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U.S. ARMY

DEVCOM GROUND VEHICLE SYSTEMS CENTER

U.S. ARMY DEVELOPMENT COMMAND GROUND VEHICLE SYSTEMS CENTER

Novel Catalyst Materials for Increasing Sulfur Tolerance in Solid Oxide Fuel Cells (Year 2 Final)

15 MAY 2023

Controlled by:	DEVCOM GVSC
Controlled by:	FPT Fuel's and Lubricant's Branch
CUI Category:	Controlled Technical Information
Distribution Statement:	A
POC:	Talia Marie Sebastian, PhD
POC:	Theodore Burye, PhD

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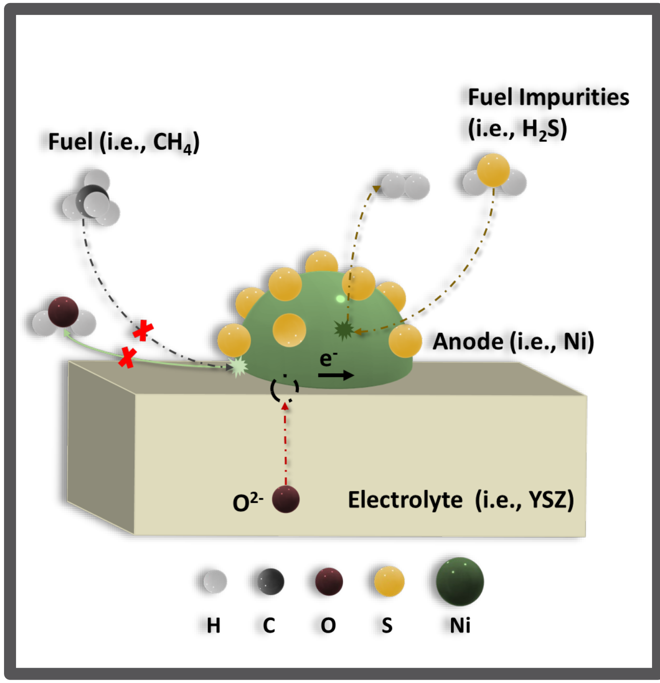
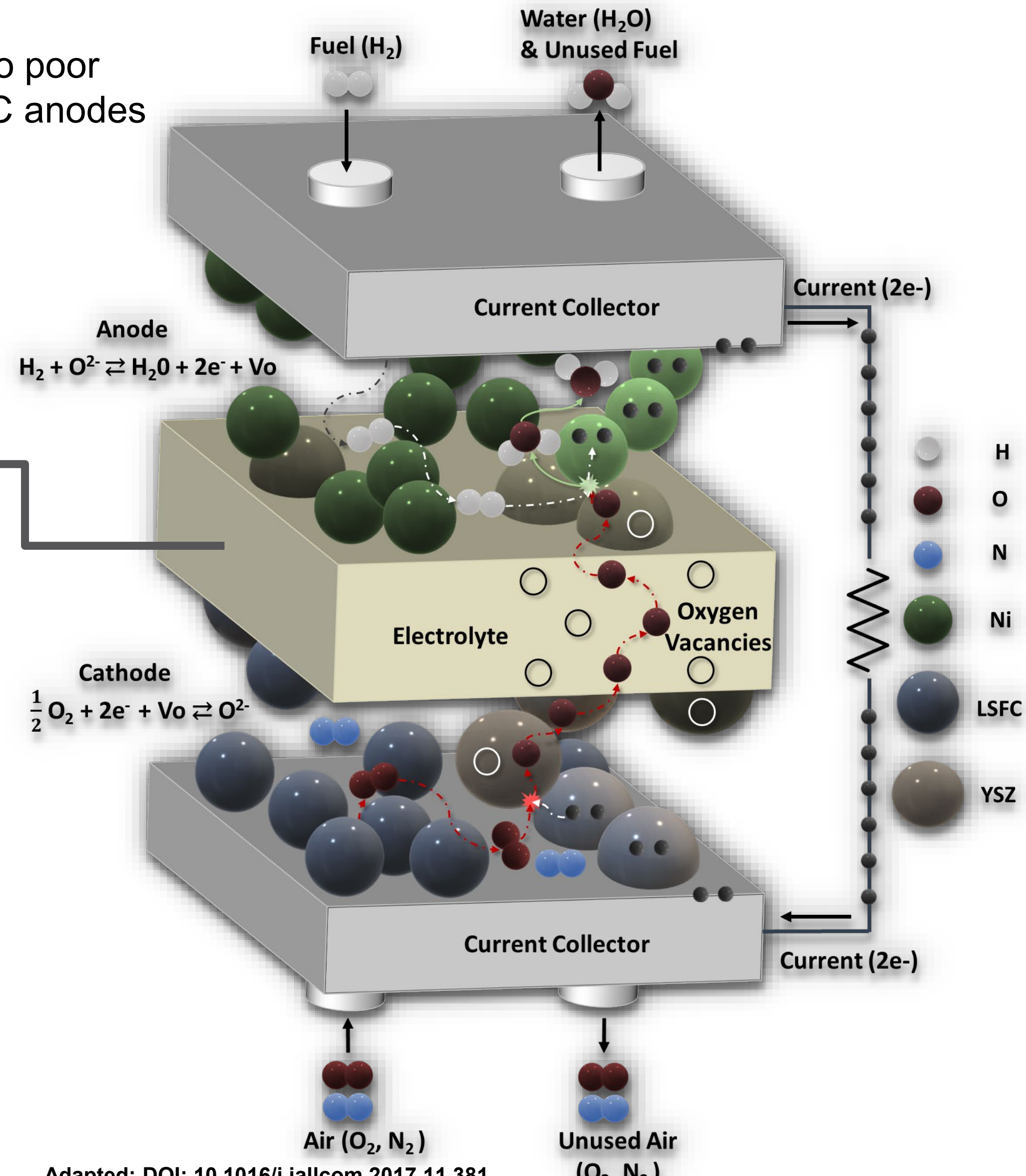
Introduction to Research Problem

Fuel Flexibility and Sulfur Poisoning

- Poisoning from sulfur impurities in fuel leads to poor performance and degradation of current SOFC anodes





Adapted: DOI: 10.1016/j.jallcom.2017.11.381

Mechanism of Chemisorption:

$$H_2S_{(g)} \leftrightarrow HS_{(ads)} + H_{(g/ads)} \leftrightarrow S_{(ads)} + H_{2(g)}$$

Mechanism of Sulfidation:

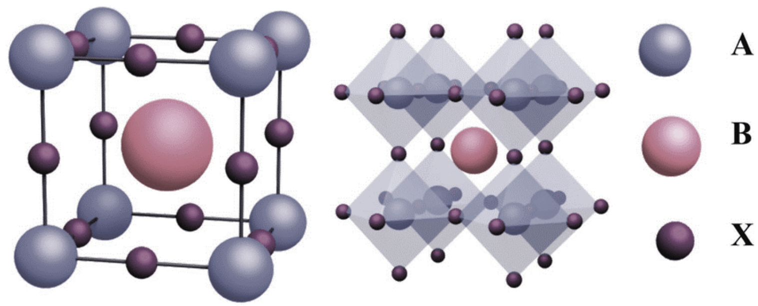
$$Ni_{(s)} + H_2S_{(g)} \leftrightarrow NiS_{(s)} + H_{2(g/ads)}$$

$$3Ni_{(s)} + xH_2S_{(g)} \leftrightarrow Ni_3S_{x(s)} + xH_{2(g)}$$

Experimental Approach to Research Problem

Materials-Based Mitigation Strategies

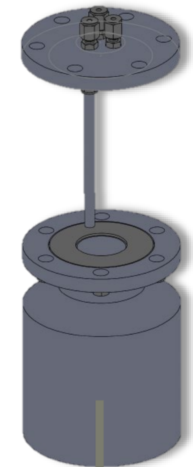
- Alloying nickel with noble or base metals
- Replacing nickel with base metals or nonmetal electronic conductors
- Replacing with mixed ionic-electronic conductors (i.e., Perovskite Oxides)



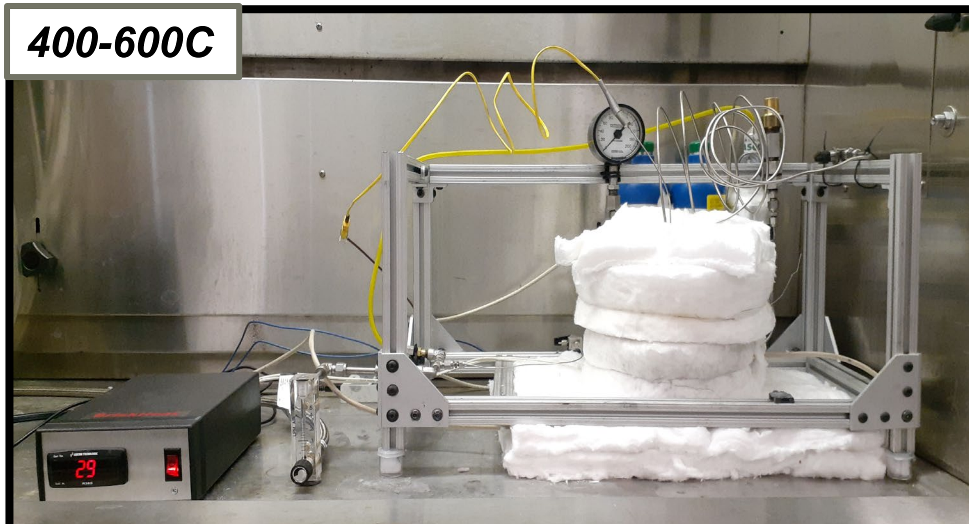
Adapted: DOI: 10.1002/advs.201700256

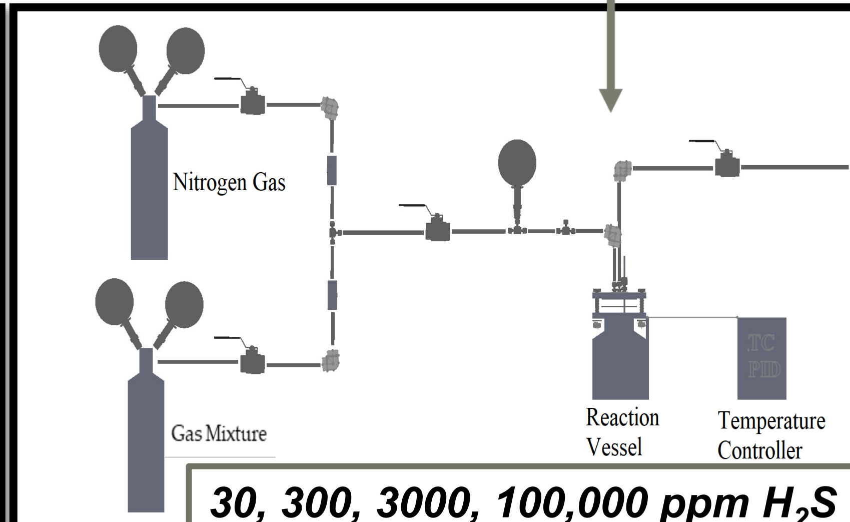
Lanthanum Strontium Vanadate
$La_{0.7}Sr_{0.3}VO_{3.85-\delta}$ (LSV)

~5g LSV



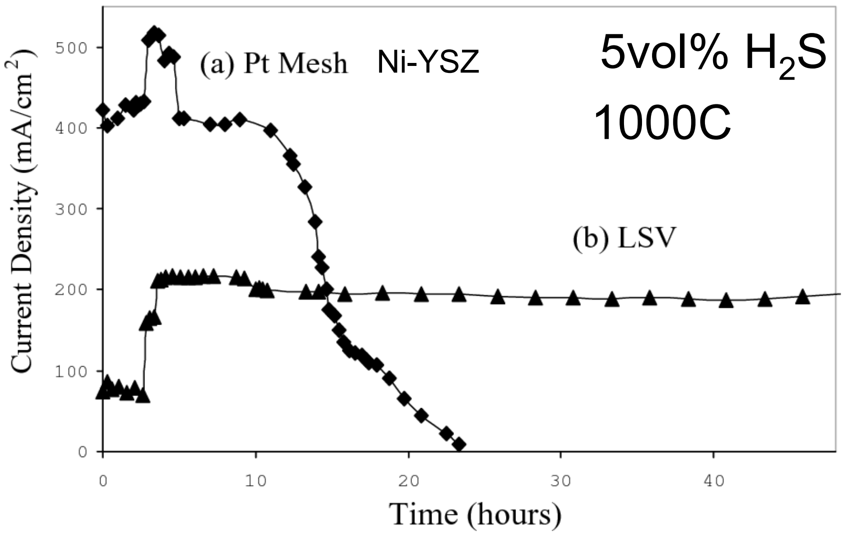
400-600C

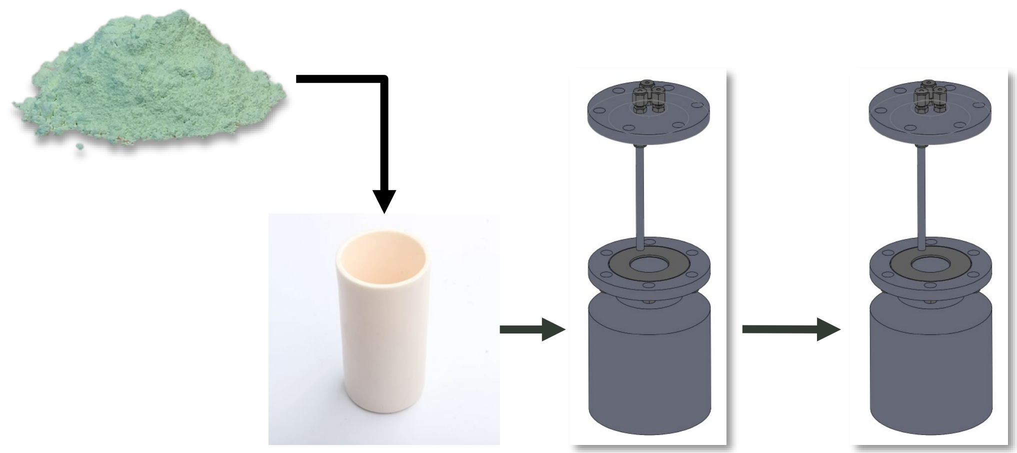


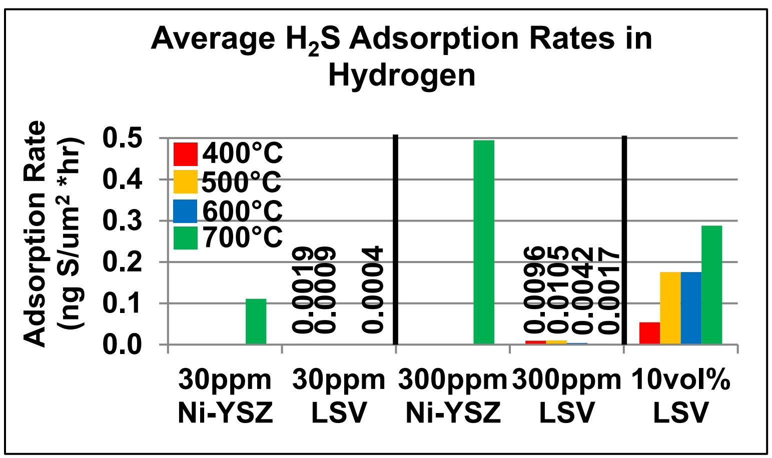


30, 300, 3000, 100,000 ppm H_2S

Motivation – LSV Anode Catalyst Sulfur Tolerance





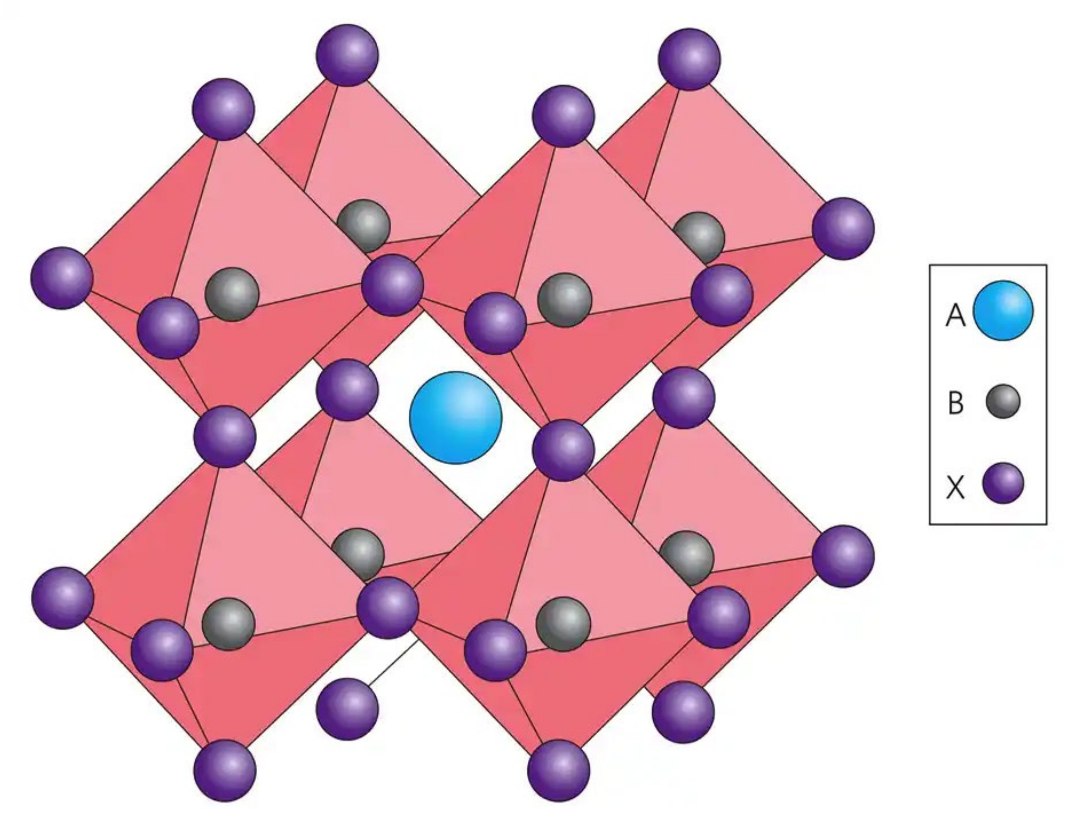


- This study experimentally tests LSV powder:
  - Heated under exposure to H_2S
  - Changed atmosphere to CH_4
  - Heated up to 100 hours
  - Sulfur amount characterized using EDS post-experimentation
  - LSV structure characterized using XRD post-experimentation
  - Modeling of H_2S and LSV interaction conducted in parallel
  - Compare adsorption response again previous study

Aguilar, J. Power Sources, 135, (2004), 17-24

Motivation– Perovskite and SOFC Materials

SOFC Catalysts - Perovskite (ABX_3)

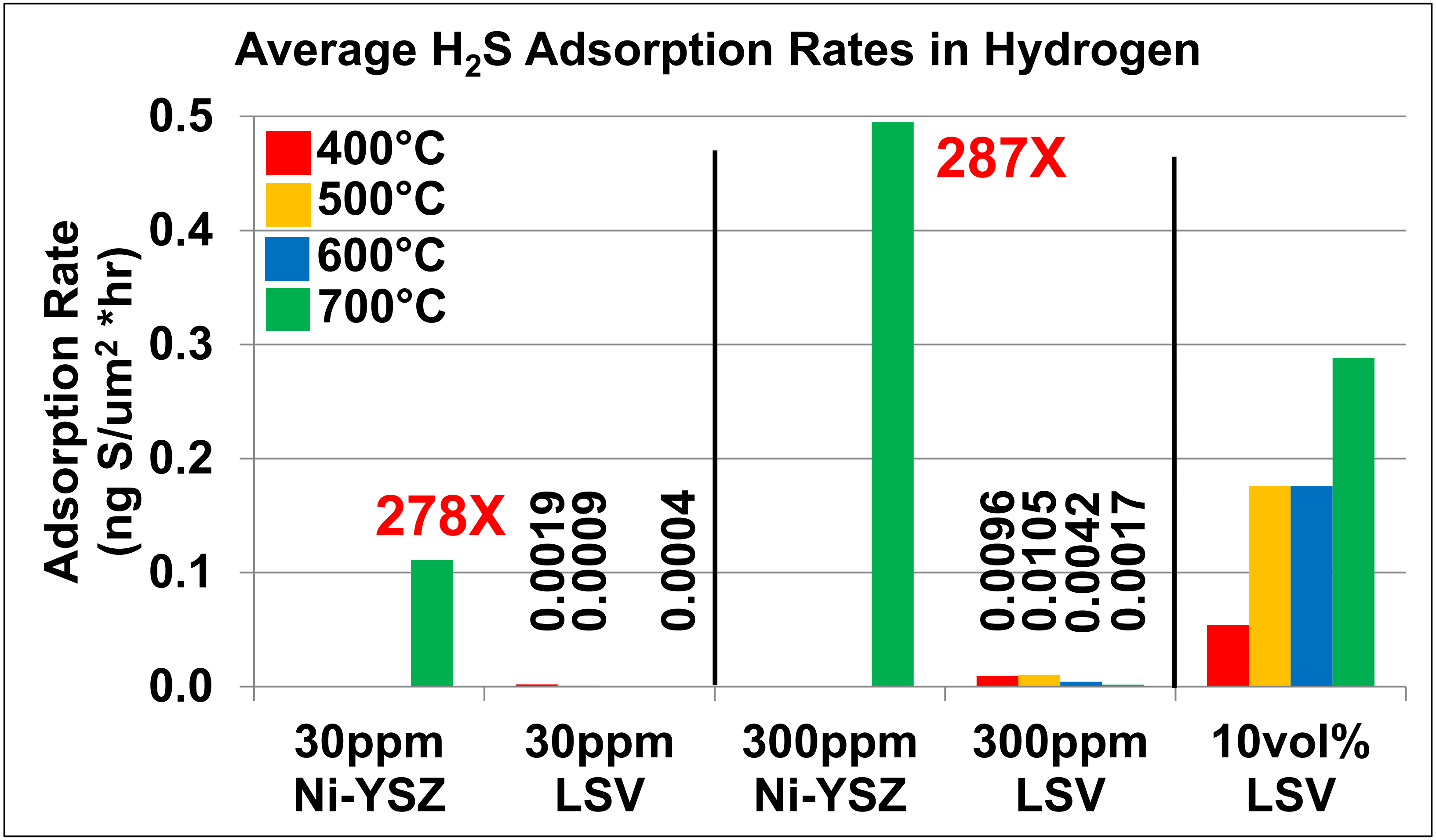


Common Catalyst Formulations

- $LaSrMnO_3$ (LSM)
- $LaSrFeO_3$ (LSF)
- $LaSrCoFeO_3$ (LSFC)
- $LaSrCoO_3$ (LSC)
- $BaSrCoFeO_3$ (BSFC)
- $SmSrCoO_3$ (SSC)
- $LaSrTiO_3$ (LST)
- $LaSrVO_3$ (LSV)

- Perovskites can be used as catalysts for anode and cathode electrodes
  - Potentially be a replacement for Ni-YSZ
- A-site and B-site can be doped with other elements for different effects
- No limit to the fun!!! Some exotic perovskite formulations have 6-7 elements

Motivation – Previous ILIR Year Experimental Testing



- Hydrogen atmosphere testing showed promising results compared to current anode material, Ni-YSZ, even at elevated sulfur concentrations.
- Hydrogen usually produces higher performance in fuel cells (reducing properties/no coking/etc)
  - Methane atmosphere tested to push LSV and see how it responds to light hydrocarbon

Characterization Techniques – SEM, EDS, XRD

SEM – Scanning Electron Microscopy

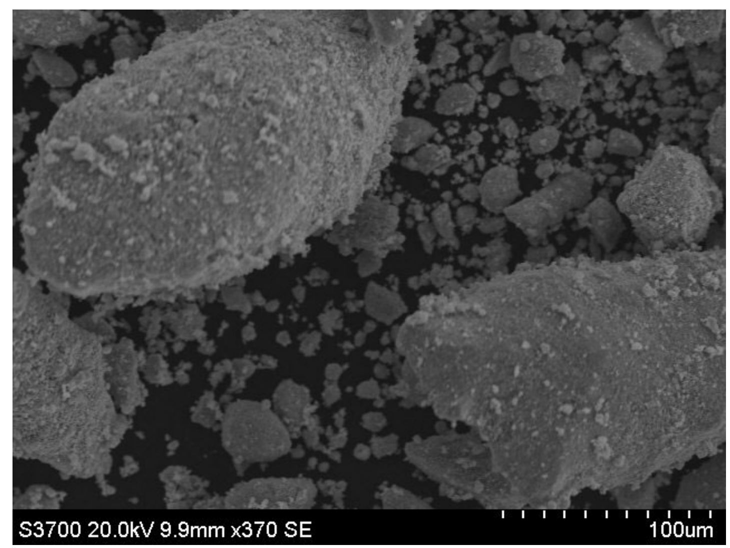
- Calculate average LSV surface area
  - Calculate average LSV H_2S adsorption rate

EDS – Energy Dispersive Spectroscopy

- Determine average LSV sulfur amount
  - Calculate average LSV H_2S adsorption rate

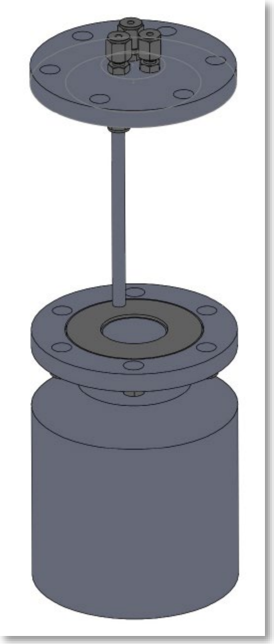
XRD – X-ray Diffraction

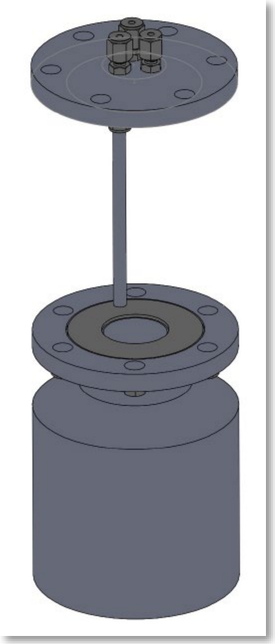
- Determine LSV structure
- Determine LSV oxygen content



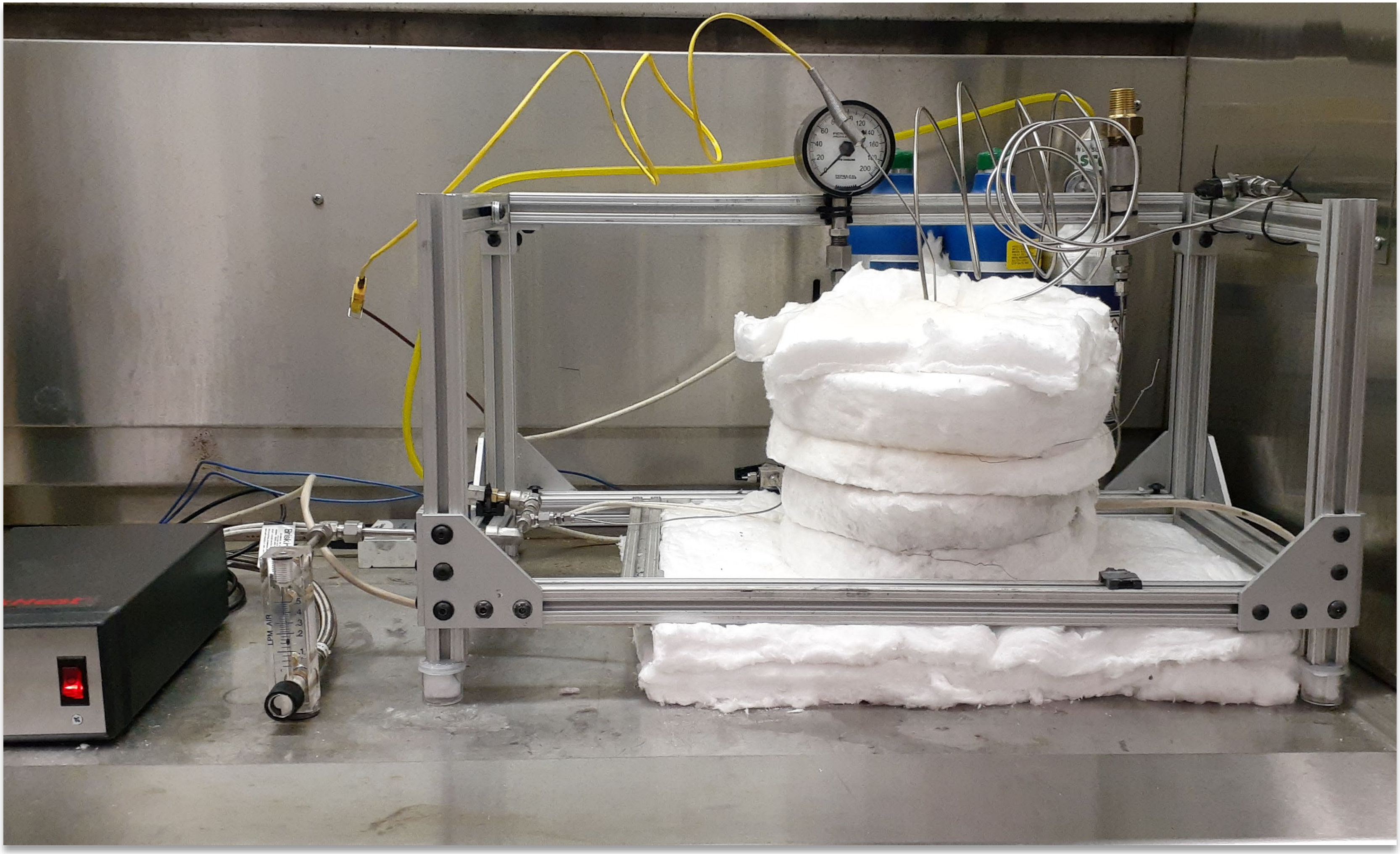
Experimental Setup – Sample Testing Preparation

LSV





Experimental Setup – Initial Design (Heat Tape)



Experimental Setup – Initial Design (Seal Failure)

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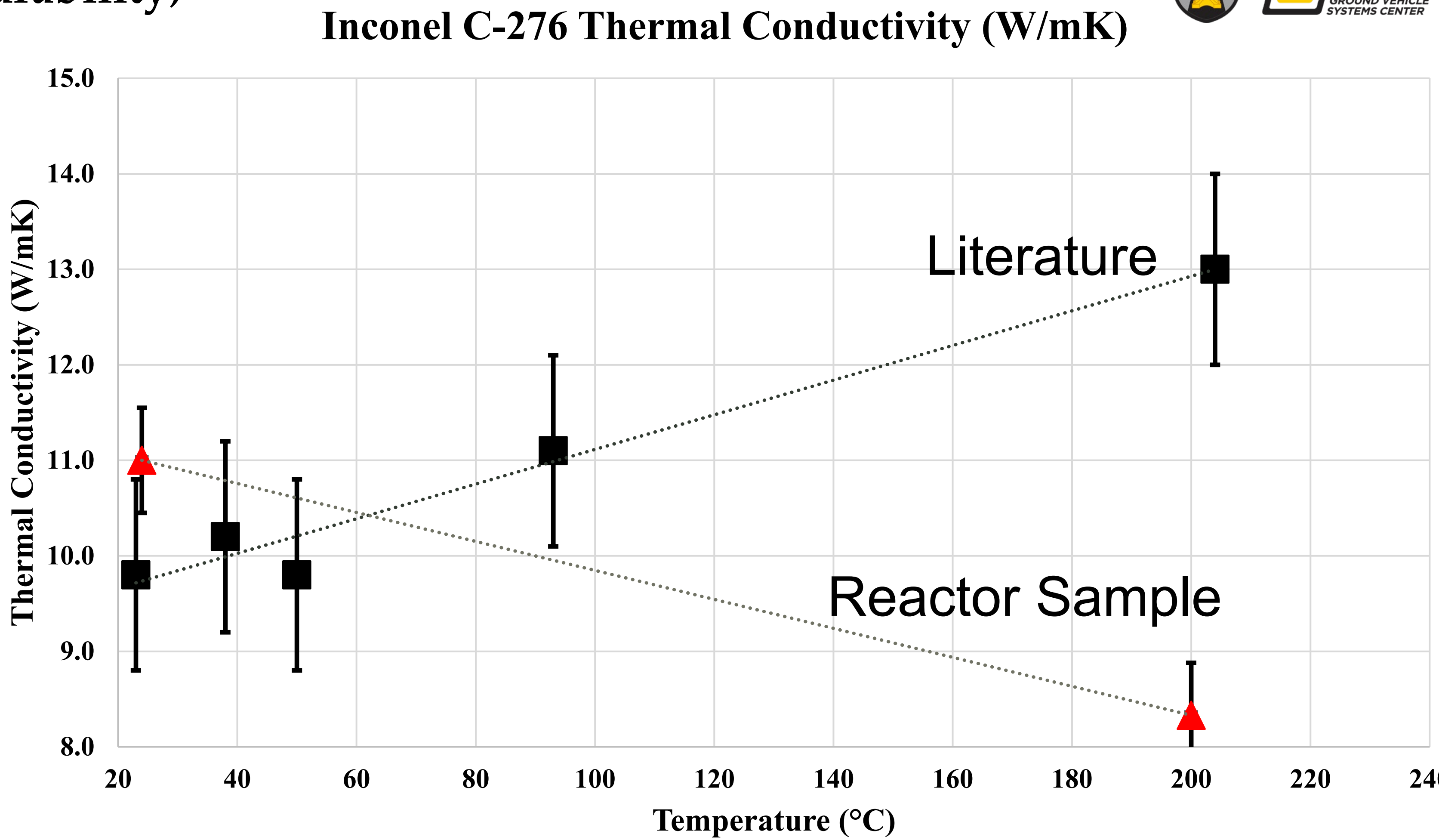
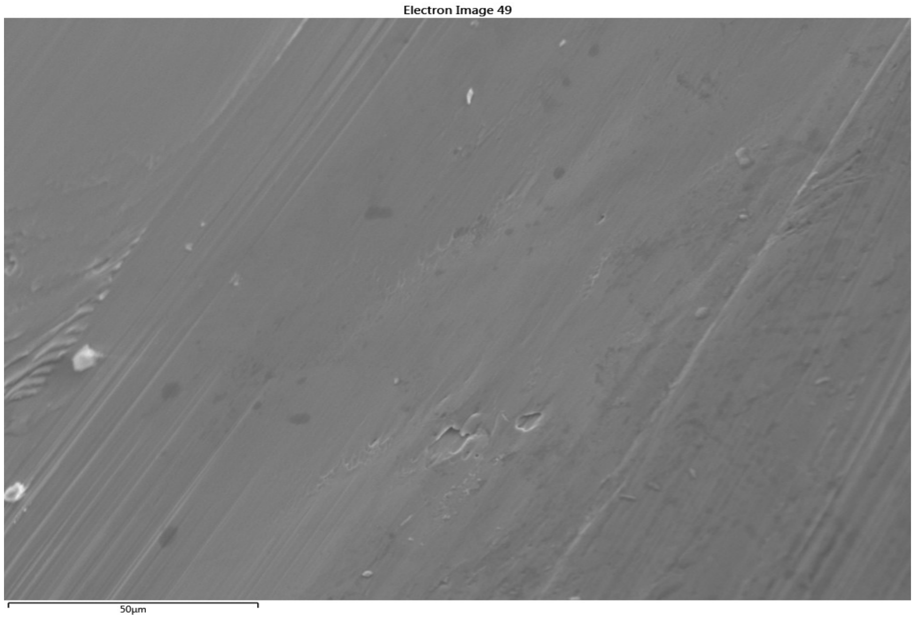
Experimental Setup – Initial Design (Heat Tape Durability)



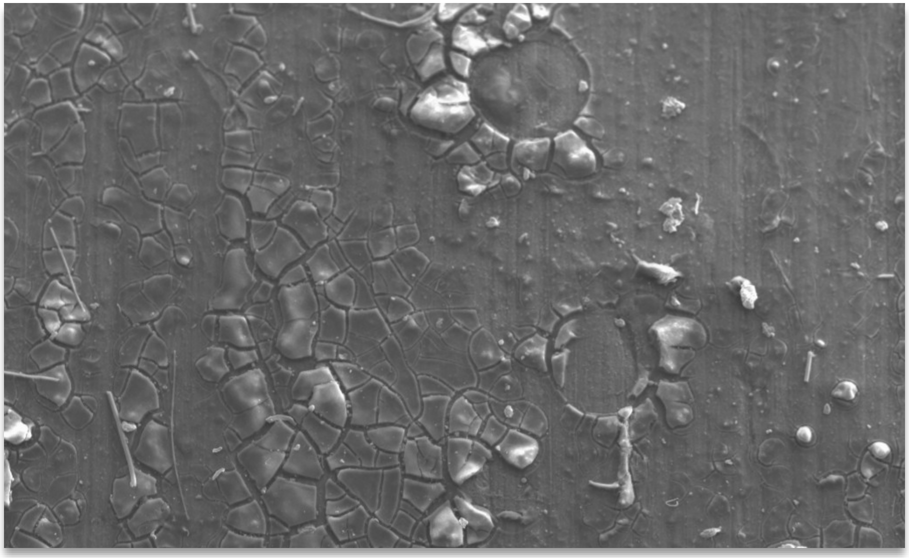
- Lower thermal conductivity thought to create “hot-spots” on heat-tape causing premature failure.

Experimental Setup – Initial Design (Heat Tape Durability)

Initial Reactor Body



Final Reactor Body



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Experimental Setup – Revised Design (Hot Air Blower)

Experimental Results – Operating Parameters

- Gas Pressure = 45 PSI
- Flow Rate = 300 mL/min

Design Type	H_2S Concentration (ppm)	Temperature (C)	Time (hours)
Heat Tape	30	400	25-100 hours
Heat Tape	30	500	25-100 hours
Heat Tape	30	600	25-100 hours
Heat Tape	30	700	25-100 hours
Air Blower	300	400	25-100 hours
Air Blower	300	500	25-100 hours
Air Blower	300	600	25-100 hours
Heat Tape	300	700	25-100 hours
Air Blower	3000	400	10-30 hours
Air Blower	3000	500	10-30 hours
Air Blower	3000	600	10-30 hours
Air Blower	3000	700	10-30 hours

Experimental Results – Adsorption Rate Calculation

$$R_{ads} = \frac{Mass_{sulf,norm}}{\mathrm{Time}_{duration}}$$

$$Mass_{sulf,norm} = \frac{Mass_{sulf}}{SA}$$

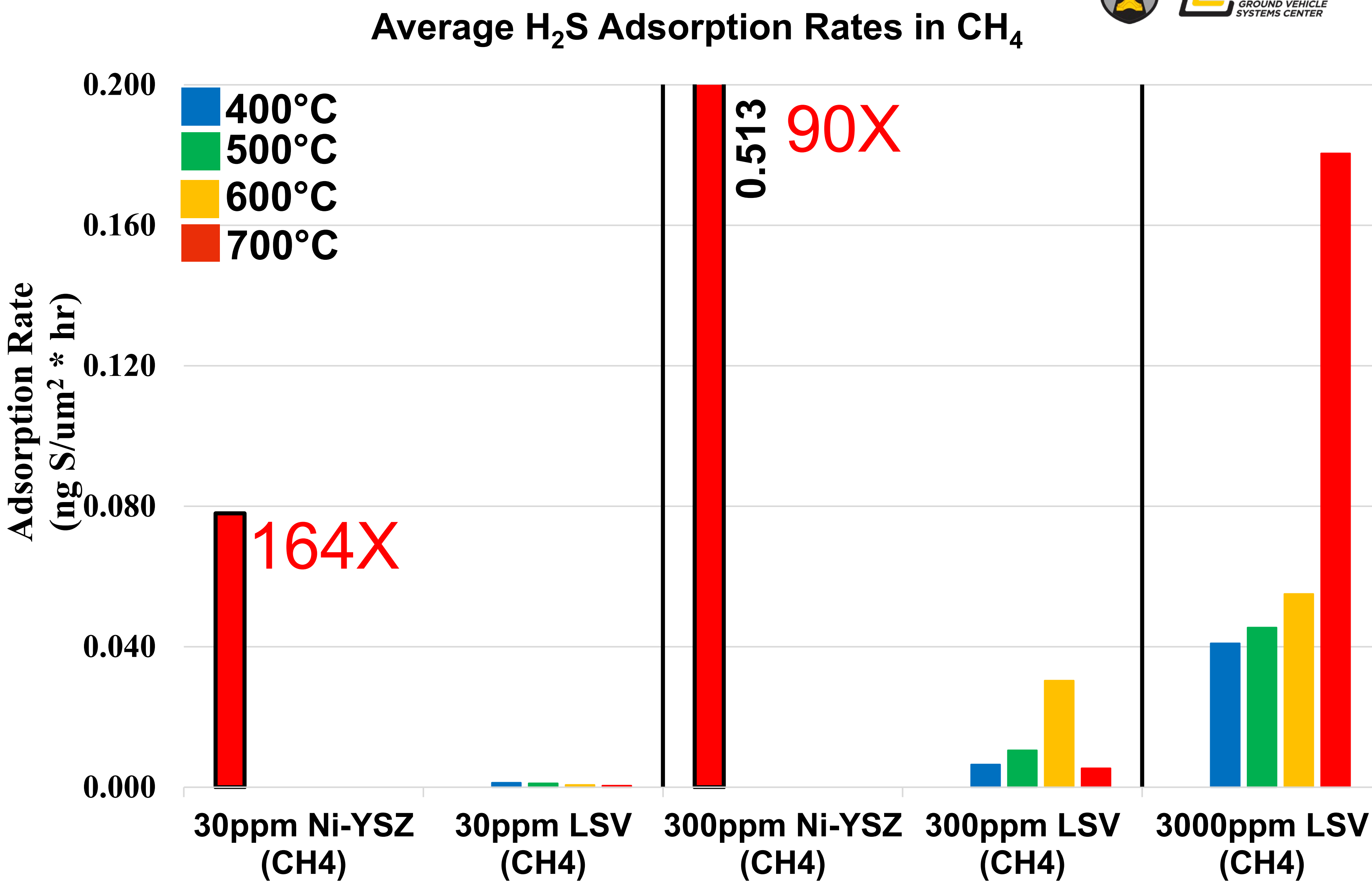
$$Time_{duration} = Gas\ Exposure\ Time\ (hrs)$$

$$Mass_{sulf} = Sulfur\ Mass\ (ng)$$ ← **EDS**

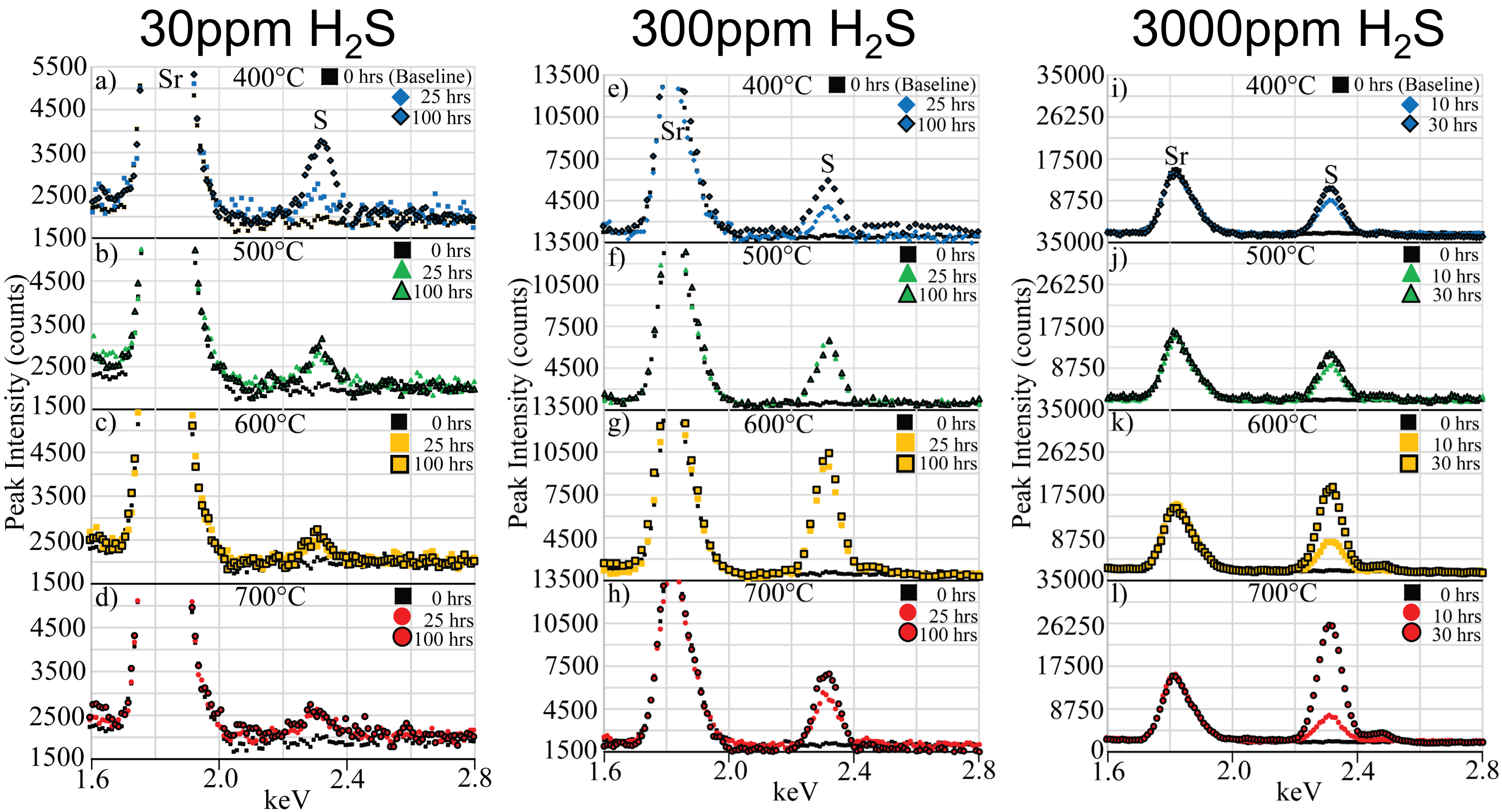
$$\mathrm{SA} = Surface\ Area\ (\mu m^2)$$ ← **SEM**

- EDS Provides Weight % Sulfur - Convert to Sulfur Mass
- SEM Provides Agglomerate Size - Determine Surface Area

Experimental Results – CH_4 Adsorption Rate Results



Experimental Results – EDS CH_4 Results



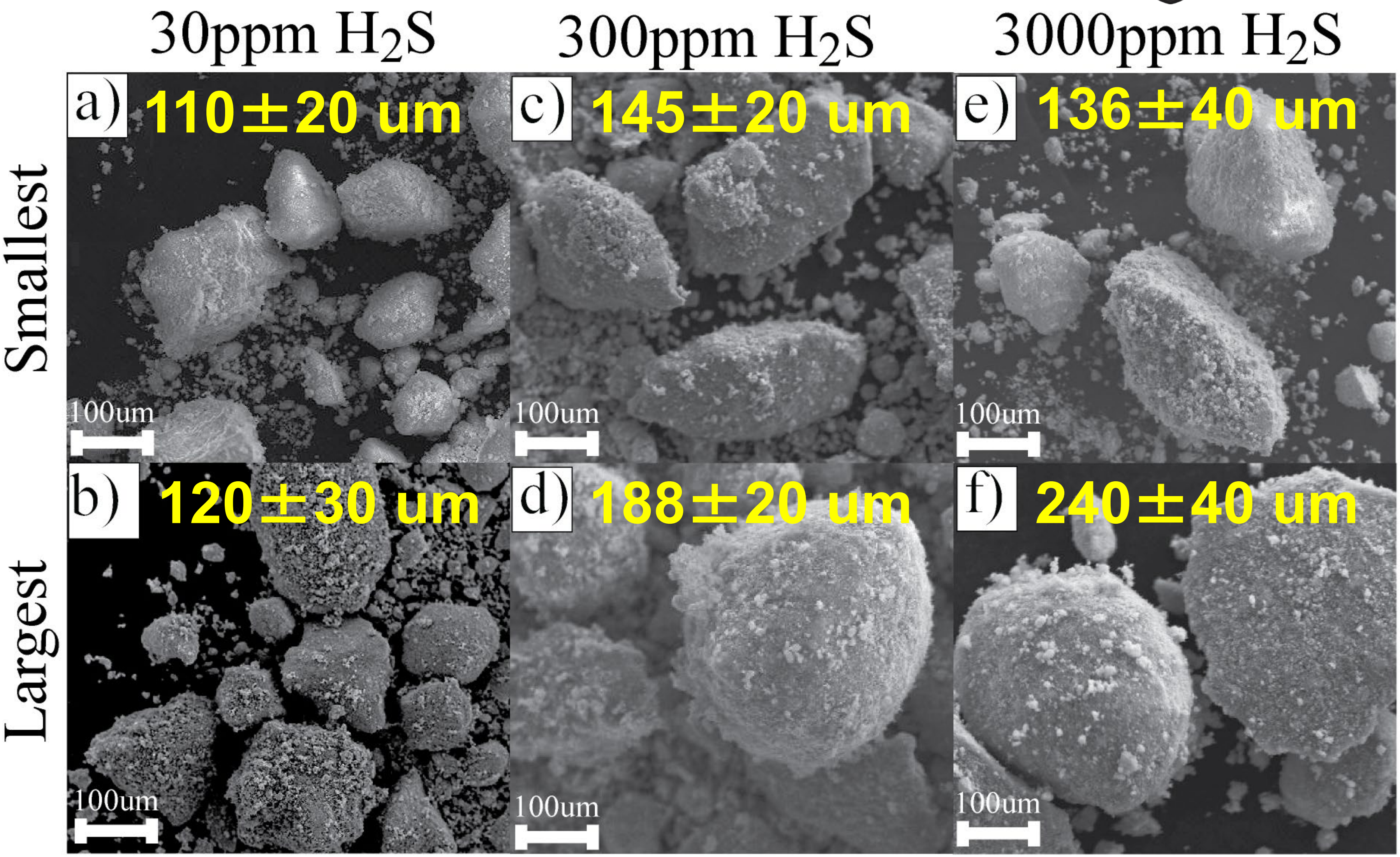
Experimental Results – EDS CH_4 Results (cont.)

- 30-300ppm H_2S - sulfur concentration remains relatively constant 400-500C.

- 30-300ppm H_2S – sulfur concentration reduced after cubic phase transition.
  - 600C – 30ppm H_2S
  - 700C – 300ppm H_2S

- 3000ppm H_2S – sulfur concentration gradually increases with increasing temperature up to 600C.
  - Large increase at 700C (may start at 600C). New phase formed shown in XRD results.

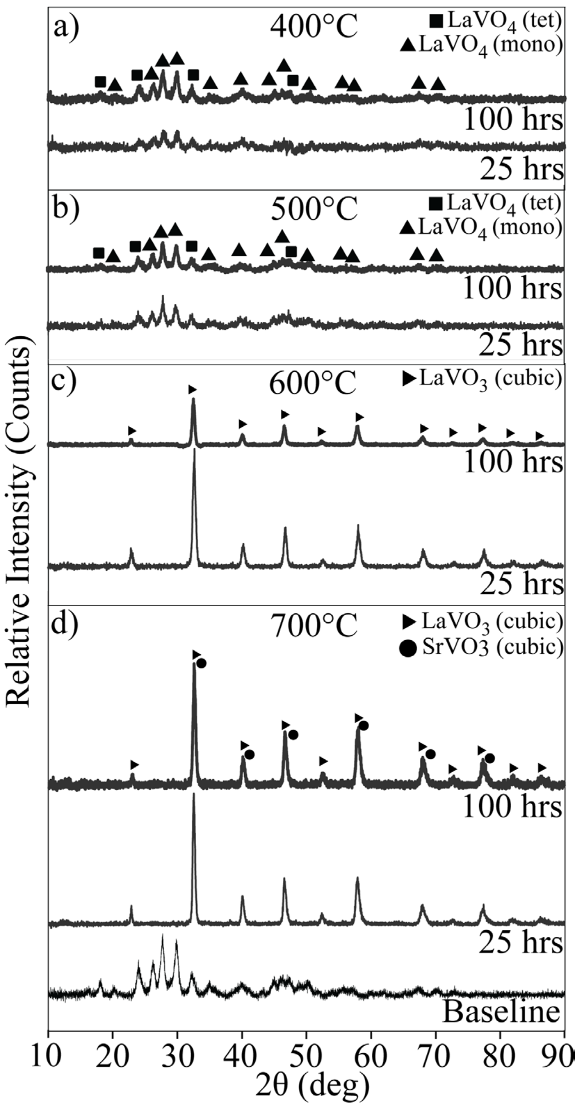
Experimental Results – SEM CH_4 Results



Experimental Results – SEM CH_4 Results (cont.)

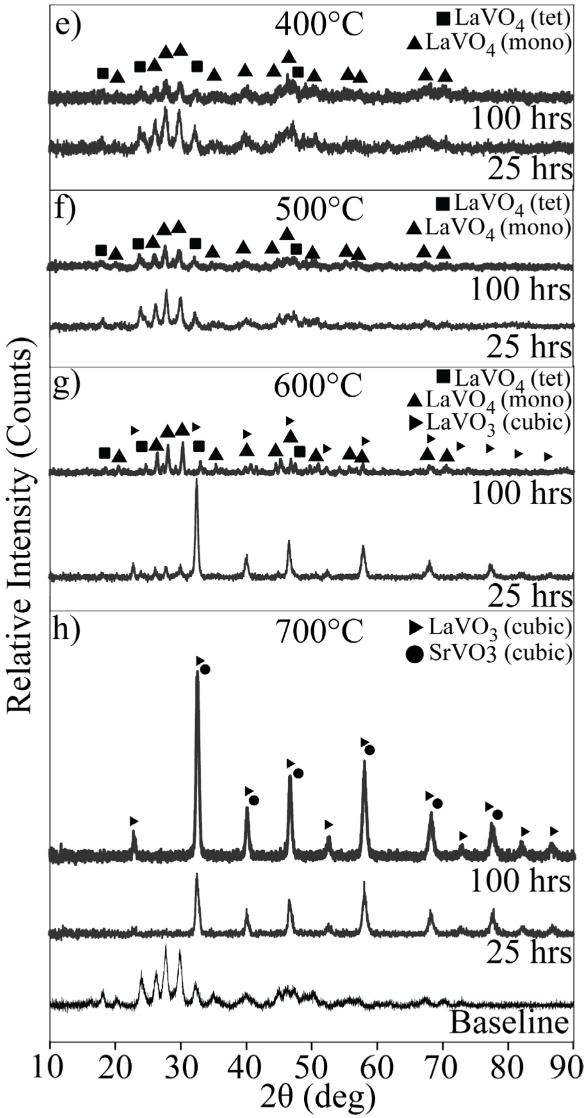
- Overall agglomerate shape is non-uniform
- LSV agglomerate size appears to grow with increasing H_2S concentration
  - 30ppm H_2S – 10 um size range
  - 300ppm H_2S – 43 um size range
  - 3000ppm H_2S – 94 um size range
- Agglomerate sizes partly influential on calculated adsorption rates.
  - Unlike previous ILIR results with H_2 which showed statistically similar agglomerate sizes with H_2S concentration and operating temperature.

Experimental Results – 30ppm H_2S CH_4 XRD Results



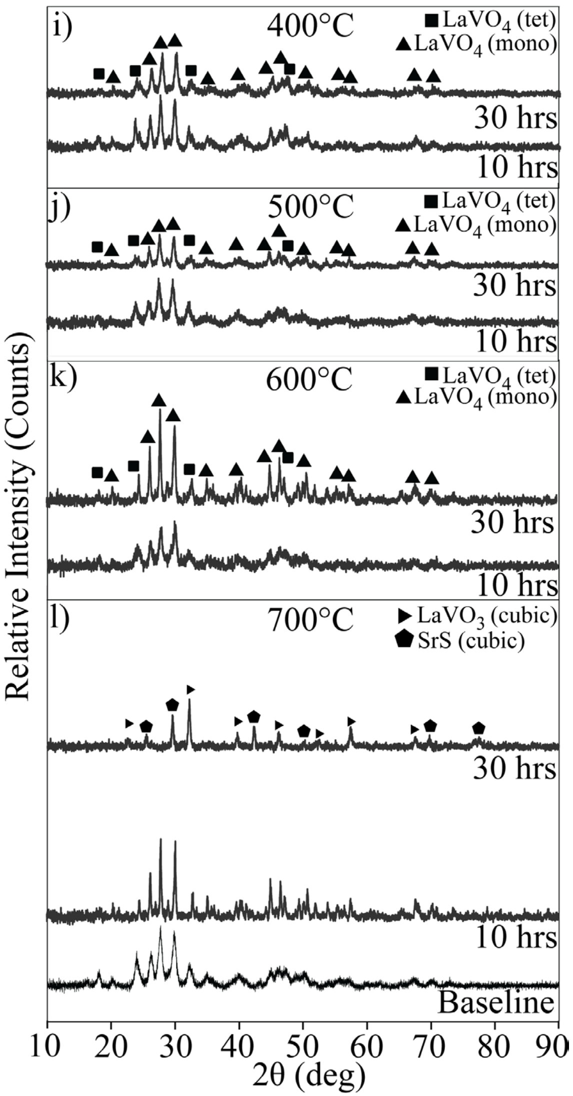
- LSV stays relatively consistent in peaks height between 400-500C.
- LSV crystal structure changes:
  - 400C – Monoclinic/Tetragonal
  - 500C – Monoclinic/Tetragonal
  - 600C – Cubic
  - 700C – Mostly Cubic

Experimental Results – 300ppm H_2S CH_4 XRD Results



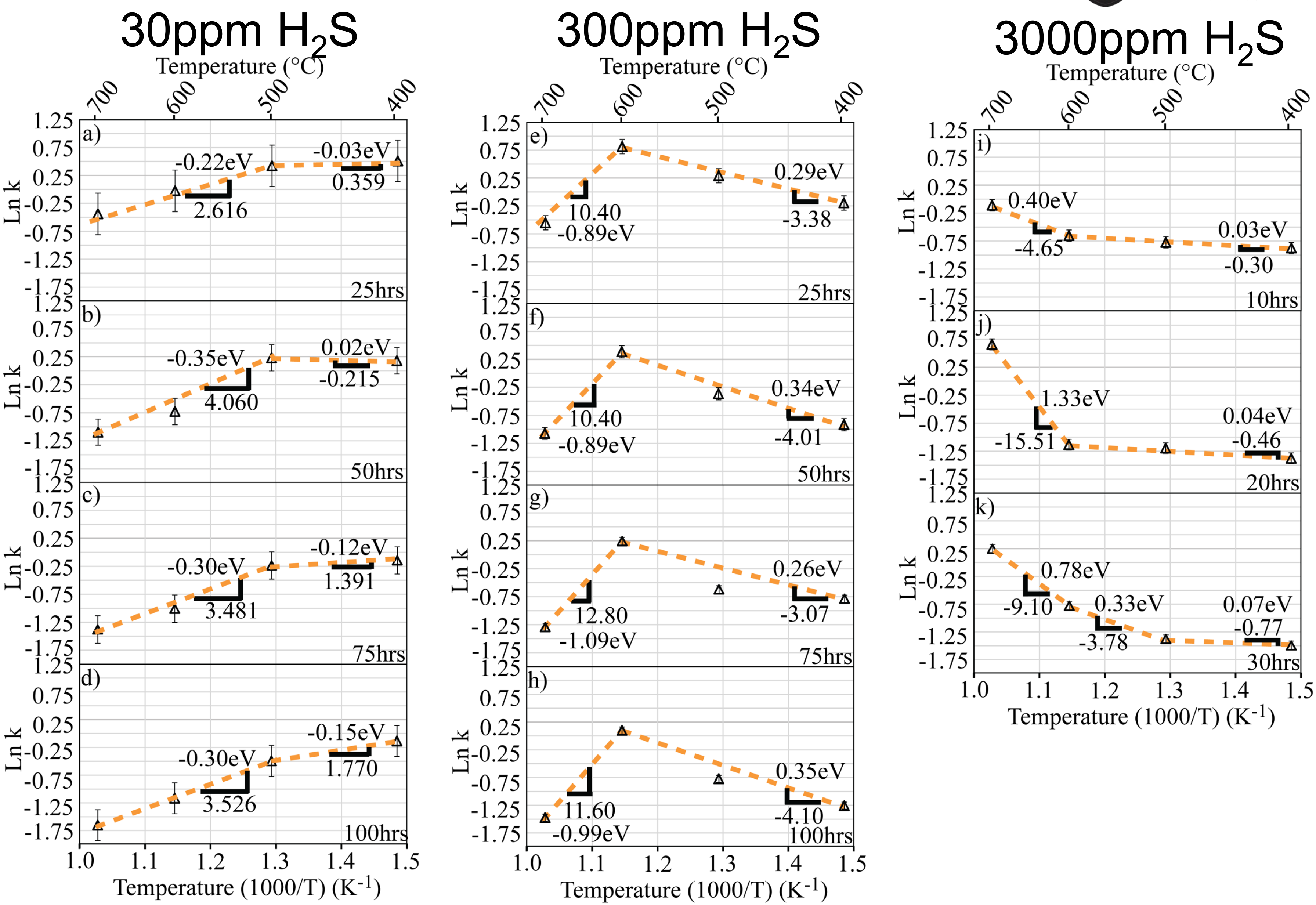
- LSV stays relatively consistent in peaks height between 400-500C.
- LSV is transitioning between cubic and monoclinic/tetragonal at 600C.
  - 25hr – Mostly cubic
  - 100 hr – Monoclinic/Tetragonal
  - Increased adsorption rate impacted by small amount of monoclinic/tetragonal at 25hr.
- LSV crystal structure changes:
  - 400C – Monoclinic/Tetragonal
  - 500C – Monoclinic/Tetragonal
  - 600C – Cubic/Monoclinic/Tetragonal
  - 700C – Mostly Cubic

Experimental Results – 3000ppm H_2S CH_4 XRD Results



- LSV stays relatively consistent in peaks height between 400-500C.
- LSV appears to change peak height ratio at 600C 30hr. Strontium sulfide might be included.
- LSV crystal structure changes:
  - 400C – Monoclinic/Tetragonal
  - 500C – Monoclinic/Tetragonal
  - 600C – Monoclinic/Tetragonal
    - Maybe Strontium Sulfide
  - 700C – Monoclinic/Tetragonal/Cubic/ Strontium Sulfide

Experimental Results – CH_4 Activation Energy Results



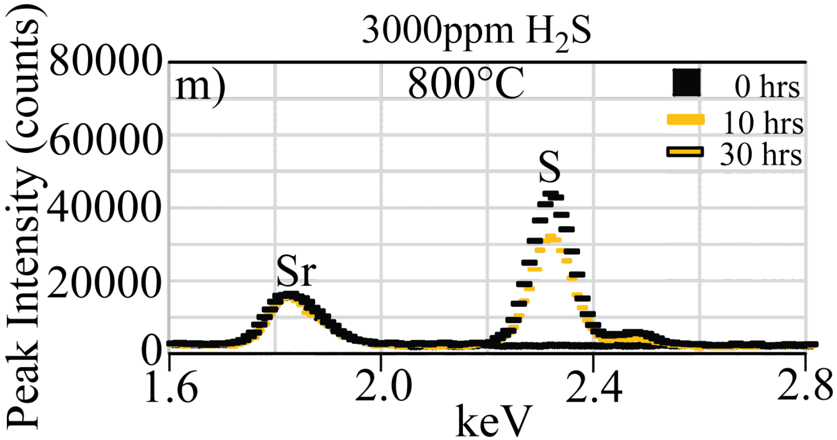
Experimental Results – CH_4 Activation Energy Results (cont.)

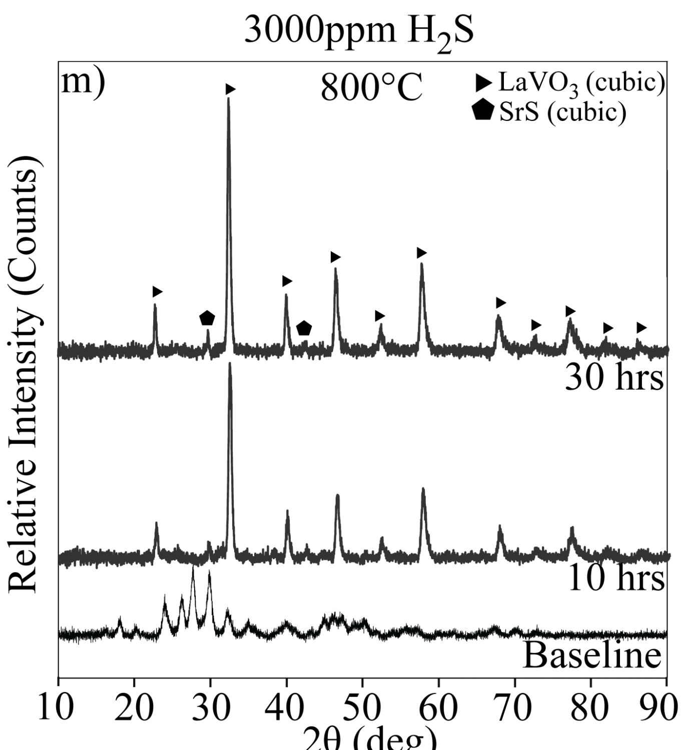
- Two activation energies for most of the samples
  - Transition temperature between energies is increased as H_2S concentration increases.

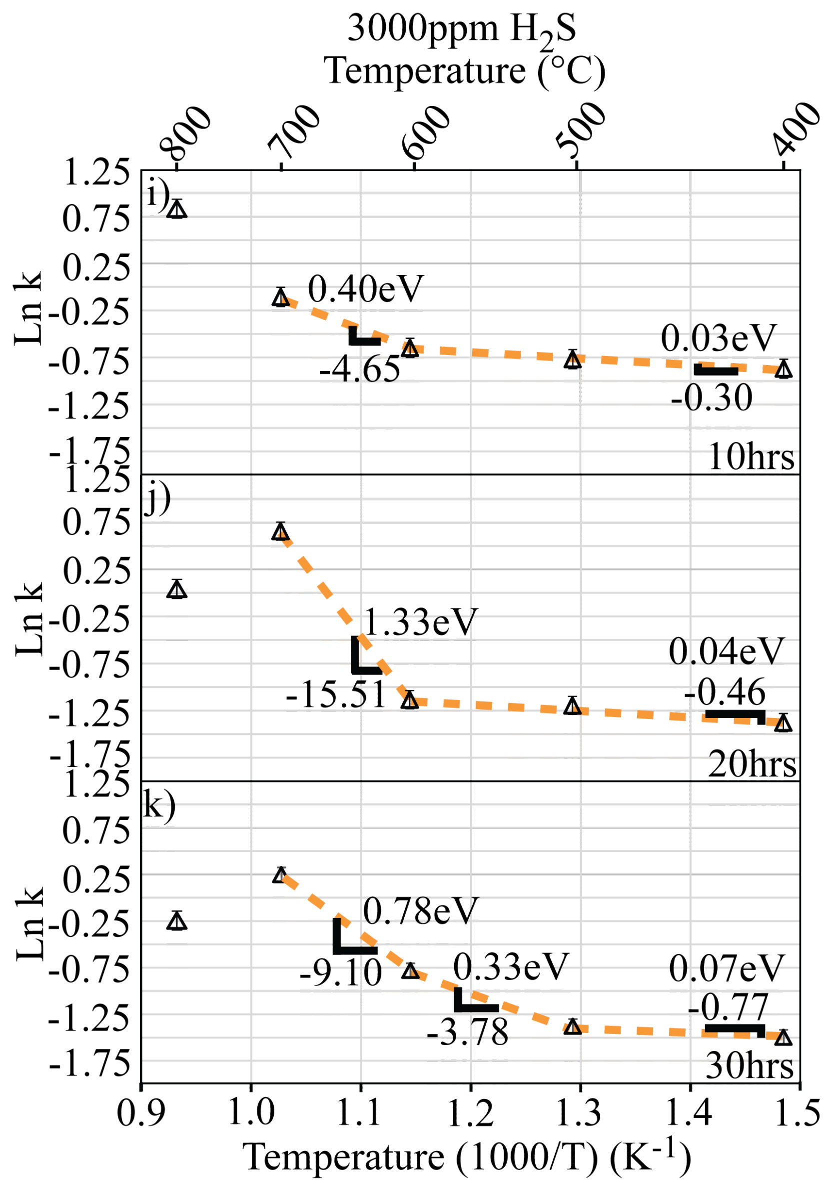
- Activation energies lower than Ni-YSZ with H_2S.
  - LSV 30-300ppm H_2S concentrations ($-1<x<1$ eV)
  - Ni-YSZ (-3.240 eV)

- Three energies are thought to exist for the 3000ppm H_2S 30hr sample.
  - This supports the hypothesis mentioned before that there may be some strontium sulfide in the 600C 30hr sample.
  - 400-500C
  - 500-600C
  - 600-700C

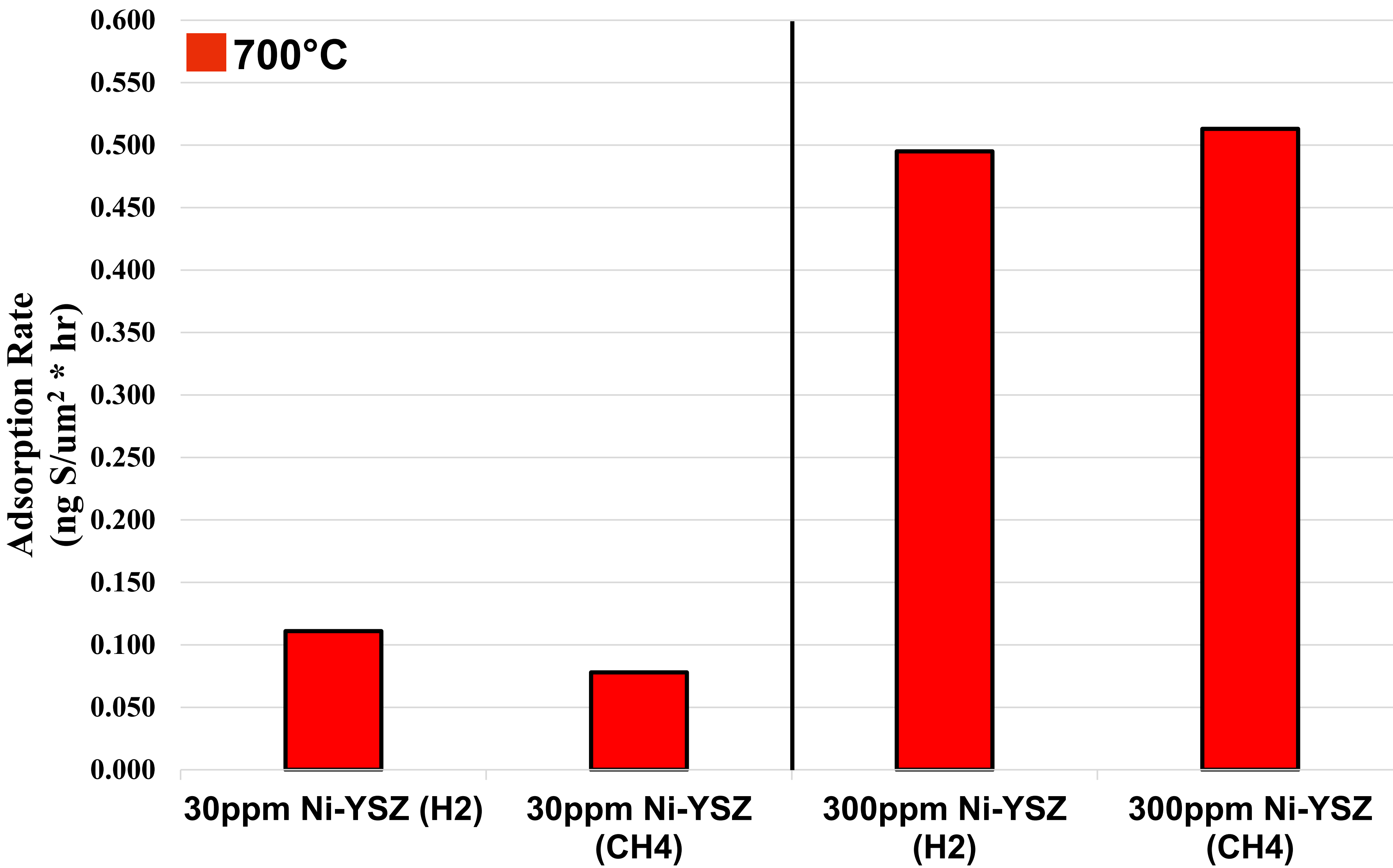
Experimental Results – 3000ppm H_2S CH_4 (Testing Beyond 700C)



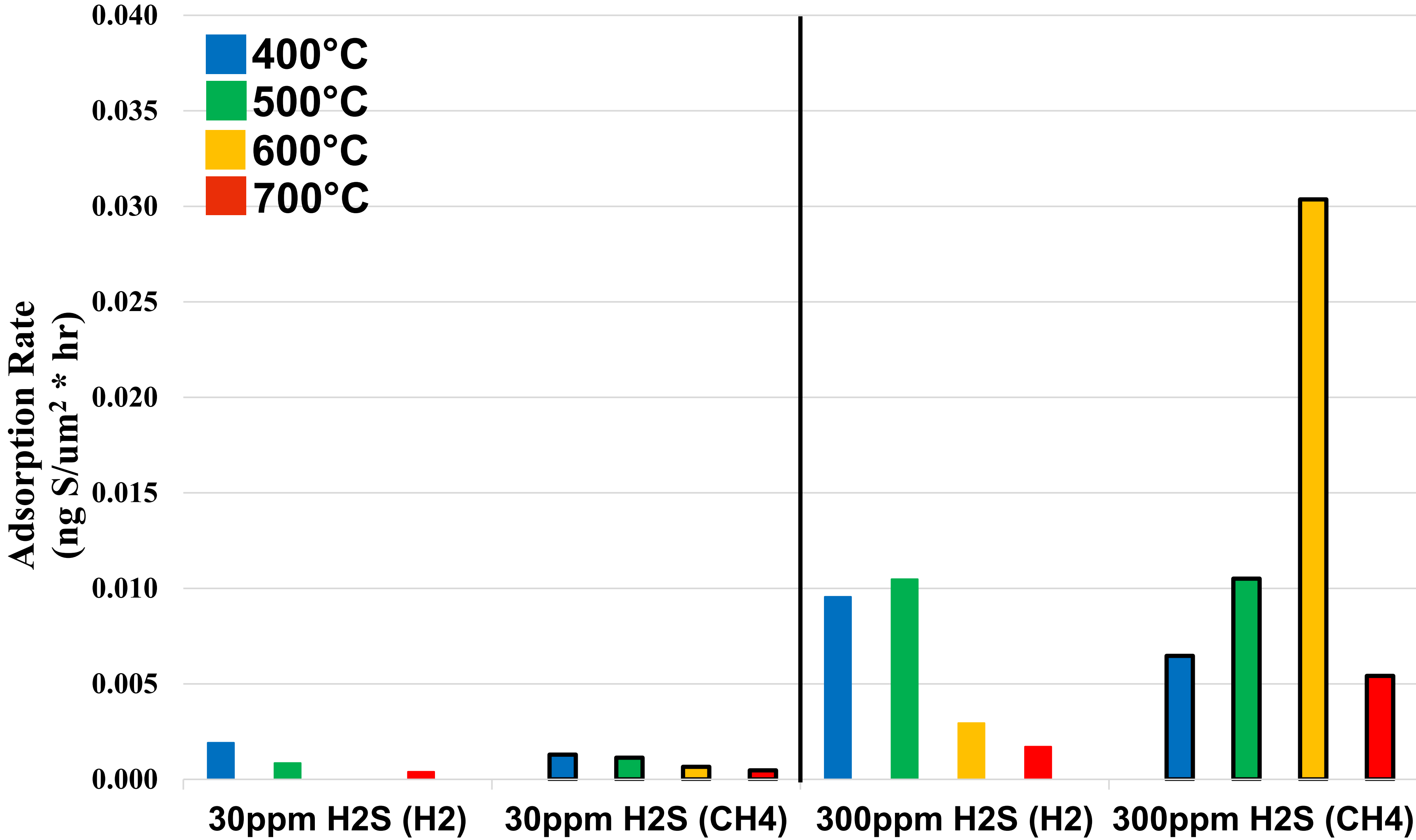




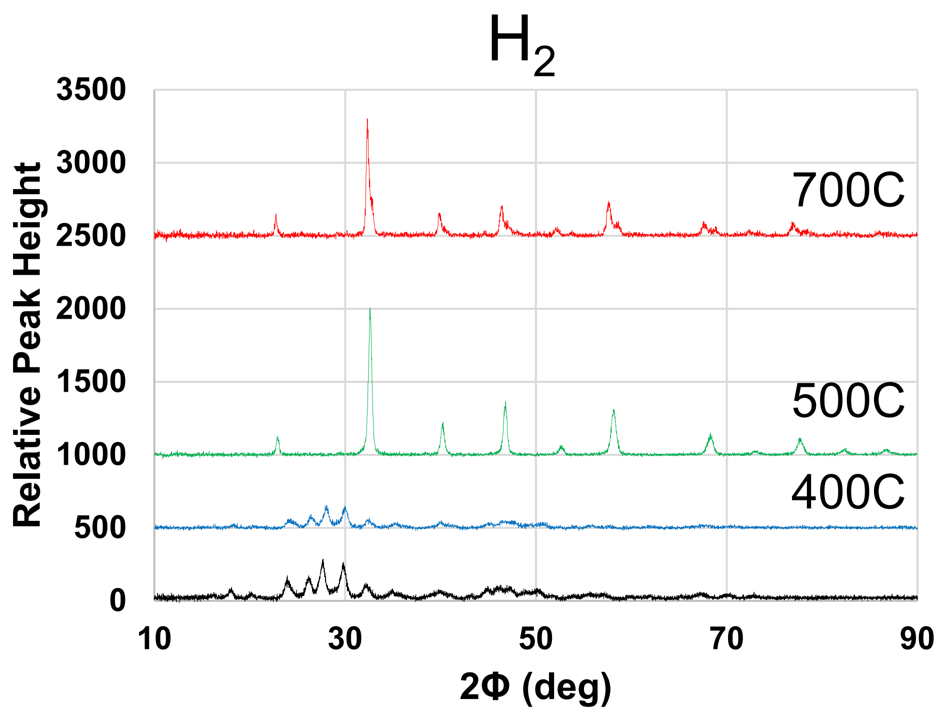
Experimental Results – Ni-YSZ Adsorption Rate Comparison with Previous H_2 Results

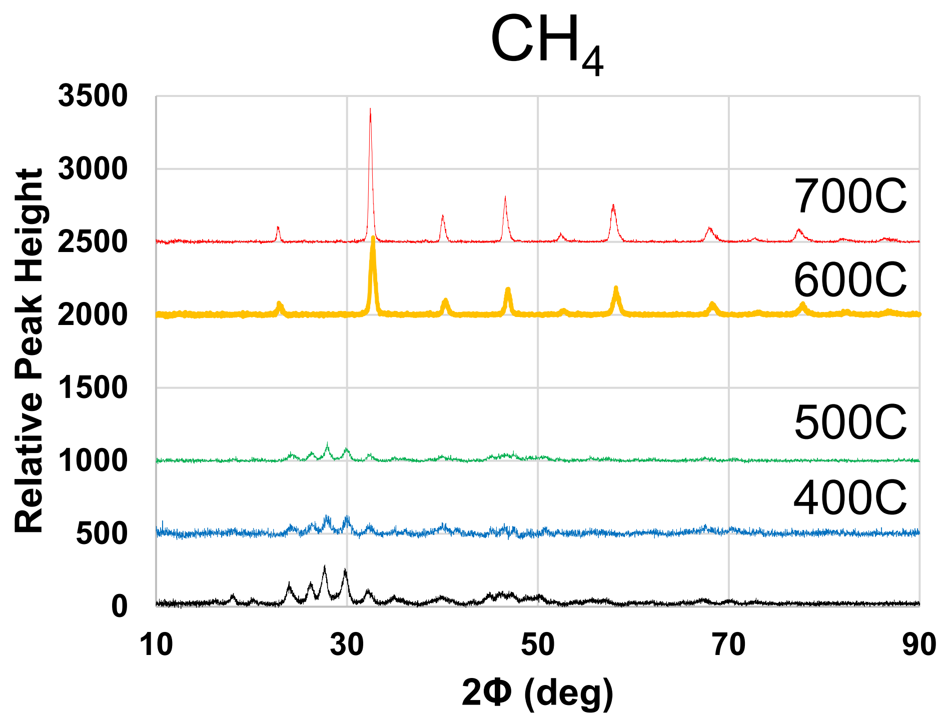


Experimental Results – LSV Adsorption Rate Comparison with Previous H_2 Results

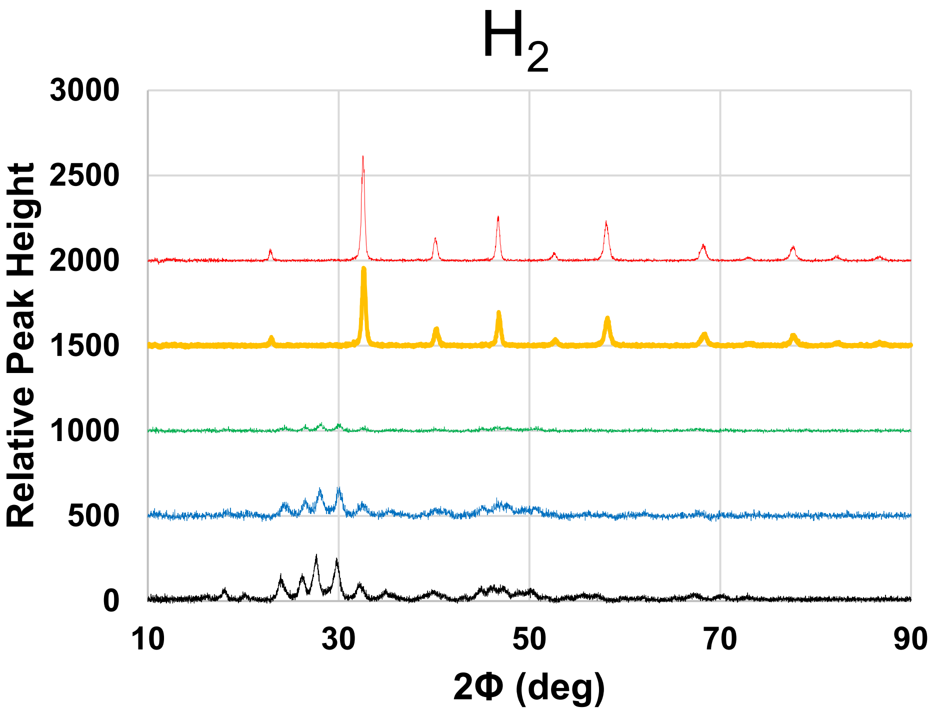


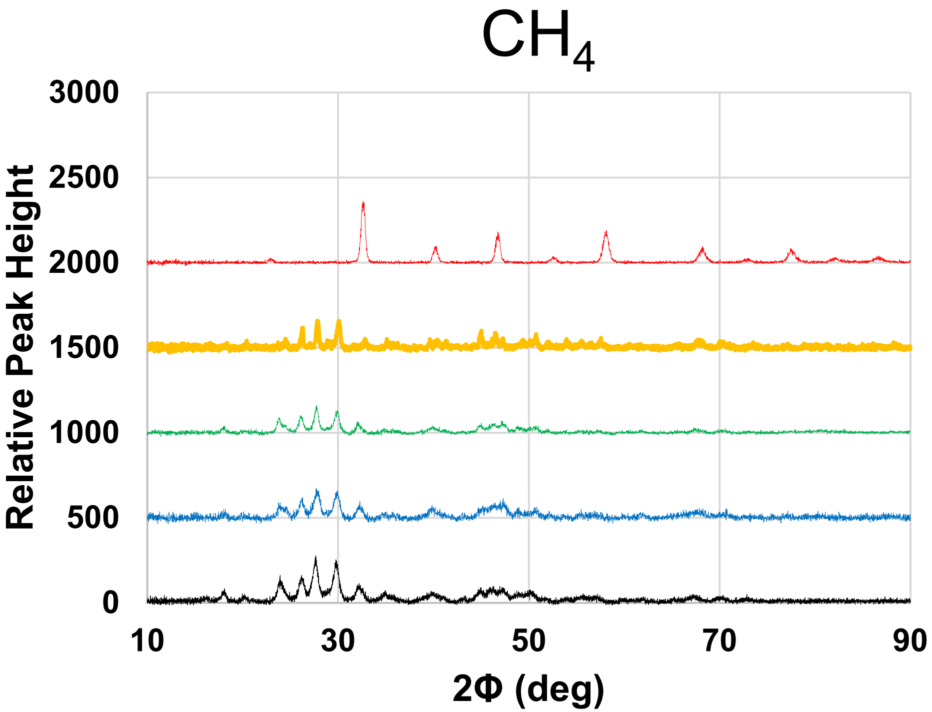
Experimental Results – 30ppm H_2S CH_4 XRD Comparison with Previous H_2 Results





Experimental Results – 300ppm H_2S CH_4 XRD Comparison with Previous H_2 Results

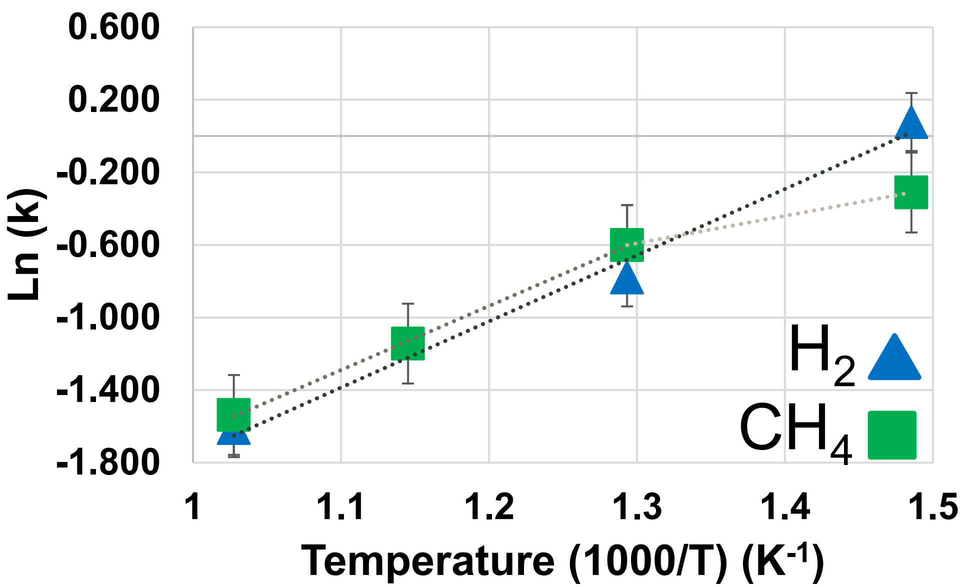




Experimental Results – Activation Energy Comparison with Previous H_2 Results

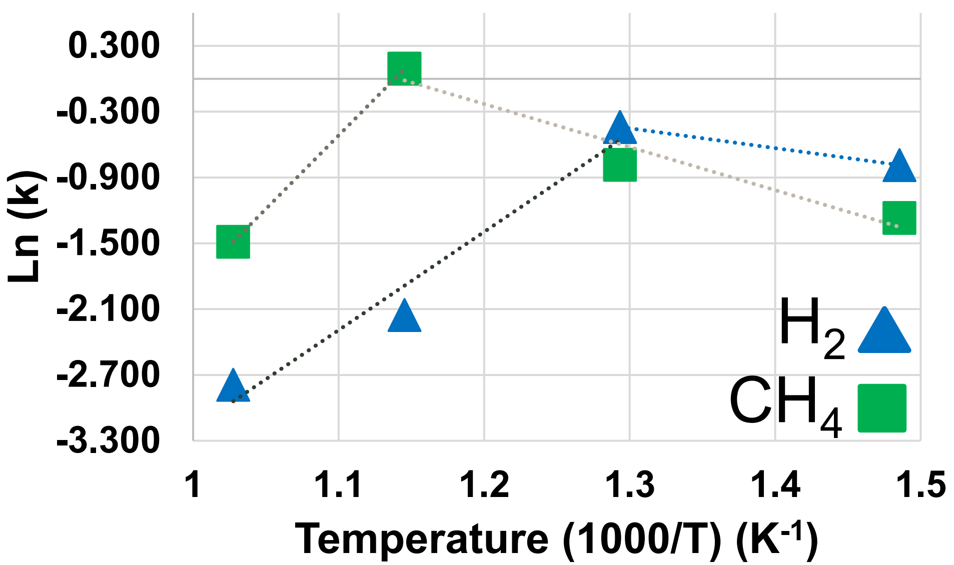
30ppm H_2S

- Reduced CH_4 adsorption/kinetics at low temperature results from CS_2 formation
- Overall, very similar



300ppm H_2S

- Reduced CH_4 adsorption/kinetics at low temperature results from CS_2 formation
- Reaction between LSV and H_2S overcomes CS_2 formation at elevated temperature
- Cubic phase peak height at 700C diminished for CH_4



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Experimental Conclusions

1. 30-300ppm H_2S in CH_4 is 90-164x more sulfur tolerant than Ni-YSZ
   - 30-300ppm H_2S in H_2 - 278-287x more tolerant
   - Closer to H_2 at 30ppm H_2S
   - Deviates significantly ≥300ppm H_2S

2. CH_4 pushes cubic phase to increased elevated temperatures

3. CH_4 has lower crystalline cubic phase which lowers sulfur tolerance

4. Further investigation into doping LSV may be considered. CH_4 fuel should be used more cautiously than hydrogen.

Acknowledgements

Office of the Chief Scientist, GVSC

Fuel Cell Technologies Branch, GVSC

Fuels and Lubricants Branch, GVSC

Water Treatment and Handling Branch, GVSC

Characterization and Failure Analysis Branch, GVSC

Backup Slides

Experimental Results – Adsorption Rates 10vol% 700C

Experimental Results – Optical Microscopy

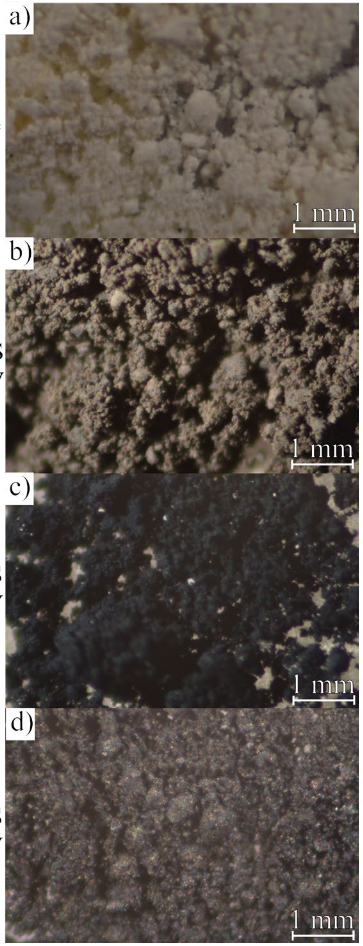
30ppm

Untested LSV Oxide Powder

30ppm H_2S 400°C LSV Oxide

30ppm H_2S 500°C LSV Oxide

30ppm H_2S 700°C LSV Oxide



300ppm

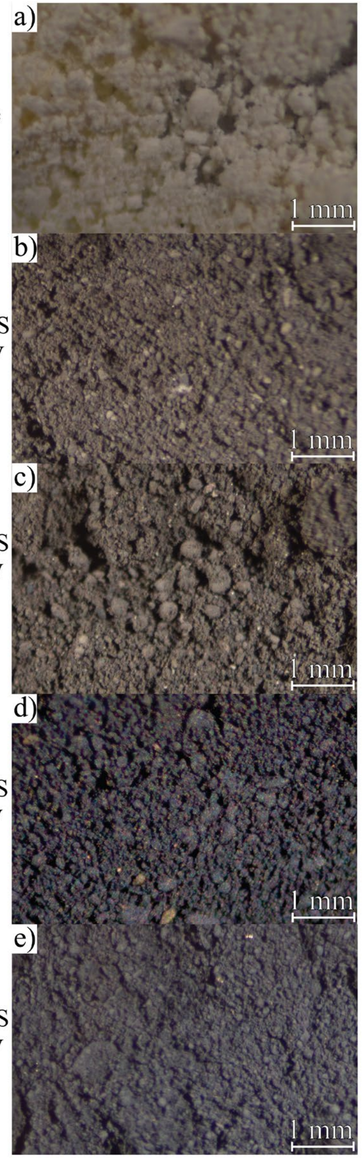
Untested LSV Oxide Powder

300ppm H_2S 400°C LSV Oxide

300ppm H_2S 500°C LSV Oxide

300ppm H_2S 600°C LSV Oxide

300ppm H_2S 700°C LSV Oxide



10vol%

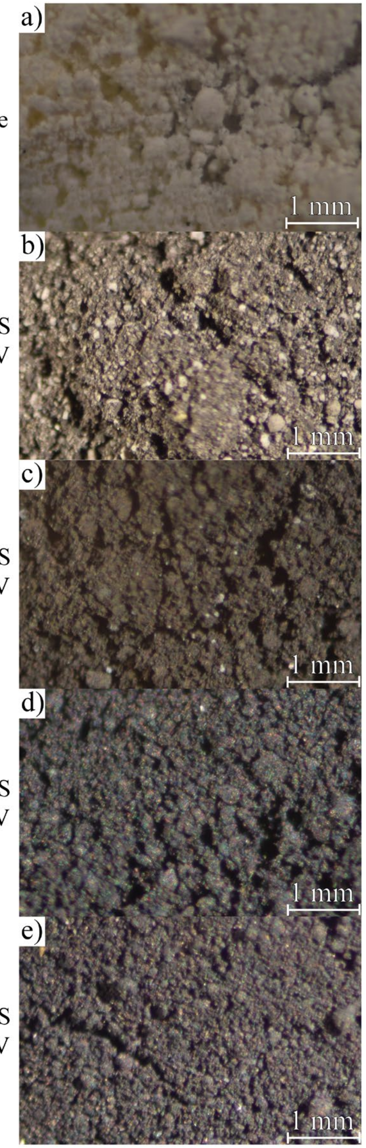
Untested LSV Oxide Powder

10vol% H_2S 400°C LSV Oxide

10vol% H_2S 500°C LSV Oxide

10vol% H_2S 600°C LSV Oxide

10vol% H_2S 700°C LSV Oxide



Experimental Results – Optical Microscopy

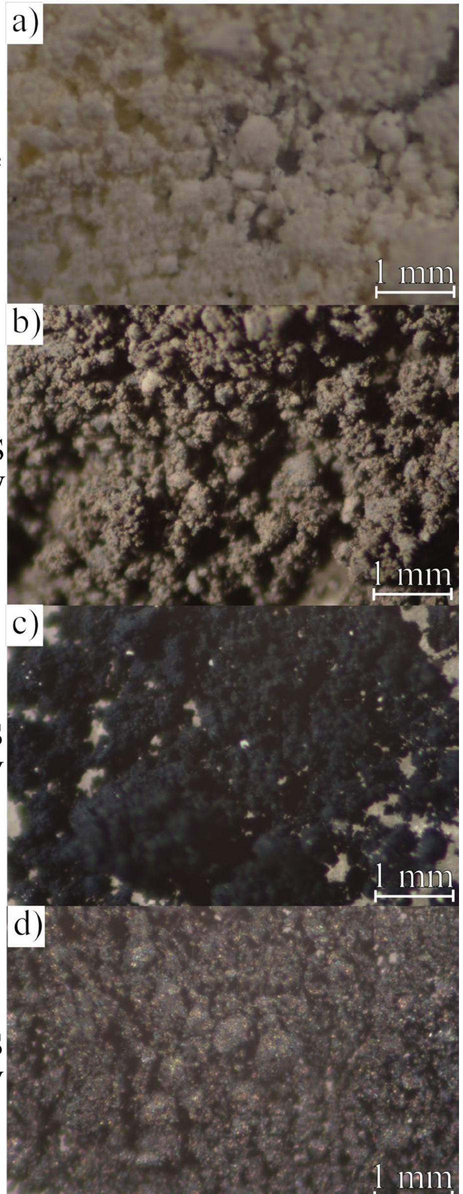
La = +3 Sr = +2

Untested LSV Oxide Powder

30ppm H_2S 400°C LSV Oxide

30ppm H_2S 500°C LSV Oxide

30ppm H_2S 700°C LSV Oxide



Cream

V = +5

Brown/Yellow

V = +5

Dark Blue

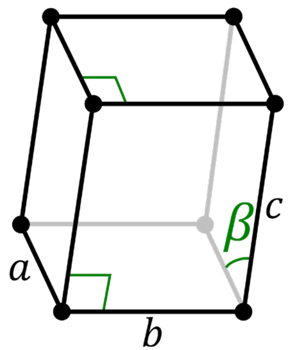
V = +4

Black

V = +3

Experimental Results – Crystal Structures

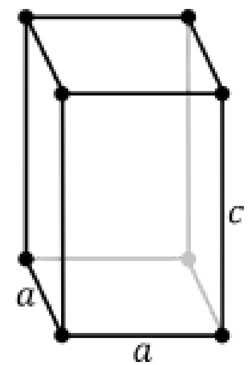
Monoclinic



$a \neq b \neq c$

$\alpha = \gamma = 90 \neq \beta$

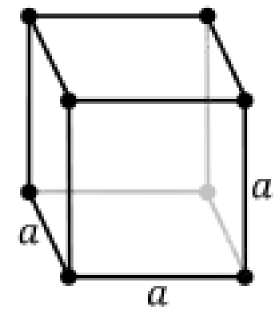
Tetragonal



$a = b \neq c$

$\alpha = \gamma = \beta = 90$

Cubic



$a = b = c$

$\alpha = \gamma = \beta = 90$

Experimental Results – Activation Energy Calculation

$$R_{ads,act} = k * P^{x}_{gas,partial}$$

↓

$$P_{gas,partial} = P_{gas} * X_{H_2S}$$

$$\mathrm{X} = kinetic\ order\ (assume\ 1)$$

$$\mathrm{k} = kinetic\ rate\ constant$$

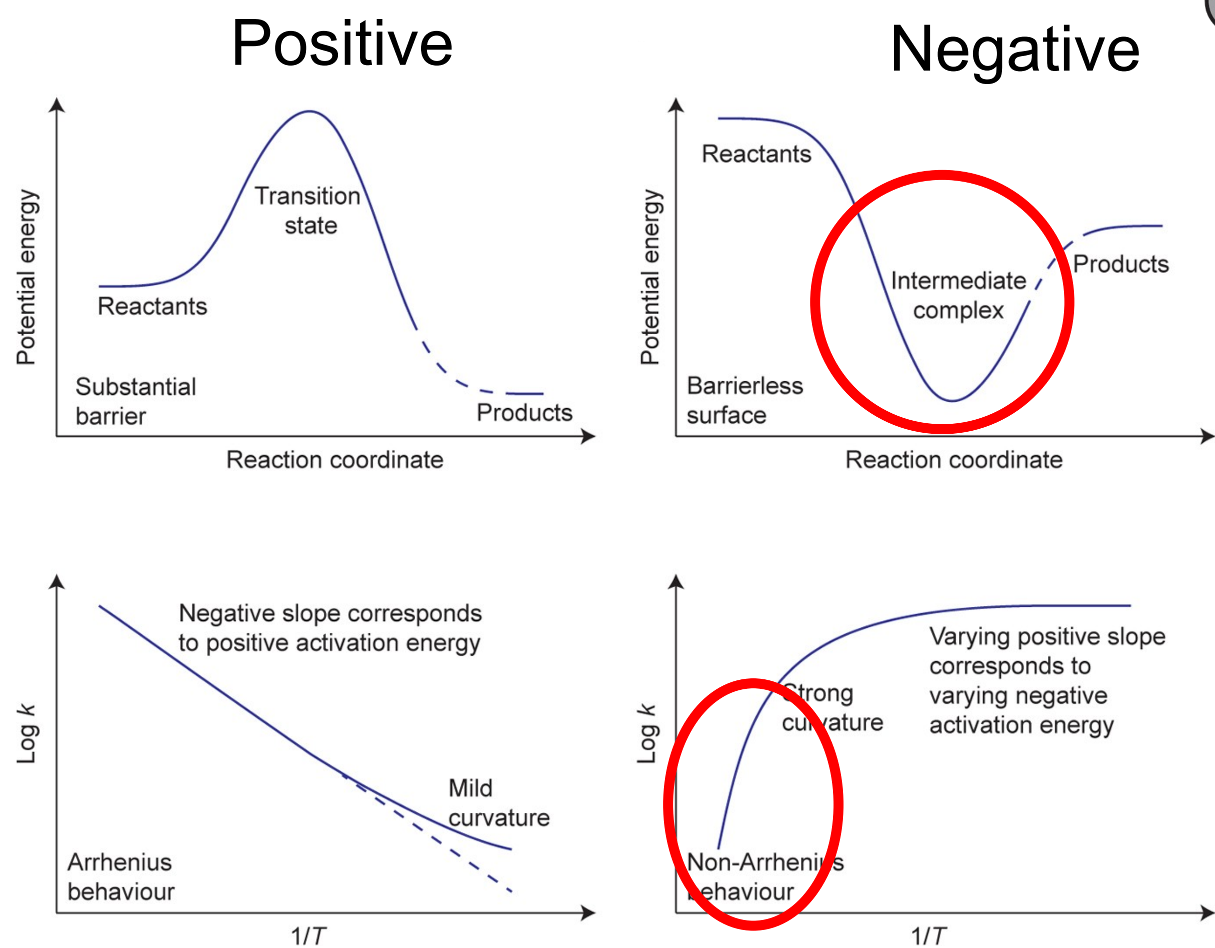
↓

$$X_{H_2S} = H_2S\ Mol\ Fraction$$

$$P_{gas} = Gas\ Pressure\ on\ Sample\ (45\ PSI)$$

- Experimental and Kinetic Model Adsorption Rate Assumed Equal
- Kinetic Rate Constant Fitted to Match Experimental Adsorption Rate
  - Rate Constant Used to Determine Activation Energy

Experimental Results – Negative Activation Energy



- Negative Activation Energy
  - Barrierless Reaction
  - Capture of Molecules in a Potential Well
  - Higher Temperature Drives more Molecules from Well
  - Less Negative Value has Greater Reaction Barrier

Experimental Results – Activation Energy Calculation

$$k = A * e^{\frac{-E_a}{R*T}} \rightarrow Ln(k) = \frac{-E_a}{R*T} + Ln(A)$$

R = Ideal Gas Constant

T = Temperature

E_a = Activation Energy (AE) (Energy Barrier for Reaction to Occur)

A = Pre-Exponential Factor (PEF) (Frequency of Collisions)