolina A&T NSF CREST Center for biofuels.

LA Tech REU and RET programs (including “STEM Week”) focused on “Energy Materials.”



On the way to NIST neutron tomography

"ICTMS" Ghent, Belgium, July, 2013
Ham: neutron tomography and hydrogen storage
Olatinwo: X-ray interferometry movies and flame retardants
Butler: new algorithm for X-ray interferometry



APS: "Fire at the beamline"
X-ray interferometry movies and flame retardants.

Prof. Les Butler's activities:

- NIST neutron imaging (2)
- Synchrotron Radiation Instr mtg
- Summer 2012: 2 REU, 2 RET

(REU wins NSF grad. fellowship)

- Summer 2013: 1 REU, 1 RET, 1

high school student:

- spherical harmonic for particle
- iPad iBook visualization