REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
05/24/2023	Presentation	Dec, 2022 - May, 2023

4. TITLE AND SUBTITLE

Contrasting Intermediate-Temperature La0.7Sr0.3VO3.86-δ (LSV) Catalyst Elevated Sulfur Tolerance using Gaseous and Liquid Fuel Explored through Experimental and Modeling Characterization over Time

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
6.1 Funding

6. AUTHOR(S)

Theodore E. Burye
Talia M. Sebastian

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

US Army Development Command (DEVCOM)
Ground Vehicle Systems Center (GVSC)
Ground Vehicle Power and Mobility (GVPM)
Force Projection Technology (FPT)
6501 E. 11 Mile Road
Warren, MI 48397

8. PERFORMING ORGANIZATION REPORT NUMBER

OPSEC 7546

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Army Development Command (DEVCOM)
Ground Vehicle Systems Center (GVSC)
Ground Vehicle Power and Mobility (GVPM)
Force Projection Technology (FPT)
6501 E. 11 Mile Road

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION A. Approved for public release; distribution unlimited. OPSEC #7546

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: Available for Public Release			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	Same as Report (SAR)	30	Theodore Burye
UNCLS	UNCLAS	UNCLAS			**19b. TELEPHONE NUMBER** *(include area code)* 586-282-3047

U.S. ARMY

DEVCOM GROUND VEHICLE SYSTEMS CENTER

U.S. ARMY DEVELOPMENT COMMAND GROUND VEHICLE SYSTEMS CENTER

Contrasting Intermediate-Temperature $La_{0.7}Sr_{0.3}VO_{3.86-\delta}$ (LSV) Catalyst Elevated Sulfur Tolerance using Gaseous and Liquid Fuel Explored through Experimental and Modeling Characterization over Time

28 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

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Motivation - SOFC Sulfur Contamination

Fuel Flexibility and Anode Deactivation

- State-of-the-art (Ni/YSZ)
  - Nickel highly active toward electrochemical oxidation of sulfur, leading to sulfur poisoning and deactivation
  - Chemisorption (<50 ppm(v)), Sulfidation (>50 ppm(v))
  - Concentrations as low as 2 ppm(v) can cause irreversible damage.

Material Strategies for Sulfur Tolerance

- 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)

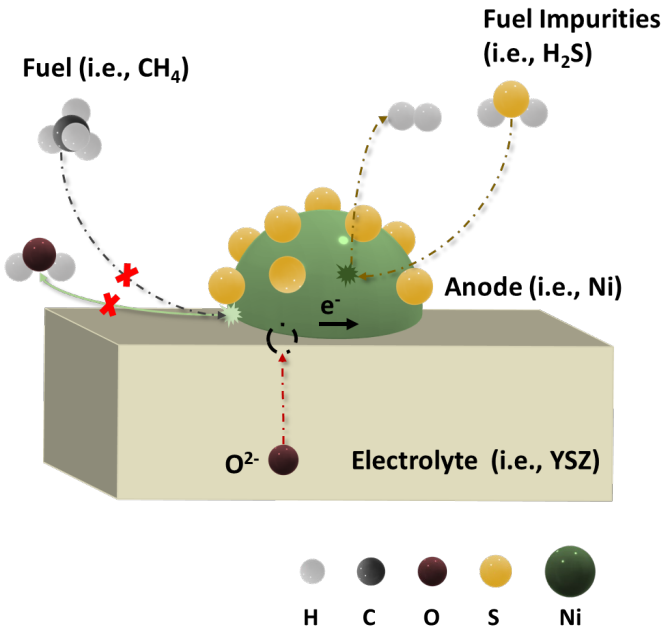
Mechanism of Chemisorption:

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

Mechanism of Sulfidation:

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

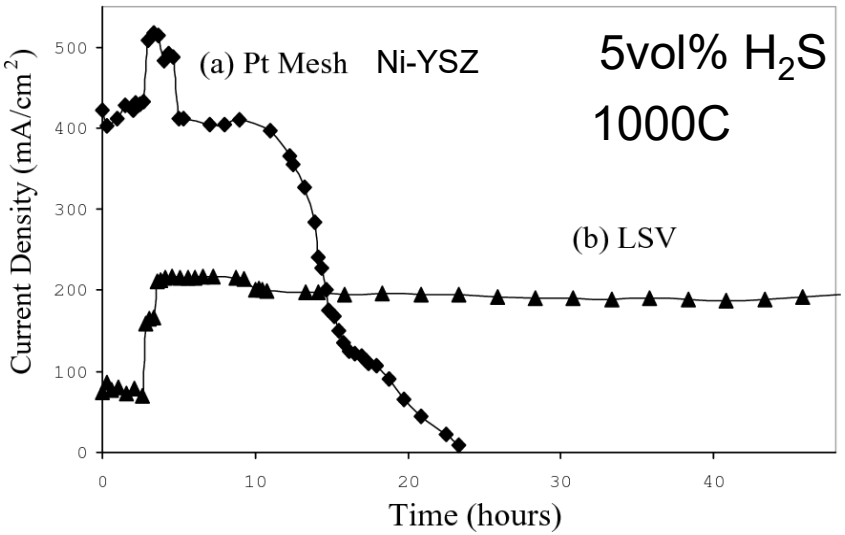
$$3Ni_{(s)} + xH_2S_{(g)} \leftrightarrow Ni_3S_{x(s)} + xH_{2(g)}$$

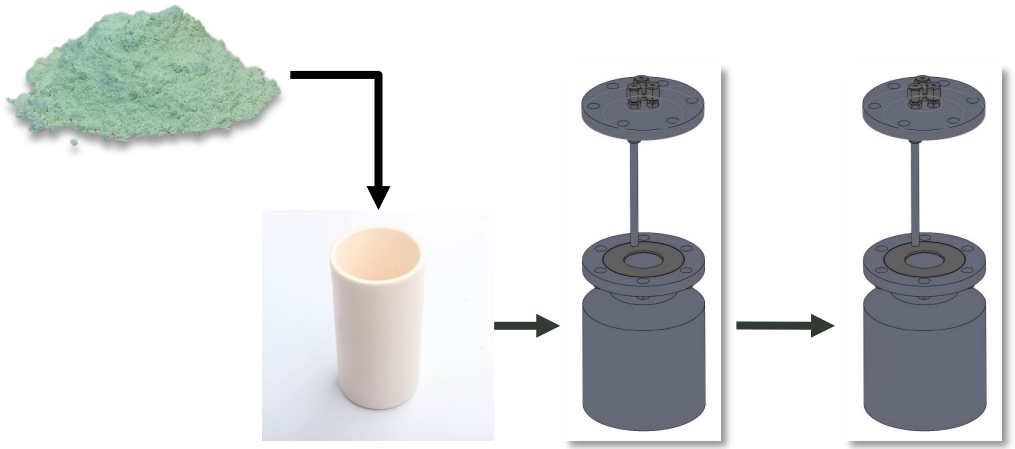


Adapted: DOI: 10.1016/j.jallcom.2017.11.381

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Motivation – LSV Anode Catalyst Sulfur Tolerance





This study experimentally tested LSV powder:

- Heated under exposure to H_2S (hydrogen sulfide) and C_4H_4S (thiophene)
  - Up to 100 hours
- Changed atmosphere between H_2, CH_4 and CH_3OH
  - Investigated gaseous vs. liquid fuel impact
  - Investigated polar vs. non-polar fuel impact

This study characterized post-experimentation LSV samples:

- Sulfur adsorption characterized using SEM/EDS
- Sulfur adsorption characterized using XRD
- LSV interaction in different atmospheres modeled in parallel to experimentation

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

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

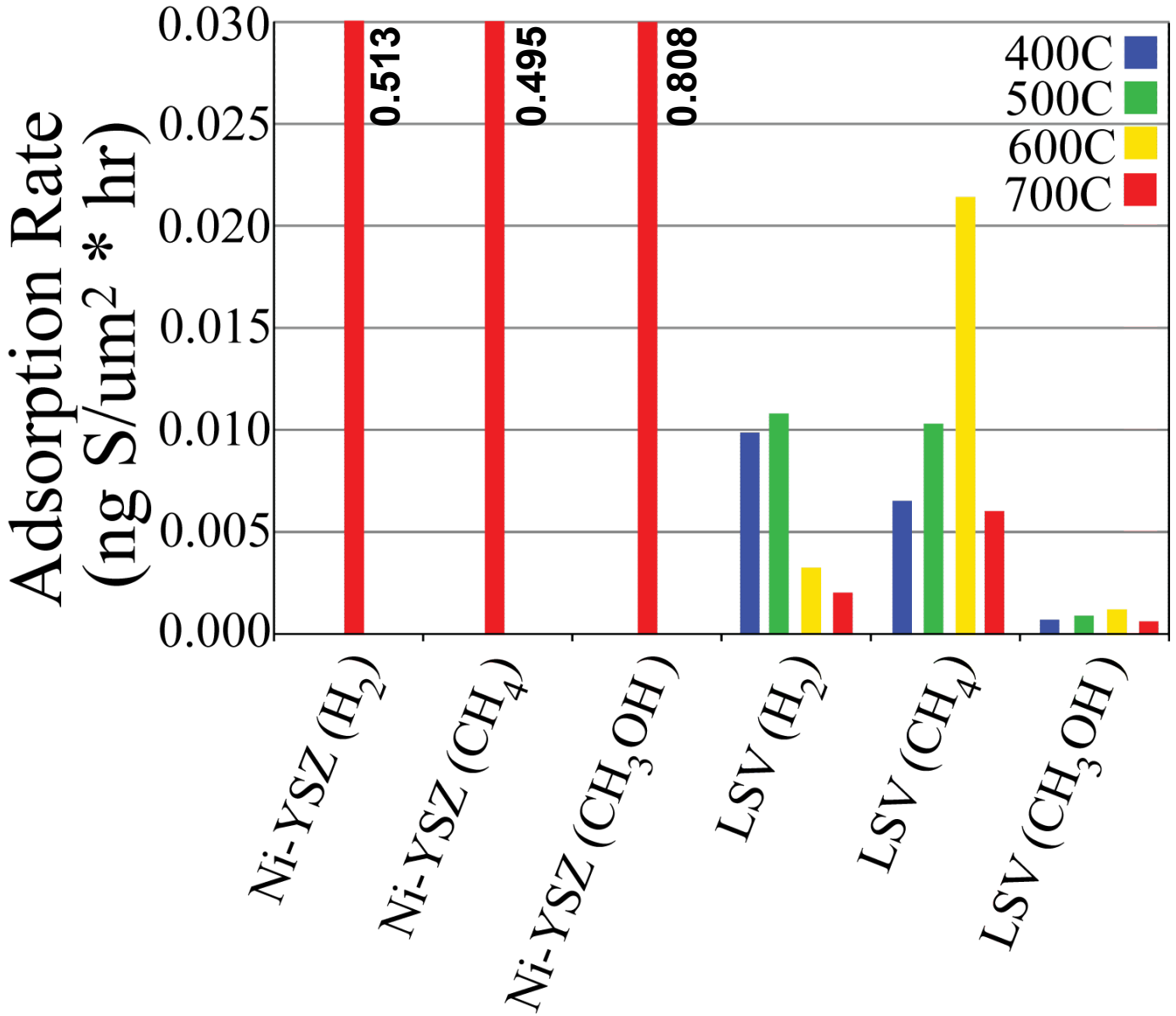
Experimental Results – Operating Parameters

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

Contaminant Concentration (ppm)	Mixture	Temperature (C)	Time (hours)
300	H_2S/H_2	400	25-100 hours
300	H_2S/H_2	500	25-100 hours
300	H_2S/H_2	600	25-100 hours
300	H_2S/H_2	700	25-100 hours
300	H_2S/CH_4	400	25-100 hours
300	H_2S/CH_4	500	25-100 hours
300	H_2S/CH_4	600	25-100 hours
300	H_2S/CH_4	700	25-100 hours
300	C_4H_4S/CH_3OH	400	25-100 hours
300	C_4H_4S/CH_3OH	500	25-100 hours
300	C_4H_4S/CH_3OH	600	25-100 hours
300	C_4H_4S/CH_3OH	700	25-100 hours

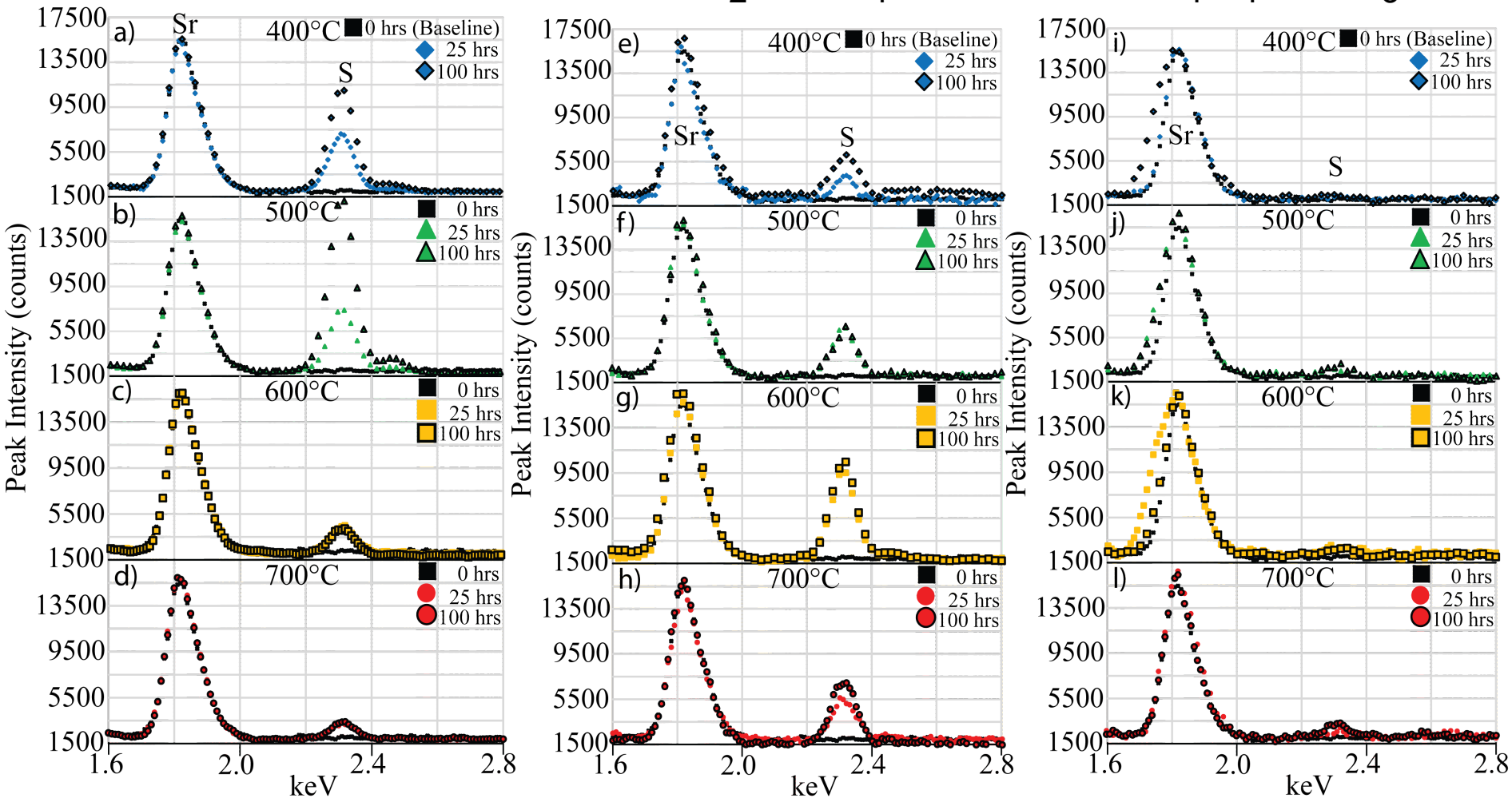
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – Adsorption Rates



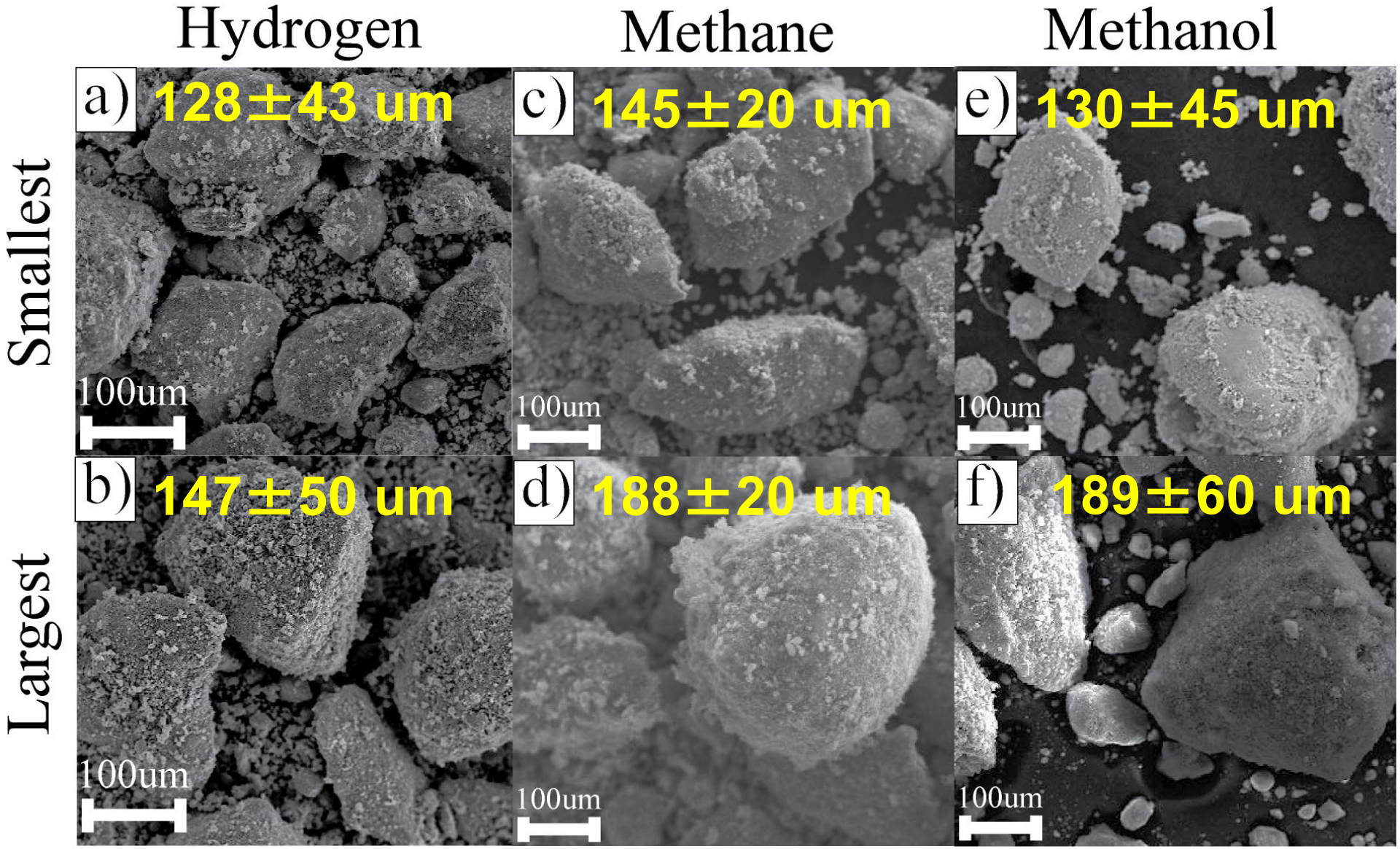
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – 300ppm LSV Raw EDS



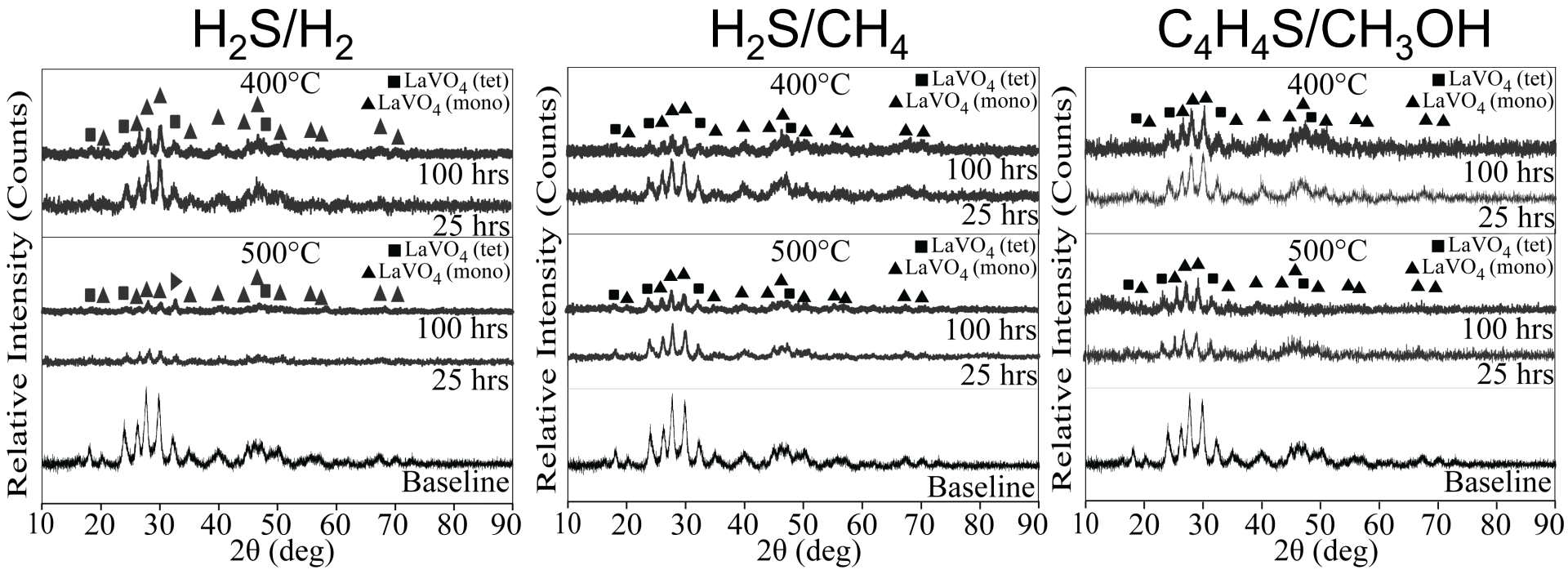
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – 300ppm LSV Agglomerate Size



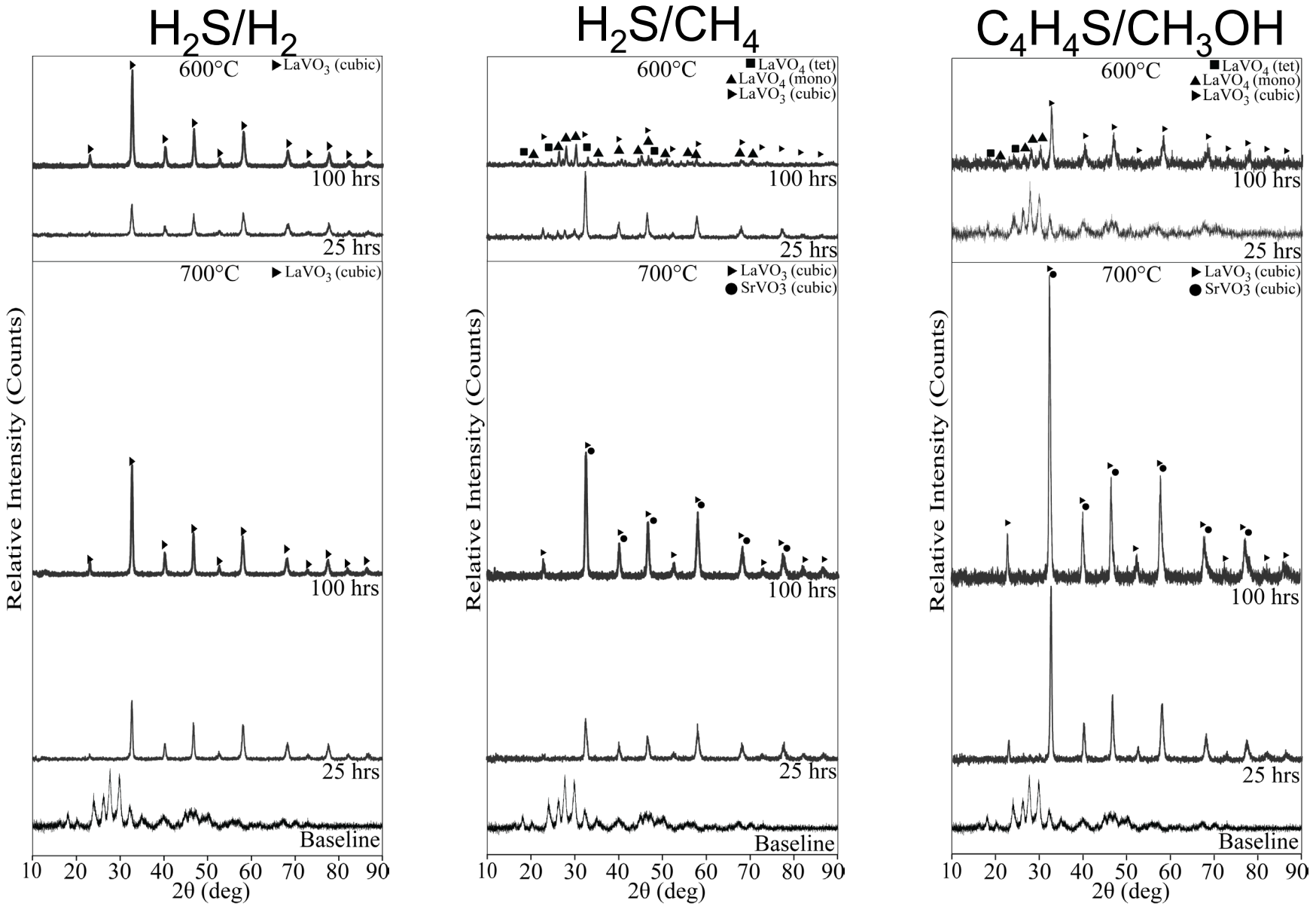
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – 300ppm LSV Low-Temperature Raw XRD



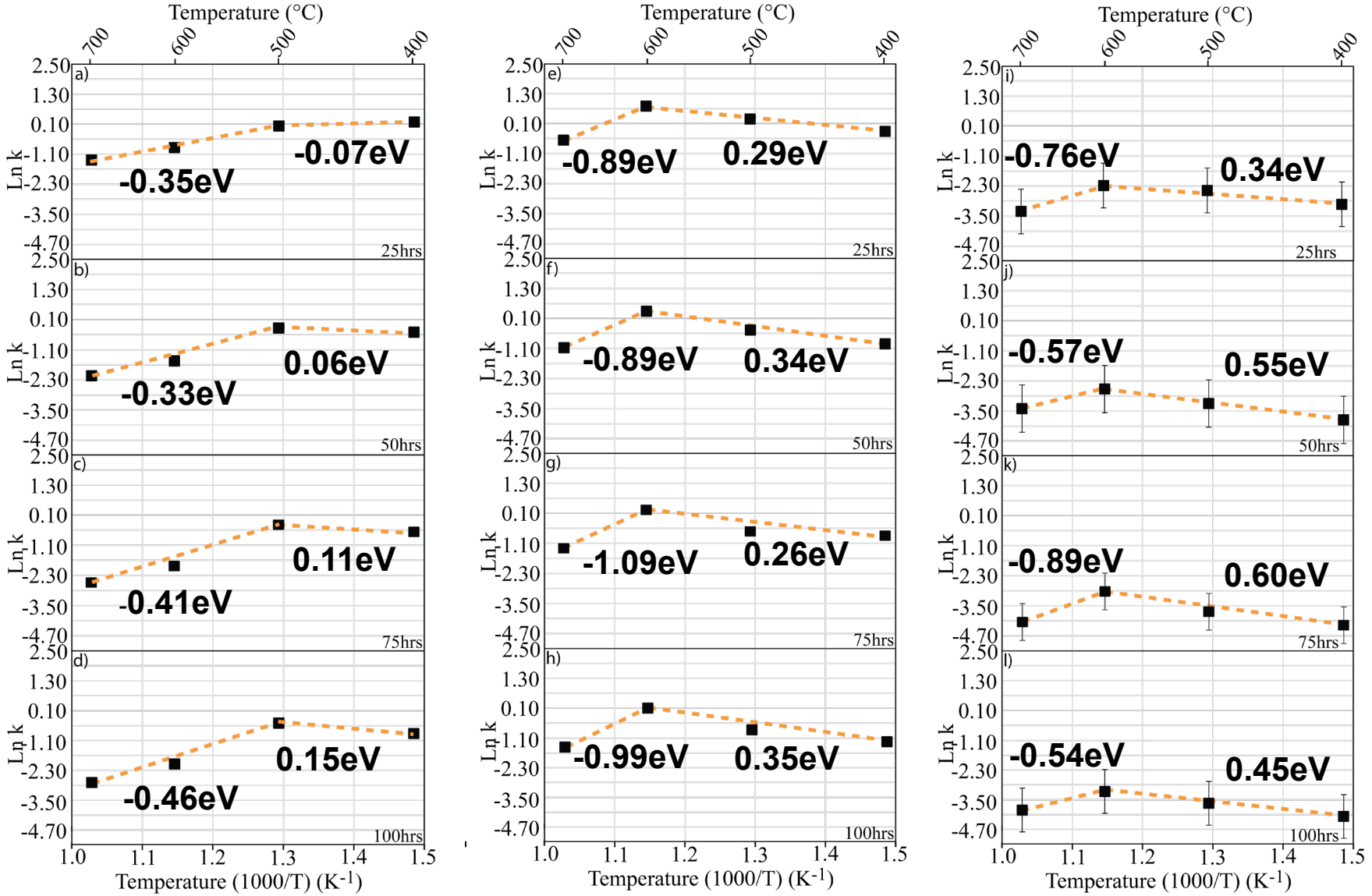
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – 300ppm LSV High-Temperature Raw XRD



DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

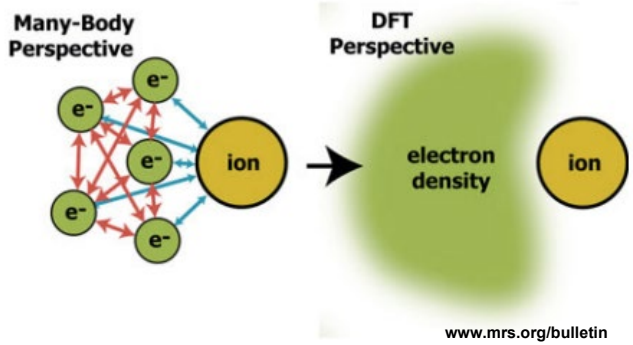
Experimental Results – 300ppm LSV Activation Energies



DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Theoretical Approach to Research Problem

Atomistic Modeling and Simulation



Density Functional Theory in Catalysis

- Atomic structures and surfaces
- Active sites and chemical states
- Adsorption and diffusion
- Electronic structure and distribution

Density Functional Theory Literature Ni/YSZ

- Adsorption of H_2S on nickel surfaces
- Two-step dissociative adsorption reaction
- Favorable reaction process

Density Functional Theory LSV Treatment

- VASP:DFT:GGA:PBEsol+U:520

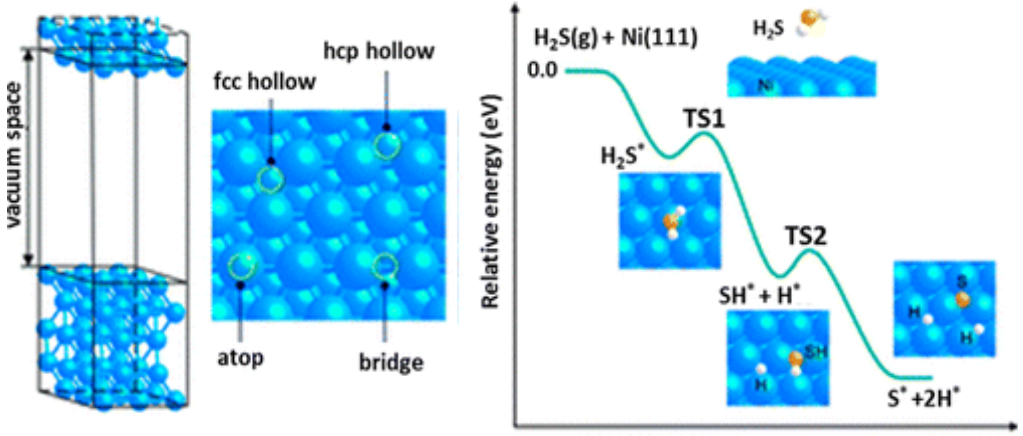


Table 3. Activation Barriers (E_a) and Reaction Energies (ΔE) for the Elementary Steps in a H_2S Dissociative Adsorption Process and Adsorption Energies (E_{ads}) of Sulfur Species (S*, HS*, and H_2S*)[a]

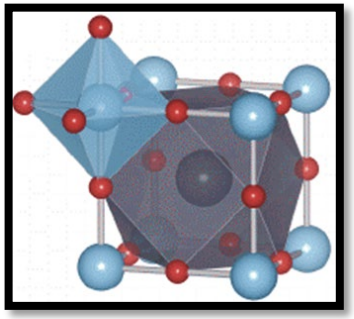
metal	E_{a1}[b]	ΔE_1[b]	E_{a2}[c]	ΔE_2[c]	E_{ads}S*	E_{ads}HS*	$E_{ads}H_2S$*
Pt(111)(93)	0.02	−0.90	0.04	−1.19	5.14	3.00	0.90
Pd(111)(94)	0.37	−1.25	0.04	−0.73	5.15	3.02	0.71
Rh(211)(95)	0.01	−1.50	0.32	−1.50	6.0	3.69	1.00
Ni(100)(88)	0.29	−1.56	0.45	−1.05	5.96	3.72	0.83
Ni(111)(88)	0.15	−0.98	0.11	−0.86	5.14	2.95	0.67

[a] All values in eV.
[b] E_{a1} and ΔE_1 correspond to $H_2S^* \rightarrow HS^* + H^*$.
[c] E_{a2} and ΔE_2 correspond to $HS^* \rightarrow H^* + S^*$.

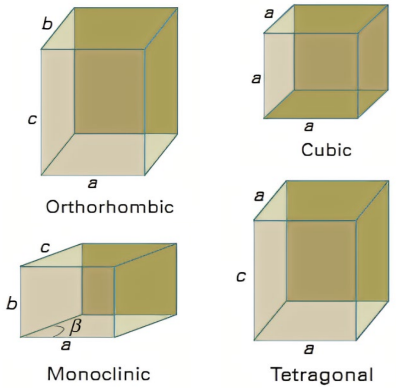
DOI:10.1021/acs.chemrev.6b00284

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Theoretical Details



DOI:10.1103/PhysRevB.89.134103



Lanthanum Vanadate ($LaVO_3$) - Reduced

- Orthorhombic: stable (Pnma)
  - a = 5.677 Å, b = 7.942 Å, c = 5.591 Å
  - α = 90.053°, β = 90.115°, γ = 90.003°
- Cubic: metastable ($Pm\bar{3}m$)
  - a = 3.950 Å, b = 3.950 Å, c = 3.950 Å
  - α = 90.000°, β = 90.000°, γ = 90.000°
  - Decomposes to orthorhombic

Lanthanum Orthovanadate ($LaVO_4$) - Oxidized

- Tetragonal: stable ($I4_1/amd$)
  - a = 6.268 Å, b = 6.268 Å, c = 6.268 Å
  - α = 106.091°, β = 106.091°, γ = 116.466°
- Monoclinic: metastable ($P2_1/c$)
  - a = 7.353 Å, b = 6.804 Å, c = 8.463 Å
  - α = 54.455°, β = 90.000°, γ = 90.000°
  - Decomposes to tetragonal

Lanthanum Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) - Mixed

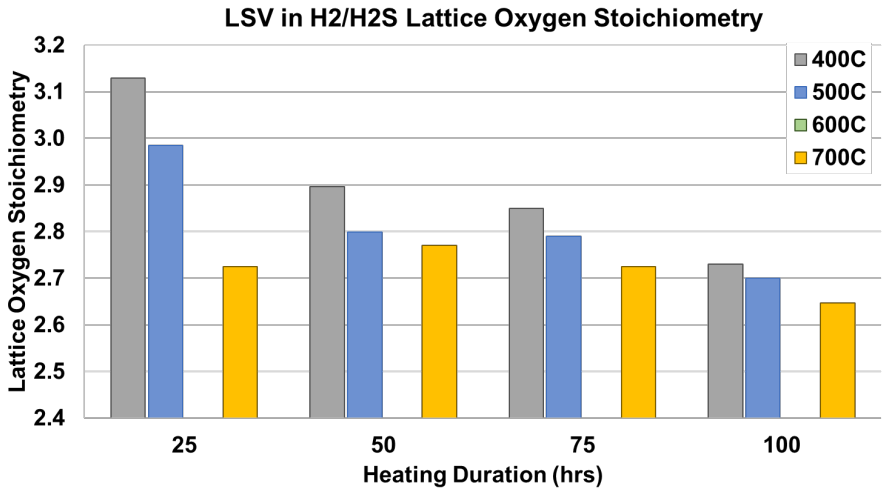
Hydrogen							
Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**		
600	30						
700	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**		
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
Methane							
Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**300**	**(1,2,0)**	**Monoclinic**	**(0,1,2)**	**Monoclinic**	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
Methanol							
Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30						
500	30						
600	30						
700	30						
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**

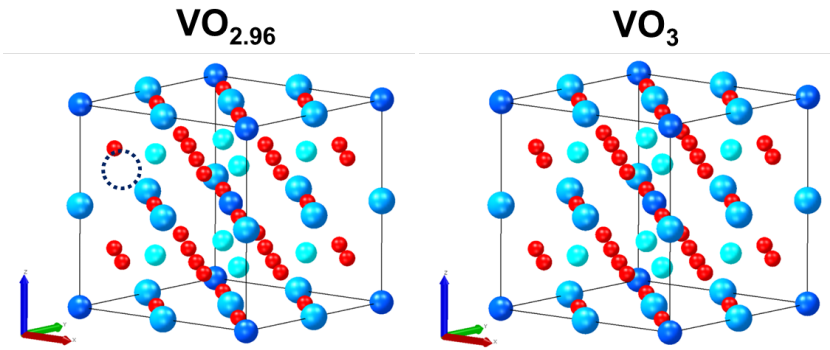
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Theoretical Details Cont.

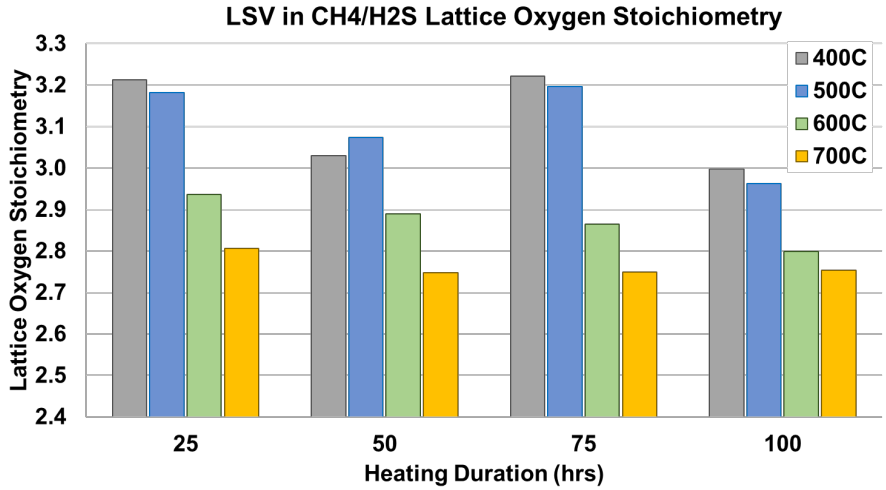
Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Mixed

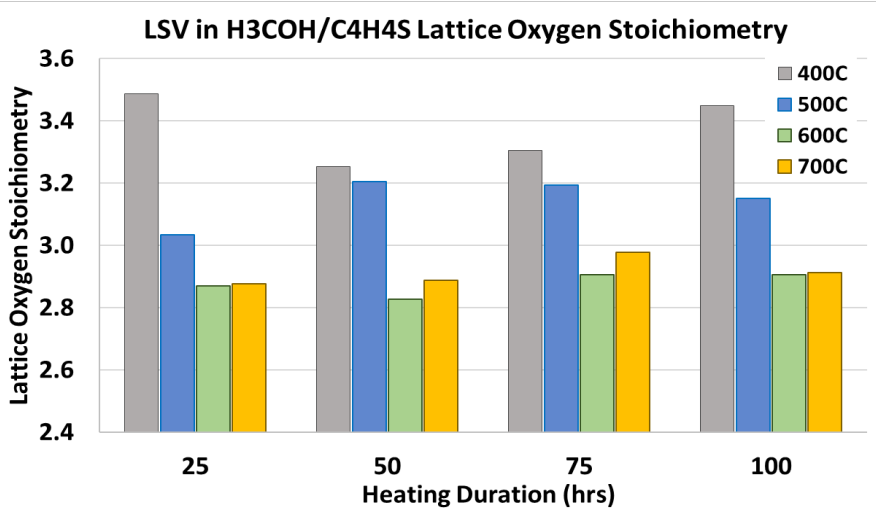
- Gas/temperature dependent oxygen stoichiometry
- Increased sulfur accumulation with increasing oxygen





- Monoclinic → Tetragonal → **Cubic**



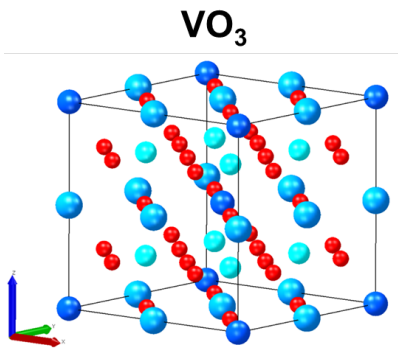


DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Theoretical Details Cont.

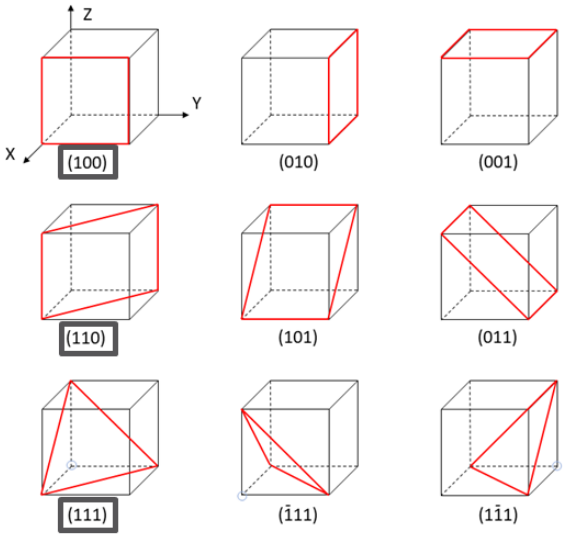
Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110}, {211} Facets

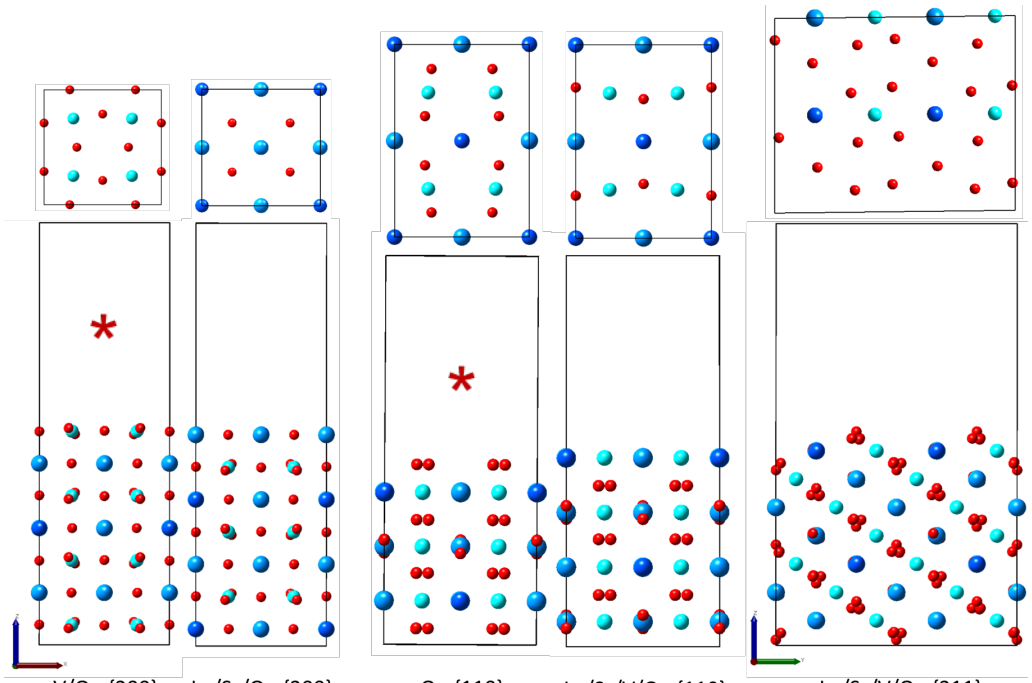
- Prominent cubic facets **{110}**, **{200}**, **{211}**

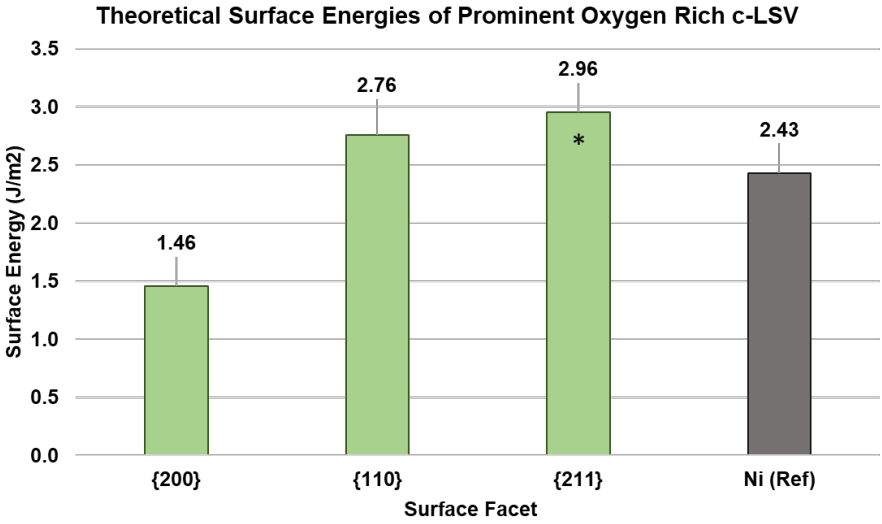


$$\sigma = \frac{E_{slab} - n(Ebulk)}{2A}$$

$$\sigma = \frac{E_{slab-V/O} + E_{slab-La/Sr/O}}{2}$$







DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

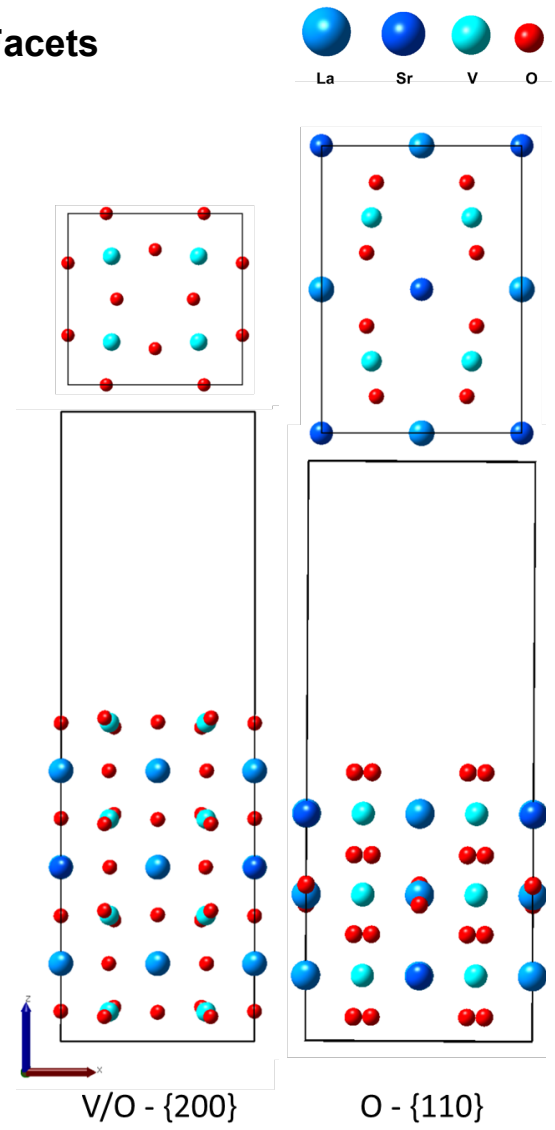
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	CH4*	CH3OH*
{200} V/O				
	Atop V	-0.45	-0.18	-0.83
	Atop O	-0.43	-0.02	-0.11
	Hollow	0.03	-0.03	-0.09
	Average	**-0.28**	**-0.08**	**-0.34**
{110} La/Sr/V/O				
	Atop La	-1.27	-1.15	-1.80
	Atop Sr	-1.16	-1.12	-1.67
	Bridge O	-0.83	-1.05	-1.63
	Hollow	-1.12	-1.07	-1.66
	Average	**-1.10**	**-1.10**	**-1.69**



DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

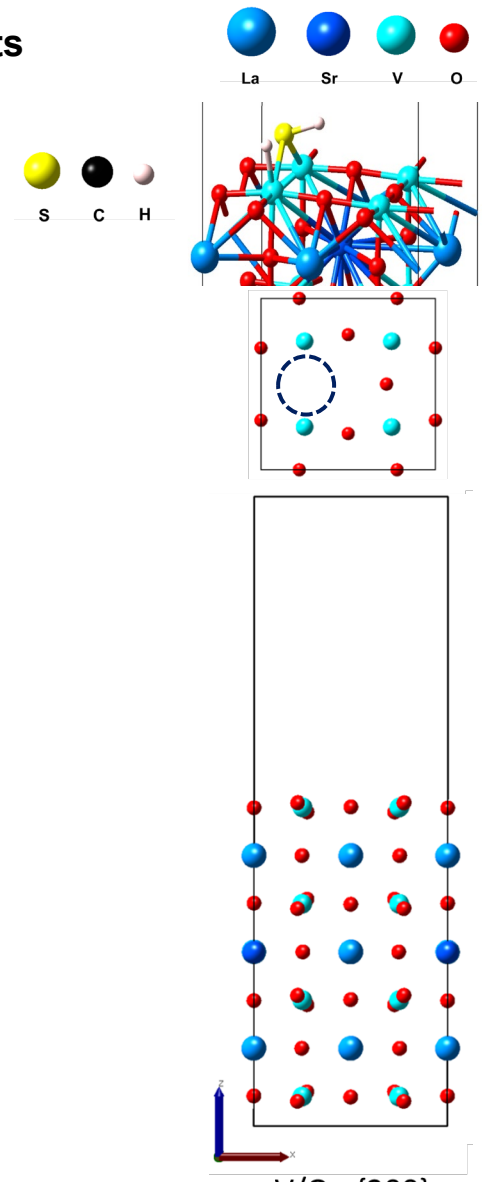
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	HS*, H*	H*, S*, H*
{200} V/O				
	Atop V	-0.46		
	Atop O	-0.43		
	Atop V_O		-1.70	
	Hollow	0.01		
Termination	**Ads Site**	**CH4***	**H3C*, H***	**CH2*, H*, H***
{200} V/O				
	Atop V	-0.23		
	Atop O	-0.03		
	Atop V_O	-0.46		
	Hollow	-0.04		
Termination	**Ads Site**	**H3COH***	**H3CO*, H***	**H2C*, H*, O***
{200} V/O				
	Atop V	-0.85		
	Atop O*	-0.87		
	Atop V_O	-1.09		
	Hollow	-0.02		



V/O - {200}

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

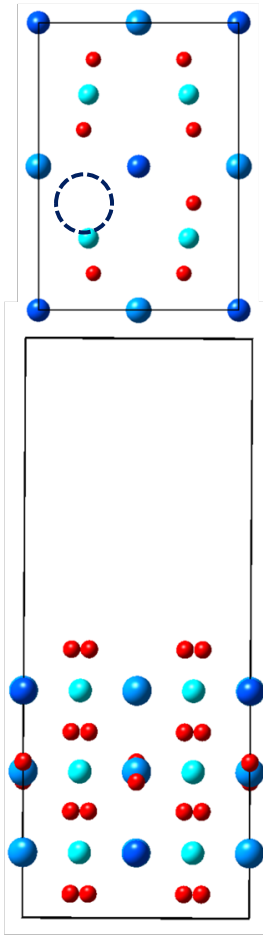
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	HS*, H*	H*, S*, H*
{110} La/Sr/V/O				
	Hollow La	-0.30		
	Hollow Sr	-0.17		
	Bridge O	-0.20		
	Atop V_O	-0.45		
Termination	**Ads Site**	**CH4***	**H3C*, H***	**CH2*, H*, H***
{110} La/Sr/V/O				
	Hollow La	-0.12		
	Hollow Sr	-0.17		
	Bridge O	-0.06		
	Atop V_O	-0.18		
Termination	**Ads Site**	**H3COH***	**H3CO*, H***	**H2C*, H*, O***
{110} La/Sr/V/O				
	Hollow La	-0.69		
	Hollow Sr	-0.90		
	Bridge O	-0.80		
	Atop V_O	-1.15		



O - {110}

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Theoretical Results

Lanthanum Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Mixed Cubic {200} H_2S Adsorption

- Higher surface energy with increasing oxygen deficit

$$E_f^O = E_{slab\text{-}O} - (E_{slab} + \mu_O)$$

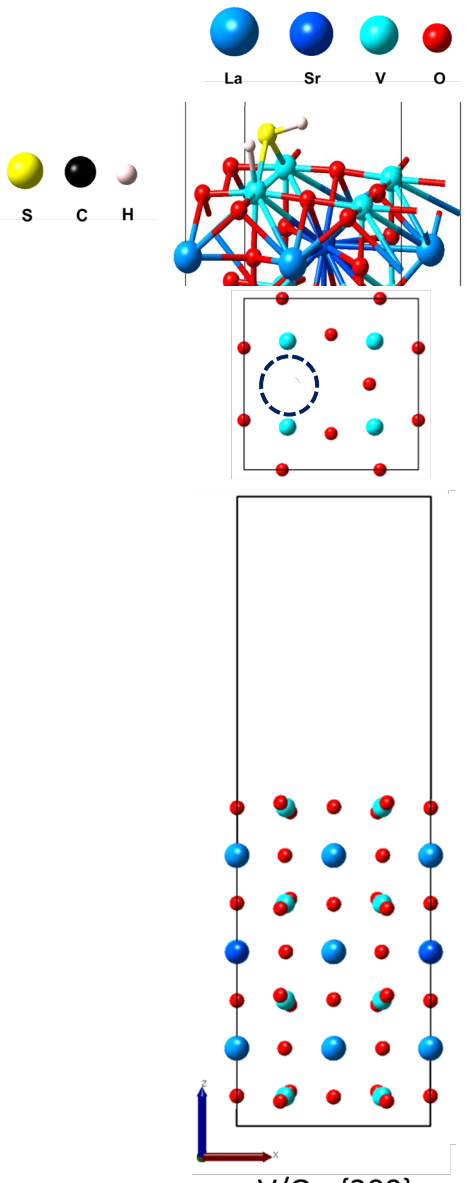
Surface Energy

Termination	Charge	σ (J/m²)	Avg. σ (J/m2)	E_f^O (eV/O atom)
{200} V/O	-7	-0.78	1.46	
	-5	0.62	2.16	5.52
	-3	1.94	2.82	4.95
	-1	3.30	3.50	5.23
	1	4.68	4.19	5.33
{200} Sr/La/O	0	3.70		

$$E_{ads} = E_{slab\,+\,molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Total Charge	Ads Site	H2S*	HS*, H*	H*, S*, H*
{200} V/O	-7	Atop V_O	-0.43		
	-5	Atop V_O		-1.70	
	-3	Atop V_O		-1.07	
	-1	Atop V_O		-1.06	
	1	Atop V_O		-1.06	



V/O - {200}

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Current Conclusions

Experimental Results Conclusions

1. LSV shows significantly improved sulfur tolerance, compared to Ni-YSZ, across multiple fuel types (gaseous or liquid).

2. Methanol shows the most promise.
    1. Thiophene not as reactive.
    2. Methanol limiting sulfur interactions with LSV.

3. Generally, sulfur tolerance is lower ≤600C.
    1. Cubic phase more sulfur tolerance. Occurs ≥600C.
    2. Methanol is an exception.

Modeling Results Conclusions

1. LSV adsorbs H2S, methane, and methanol through molecular adsorption on oxygen rich surfaces.

2. Slightly stronger adsorption of methanol than H2S, likely due to higher dielectric constant of methanol.

3. Oxygen rich LSV can adsorb H2S through barrierless one-step dissociative chemisorption, reacting with surface oxygen, leading to La/Sr-SH and V-OH bonds, in presence of oxygen vacancies.

4. LSV adsorbs H2S on oxygen deficient surfaces through molecular adsorption, as well as with barrierless one-step dissociative chemisorption, reacting with surface La/Sr, leading to La/Sr-SH and La/Sr-OH bonds in the presence of oxygen vacancies.

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

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

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Backup Slides

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

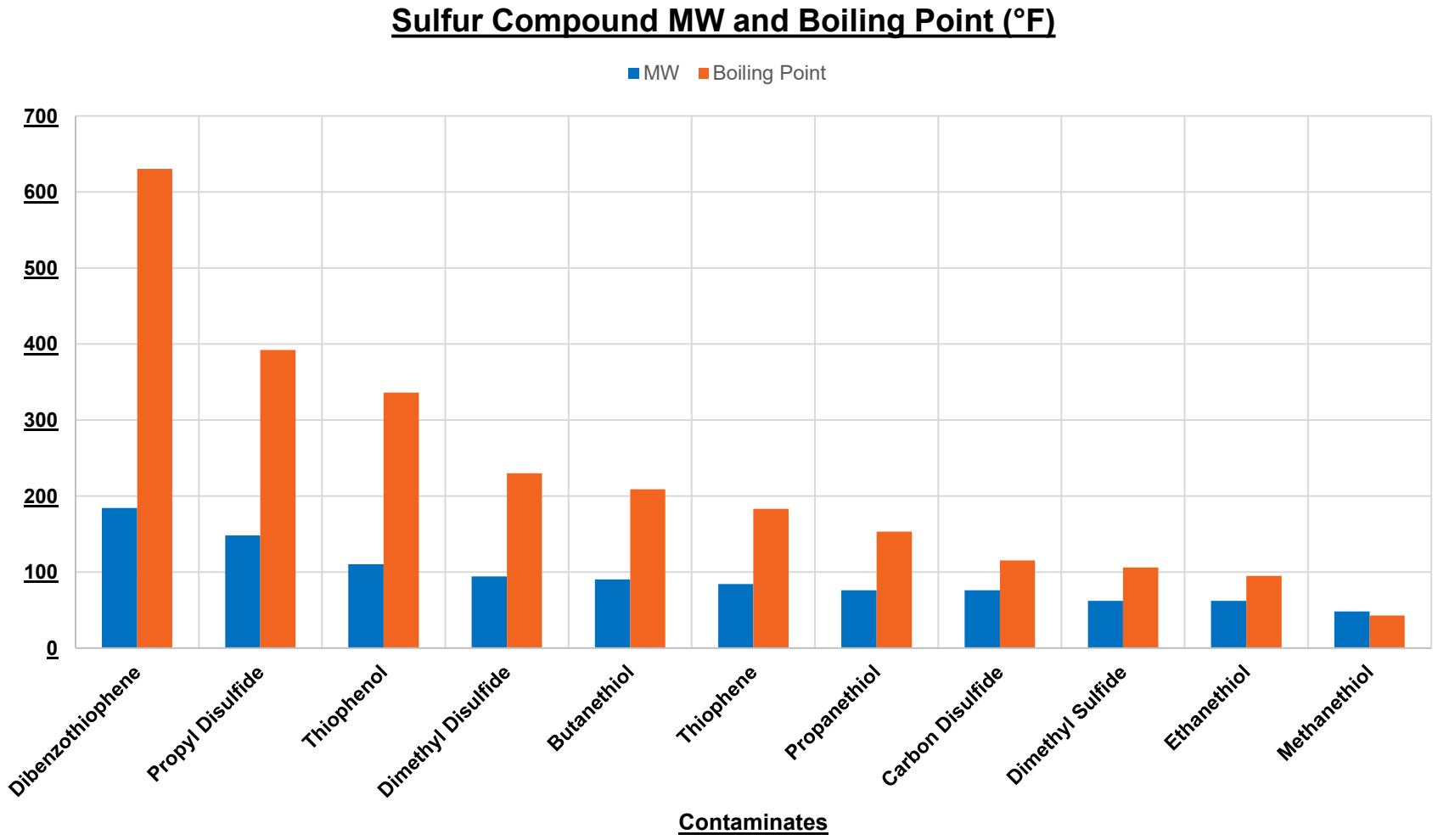
Contaminate Selection Parameters

Contaminate Name	Room Temperature Phase	Boiling Temperature (°F)	Decomposition Temperature (°F)
Methanol	Liquid	148.5	1202-1382
Dibenzothiophene	Solid	630.5	
Allyl Propyl Disulfide	Liquid	392	
Dimethyl Disulfide	Liquid	230	1150[2]
Butanethiol	Liquid	208.8	
Thiophene	Liquid	183	2060
Propanethiol	Liquid	153	
Carbon Disulfide	Liquid	115.23	>1832
Dimethyl Sulfide	Liquid	106	1470
Ethanethiol	Liquid	95	1340-1880
Hydrogen Sulfide	Gas	-75.19	
Methanethiol	Gas	42.71	1349-1524

Vasiliou, J. Phys. Chem. A, vol, 121, 7655-7666 Chevron Phillips, DMS Technical Data Sheet Proceedings of the Royal Society of London. Series A, vol. 147, 1934 Vasiliou, J. Phys. Chem. A, vol.121, 4953-4960, 2017

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

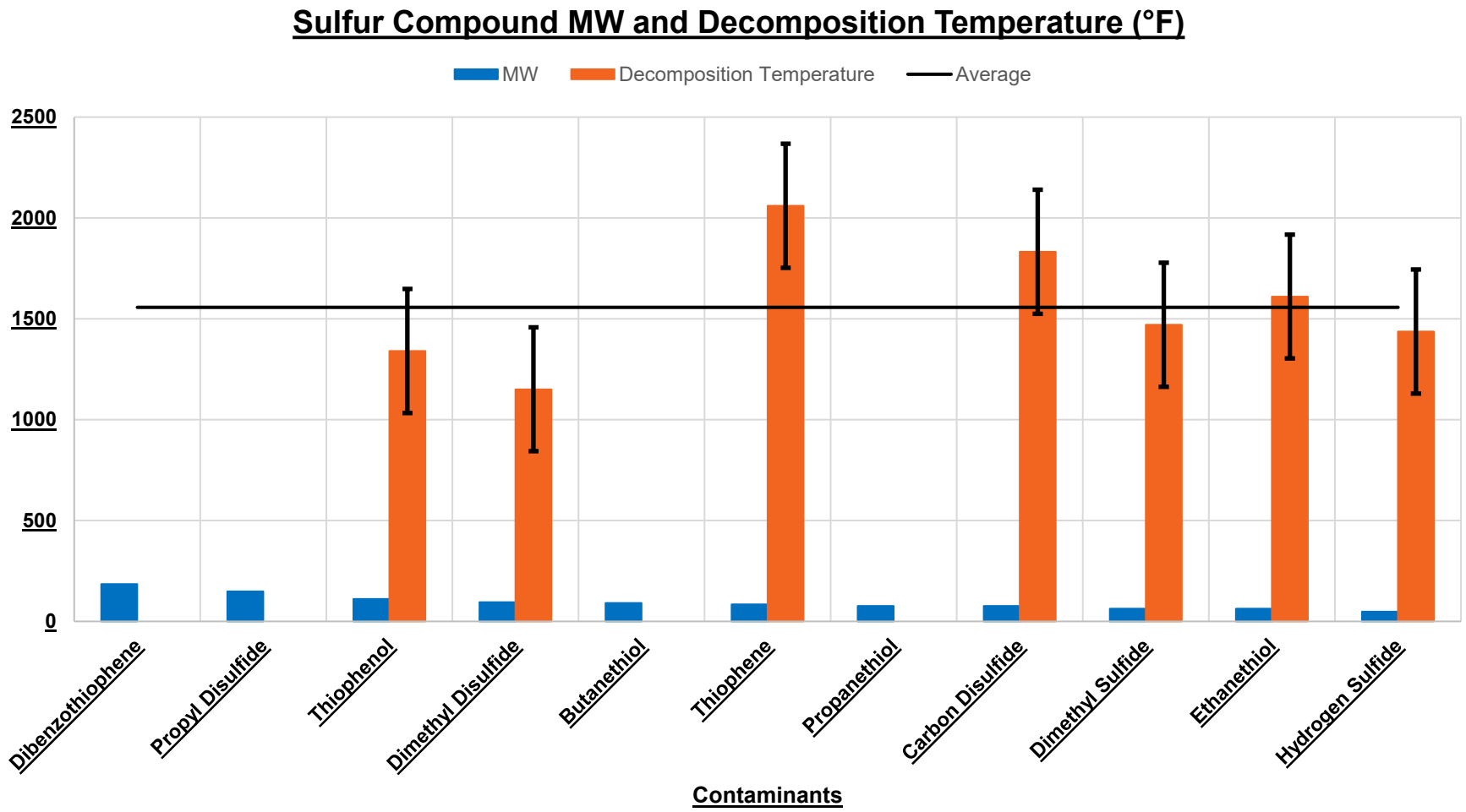
Contaminate Selection MW and Boiling Point Comparison



Vasiliou, J. Phys. Chem. A, vol, 121, 7655-7666 Chevron Phillips, DMS Technical Data Sheet Proceedings of the Royal Society of London. Series A, vol. 147, 1934 Vasiliou, J. Phys. Chem. A, vol.121, 4953-4960, 2017

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Contaminate Selection MW and Decomposition Temperature Comparison



Vasiliou, J. Phys. Chem. A, vol, 121, 7655-7666 Chevron Phillips, DMS Technical Data Sheet Proceedings of the Royal Society of London. Series A, vol. 147, 1934 Vasiliou, J. Phys. Chem. A, vol.121, 4953-4960, 2017

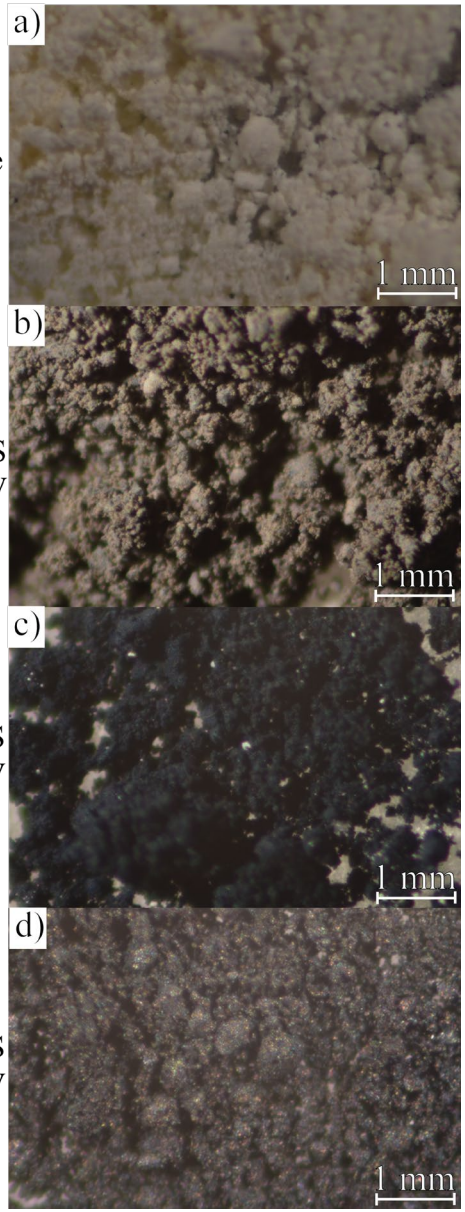
DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – Adsorption Rates 10vol% 700C

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

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

Brown/Yellow

Dark Blue

Black

V = +5

V = +5

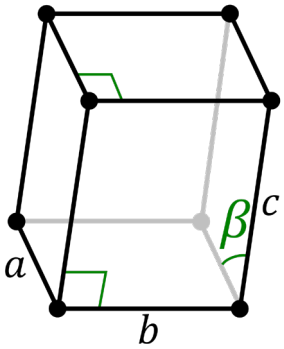
V = +4

V = +3

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – Crystal Structures

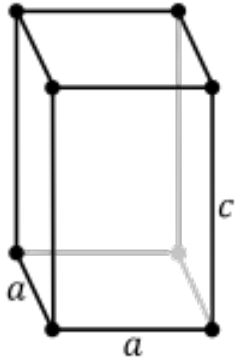
Monoclinic



a ≠ b ≠ c

α = γ = 90 ≠ β

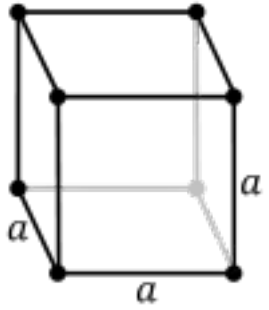
Tetragonal



a = b ≠ c

α = γ = β = 90

Cubic



a = b = c

α = γ = β = 90

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – Activation Energy Calculation

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

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

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

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

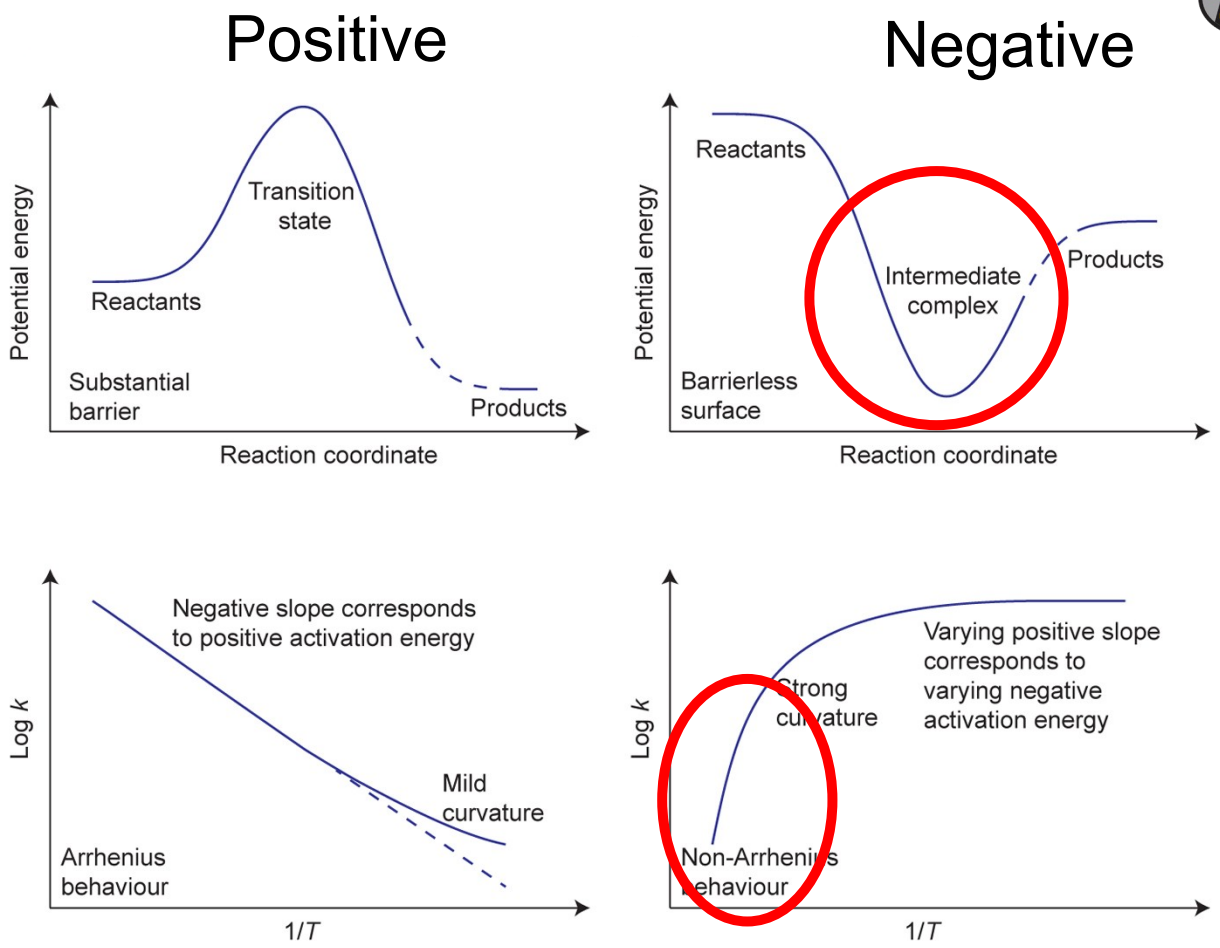
$$X_{H_2S} = H_2S\ Mol\ Fraction$$

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

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

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

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

DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546

Experimental Results – Activation Energy Calculation

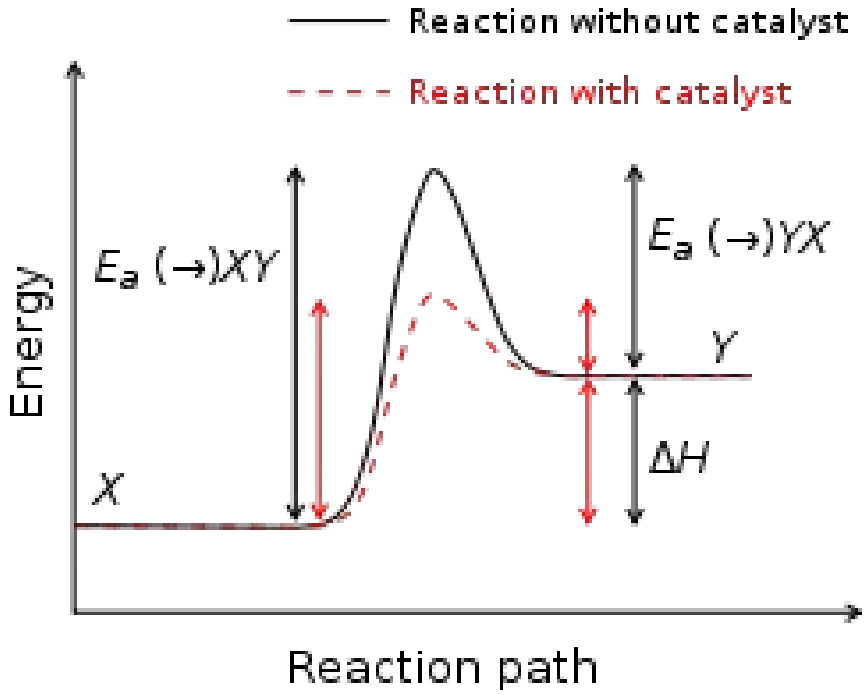
$$k = A * e^{\frac{-E_a}{R*T}} \rightarrow Ln(k) = \frac{-E_a}{R*T} + Ln(A)$$

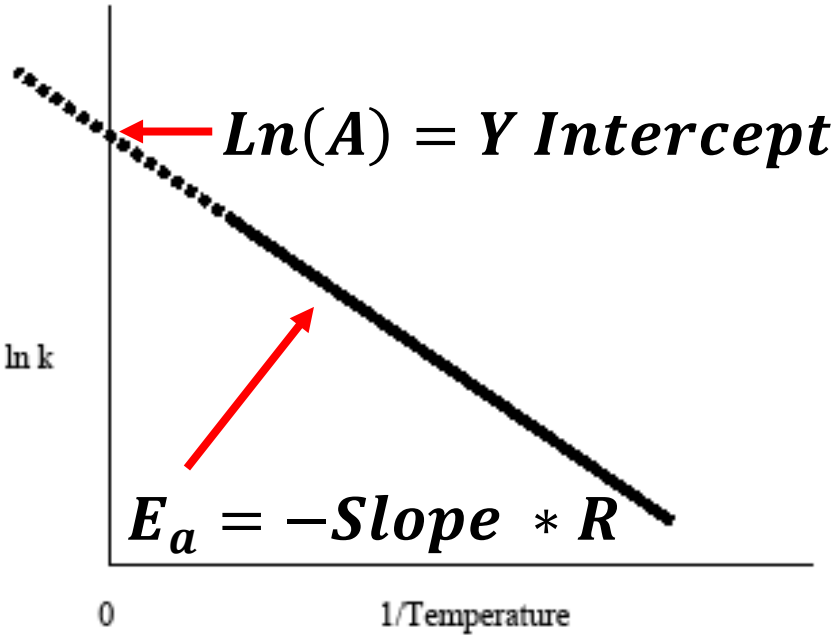
R = Ideal Gas Constant

T = Temperature

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

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





DISTRIBUTION A. Approved for Public Release; Distribution Unlimited. OPSEC #7546