Energy & Environmental Research Center (EERC)

Coal Syngas Cleanup for Commercially Viable SOFC Performance

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FY24 FECM Spring R&D Project Review

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

ACKNOWLEDGMENTS AND DOE DISCLAIMER

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PROJECT OBJECTIVES

- Design, configure, optimize, and demonstrate long-term operational viability of a syngas cleanup train.
- Produce coal syngas sufficiently clean to match SOFC performance using deodorized natural gas.
- Perform thermodynamic simulation and postmortem analysis to understand coal trace contaminant interaction with anode materials.
- Create multiphysics model to simulate SOFC performance and degradation with coal trace contaminants.
- Conduct a techno-economic analysis (TEA) of the integrated syngas production and cleanup system.

FUEL PRODUCTION AND CLEANUP TECHNOLOGY – FLOWCHART

Gasifier Options Include:
- Pressurized Fluid Bed (PFB)
- Entrained Flow
- Downdraft Fixed Bed

Coal
Steam/ Air or Oxygen
PFB Gasifier 1450 - 1750°F
Syngas Cleanup Train*
Syngas Dryer <450 °F
Syngas Compressor 3200 psig
Syngas Delivery Manifold < 200 psig
Syngas Storage Manifold 2800 psig
Syngas Gas Bottle Fill Station < 3300 psig
Syngas Storage Tanks 90 °F
Syngas Gas Bottle Drain Station < 3300 psig
Thermal Oxidizer 1800 - 2000 °F
Bypass
Natural Gas
NG Sulfur Capture Station 100 °F
Gas Delivery Manifold** < 200 psig
Gas Cylinders (N_2, H_2, CO, CO_2, CH_4) and Contaminants
SOFC Test Stands
Deltech Test Stand Up to four cells or stacks, up to 38 cm^2/cell
Horiba Test Stand Cell or stack, up to 100 cm^2/cell, up to 1kW total output
Fiaxell Test Stand Cell or stack, up to 100 cm^2/cell

Gasification and Reforming
Cleanup Technology
Storage
Fuel Delivery

*Syngas Cleanup Train
From Gasifiers
Particulate Filter 700 °F
CO Shift Reactor 650 °F
Regenerable Sulfur Removal 650 °F
Polishing Sulfur Removal 450 - 500 °F
Fixed Bed Trace Metal Removal 450 - 500 °F
Gas Cooling/ Quench for H_2O, H_2O Solubles, Tar Removal 60 - 70 °F
CO_2 Scrubber 50 - 60 °F
To Syngas Dryer
Bypass
Bypass
Bypass
Bypass

EERC SOFC Test Stands Integrated with Syngas Production, Cleanup, Storage, and Fuel Delivery System

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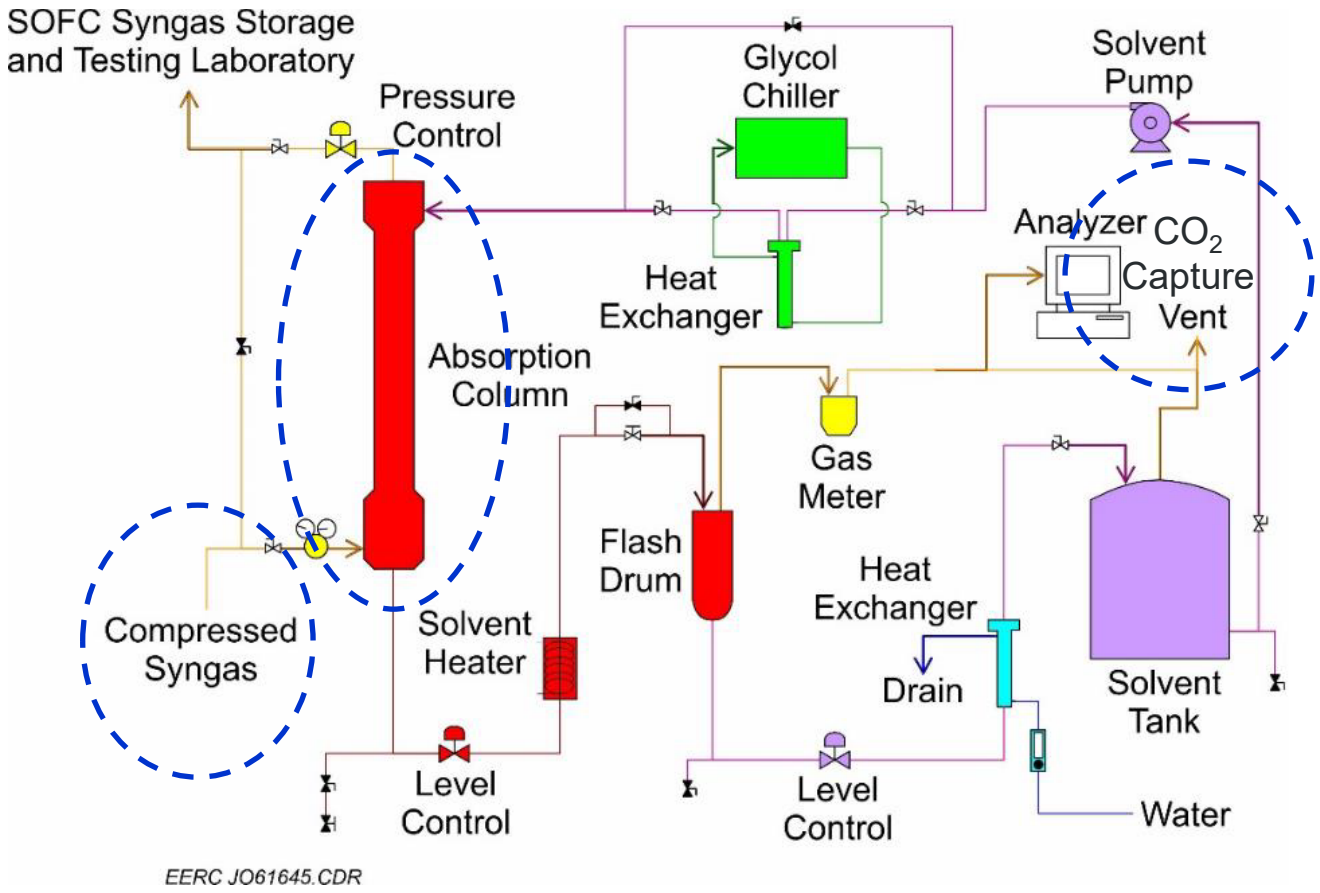
EERC GASIFICATION CAPABILITY – CARBON CAPTURE

- **Produce syngas to operate SOFC system with low CO_2 emission**

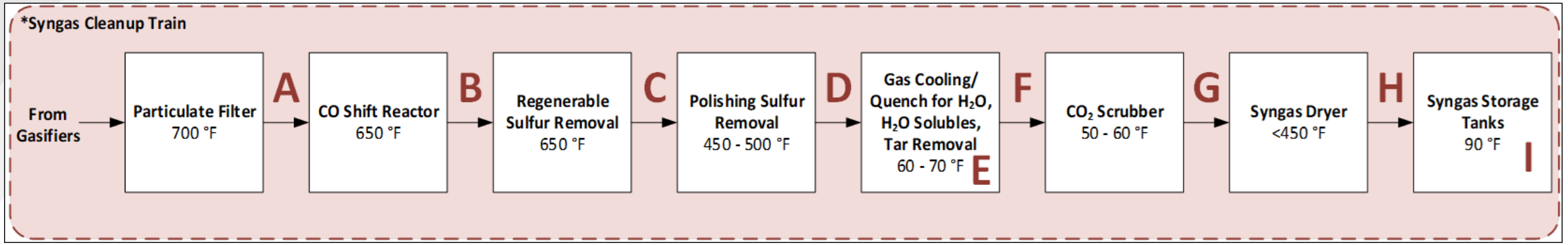
- 12-day PFB gasification run to generate and store coal-derived syngas
  - Produced approximately **17,000 scf/2000 psi** syngas
  - Stored syngas to be utilized for SOFC operation and testing

Syngas Gas Component	Mole Percent
Hydrogen	59.5
Carbon Dioxide	0.9
Ethane	0.0
Argon	0.4
Nitrogen	32.5
Methane	5.2
Carbon Monoxide	1.7



CO_2 Capture Sub-System

COAL SYNGAS CHARACTERIZATION

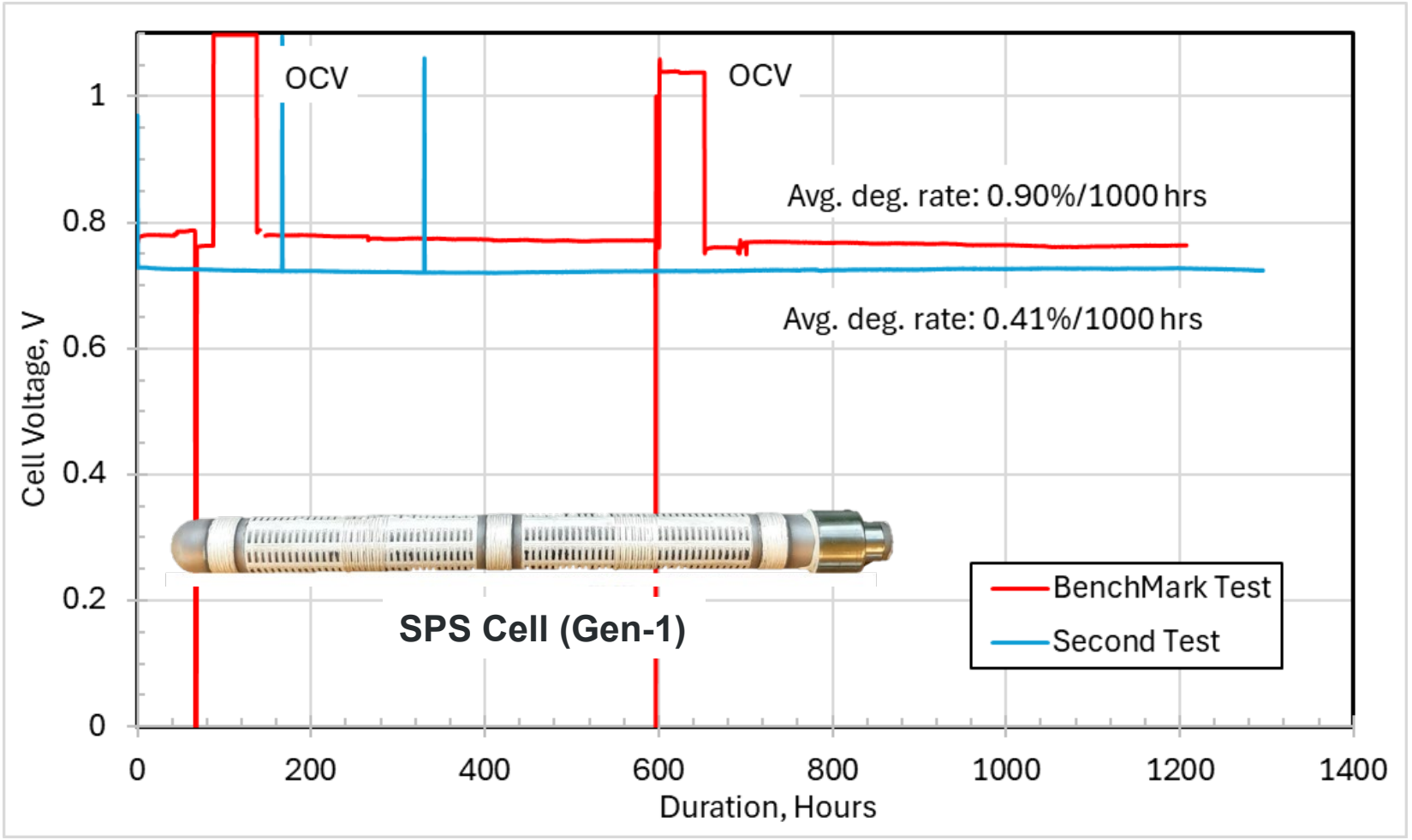


	Allowable Threshold	Detection limit, ppb	A	B	C	D	E	F	G	H	I
Ammonia	5,000 ppmv		< 2500 ppmv						< 50 ppmv		
Antimony	1,000 ppbv		< 5 ppbv							< 1 ppbv	
Arsenic	10 ppbv	1	< 5 ppbv							< 1 ppbv	
Arsine	10 ppbv	5	< 5 ppbv						< 5 ppbv		
Benzene	15 ppmv		< 850 ppmv					< 850 ppmv	< 200 ppmv	< 15 ppmv	
Cadmium	200 ppbv		< 1 ppbv						< 1 ppbv		
Carbon Disulfide	100 ppbv	150	< 150 ppbv						< 150 ppbv		
Hydrochloric Acid	100 ppbv	50	< 5 ppmv	< 50 ppbv					< 50 ppbv		
Hydrogen Sulfide	100 ppbv	10	< 6 ppmv		< 0.5 ppmv	< 10 ppbv			< 10 ppbv		
Mercaptans	100 ppbv	20	< 25 ppmv	< 5 ppmv	< 20 ppbv				< 20 ppbv		
Mercury	7 ppmv		< 2 ppmv				< 0.05 ppbv				
Nickel	5 ppbv		< 1500 ppmv				< 200 ppmv			< 0.1 ppbv	
Nickel tetracarbonyl	10 ppbv				< 160 ppbv				< 10 ppbv		
Phosphine	0.5 ppbv	0.5	< 10 ppbv			< 0.5 ppbv			< 0.5 ppbv		
Phosphorus	0.5 ppbv	30	< 0.2 ppmv							< 30 ppbv	
Silicon	30 ppbv		< 8 ppmv		< 6 ppmv		< 2 ppmv			< 0.1 ppmv	
Toluene	100 ppmv		< 2000 ppmv					< 1800 ppmv		< 10 ppmv	
Xylene	10 ppmv		< 3000 ppmv		< 2000 ppmv				< 2000 ppmv	< 100 ppmv	

Major Coal Contaminants, ppb level

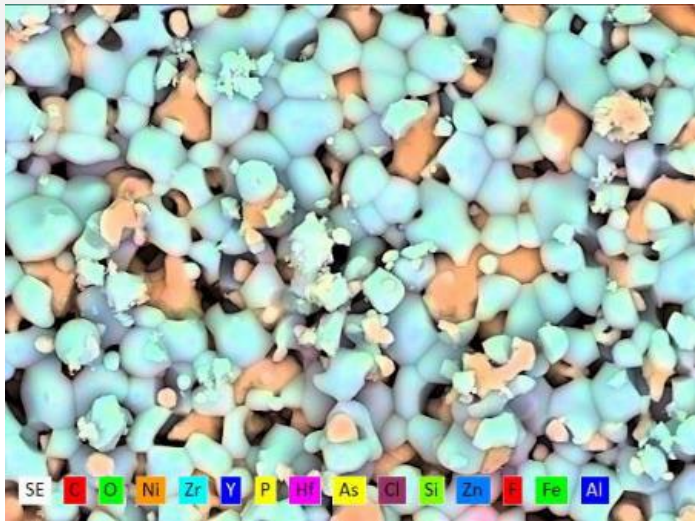
SOFC LONG-TERM DURABILITY TEST USING COAL-DERIVED SYNGAS

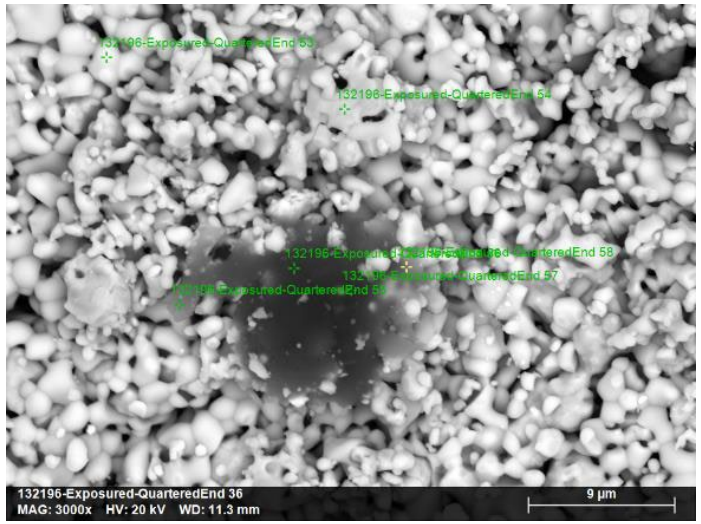
- Operation conditions
  - 750°C
  - 230 mA/cm^2
  - 40% - 75% fuel utilization
  - Voltage degradation rate is 0.41%/1000hrs for second test, which is comparable to that with natural gas fuel

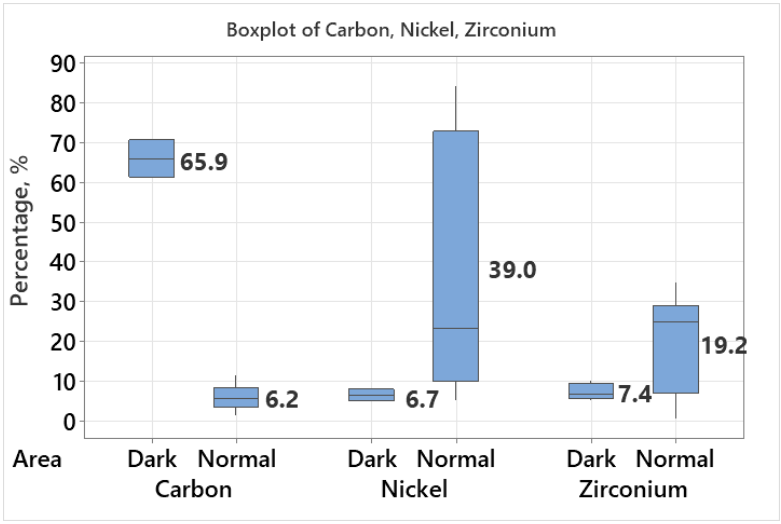


POST-MORTEM ANALYSIS OF SOFCS WITH COAL SYNGAS AND NATURAL GAS

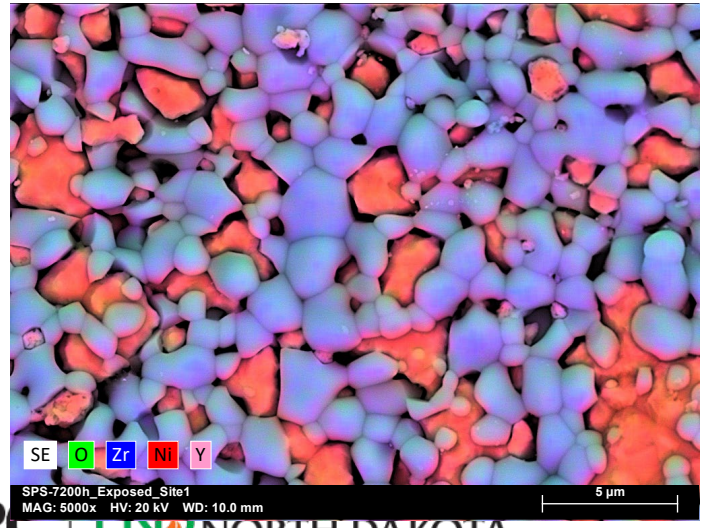
Syngas

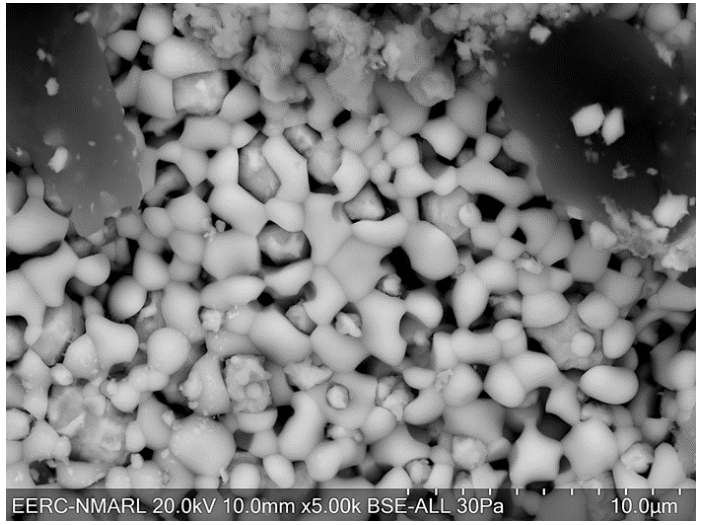


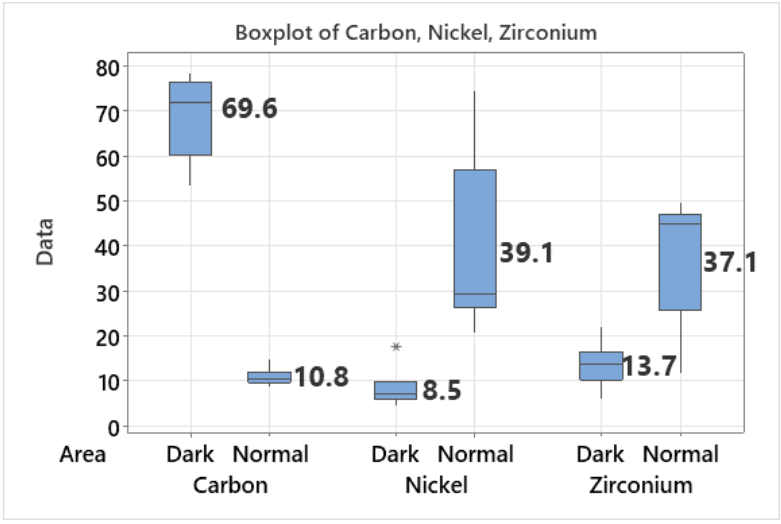




Natural Gas







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SOFC TEST MATRIX WITH COAL CONTAMINANTS

- Define “clean coal syngas” as fuel for SOFC system operation.
- Generate database for initial coal syngas specification
- Calibrated contaminants gas balanced by N_2
- Maintain syngas flow rate/concentration constant

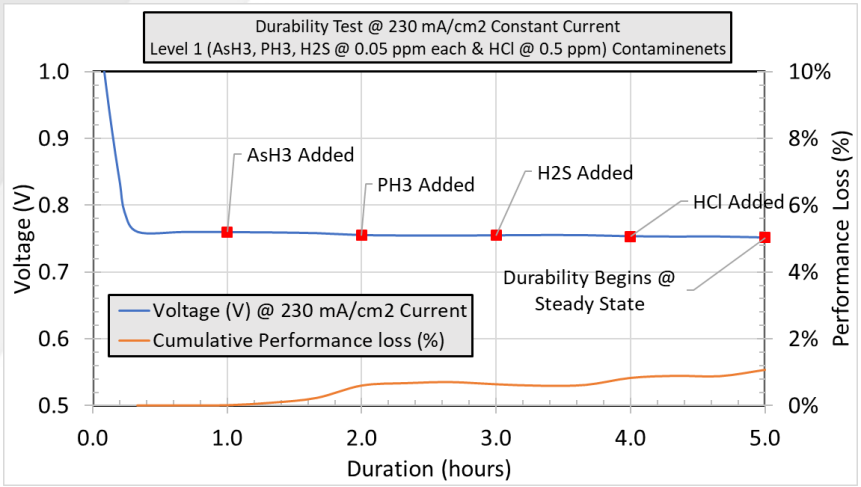
	Detection limit, ppb	Concentration, ppb/ppm
AsH_3	5	< 5 ppb
PH_3	0.5	< 0.5 ppb
H_2S	10	< 10 ppb
HCl	50	< 50 ppb

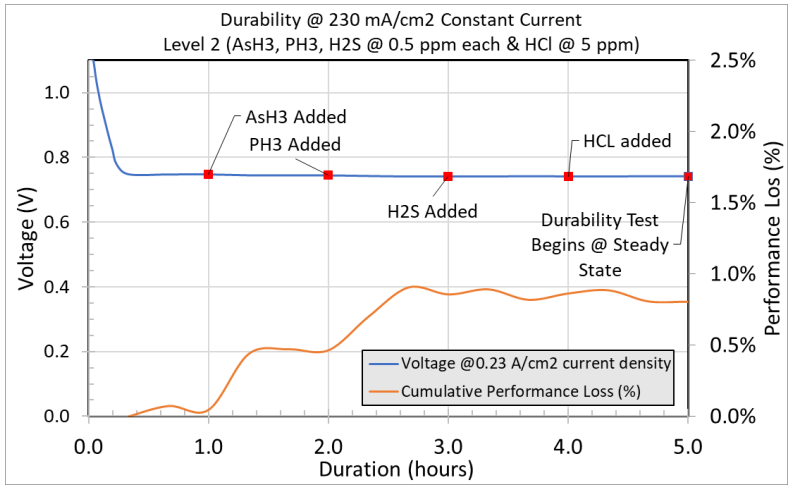
Selected coal contaminants for testing

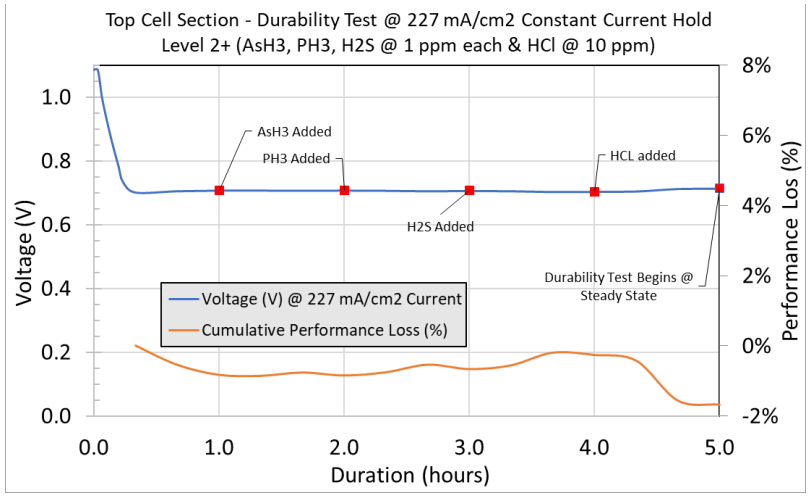
	AsH_3	PH_3	H_2S	HCl
Level 1 (ppm)	0.05	0.05	0.05	0.5
Level 2 (ppm)	0.5	0.5	0.5	5
Level 2+ (ppm)	1.0	1.0	1.0	10
Level 3 (ppm)	5.0	5.0	5.0	50

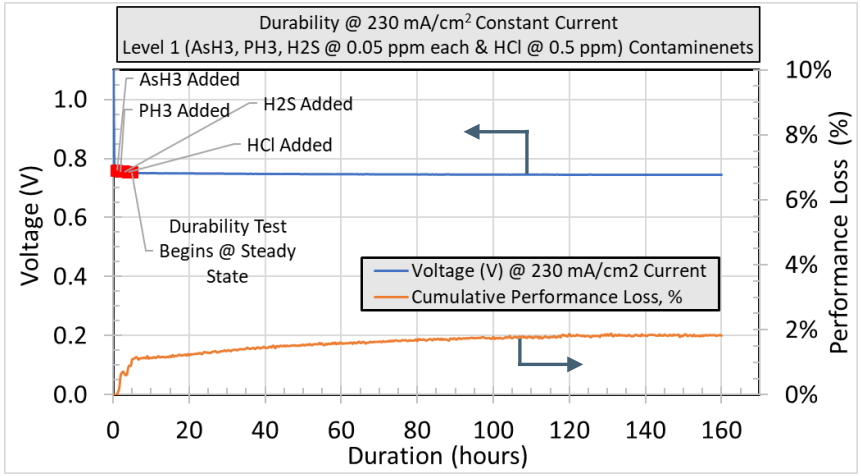
Test matrix

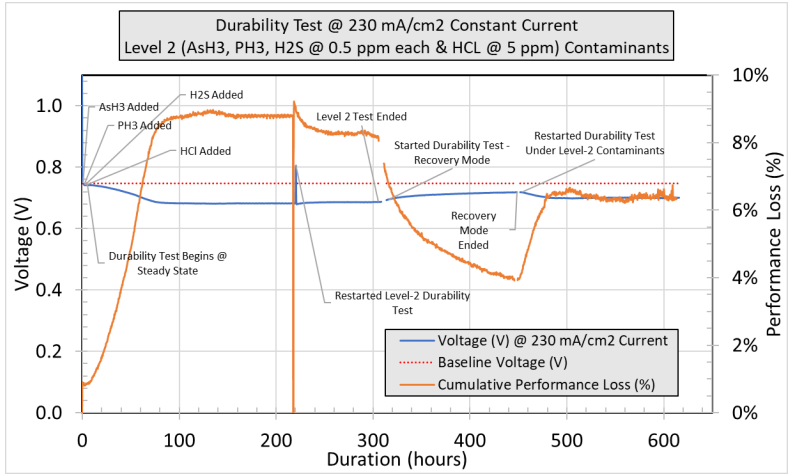
SOFC DURABILITY WITH COAL CONTAMINANTS

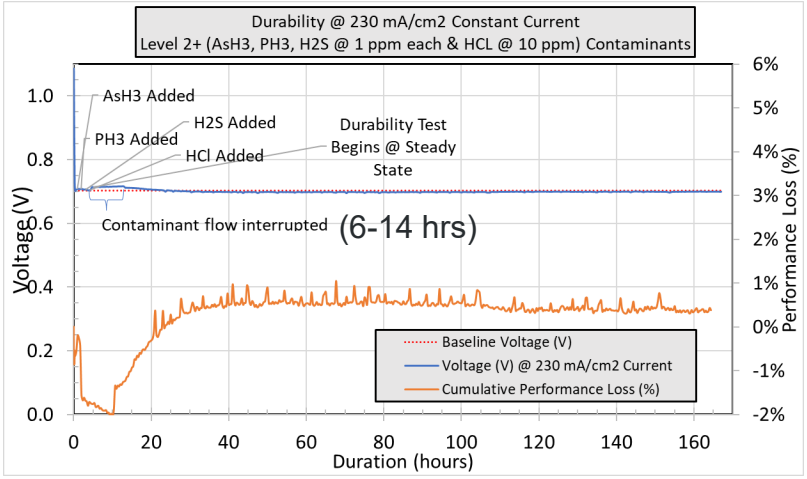












Level 1

Level 2

Level 2+

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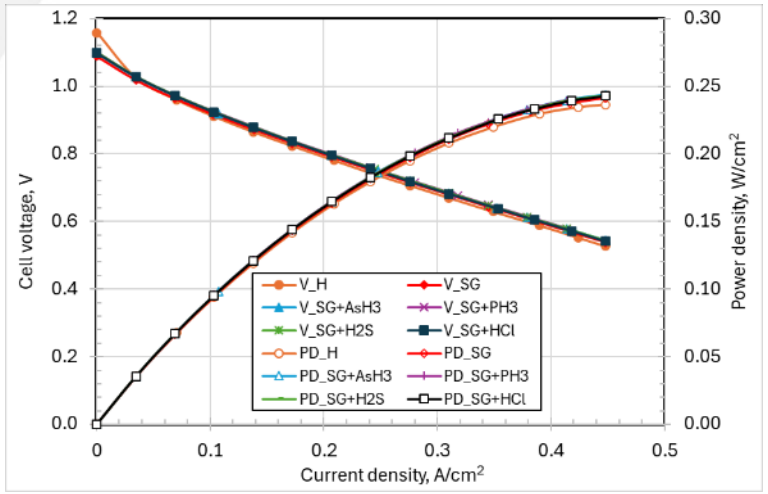
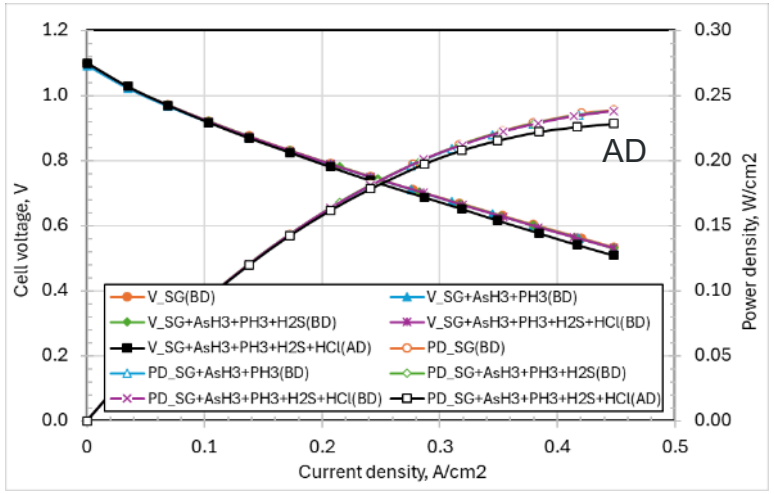
SOFC PERFORMANCE BEFORE AND AFTER DURABILITY

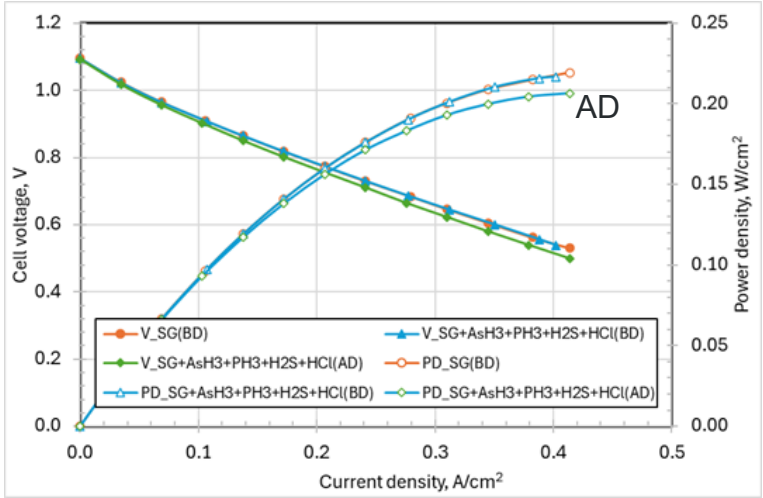
Single contaminant

Combined contaminant

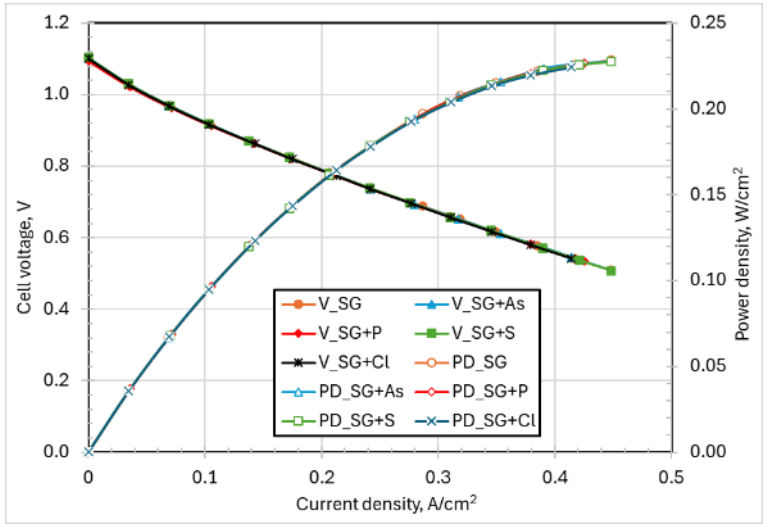
Level 1

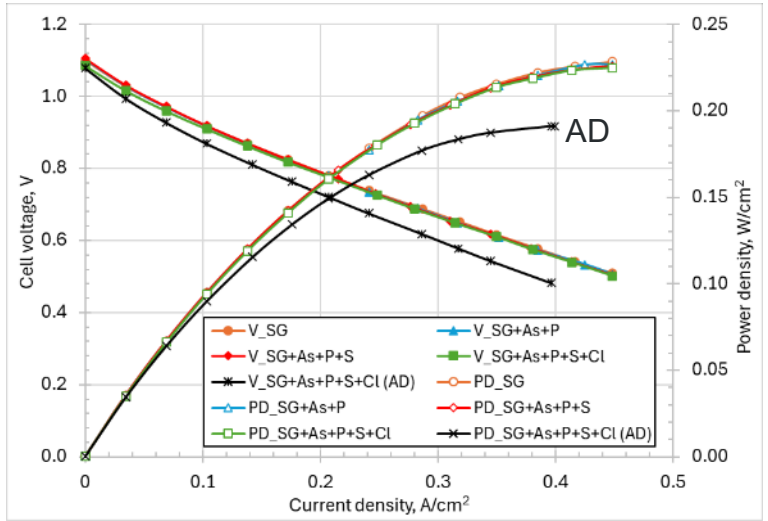


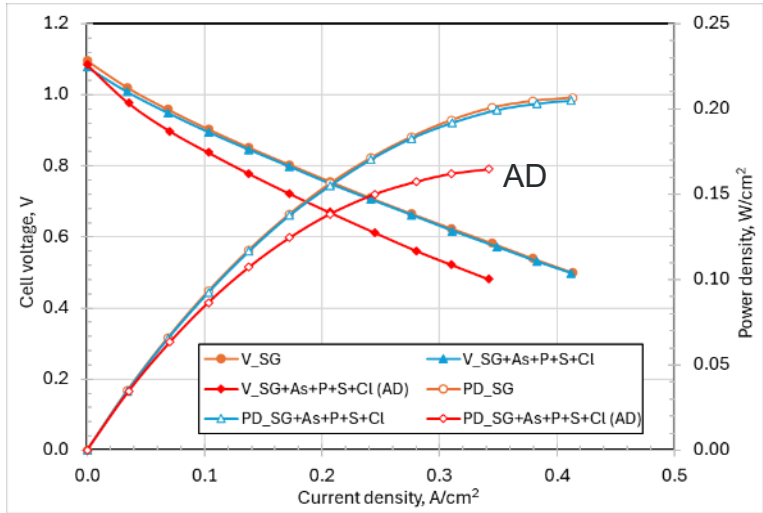




Level 2





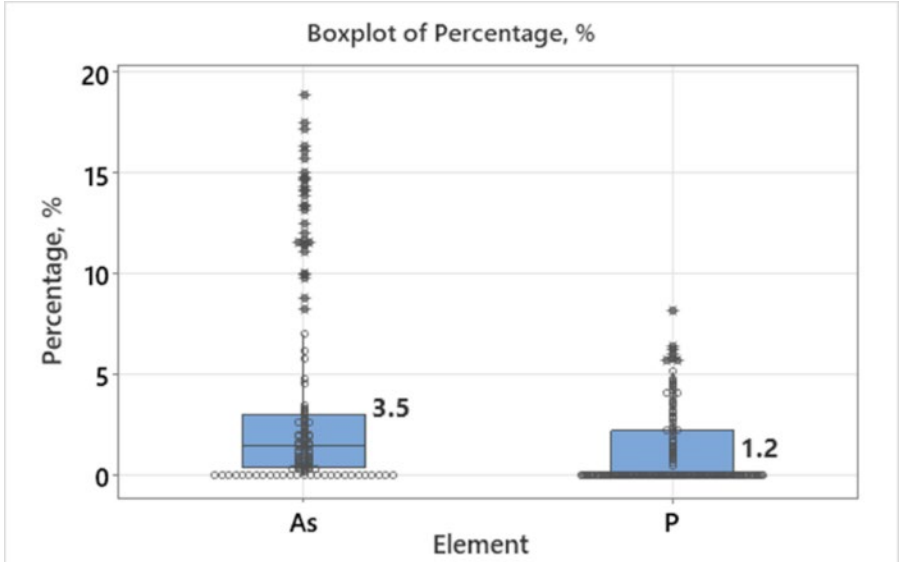


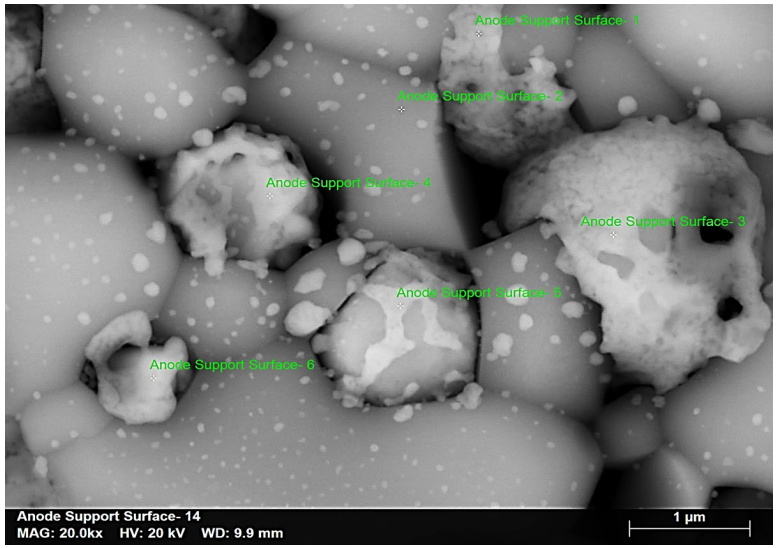
Top cell section

Bottom cell section

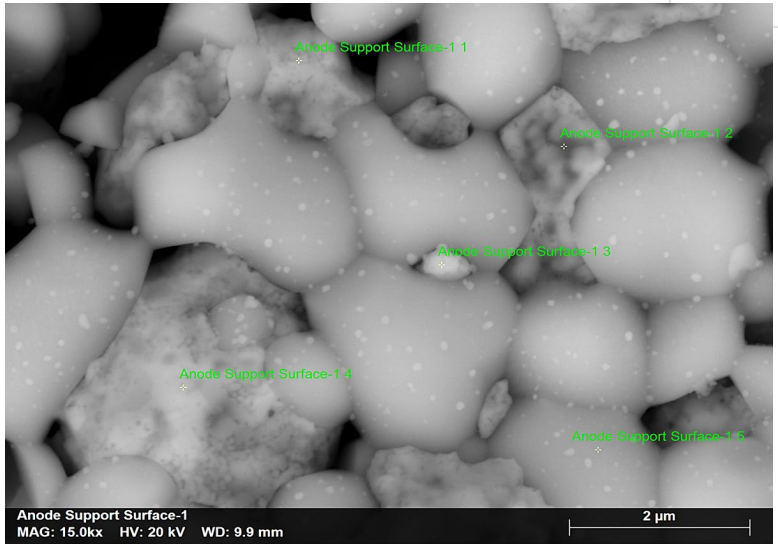
POST-MORTEM ANALYSIS AFTER CONTAMINANTS TESTING

- As and P deposited on anode support surface or pore space
- S and Cl were not detected by SEM/EDS on surface
- A “skin” was observed around Ni particle
- Statistical data analysis indicates more As deposition than P

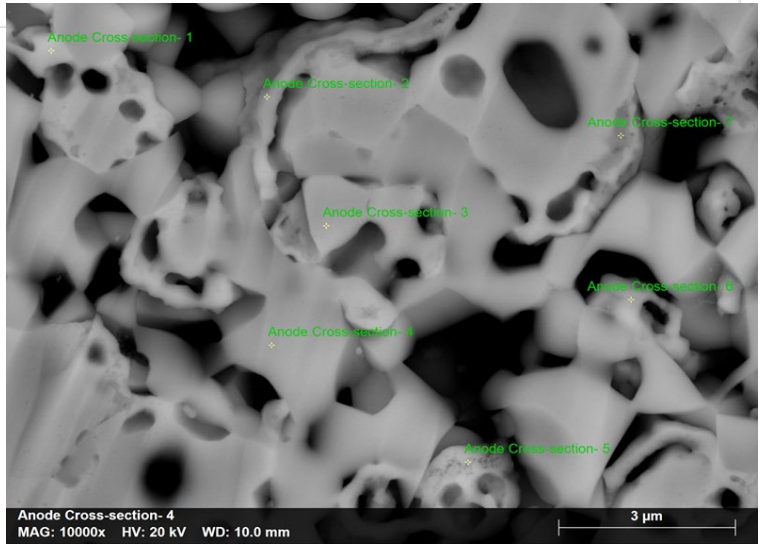




Rich in As

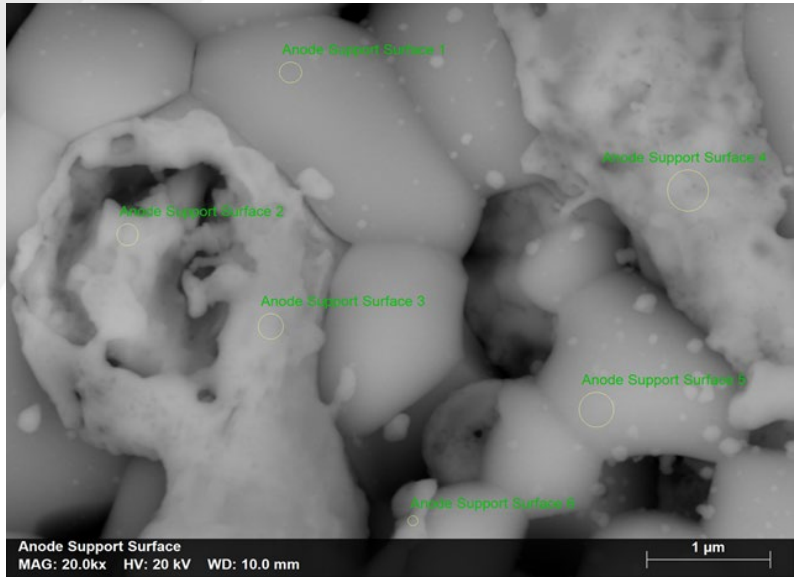


Rich in P

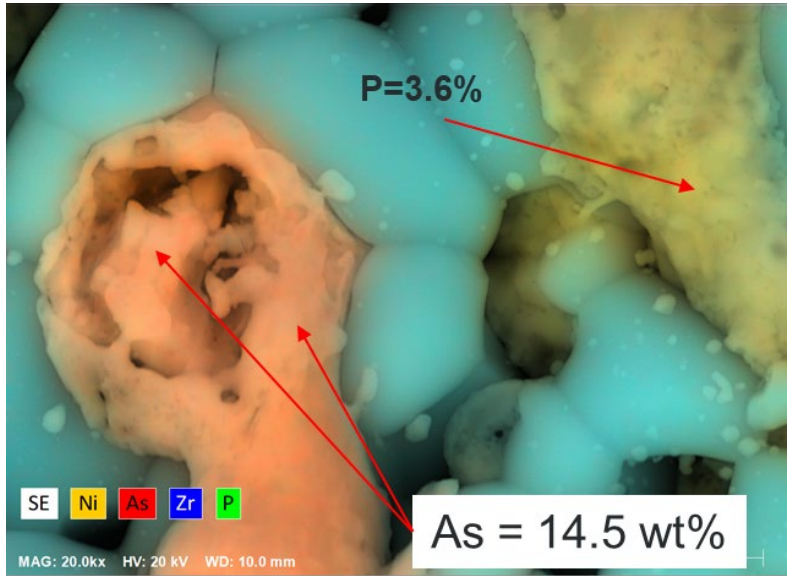


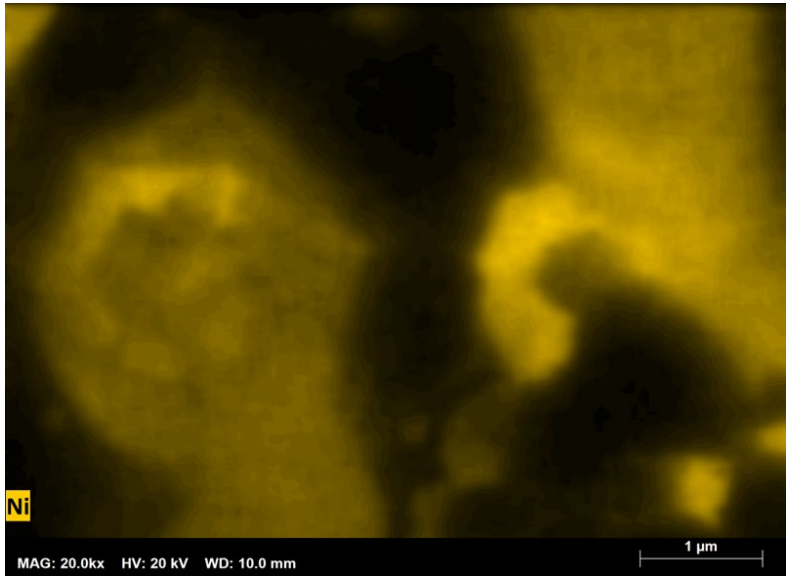
No contaminant identified by SEM/EDS

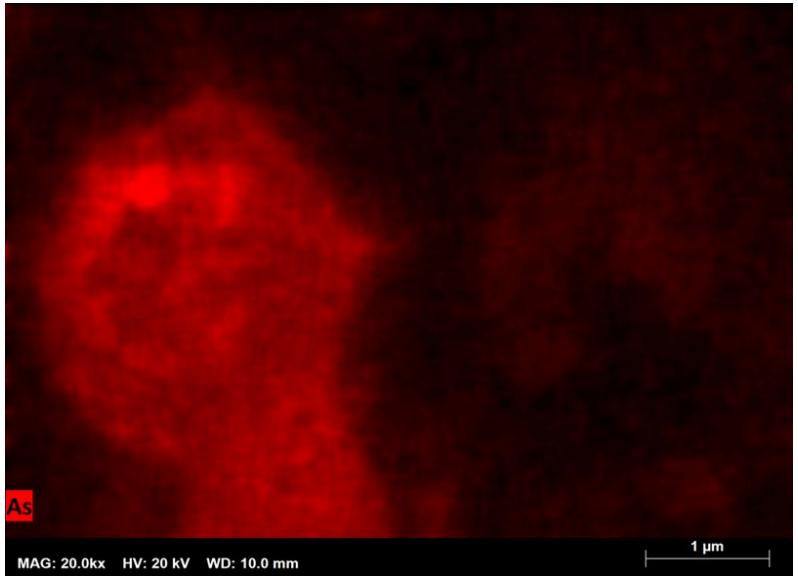
EDS ELEMENT MAPPING



- EDS element mapping indicates As and P deposited on Ni particles
- As and P intend to be deposited on separate Ni particle



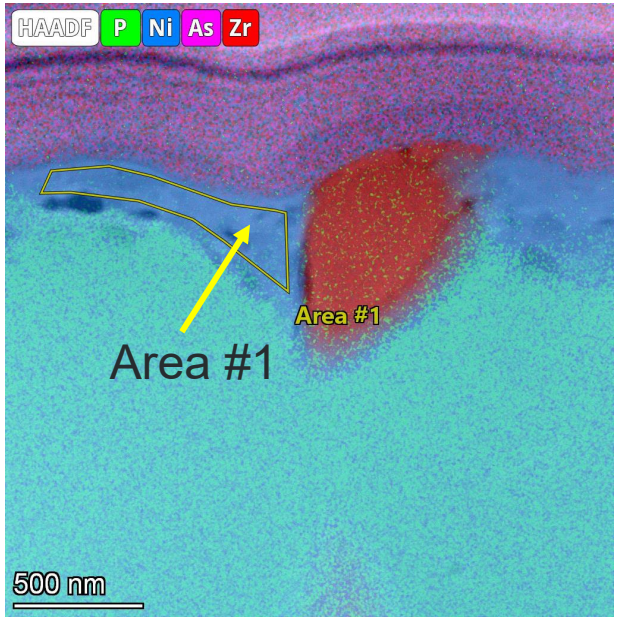


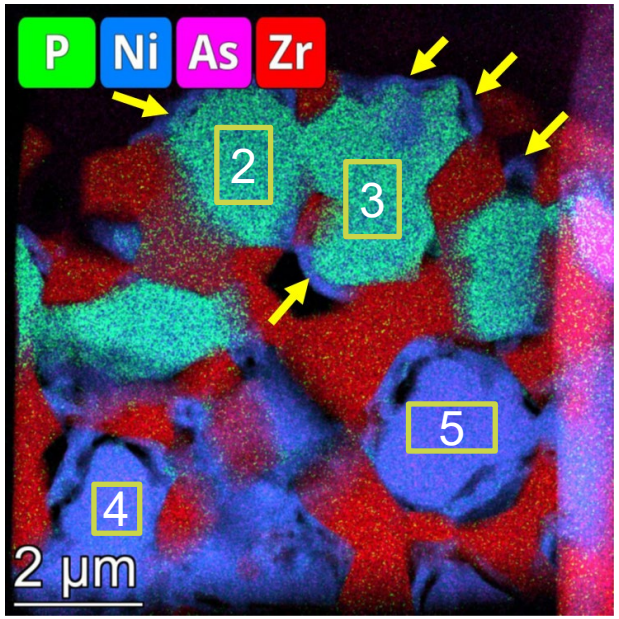


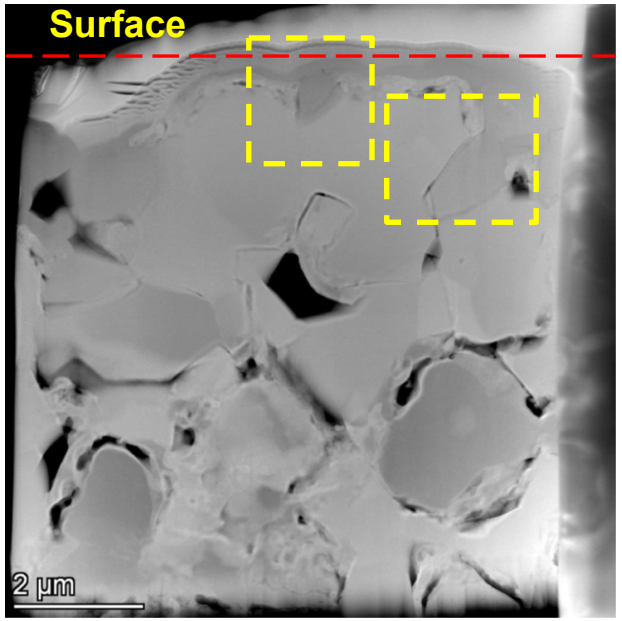
POST-MORTEM ANALYSIS – TEM/EDS

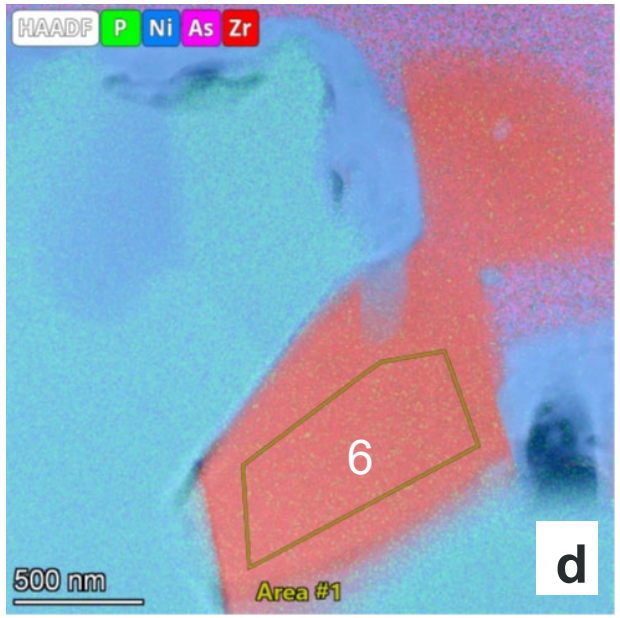
- The “skin” is Ni metal rich in As
- The Ni particles on anode support surface are rich in P
- Ni particles away from the surface are rich in As
- Ni and As were also detected in YSZ phase

	EDS Analysis, at%					
	P	Ni	Cu	As	Y	Zr
Area 1	0	87.5	0.0	**2.3**	0.3	0.5
Area 2	**13.1**	74.2	8.3	0.9	0.4	0.4
Area 3	**13.6**	81.0	0.0	0.9	0.6	0.7
Area 4	0.2	93.4	0.0	**2.8**	0.9	0.8
Area 5	0.0	92.9	0.0	**3.0**	0.9	1.0
Area 6	0.0	4.1	0.0	0.5	13.5	81.9



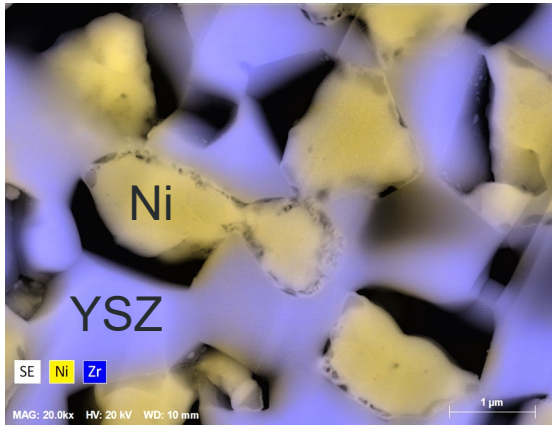




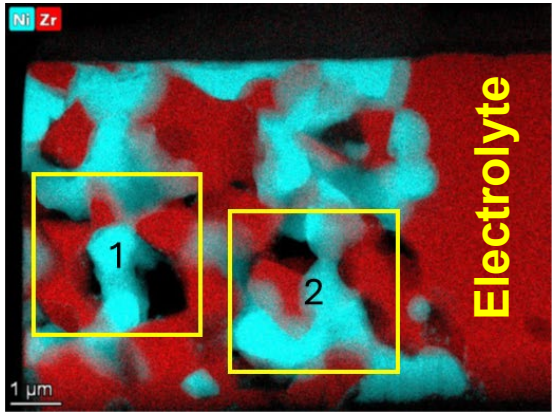


POST-MORTEM ANALYSIS OF ACTIVE ANODE – TEM/EDS

- P, S, and Cl were not detected in active anode
- Possible As present (0.1 – 0.3 at%)
- Interaction at Ni/YSZ interface was identified in both TEM and SEM images.

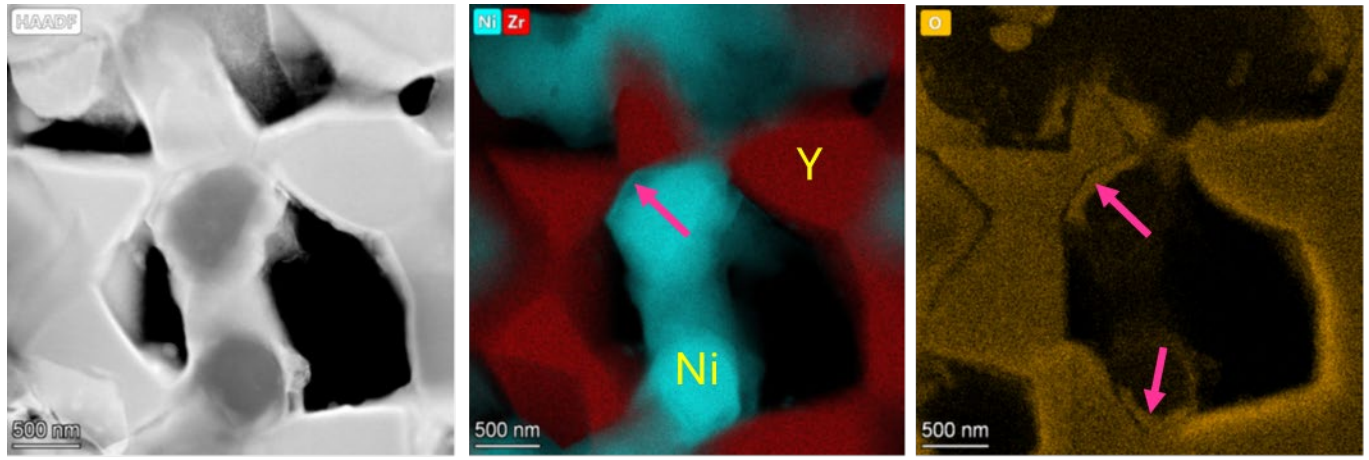


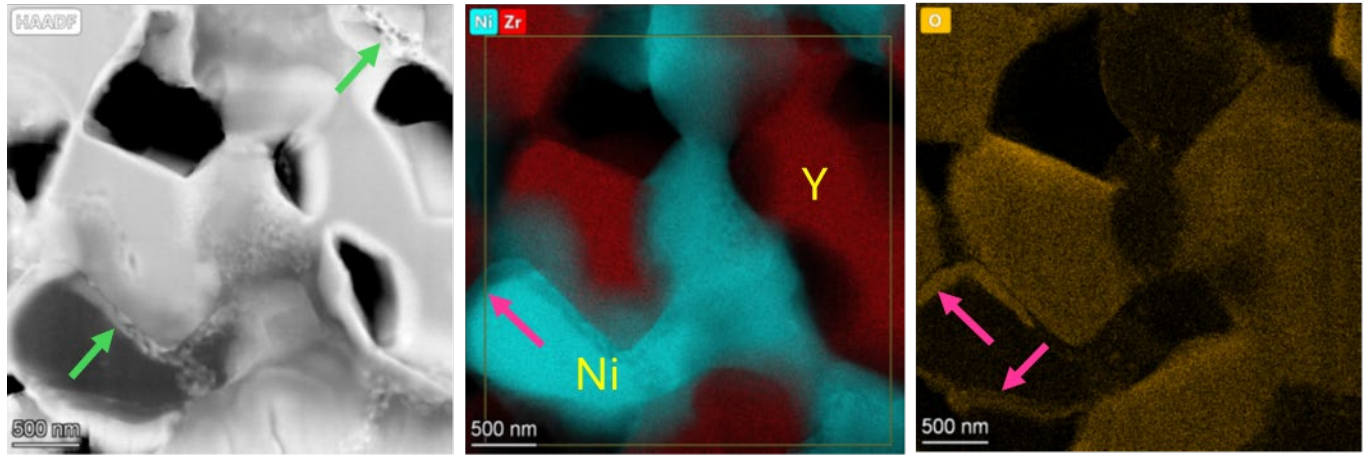
Active anode (SEM)



Ni & Zr mapping (TEM)

Yellow box 1

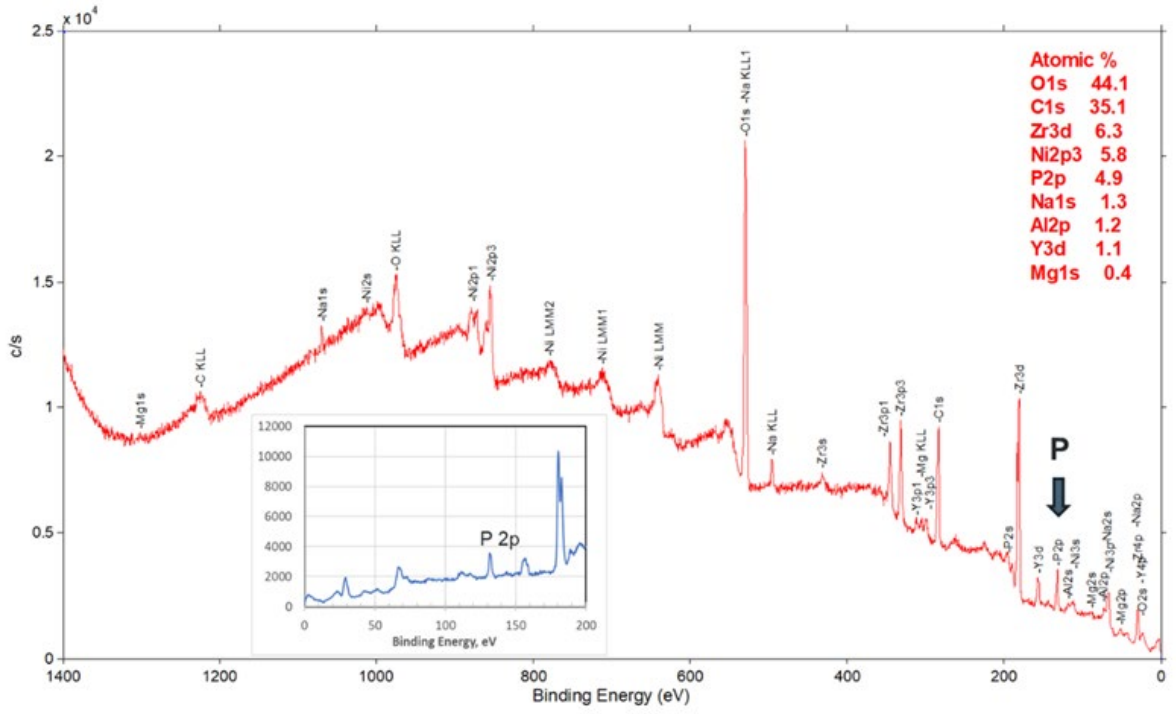




Yellow box 2

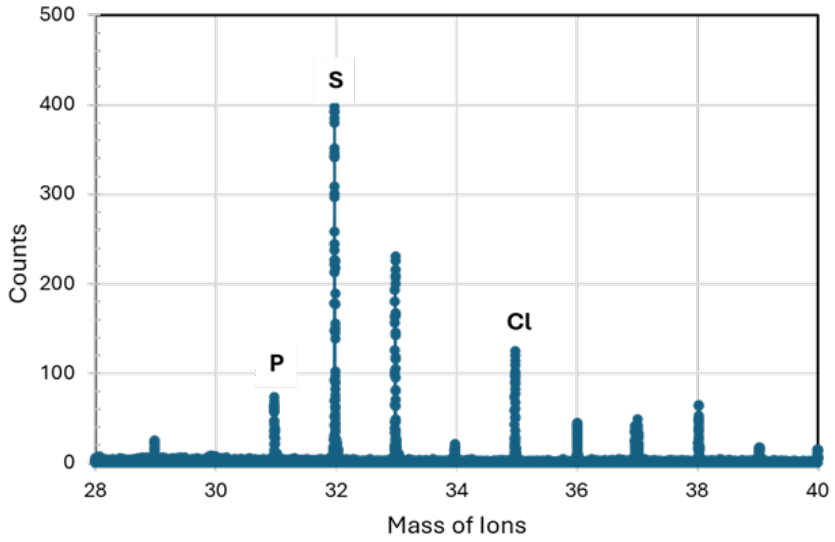
SURFACE ANALYSIS – XPS AND TOF-SIMS

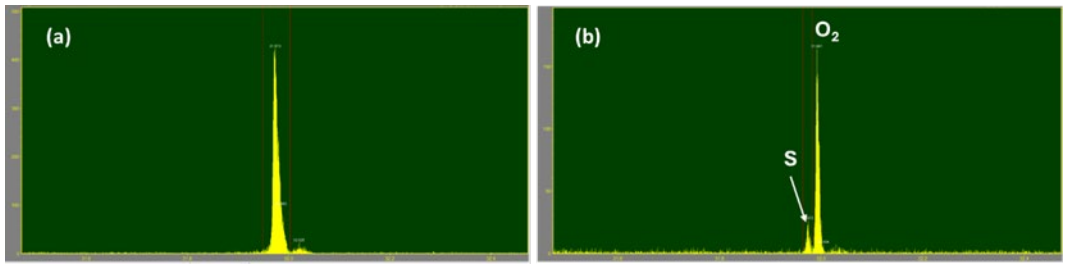
- Only P was detected by XPS: 4.6 at%.
- Other impurities include Al, Mg, Na, and Si



	Ni 2p3	Zr 3d	Y 3d	P 2p	Al 2p*	Mg 1s*	O 1s*	C 1s	Na 1s	Si 2p
Area 1	5.8	6.3	1.1	4.9	1.2	0.4	44.1	35.1	1.3	-
Area 2	6.5	6.7	1.2	4.1	1.0	0.8	44.7	32.9	1.5	0.4
Area 3	6.2	6.2	1.1	4.7	0.7	0.7	44.0	35.2	1.3	-

- P, S, Cl were detected on anode support surface by ToF-SIMS
- Other trace elements include Cu, Mg, Al, and Si





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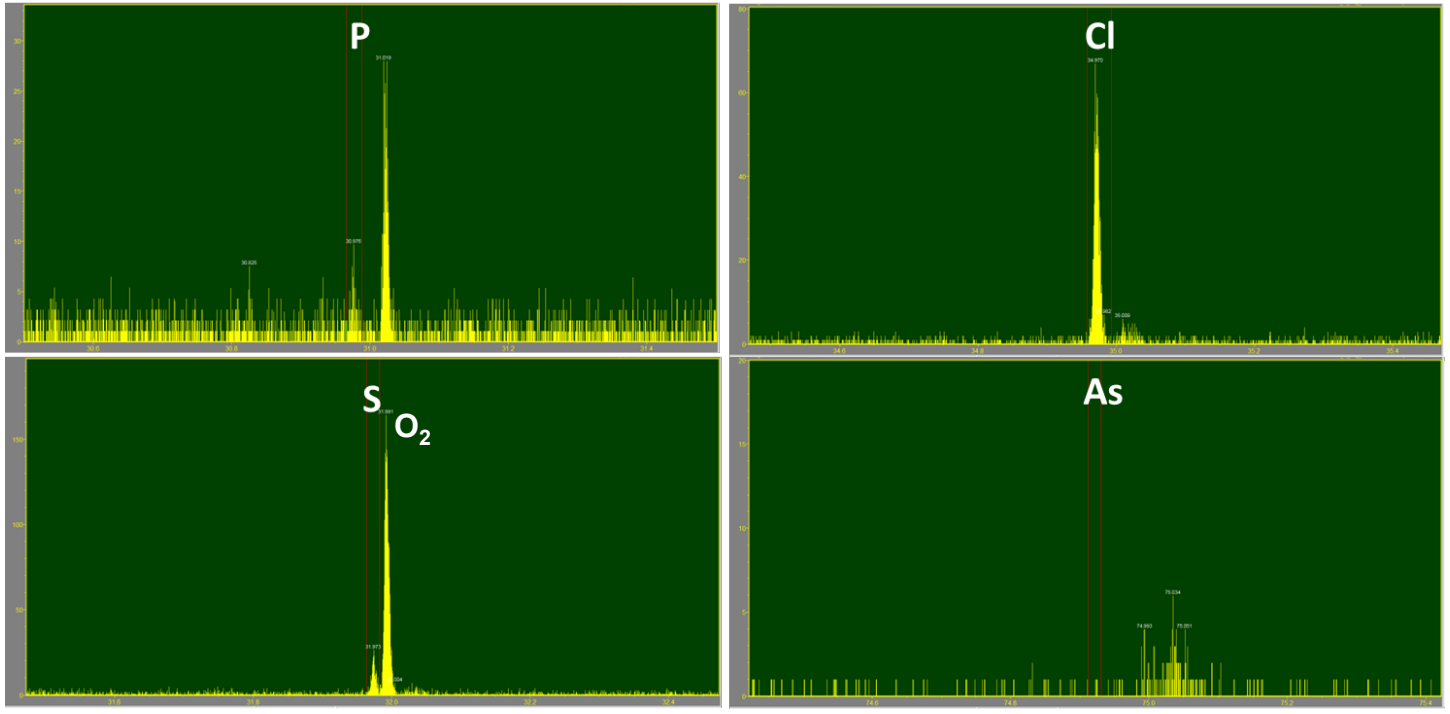
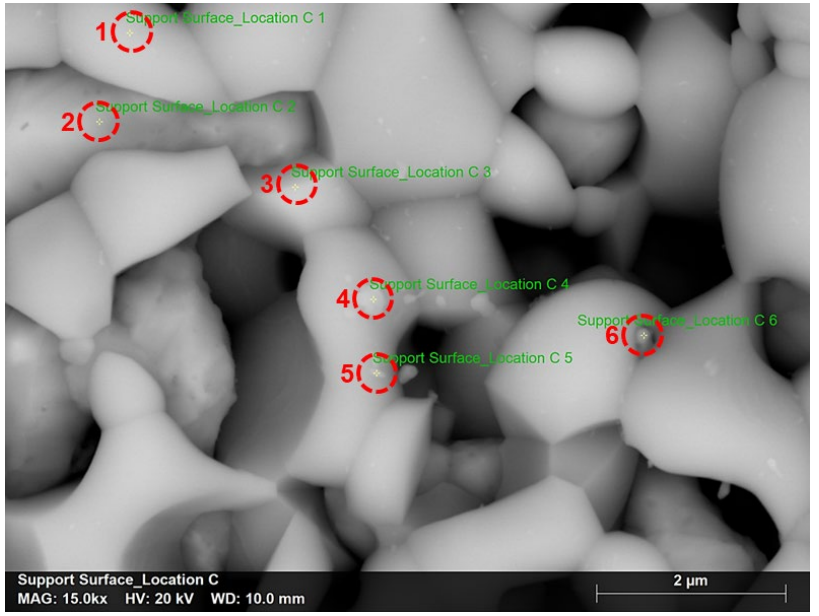
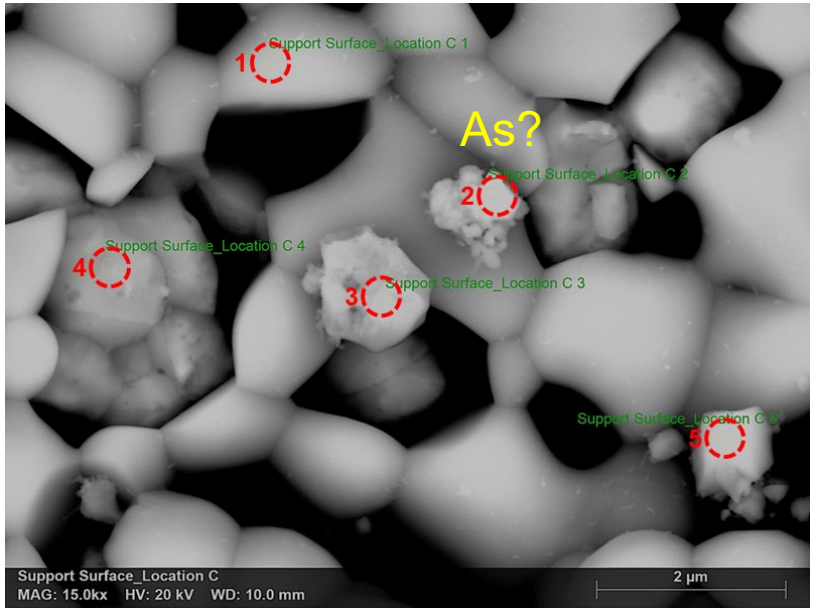
POST-MORTEM ANALYSIS – SOFC SAMPLE NEAR FUEL OUTLET

- SEM/EDS
  - P, S, and Cl: not detected. Mg, Al, Na, Cu, Sr detected.
  - Possible As ≤ 0.28 wt%
- ToF-SIMS
  - S and Cl peaks detected
  - P peak possible. As peak not detected.
  - Mg, Al. Si, Na, Co detected.

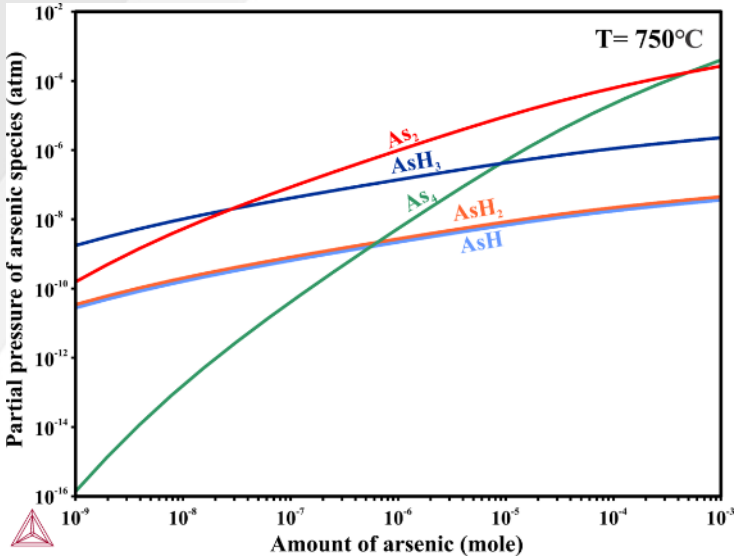


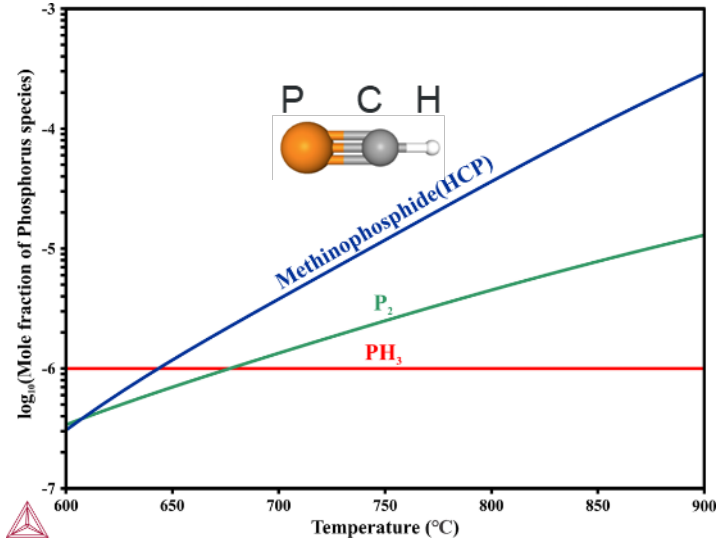


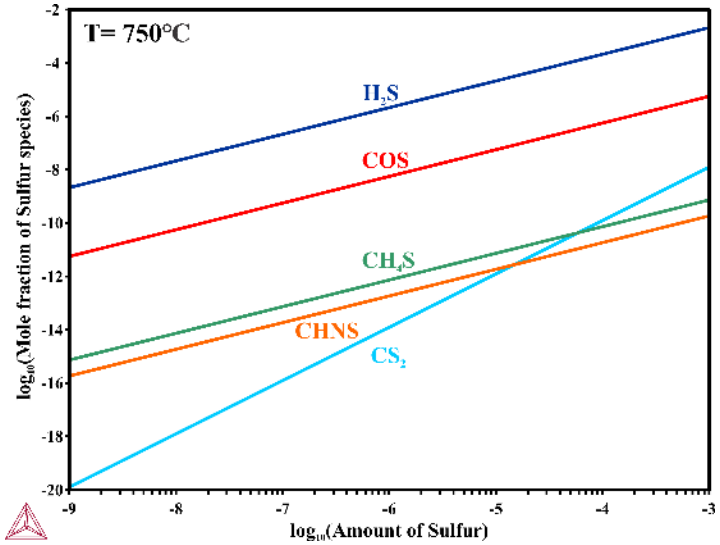


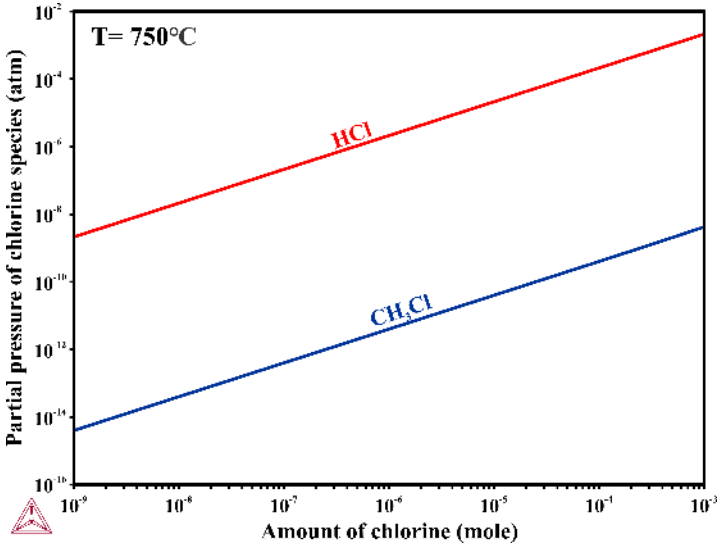
CONTAMINANT SPECIES IN SYNGAS INTERACTION WITH NI

Contaminant species in coal syngas at 750°C

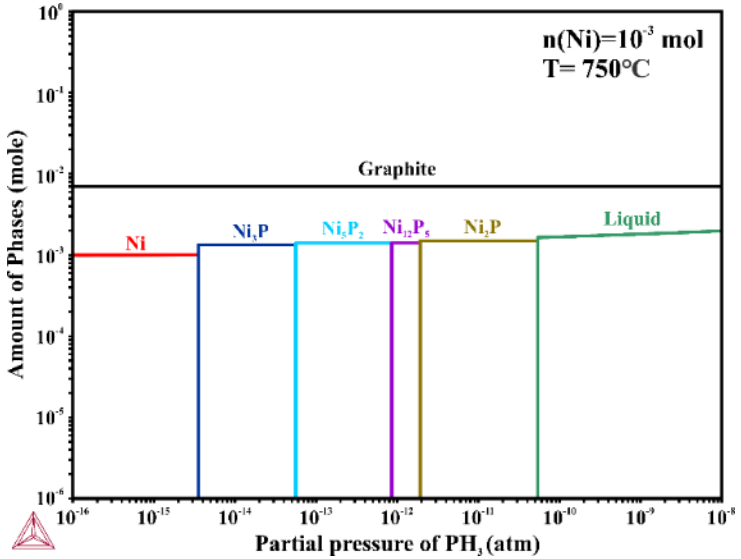


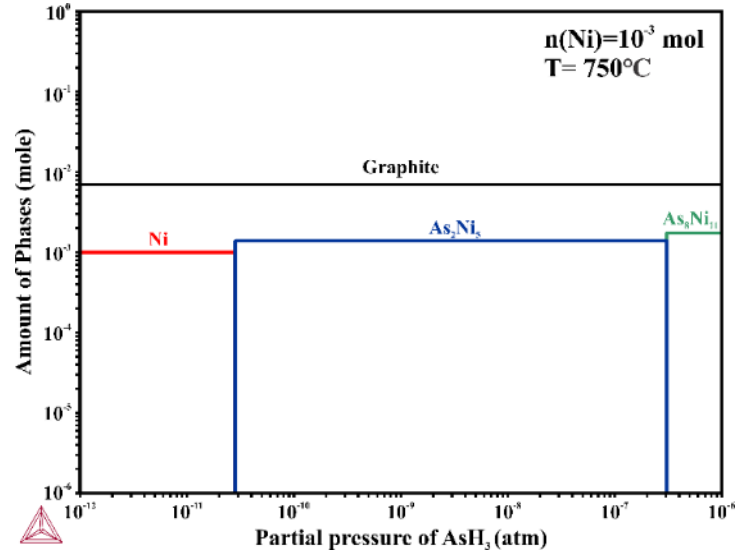






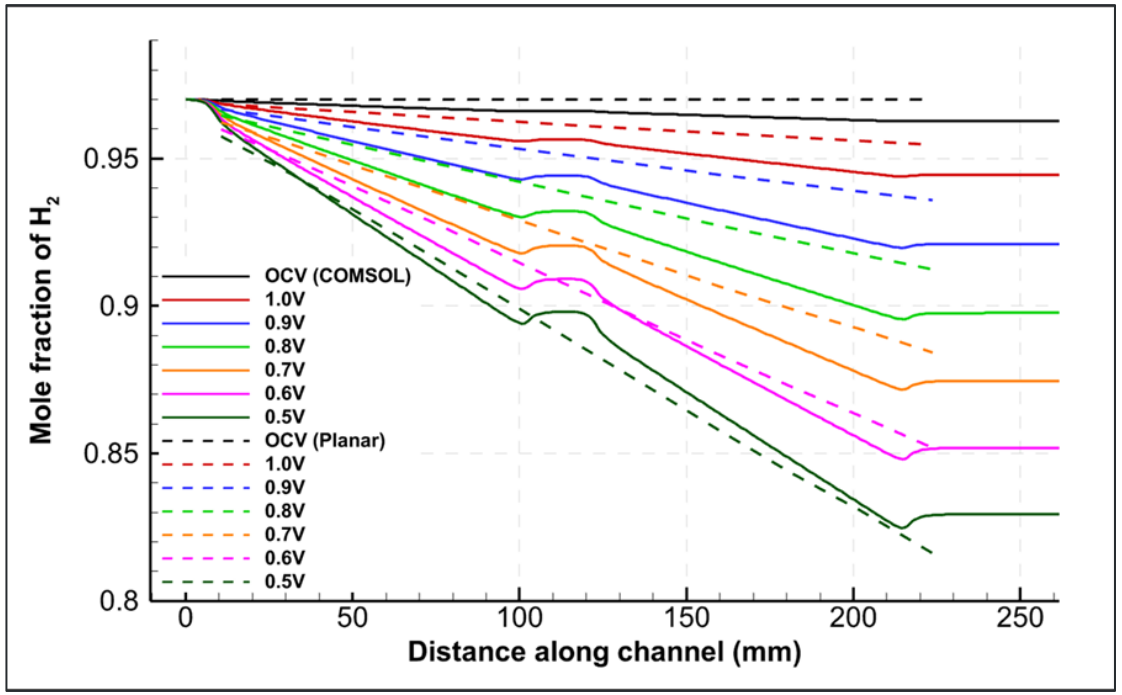
Interaction of contaminants with Ni at 750°C





MULTIPHYSICS MODEL – SIMULATION OF SOFC DEGRADATION WITH COAL CONTAMINANTS

- Planar cell model was modified to tubular cell geometry and calibrated by experimental data.
- Planar model was used to simulate SOFC degradation with coal contaminants
- Sensitivity of two key factors were investigated: contaminant concentration and anode thickness



level of contaminant (AsH_3)

	30μm	200μm	800μm	1.2mm
1ppb	65kh	750kh	4500kh	11000kh
0.05ppm	1300h	15kh	90kh	220kh
0.5ppm	150h	1500h	9000h	22kh
5ppm	20h	200h	1200h	2200h
10ppm	10h	105h	650h	1100h

electrode thickness

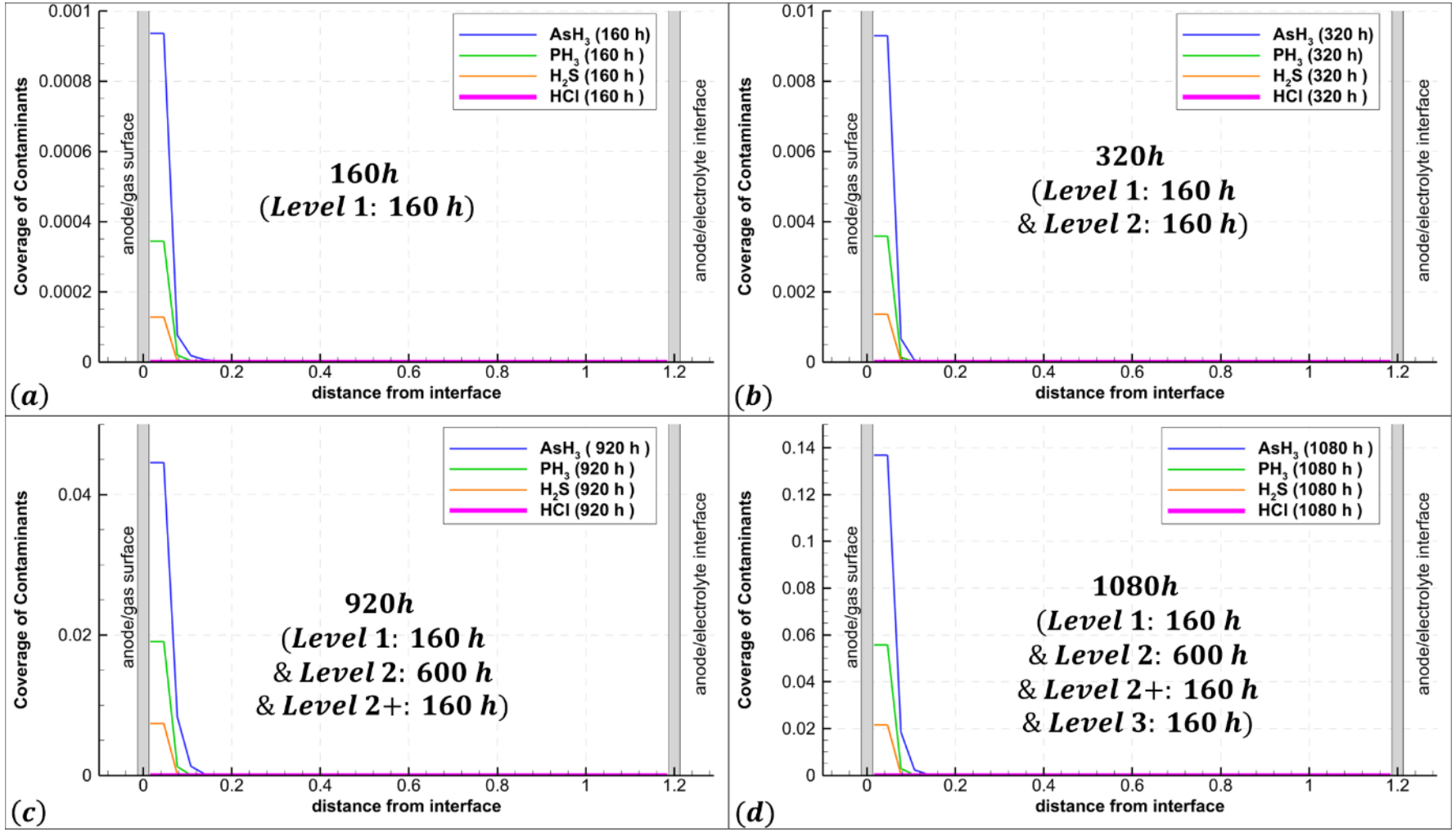
level of contaminant (PH_3)

	30μm	200μm	800μm	1.2mm
1ppb	500kh	5000kh	16500kh	43000kh
0.05ppm	10kh	100kh	530kh	860kh
0.5ppm	1000h	10kh	50kh	86kh
5ppm	100h	1150h	5300h	8600h
10ppm	50h	560h	2600h	4000h

electrode thickness

SIMULATION OF SOFC DEGRADATION WITH COAL CONTAMINANTS USING MULTIPHYSICS MODEL

- The contaminant coverage is localized in the support layer near the surface, which is increased with increasing of contaminant concentration;
- The contaminant coverage on Ni phase is negligible in active anode, or near the electrode/electrolyte interface;
- AsH_3 has highest coverage on Ni surface, then PH_3, and H_2S. HCl coverage on Ni throughout the anode is negligible.



SUMMARY

- Performed long-term durability test using coal-derived syngas with comparable degradation rate as natural gas.
- Designed a matrix and tested SOFC performance and short-term durability with single or multiple contaminant at three level of concentration.
- Performed post-mortem analysis by SEM/EDS, TEM/EDS, XPS, and ToF-SIMS and revealed the interaction mechanism of contaminants with Ni particles.
- Conducted thermodynamic and Multiphysics simulation to understand contaminant interaction with Ni metal and its impact on SOFC performance.

NEXT STEPS

- Work on a manuscript on coal contaminants interaction with anode and impact on SOFC performance.
- Complete two SOFC stack test using coal syngas and alternative fuel for up to 1,000 hours test.
- Validate 1 kW SOFC testing stand

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