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Combined Theoretical and Experimental Investigation and Design of H_2S Tolerant Anode for Solid Oxide Fuel Cells

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DOE Program Manager: L. Wilson

EERL developing the technology of the future

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OHIO UNIVERSITY 1804

Collaborators

•Damilola Daramola. MS student. Effort in the experimental scope of the project. Designed, constructed experimental set up. Builds SOFCs and tests them.

•Madhivanan Muthuvel. Post-doctoral research associate. Performs molecular modeling.

Introduction

Solid Oxide Fuel Cells (SOFCs) are the most viable fuel cell technology to handle coal syngas

- Functions at high temperatures

  (600°C – 1000°C)
- Tolerable to contaminants like Carbon monoxide (CO) and Carbon dioxide (CO_2)
- Presence of Hydrogen sulfide (H_2S) is harmful to SOFC anode

Therefore, it is imperative that a sulfur-tolerant anode be developed

Introduction

Typical SOFCs are made up of

- Electrolyte – Yttria-Stabilized Zirconia (YSZ)
- Anode – Nickel Oxide + Yttria-Stabilized Zirconia (Ni-YSZ)

Background

Experimental research for the design of SOFC anodes -

- Mainly, trial and error methods
- Anode degradation mechanism is unclear
- Molecular modeling has not been utilized

Overall Objectives

- Our overall objective is to use a systematic approach that combines molecular modeling of the materials with experimentation to design a sulfur tolerant anode that is able to work with coal syngas
- Molecular modeling can provide an understanding of the performance of the material and minimize the costs of experiments

Specific Objectives

- Obtain a better understanding of anode behavior in the presence of coal syngas
- Characterize and optimize the performance of the anode
- Determine the interactions between H_2, H_2S and CO with Nickel Yttria Stabilized Zirconia (Ni-YSZ)
- Validate the theoretical models with experimental data

Molecular Modeling

This was carried out using two methods:

1. Quantum Chemistry
   - Structural Analysis
   - Software: Gaussian 03
2. Molecular Dynamics
   - Gas molecule and Anode surface interactions
   - Software: Cerius^2 (Version 4.8)

Quantum Chemistry

- Computes the energy of a particular molecular structure by using quantum laws
- Performs geometry optimization
- Computes vibration frequencies of molecules
- Electronic structure methods solve Schrödinger Equation:

$$H\psi = E\psi$$

Molecular Dynamics

- Simulates chemical structures numerically based on the fundamental laws of physics
- Computes the forces of interactions between different molecular structures
- Potential energy calculated by force field energy equations
- Kinetics energy calculated from Newton's second law

Results Quantum Chemistry

Quantum Chemistry

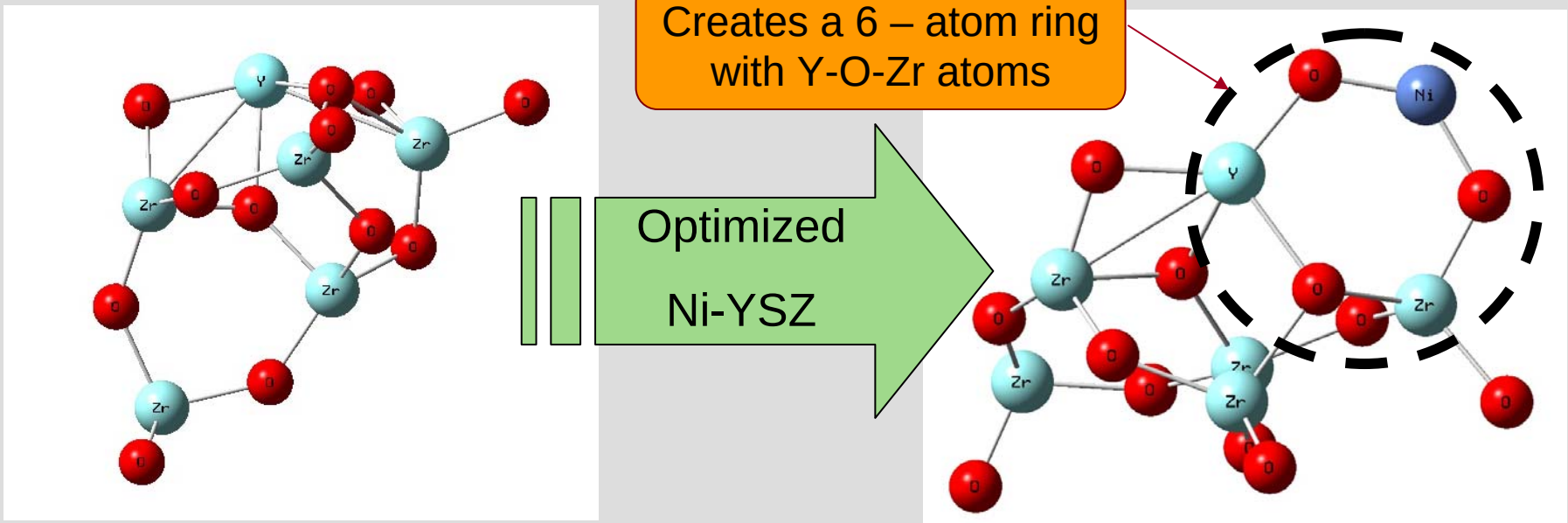
Structures of the molecules were optimized by Density Functional Methods (DFT)

- Method: B3PW91
- Basis set: LANL2DZ
- Phase: Gas phase

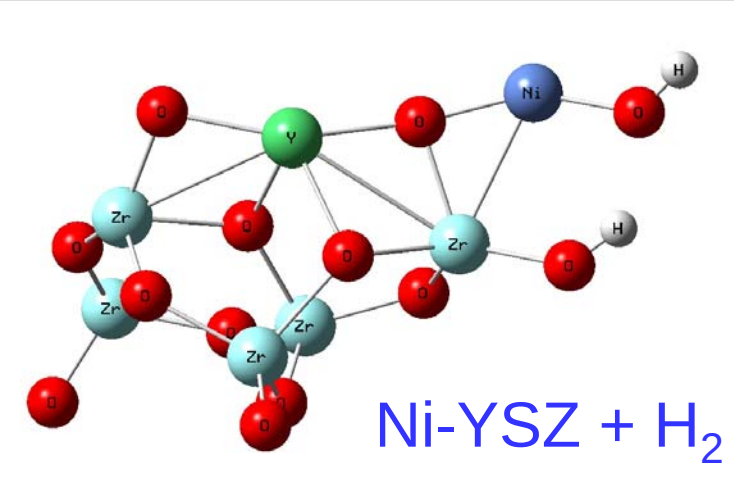
Optimization of Ni-YSZ Anode

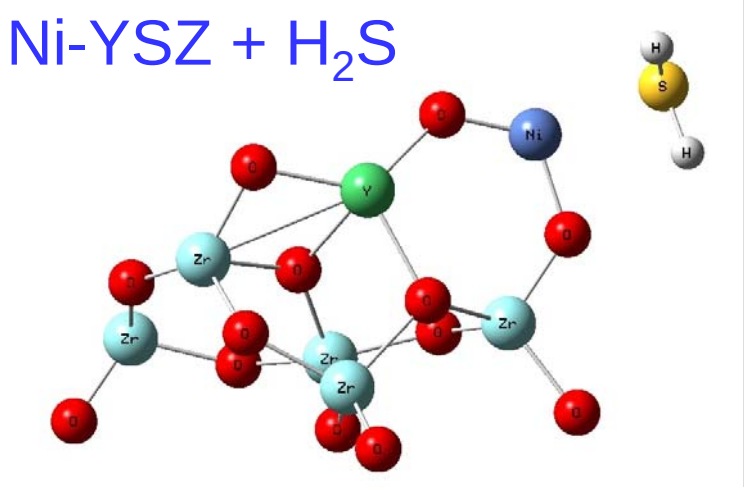
- YSZ structure was optimized
- NiO was added to YSZ unit and then this new structure was optimized

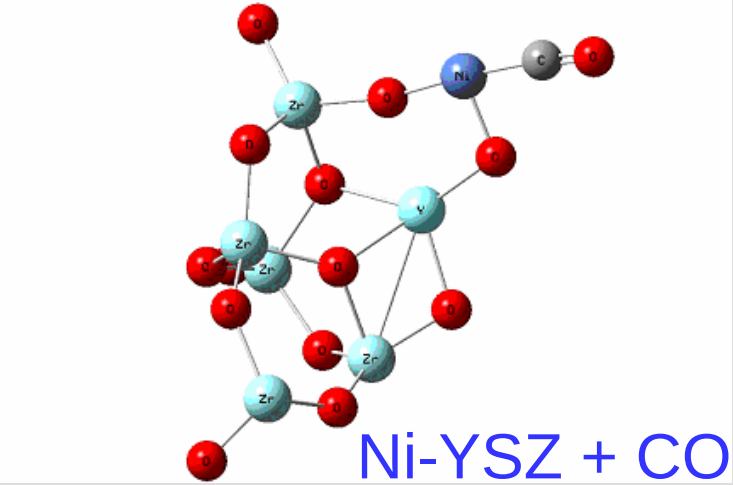
Binding Energy: -128 kcal/mol (strong bonding)



Interactions with Gas Phase Components







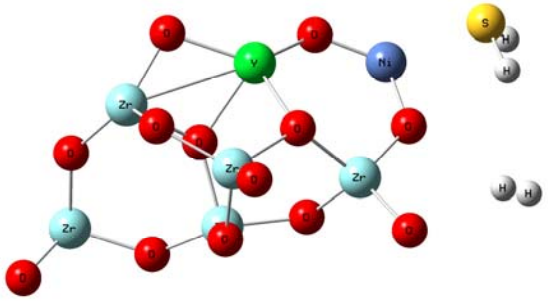
Binding Energies with Gas Phase Components

Binding Energies (Kcal/mol)

Ni-YSZ + H_2	-89.5
Ni-YSZ + H_2S	-24.2
Ni-YSZ + CO	-26.9

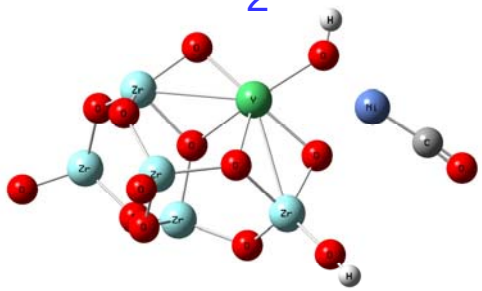
- Results suggest that anodic material reacts preferentially towards hydrogen
- Values of -24.2 and -26.9 kcal/mol also suggests that H_2S and CO oxidation respectively are thermodynamically favored
- CO oxidation is more favorable than H_2S oxidation

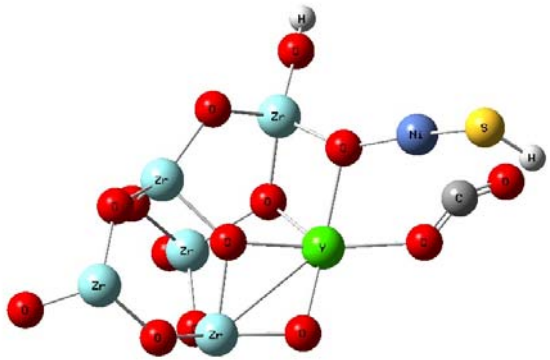
Interactions with Gas Phase Components: Combinations



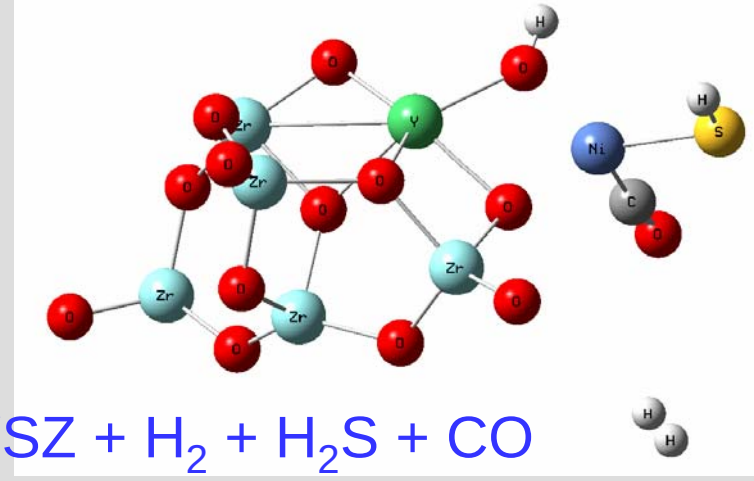
Ni-YSZ + H_2 + H_2S

Ni-YSZ + H_2 + CO





Ni-YSZ + H_2S + CO



Ni-YSZ + H_2 + H_2S + CO

Binding Energies with Gas Phase Components

Combinations: Binding Energies (Kcal/mol)

Ni-YSZ + H_2 + H_2S	**-23.2**	**Ni-YSZ + H_2**	**-89.5**
Ni-YSZ + H_2 + CO	-155.5		
Ni-YSZ + H_2S+ CO	-134.6		

– For the H_2/H_2S case, results suggest that H_2S presence slows reaction of anodic material towards hydrogen

Binding Energies with Gas Phase Components

Combinations: Binding Energies (Kcal/mol)

Ni-YSZ + H_2 + H_2S	-23.2	Ni-YSZ + H_2	-89.5
Ni-YSZ + H_2 + CO	**-155.5**	**Ni-YSZ + H_2S**	**-24.2**
Ni-YSZ + H_2S+ CO	**-134.6**	**Ni-YSZ + CO**	**-26.9**

- For the H_2/H_2S case, results suggest that H_2S presence slows reaction of anodic material towards hydrogen
- Large values of -155.5 and -134.6 kcal/mol for the two CO cases also suggests that CO presence affects the oxidation of H_2S and H_2
- As before, CO oxidation is more favorable than H_2S oxidation

Binding Energies with Gas Phase Components

Combinations: Binding Energies (Kcal/mol)

Ni-YSZ + H_2 + H_2S	-23.2	Ni-YSZ + H_2	-89.5
Ni-YSZ + H_2 + CO	-155.5	Ni-YSZ + H_2S	-24.2
Ni-YSZ + H_2S+ CO	-134.6	Ni-YSZ + CO	-26.9
Ni-YSZ + H_2+ H_2S+ CO	**-83.1**	**Reactivity of H_2 and H_2S towards anode surface is slowed**	

– CO affects the oxidation of both H_2 and H_2S in ternary system

Results Molecular Dynamics

Molecular Dynamics Calculations

Simulations performed using Cerius2 (v. 4.8)

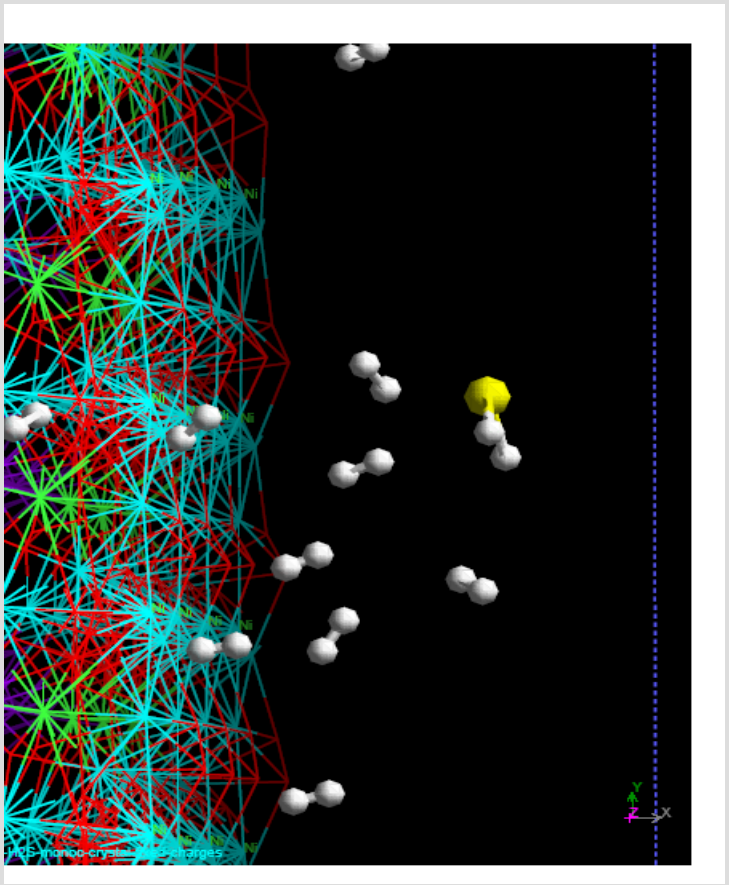
- NVT ensemble (constant number of particles, volume and Temperature)
- Each simulation began with 5000 fentoseconds of equilibration using a 0.5-fentoseconds/iteration time step and the velocity scaling temperature control method.
- 200 ps simulation (production) time; 0.5 fs iteration time
- Trajectory files were saved with a frequency of 5fs
- Unit cells of 8,000 A^3
- Periodic 3D boundary conditions

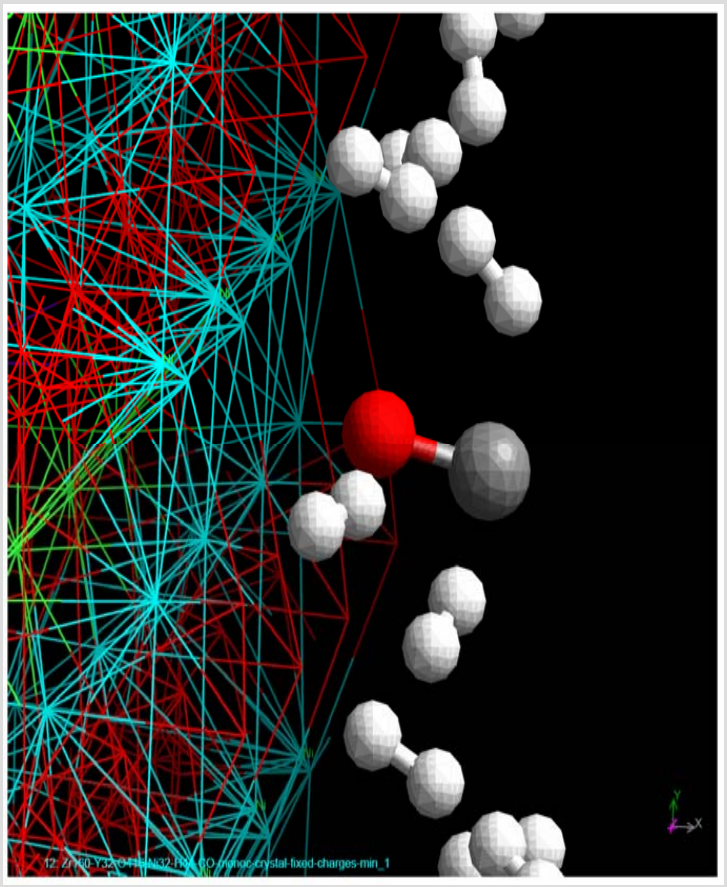
Molecular Dynamics Calculations

Simulations performed using Cerius2 (v. 4.8)

- Temperature: 850 °C
- Concentrations:
  - 2% H_2S balanced with H_2
  - 2% CO balanced with H_2
  - 2% CO, 2% H_2S balanced with H_2
  - 1% CO, 1% H_2S balanced with H_2

Snapshot of the MD Simulation at 850° C: Interactions of H_2/H_2S and H_2/CO with anode surface





H_2 molecules (gray) closer to Ni-YSZ than H_2S & CO

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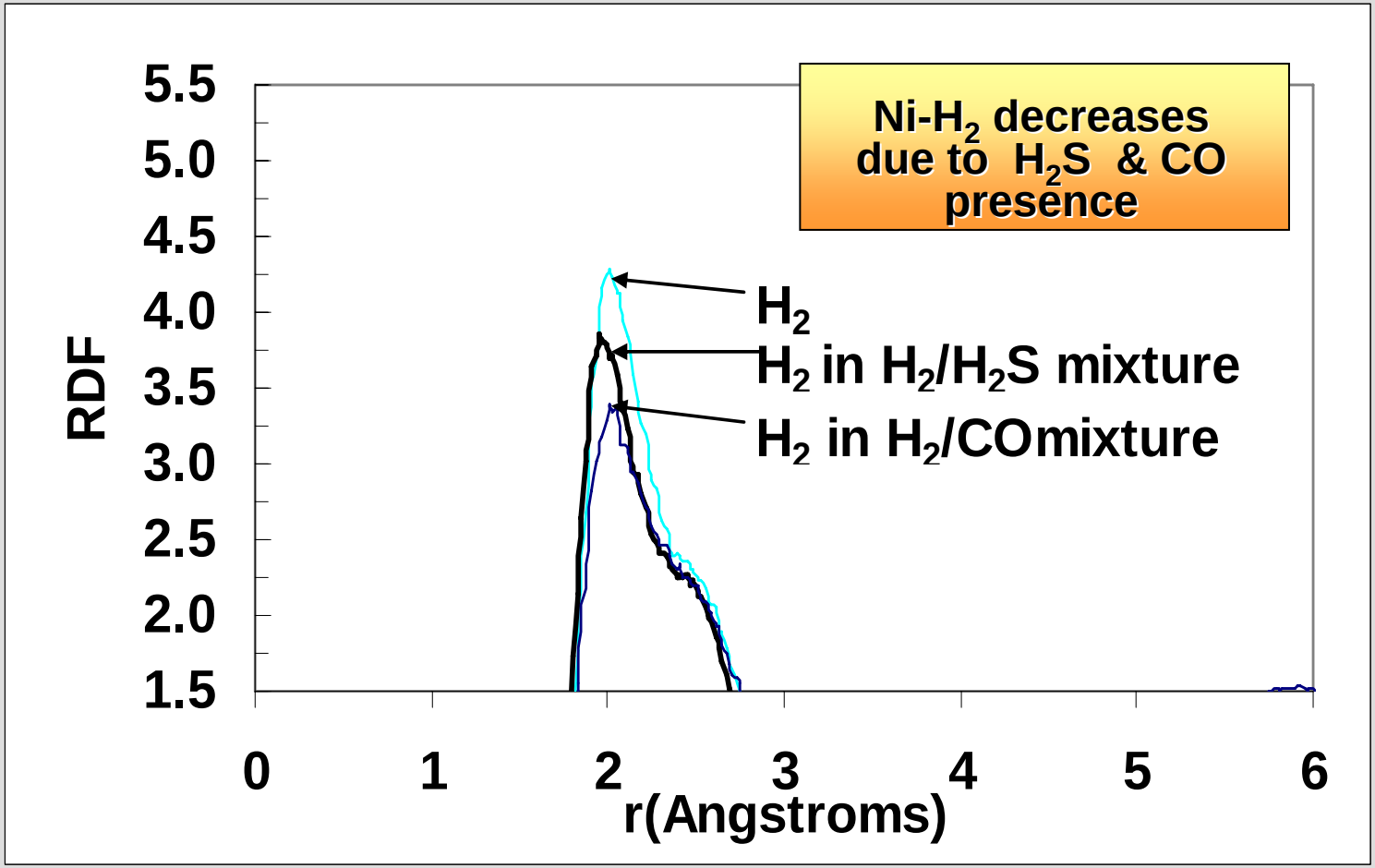
Effect on the RDF for Ni-H_2 with the presence of H_2S and CO (2%) at 850° C



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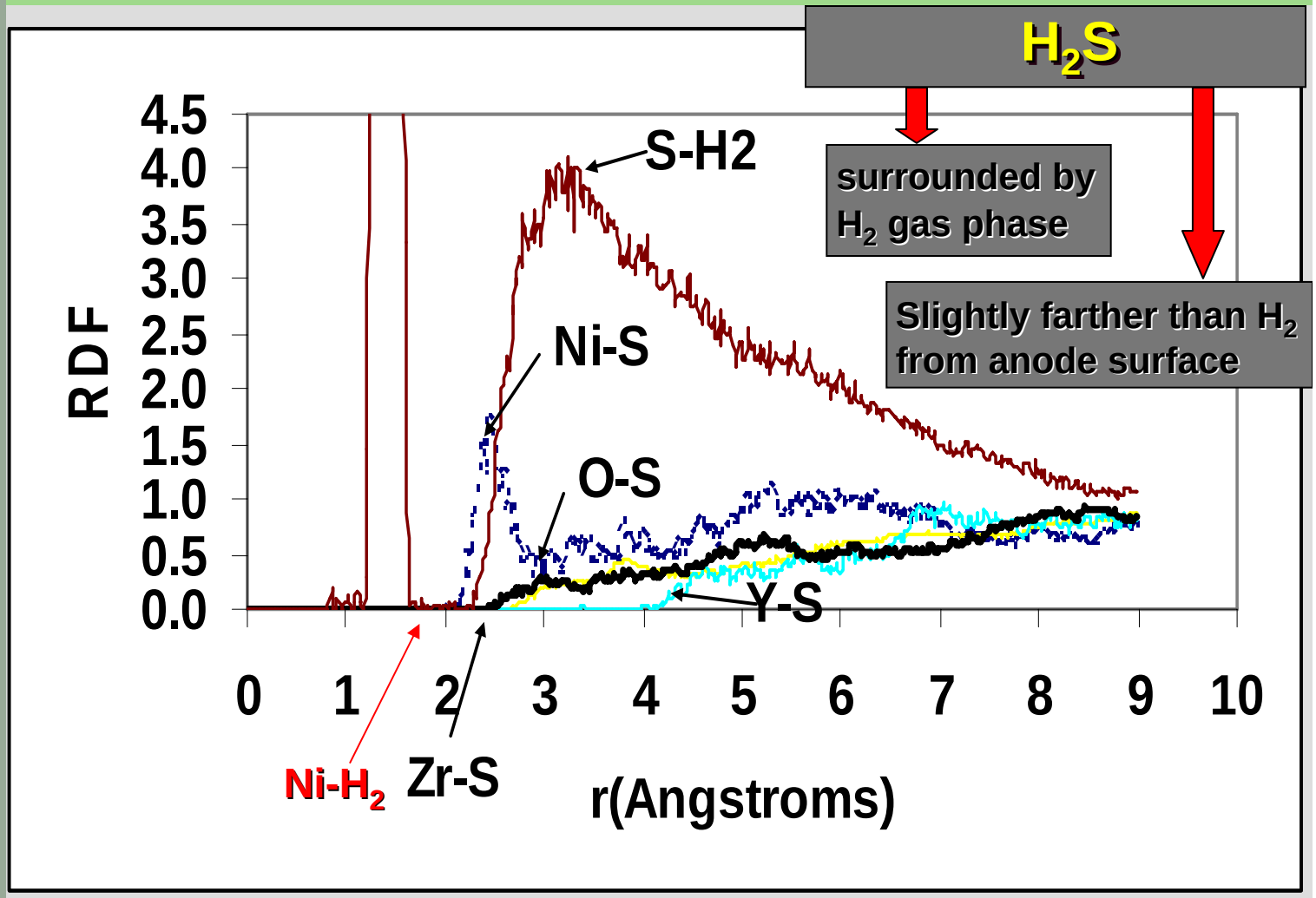
Interactions of the H_2S molecules (2%) with H_2 and anode at 850° C



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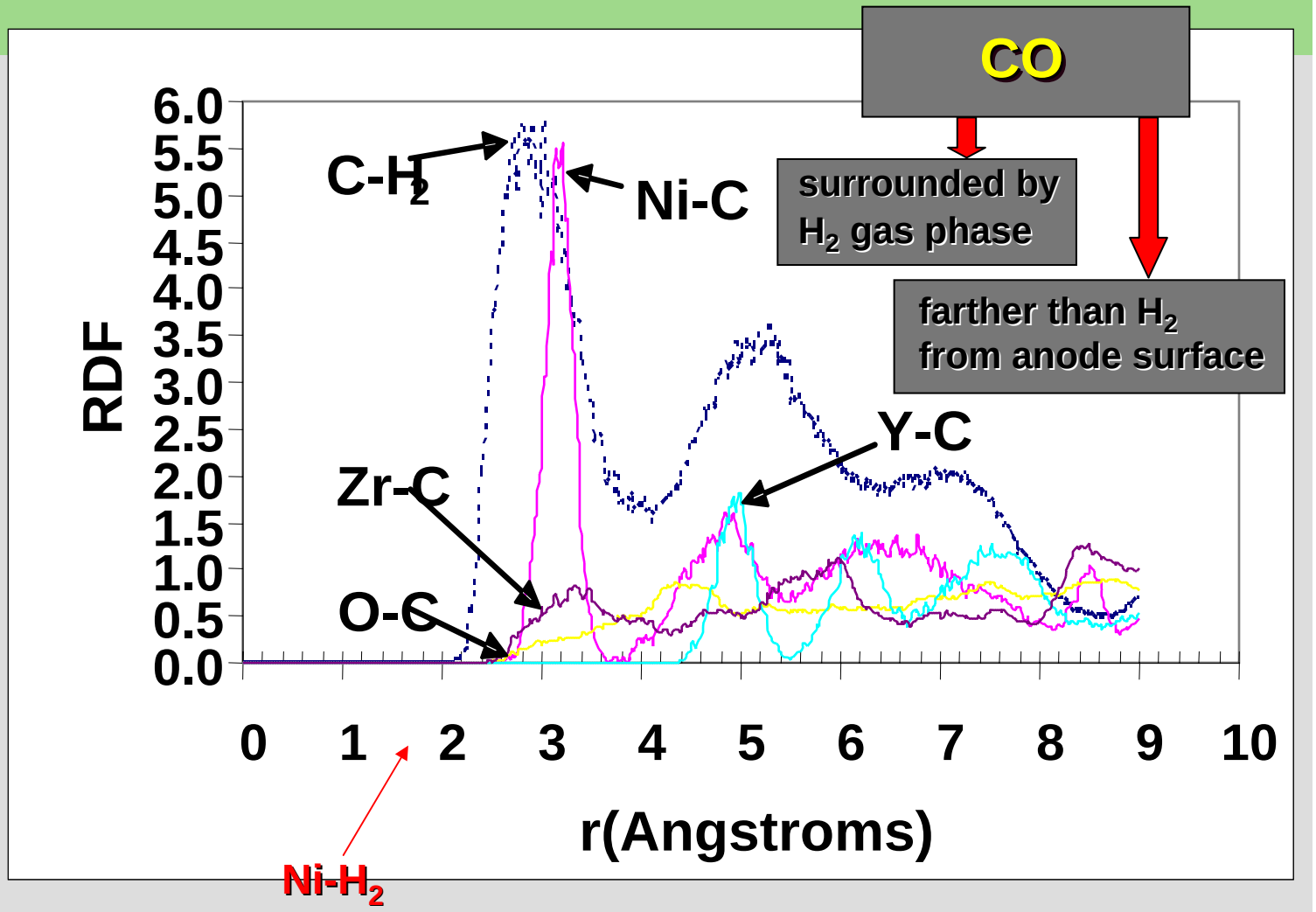
Interactions of the CO molecules (2%) with H_2 and anode at 850° C



Interaction H_2/H_2S stronger than H_2/CO

Diffusion Coefficients of the Gas Phase Mixtures: 850 ˚C

System	Diffusivity H_2 (cm^2/s)	Diffusivity H_2S (cm^2/s)	Diffusivity CO (cm^2/s)
H_2	$1.5x10^{-4}$		
H_2/H_2S (2%)	$1x10^{-4}$	$1x10^{-5}$	
H_2/CO (2%)	$5x10^{-6}$		$3x10^{-7}$
H_2/H_2S/CO (2%)	$9x10^{-6}$	$2x10^{-6}$	$6x10^{-9}$
H_2/H_2S/CO (1%)	$2x10^{-5}$	$8x10^{-9}$	$6x10^{-9}$

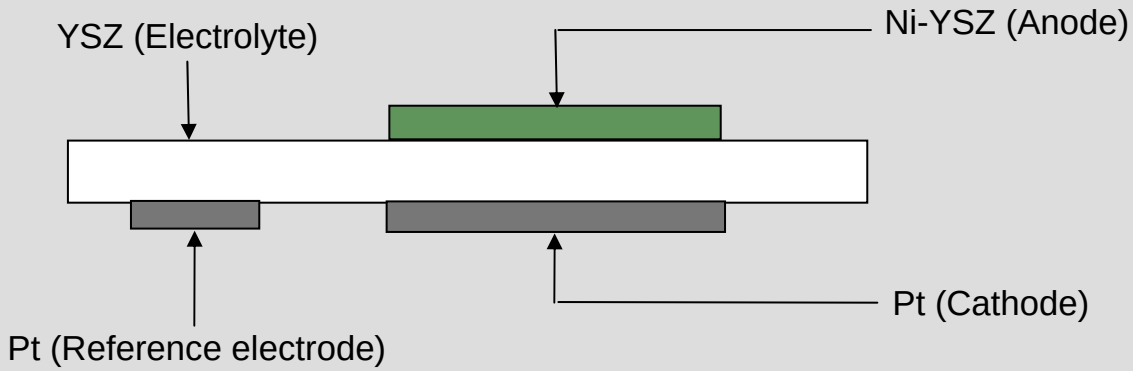
Diffusion Coefficients of the Gas Phase Mixtures

- Diffusion coefficient of H_2 in the presence of CO is smaller than in the presence of H_2S.
- Repulsion of H_2 with the H atoms in the H_2S molecule.
- Attraction of H_2 molecule to both atoms (C and O) in the CO molecule
- H_2 diffuses faster when H_2S and CO concentrations are lower; thus, CO and H_2S slows H_2 oxidation
- Interaction H_2/H_2S stronger than H_2/CO
- H_2S more surrounded by H_2 molecules at higher H_2 concentrations
- CO diffusion unchanged at higher H_2 concentrations

Experimental Setup

- A planar cell will be used to investigate the effect of the gases on the anode
- Quartz tubes to house the cell and withstand the high temperature
- Three furnaces will be used to maintain a uniform temperature of 850°C.

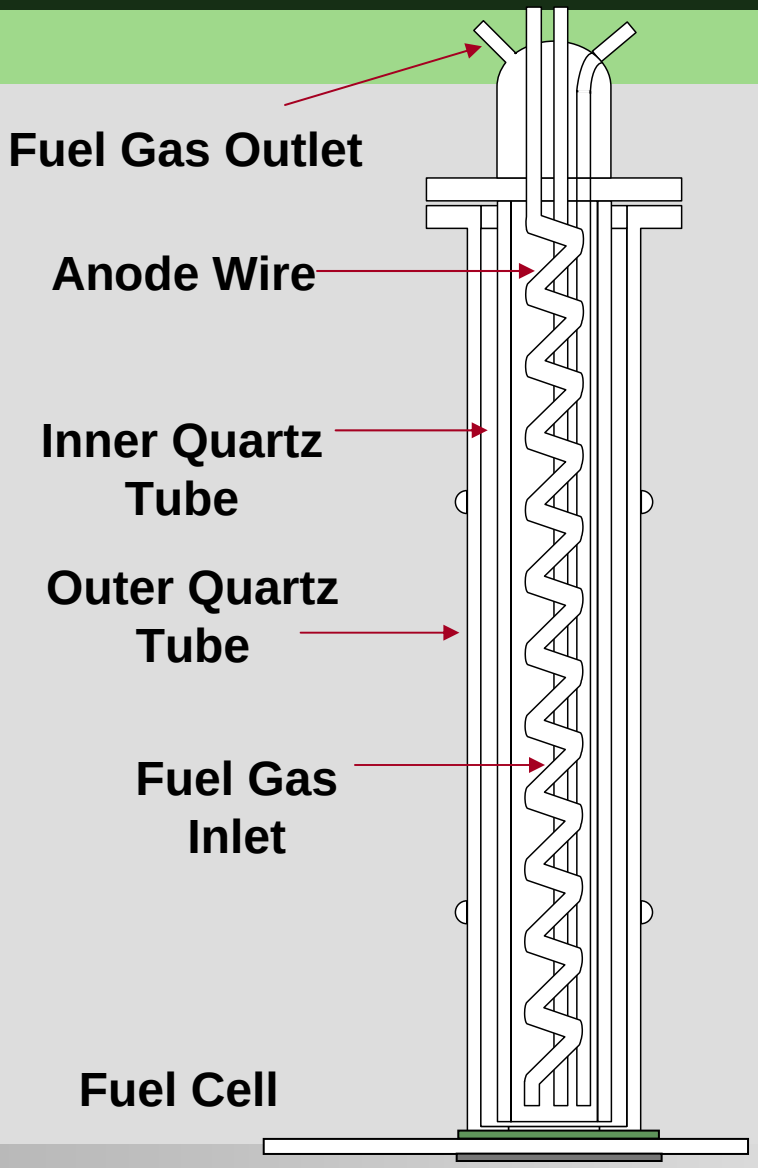
Cell

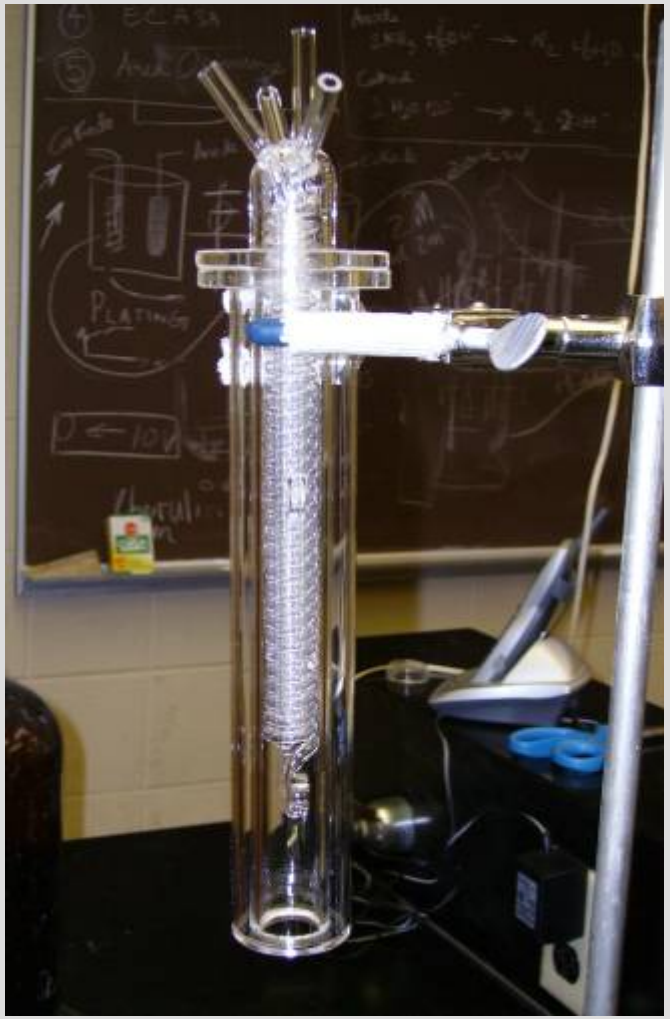


Cell Dimensions

	Electrolyte	Electrodes	
		Anode and Cathode	Reference
Diameter (mm)	30	10	2
Thickness (μm)	270	50	50

Quartz Tubing





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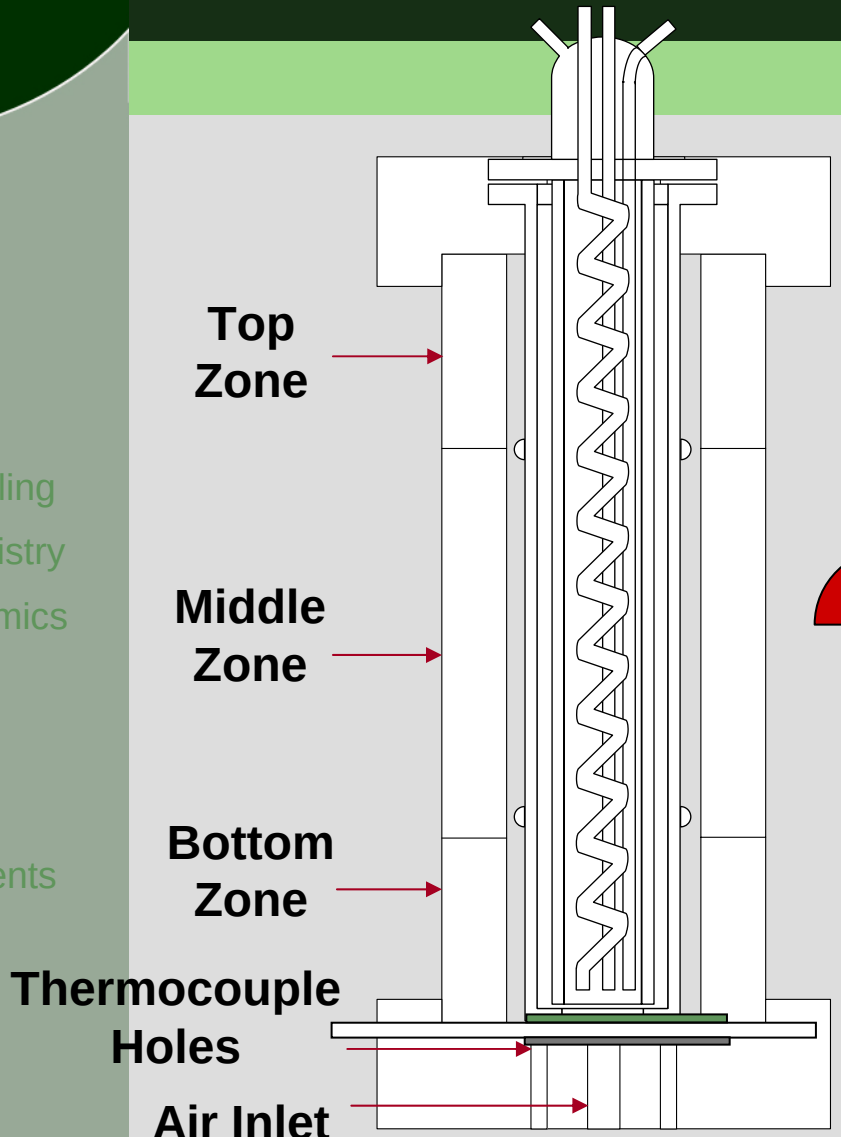
Furnace



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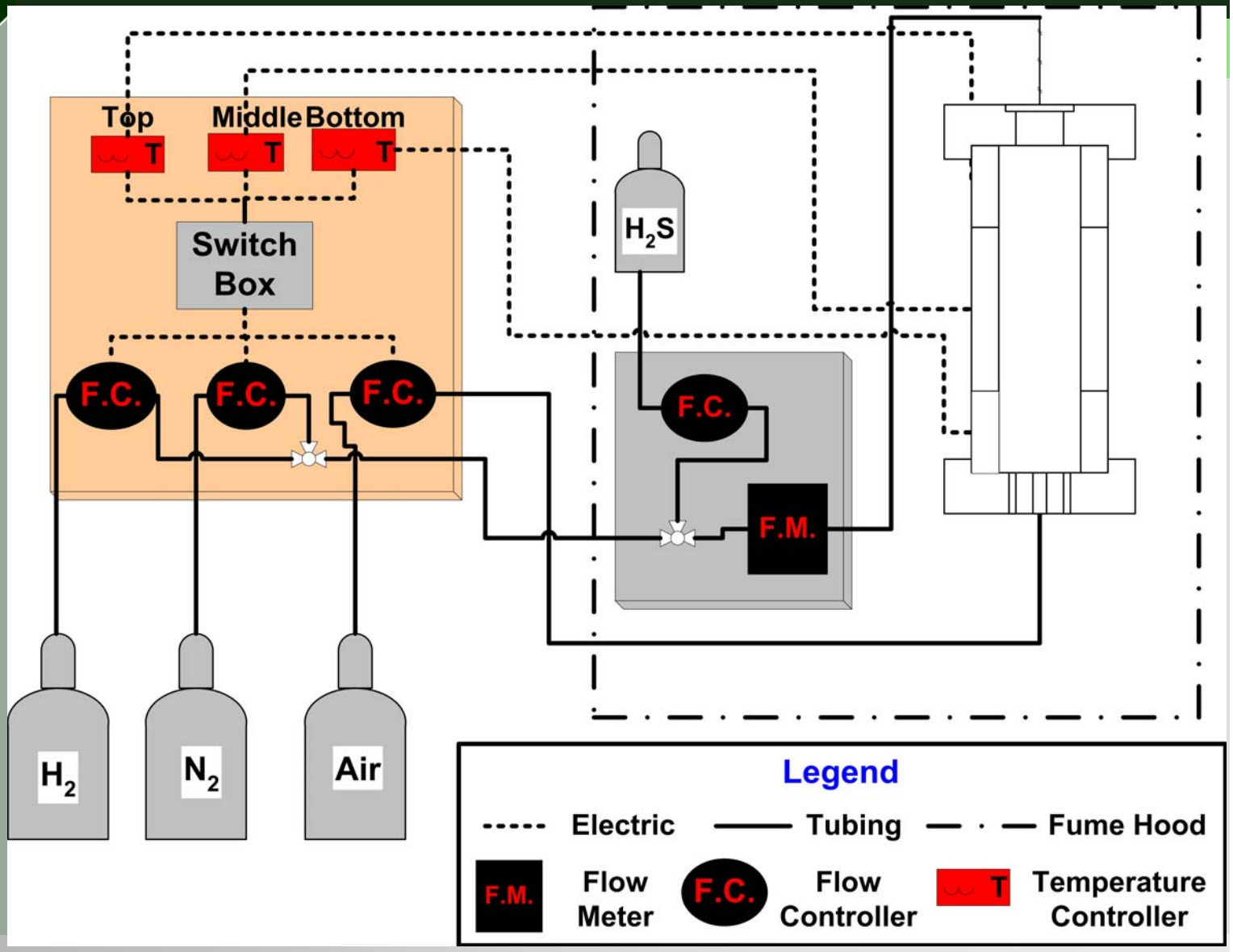
Process Schematic



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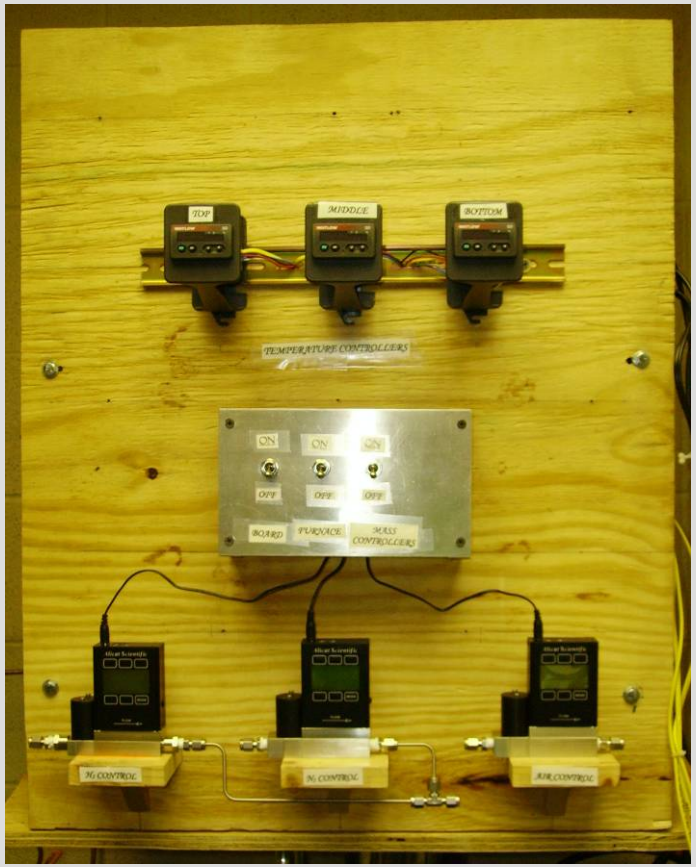
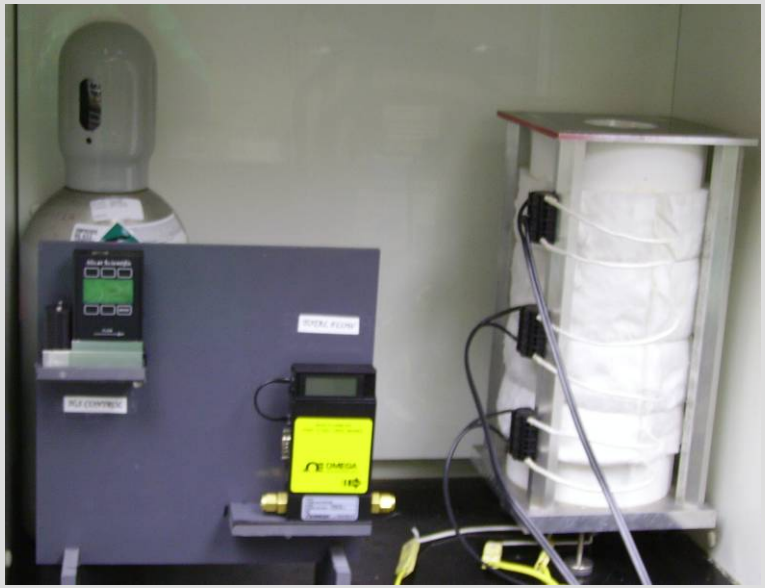
Partial Setup



Control Panel



Fume Hood

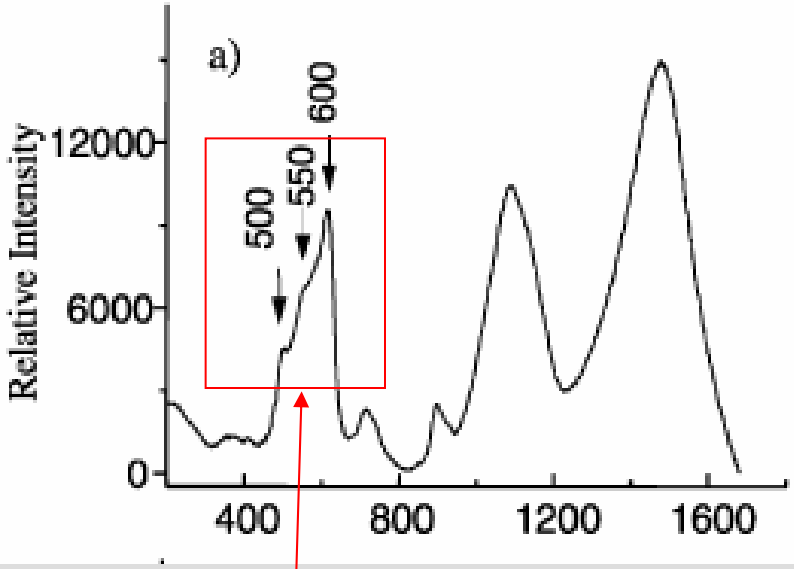
Update on Experimental Tasks

- ✓ Build setup
- ✓ Make cells:
  - ✓ Electrolyte is provided by Nextech.
  - ✓ Anode and cathode electrodes are made in the lab using screen printing
- Check sealing

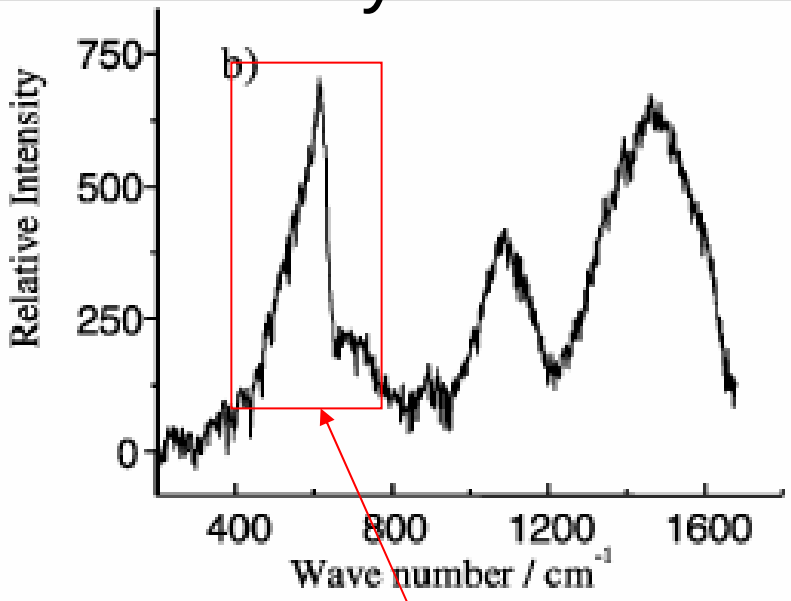
Validation of the Models

Raman Spectra of YSZ Deposited on Ni-YSZ at 400 ºC by Atomic Layer Deposition

Cermet



Layer on Ni-YSZ

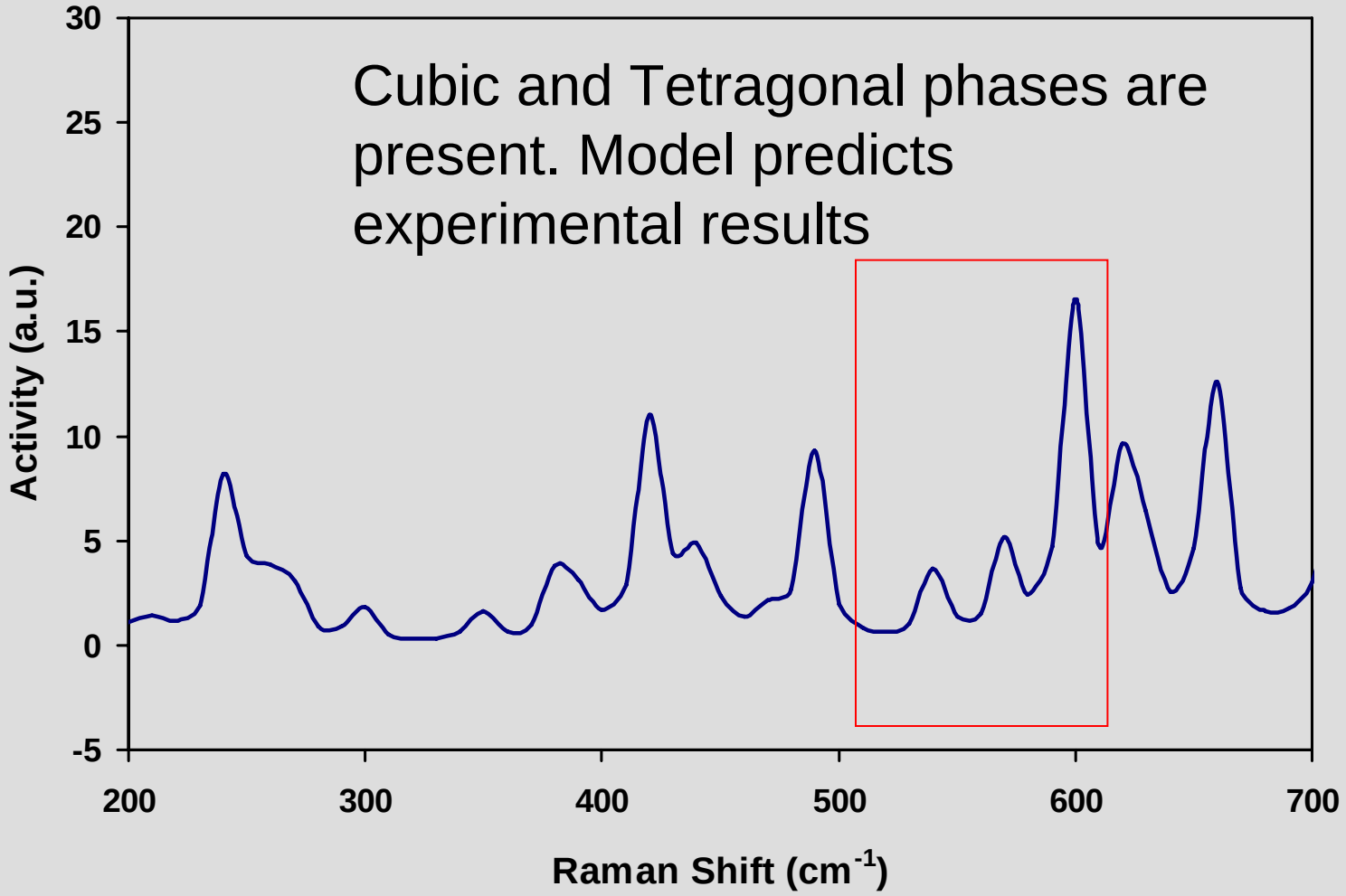


Characteristic of the cubic and tetragonal crystalline phases of the YSZ

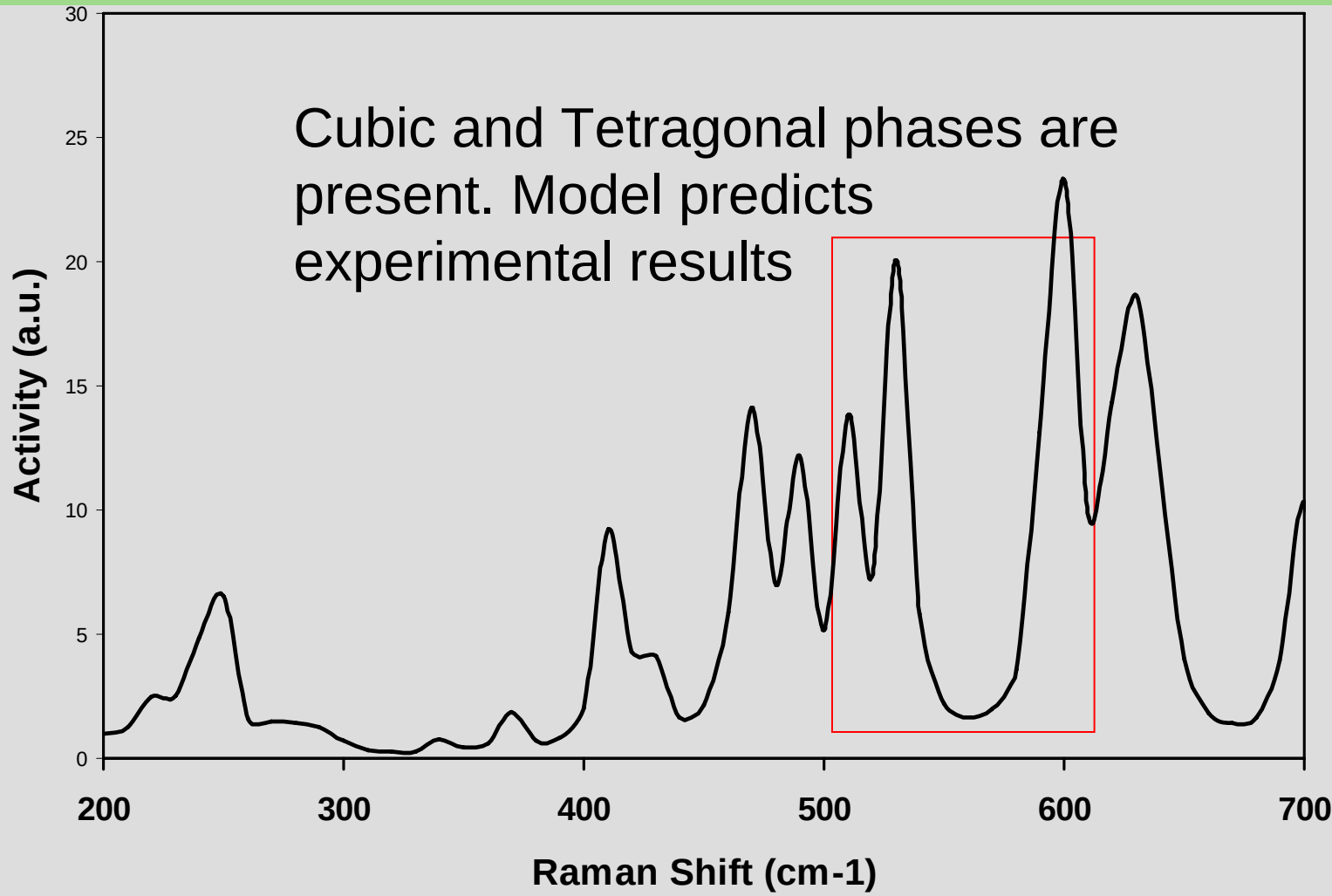
The cubic phase is dominant

Source: C. Bernay, A. Ringuede, P. Colomban, D. Lincot, and M. Casi. Journal of Physics and Chemistry of Solids, 64 (2003), 1761-1770

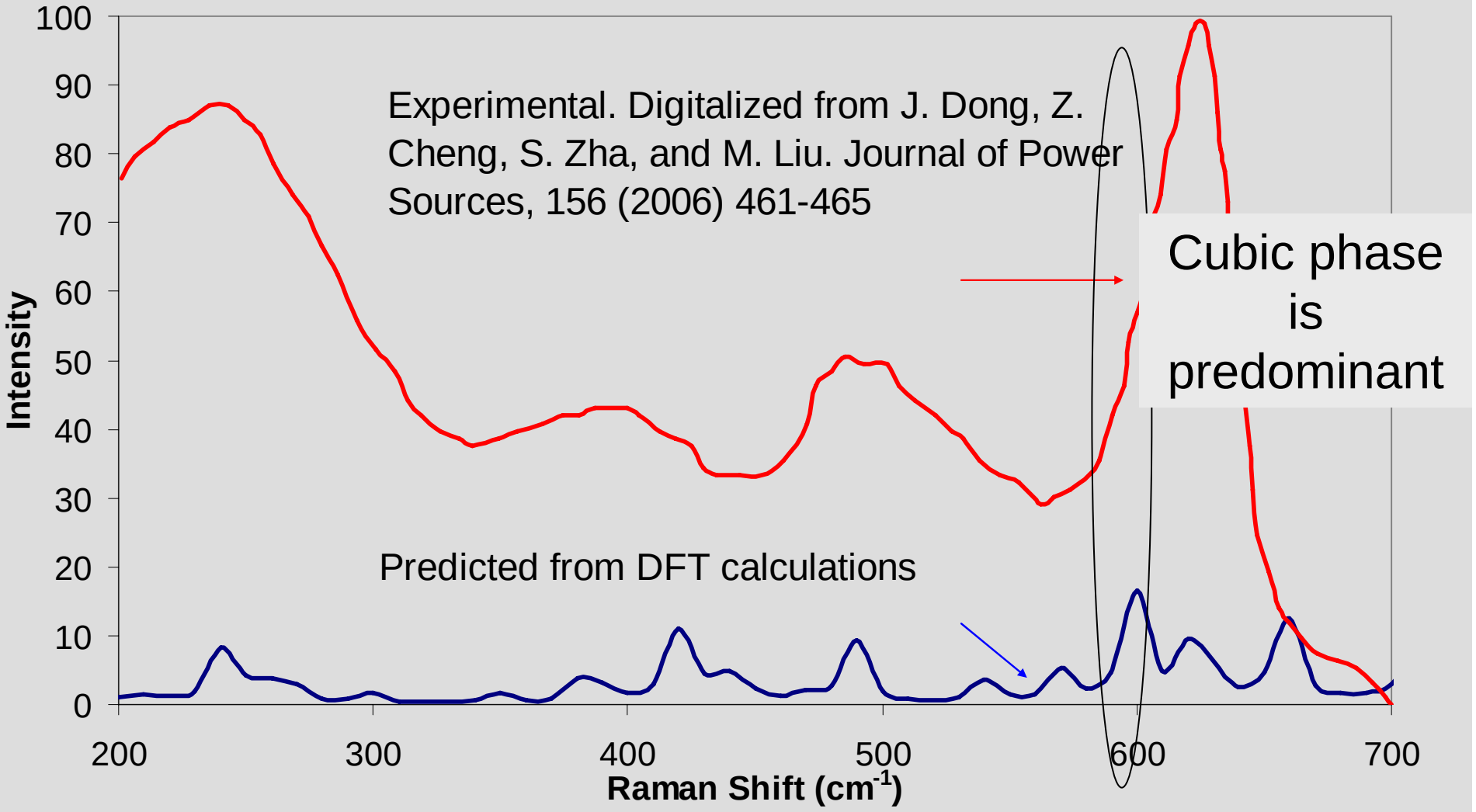
Raman Spectra of YSZ Predicted from DFT Calculations



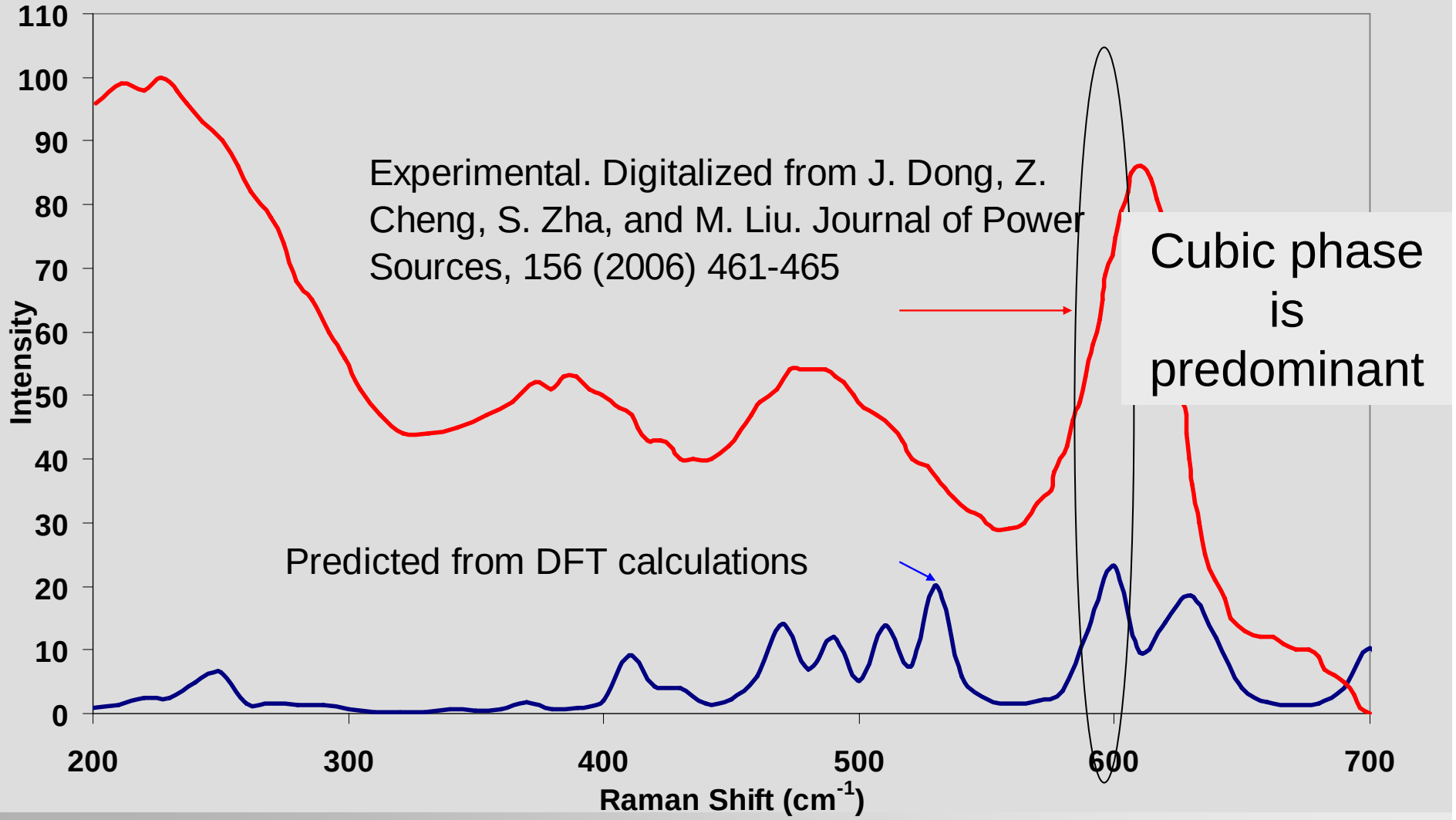
Raman Spectra of Ni-YSZ Predicted from DFT Calculations



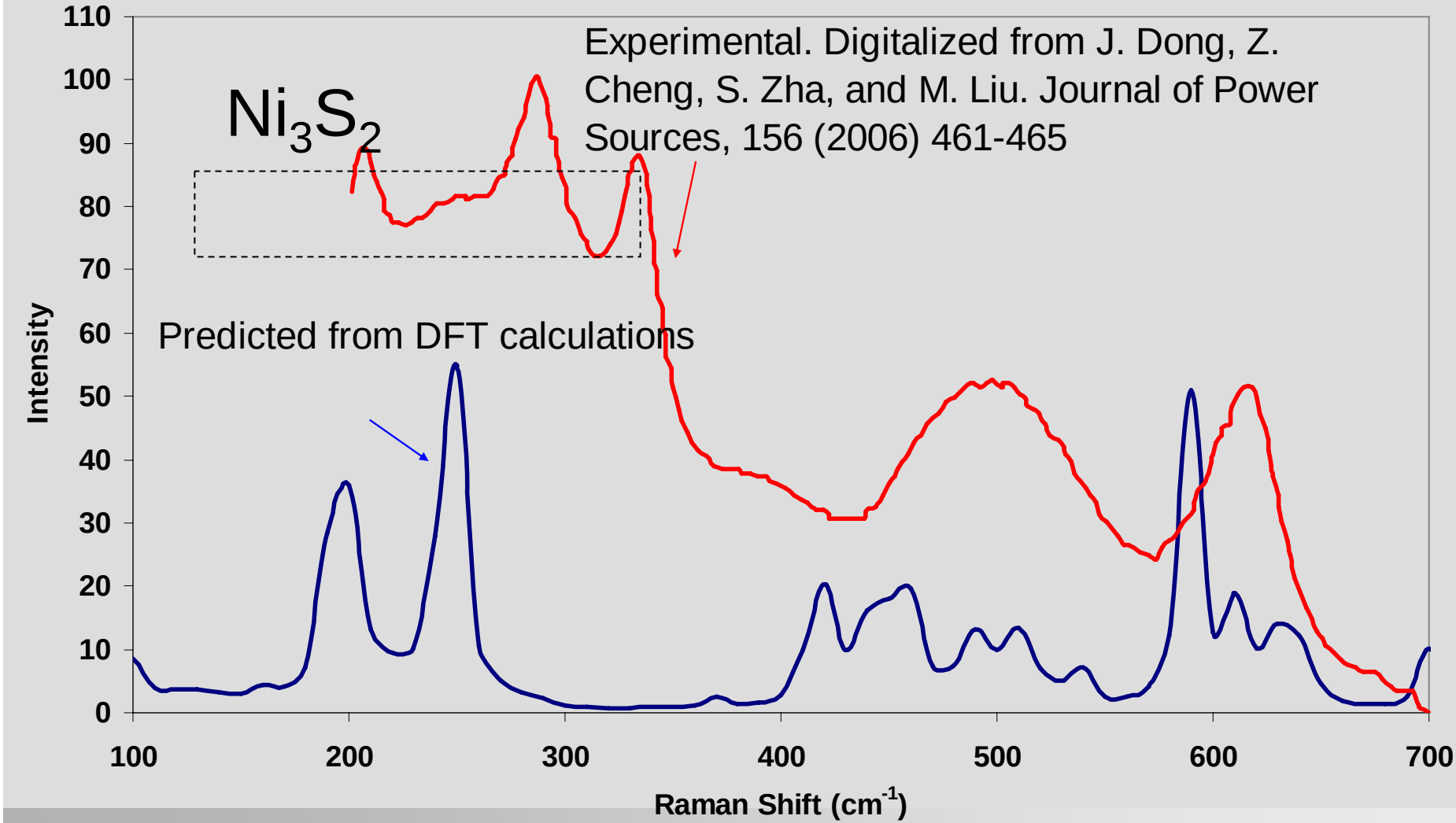
Raman Spectra of YSZ Comparison with Experimental Results



Raman Spectra of Ni-YSZ Comparison with Experimental Results



Raman Spectra of Ni-YSZ in the Presence of H_2 and H_2S. Experimental 10 ppm of H_2S, theoretical 50%



Summary

- Quantum Chemistry (QC) and Molecular Dynamics (MD) techniques combined provide useful insights of the interactions & mechanisms of H_2S/ H_2/CO reactivity towards the surface of the anode materials
- DFT calculations have predicted experimental results
- Basis for future anode & sulfur-tolerant materials development for SOFC

Future Work

- Validate the model with experimental data by
  - Comparison between theoretical and experimental Raman Spectra
  - Comparison between impedance spectroscopy and theoretical diffusion coefficients
- Identify materials that will improve the performance of the anode on the presence of coal syngas
- Build continuous model to predict the performance of the cell.

Acknowledgements

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- Electrochemical Engineering Research Lab (EERL) group members

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