Energy & Environmental Research Center (EERC)

SUBTASK 5.1 – SOLID OXIDE FUEL CELL DEVELOPMENT AND DEMONSTRATION TEST CENTER

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FY23 FECM Spring R&D Project Review
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ACKNOWLEDGMENTS AND DOE DISCLAIMER

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Activity Breakdown

- Subactivity 2.1 – Project Management and Reporting
- Subactivity 2.2 –SOFC Testing
- Subactivity 2.3 – Development of Protocols for Accelerated Stress Tests (ASTs)
- Subactivity 2.4 – Coordination with SOFC Manufacturers/Developers

Project Schedule

- M4 – Complete SOFC Performance Test

	Activity 2: Sept, 2022 - Jan 31, 2024	2022			2023												2024
	Tasks	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan
Task 1	**2.1 Project Management through 1/31/2024**				D1			D1			D1			D1			D2
Task 2	**2.2.1 SOFC performance and durability assessment using alternative fuels**																
	1) Coordination with SOFC suppliers																
	2) Parametric & durability test using ammonia									M4							
	3) Understand degradation mechanism & develop mitigation approaches																
	4) Parametric & durability test using renewable natural gas (RNG)/bio-syngas																
	5) Postmortem analysis																
	2.2.2 Proton conducting electrolyte and SOFC development																
	1) Conductivity and stability evaluation of electrolyte.																
	2) Cathode and anode materials development																
	3) Button cells testing & materials optimization																
	2.2.3 Establish the capability of SOFC processing																
	1) Cell processing lab and equipment readiness																
	2) Prepare button cells to meet the development need of 2.2.1 and 2.2.2																
Task 3	**2.3 Development of protocols for accelerated stress tests**																
	Select accelerated stress tests, design test matrix, generate test procedures																
Task 4	**2.4 Coordination with SOFC and SOFC Component Manufacturers/Developers)**																

Task 2.2 SOFC Testing – Technical Approaches

2.2.1 SOFC Performance and Durability Assessment Using Alternative Fuels

- Use commercially available SOFC cells.
- Using H_2/pipeline natural gas/coal-derived syngas as baseline.
- SOFC cell performance and durability using alternative fuels are comparable to baseline data.
- Understand degradation mechanism and generate mitigation approach.
- Potential risk using ammonia fuel.
  - Nitride formation on anode
  - NO_x formation
- Renewable natural gas.
  - Produced from feedstocks including animal waste, crops and crop residue, vegetable and food waste.
- Bio-syngas.
  - H_2–CO mixture produced by biomass gasification

Task 2.2 SOFC Testing – Technical Approaches

2.2.2 SOFC Optimization of Proton-Conducting Electrolyte

- **Characterization of proton-conducting electrolyte**
  - Thermal expansion coefficient (CTE)
  - XRD for crystalline phase
  - Chemistry
  - Material densification vs. sintering temperatures
- **Conductivity testing of proton-conducting electrolyte under low and high pO_2**
  - Conductivity vs. temperature
  - Stability vs. moisture, pO_2
  - Chemical expansion
- **Chemical compatibility with cathode and anode materials**
  - Calcine powder mixture at sintering temperature
  - XRD characterization for third phase
- **Button cell processing optimization and testing**
  - Fabricate button cells to meet electrochemical testing need
  - Test button cells in SOFC or SOEC mode to meet performance target

Task 2.2 SOFC Testing – Technical Approaches

2.2.3 Capability of SOFC Development

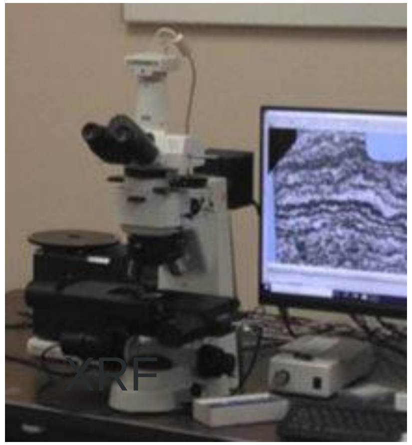
SOFC Cell Processing

- High temperature furnaces
- Screen printer
- Three-roll mill for ink development
- Dryer with forced air
- Viscometer
- Optical microscope
- Ball mill for slurry preparation

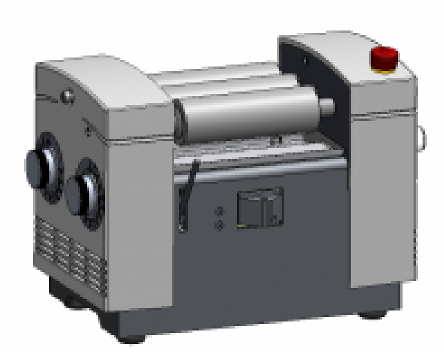
Materials Characterization

XRF

Electron Microscope



OM Image System



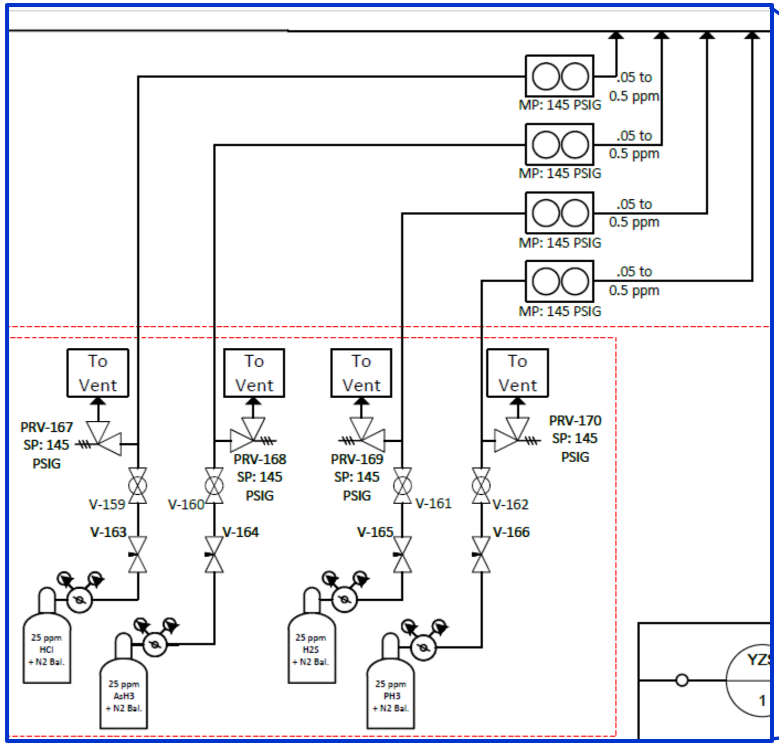
Three-Roll Mill

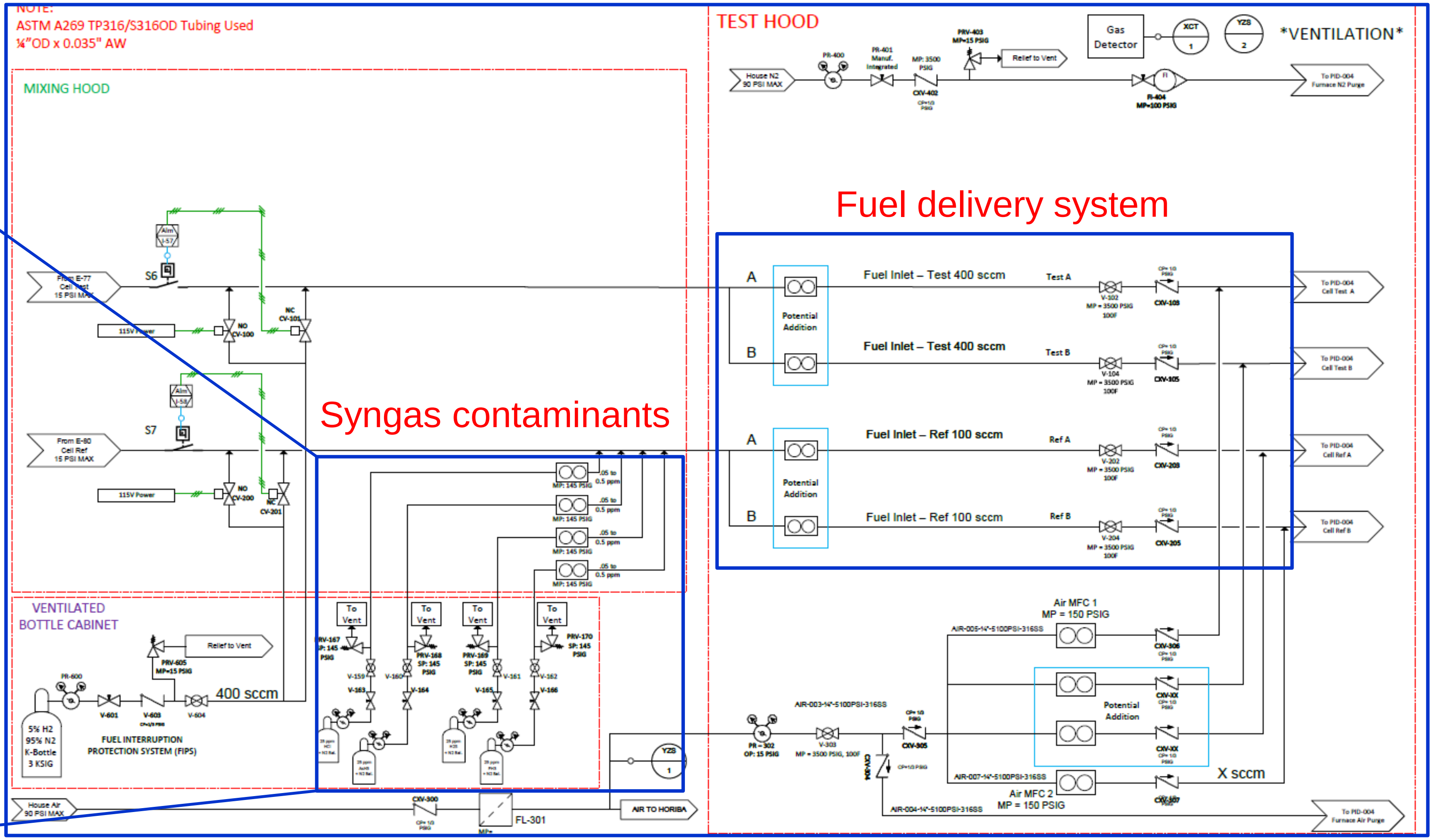
Screen Printer

XRD with Hot Stage and Data Analysis System

Updated Capability of SOFC Testing Lab

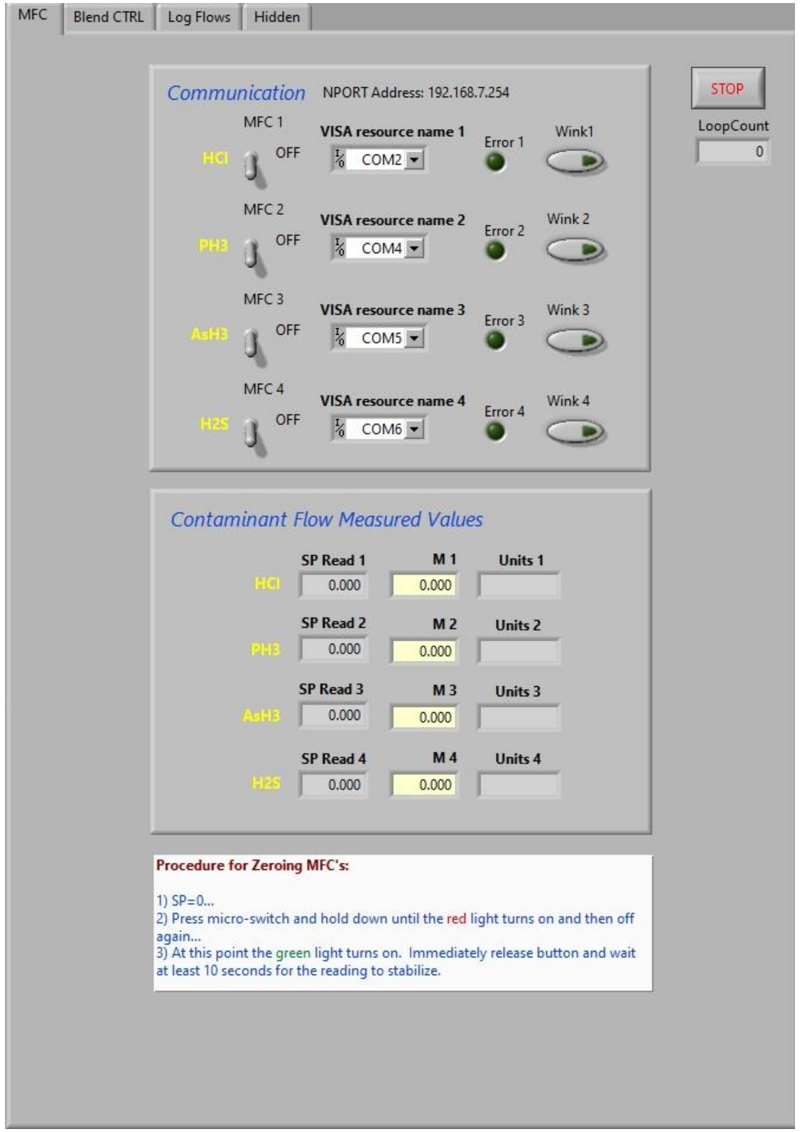
- Addition of syngas contaminants to fuel gas stream
- Multiple contaminants simultaneously

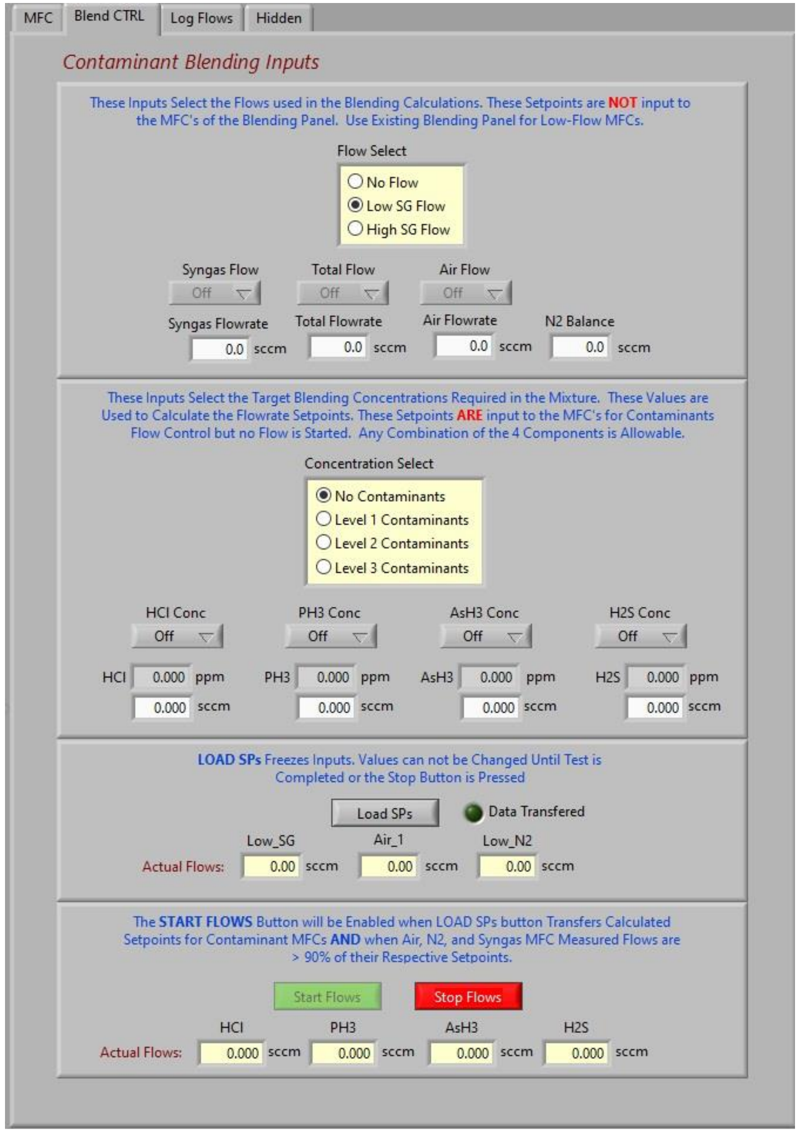




Control System for Syngas Contaminant Addition

- Completed hardware/plumbing and control system.
- Able to add up to four kinds of syngas contaminants to fuel stream.
- Contaminants can be changed via calibrated gas bottle.
- Accurate MFCs to add as low as 50 ppb contaminant.
- Safety protection.





SOFC Testing – Literature Review for NH_3-Reforming Catalyst

Ni-Based Ammonia-Reforming Catalysts					
Catalyst	Metal Content, wt%	Support Materials	Temperature, °C	NH_3 Conversion, %	References
$Ni_{0.5}Ce_{0.1}Al_{0.4}O$			500	88	J. Phys. Chem. C 2016, 120, 7685
Ni		Al_2O_3	600	97	Ind. Eng. Chem. Res. 2000, 39, 3694
Ni	10	Al_2O_3	500	93	Appl. Catal., A 2012, 447−448, 22.
Ni	90	Al_2O_3	600	93	J. Mater. Chem. A 2015, 3, 17172
Ni	38.6	Attapulgite	650	90	Int. J. Hydrogen Energy 2016, 41, 21157
Ni	40	$BaZrO_3$	550	94	RSC Adv. 2018, 8, 32102
Ni	13.2	$Ce_{0.8}Zr_{0.2}O_2$	550	96	Int. J. Hydrogen Energy 2012, 37, 15901
Ni	40	$GdAlO_3$	550	81	RSC Adv. 2018, 8, 32102
Ni	6	MgO	650	88	Ind. Eng. Chem. Res. 2000, 39, 3694
Ni	23.4	SBA-15	550	89	Appl. Catal., A 2008, 337, 138
Ni	5.2	Sepiolite	550	82	Int. J. Hydrogen Energy 2018, 43, 9954
Ni	40	$SmAlO_3$	550	81	RSC Adv. 2018, 8, 32102
Ni	40	$SrTiO_3$	550	80	RSC Adv. 2018, 8, 32102
Ni	40	$SrZrO_3$	550	90	RSC Adv. 2018, 8, 32102
Ni	5	ZSM-5	650	98	Appl. Catal., A 2018, 562, 49

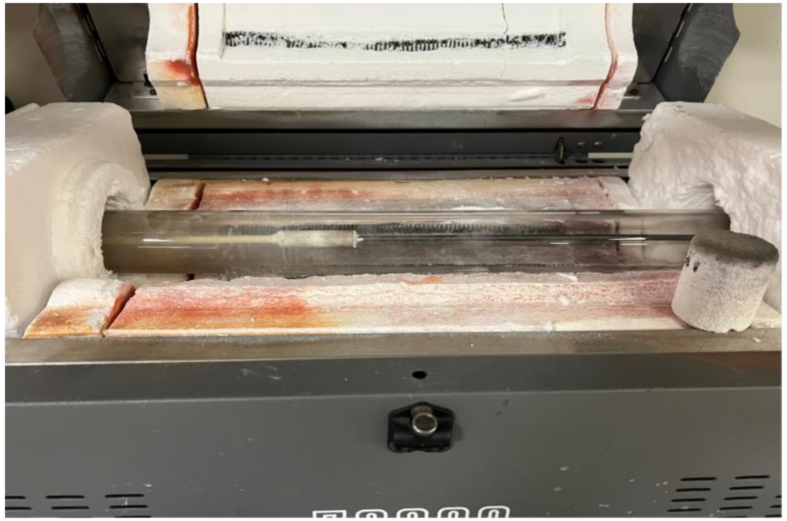
SOFC Testing – Literature Review for NH_3-Reforming Catalyst

Ru-Based Ammonia-Reforming Catalysts					
Catalyst	Metal Content, wt%	Support Materials	Temperature, °C	NH_3 Conversion, %	References
Ru	2.5	SiC	400	99.3	J. Ind. Eng. Chem. 2021, 94, 326
Ru	5.0	$Cu/LaTiO_2N$	450	97.3	Applied Catalysis B: Environmental 2004, 48, 237
Ru	5.0	Graphitic carbon (GC)	550	95.0	Appl. Catal., A. 2007, 320, 166
Ru	11.7	Graphene Aerogel	450	97.6	Appl. Catal., A. 2021, 610, 117969
Ru	5.0	Cr_2O_3	600	100.0	Appl. Catal., A. 2013, 467, 246
Ru	4.8	La_2O_3	525	90.7	Appl. Surf. Sci. 2019, 476, 928
CoMo	5.0	Al_2O_3	600	99.5	Int. J. Hydrogen Energy. 2014, 39, 12490
Ru	0.7	$LaAl_2O_3$	450	99.0	J. Membr. Sci., 2020, 614, 118483
Cs-Ru	0.4	YSZ	450	99.0	ACS Sustainable Chem. Eng. 2019, 7, 5975
Ru	2.0	Al_2O_3	450	99.0	Fuel Process. Technol., 2021, 216, 106772
Ru-Y-K	3.0	Al_2O_3	450	99.0	J. Membr. Sci., 2021, 629, 119281
Ru	1.9	YSZ	450	99.0	J. Membr. Sci., 2022, 644, 120147
Ru	1.0	YSZ	450	99.0	J. Membr. Sci., 2022, 644, 120147
Ru		SiO_2	500	96.0	Catal. Today 2011, 164, 112
Ru	2.0	Al_2O_3	500	98.0	Appl. Catal., A 2012, 447−448, 22
Ru	8.5	Al_2O_3	400	99.0	Int. J. Hydrogen Energy 2014, 39, 808
Ru	4.0	Al_2O_3	400	95.0	Top. Catal. 2008, 50, 180
Ru		C	400	90.0	Int. J. Hydrogen Energy 2013, 38, 3233
Ru	5.0	CNTs	500	88.0	J. Catal. 2004, 224, 384
Ru	5.0	GC	550	95.0	Appl. Catal., A 2007, 320, 166
Ru		Graphene	450	91.0	Catalysts 2017, 7, 1
Ru	2.0	Graphene	600	93.0	J. Am. Chem. Soc. 2013, 135, 3458

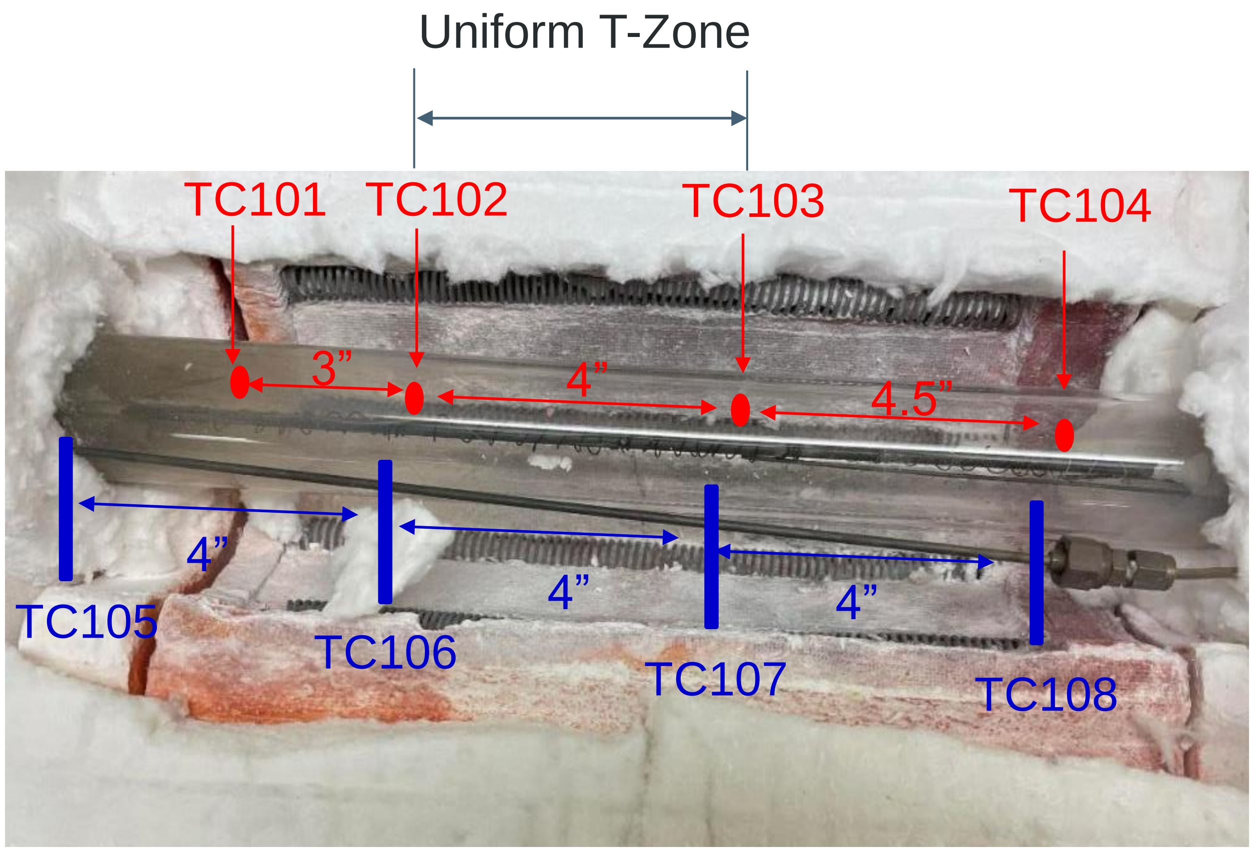
SOFC Testing – Preliminary NH_3-Reforming Test

Test Setup

- Tube furnace
- Fuel injection tube inside of quartz tube
  - NH_3 passed through injection tube
  - Gas samples collected at outlet



Furnace with Quartz Tube



- TC101-TC104: TCs attached with injection tube
- TC105-TC108: TCs attached with quartz tube

SOFC Testing – NH_3 Decomposition from 450°–750°C

- Performed in a tubular furnace with fuel injection tube.
- Inline LGA used for exhaust gas analysis.
- NH_3 concentration is “estimated” by the difference of 100% and LGA data.

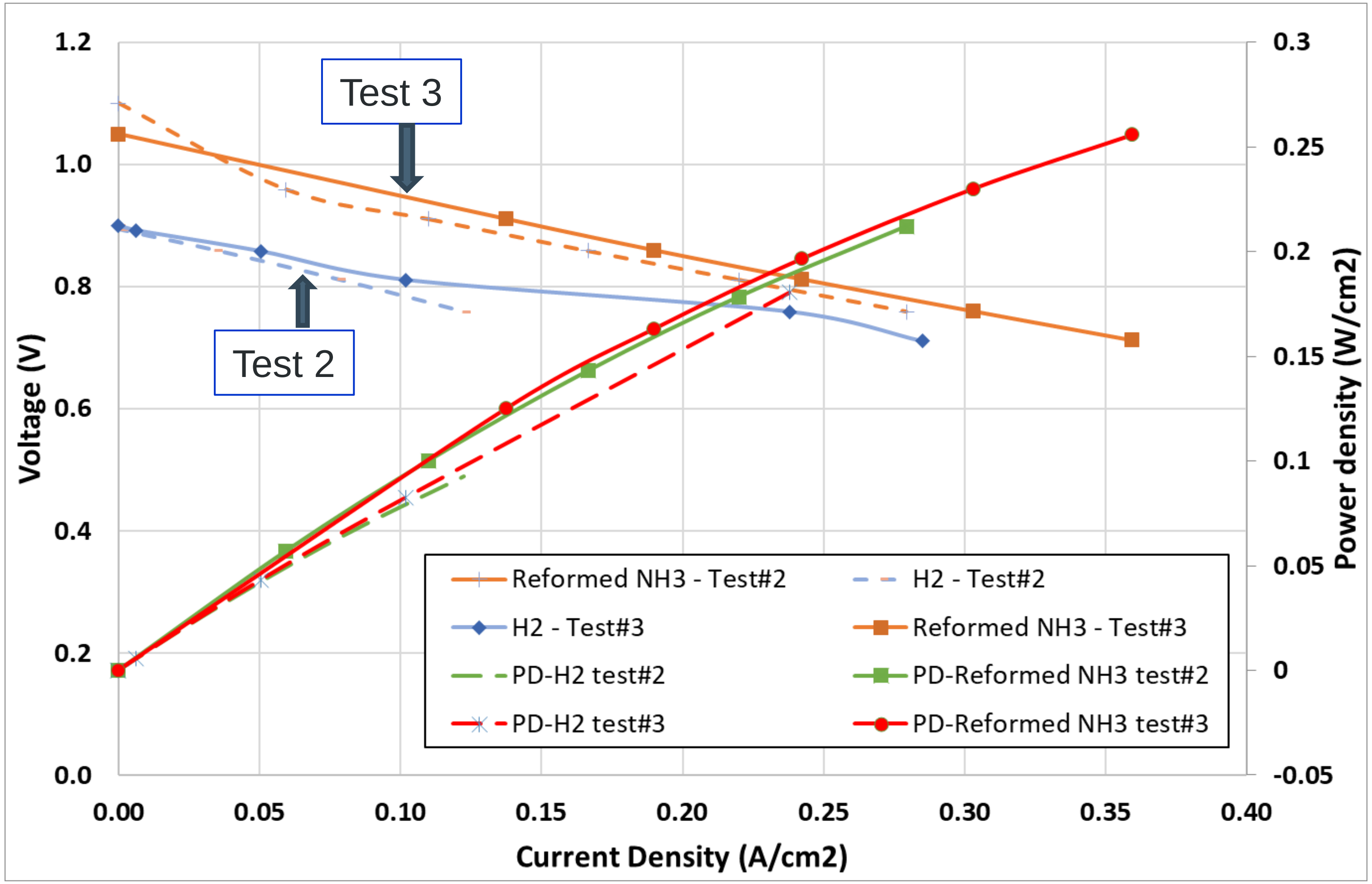
Test Performed on	T, °C	% CO	% O_2	% H_2S	% N_2	% H_2	% CO_2	Total	Est. % NH_3
1/11/2023	450	0	1	0	12	2	0	100	85
1/11/2023	500	0	1	0	13	4	0	100	82
1/11/2023	600	0	0	0	17	19	0	100	63
1/11 & 1/19/2023	650	0	0	0	21	36	0	100	42
1/19/2023	**675**	**0**	**0**	**0**	**24**	**47**	**0**	**100**	**29**
1/19/2023	700	0	0	0	27	56	0	100	17
1/11/2023	750	0	0	0	31	70	0	101	-1

SOFC Testing – Cell Performance with Different Fuel Compositions

Three tests

- Test 1: system shakedown
- Test 2: H_2 and reformed NH_3
- Test 3: modified setup

- Temperature – 675°C
- H_2 test
  - Fuel flow: 200 sccm
  - Airflow: 400 sccm
- Reformed NH_3 Test
  - Fuel Flow: 200 sccm
    - ♦ NH_3: 29%
    - ♦ H_2: 47%
    - ♦ N_2: 24%
  - Airflow – 400 sccm



Cell V/I and P/I Curves with H_2 and Reformed NH_3 Fuel

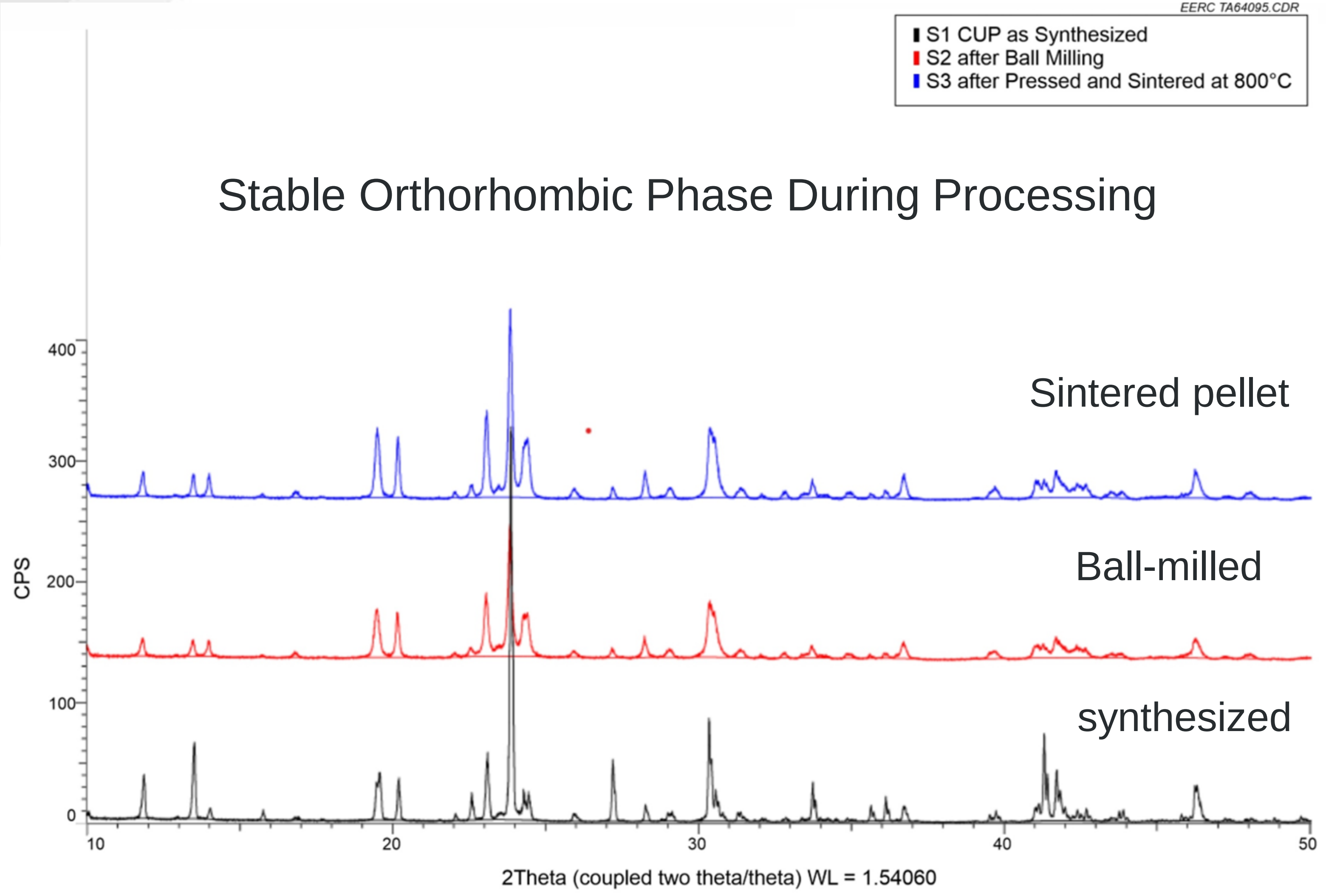
SOFC Development

- EERC selected proton-conducting electrolyte for technology development.

- State-of-the-art SOFC/SOEC is based on commercially available oxygen ion-conducting YSZ/ScSZ electrolyte.
- Operating at high temperatures.
- Higher BOP cost.
- Higher degradation rate for SOEC.

- Lower activation energy and higher conductivity at low temperatures.
- Enable low-temperature operation.
- Lower BOP cost.
- Improve thermally activated degradation mechanisms.
- Potentially longer service life.
- Phosphate-based material was selected (CUP).

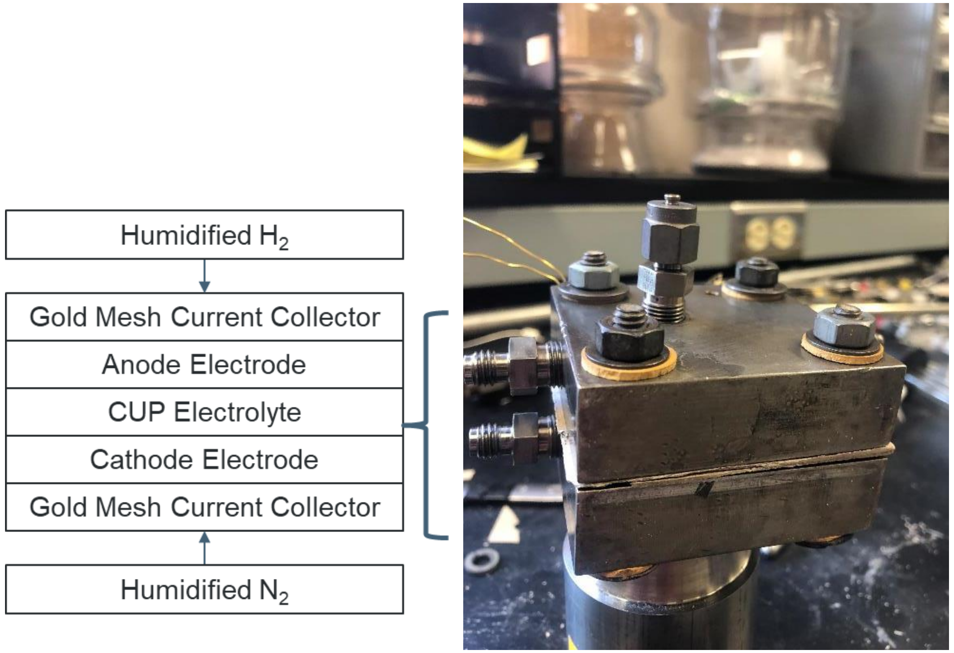
CUP Powder and Disk Preparation – Phase Stability



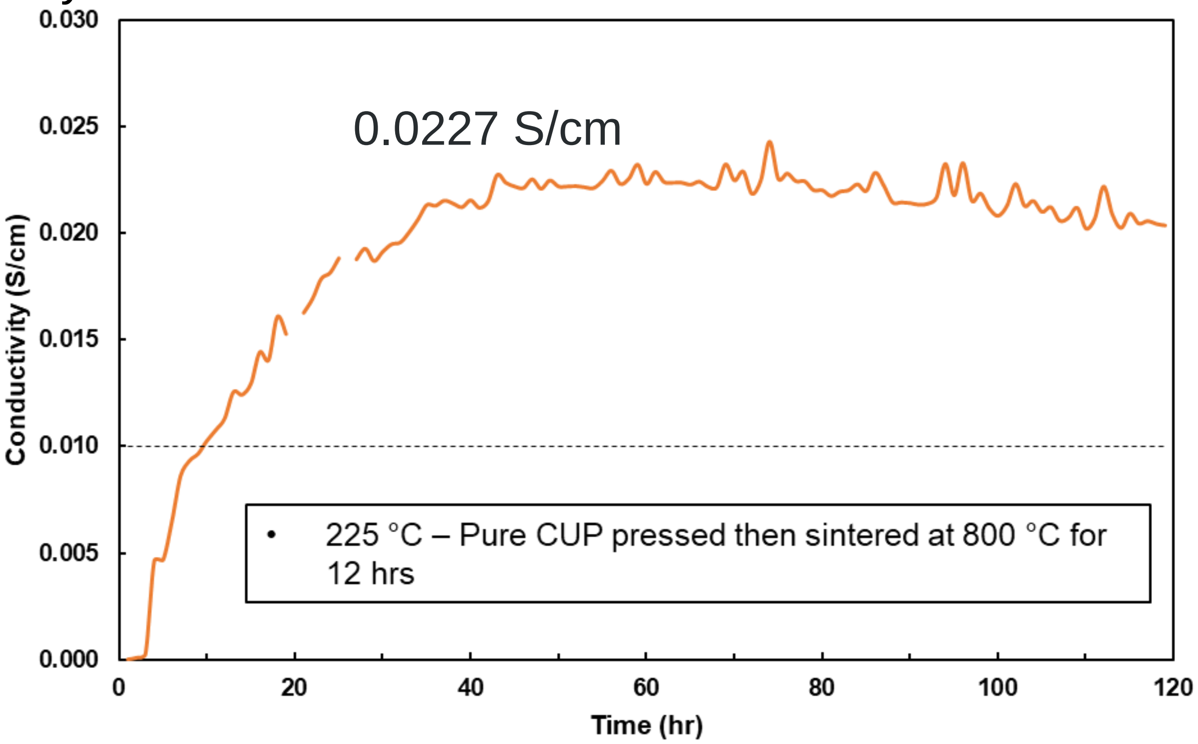
- CUP was synthesized as amorphous phase at high temperatures.
- Amorphous phase crystallized to orthorhombic phase during cooling.
- Crystals were ball-milled into CUP powder for PCE.
- CUP disks were prepared by isostatic pressing for property characterization evaluation.

Conductivity of CUP Electrolyte Disk

- Conductivity of CUP electrolyte disk was measured using EIS in H_2 gas with moisture.
  - Steady increase in proton conductivity, possibly related to the interaction of CUP with steam.
- Maximum conductivity of 0.0227 S/cm was achieved at 225°C, then showing steady degradation.
  - Performed XRD characterization after conductivity test.



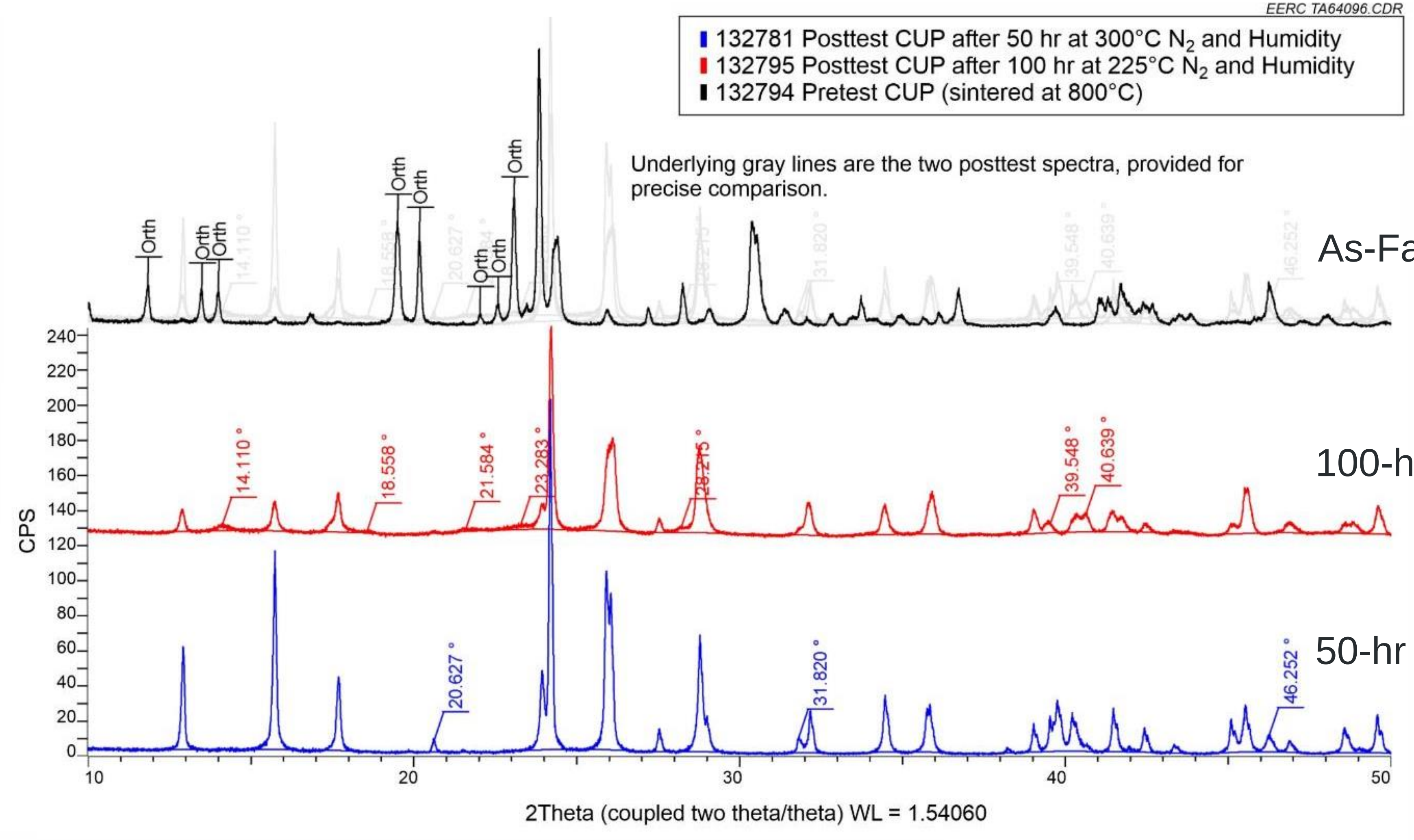
Testing Setup



Proton Conductivity Versus Time for Sintered CUP Disk

CUP Disk Stability – Before and After Testing

- XRD spectra of C-PCE disks before and after conductivity testing at 225° and 300°C, respectively.
- Noticeable phase change.



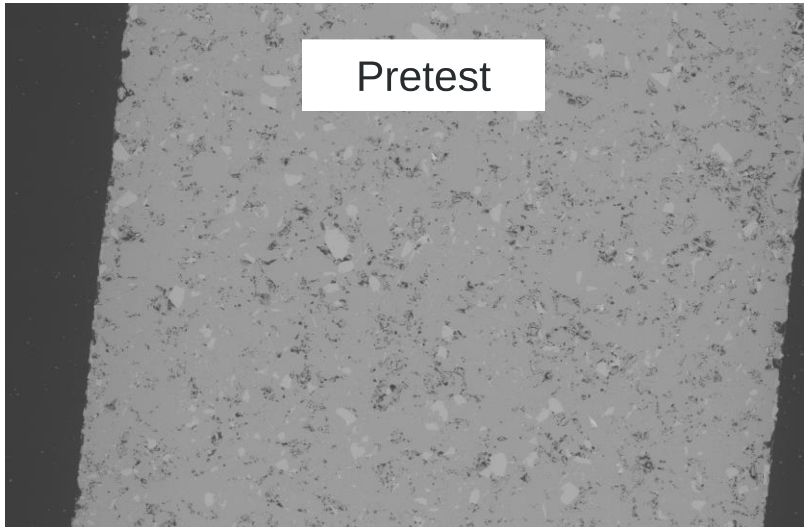
As-Fabricated Disk

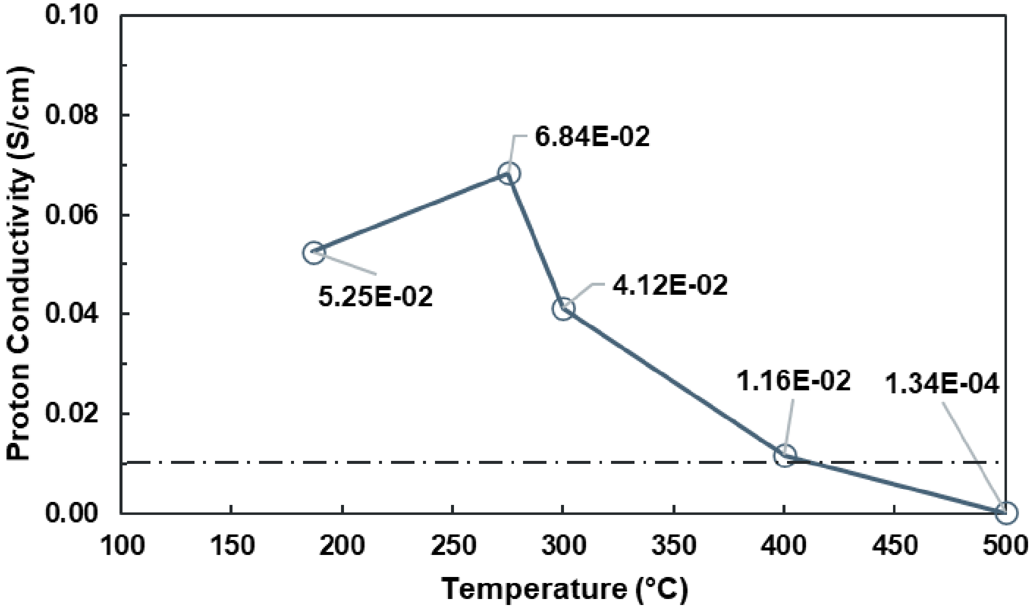
100-hr at 225°C

50-hr at 300°C

CUP Disk Densification and Improvement

- SEM examination indicates about 10% porosity for sintered CUP electrolyte disk.
- Mitigation approaches to improve densification of CUP disk:
  - Sintering aid
    - ♦ Cobalt oxide (CoO)
    - ♦ Ternary glass: P_2O_5-CaO-Na_2O (PCN): conductivity of $2.7x10^{-4}$ S/cm
  - Powder-milling study to reduce particle size
  - Sintering profile optimization





CUP Disk Cross-Section with CoO Sintering Aid

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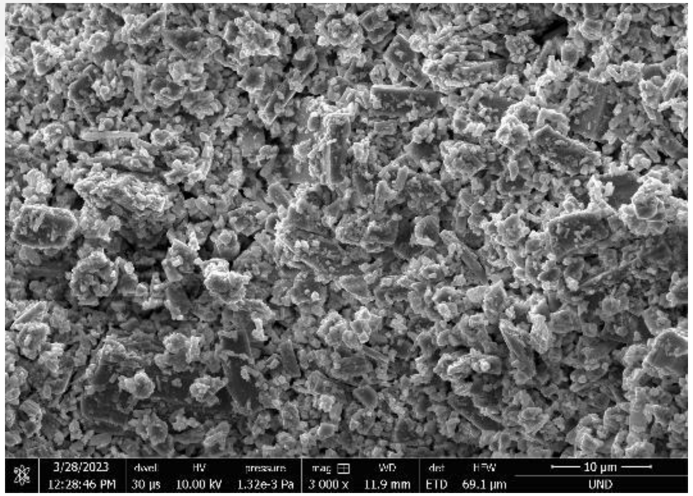
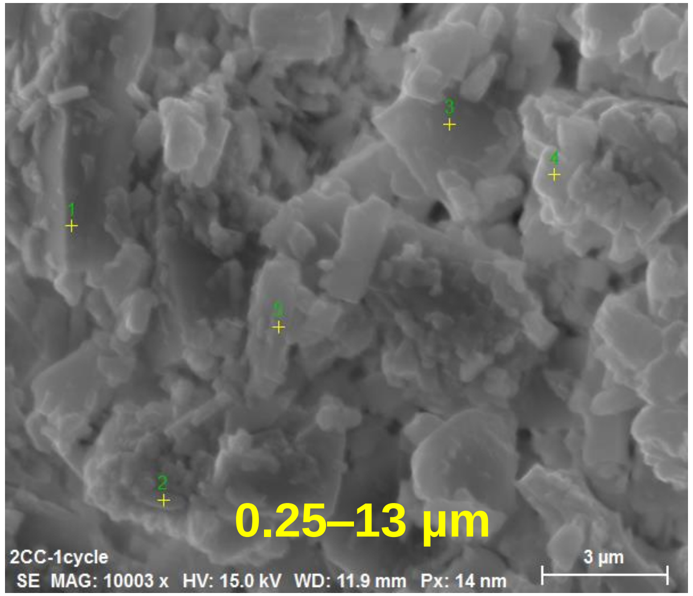
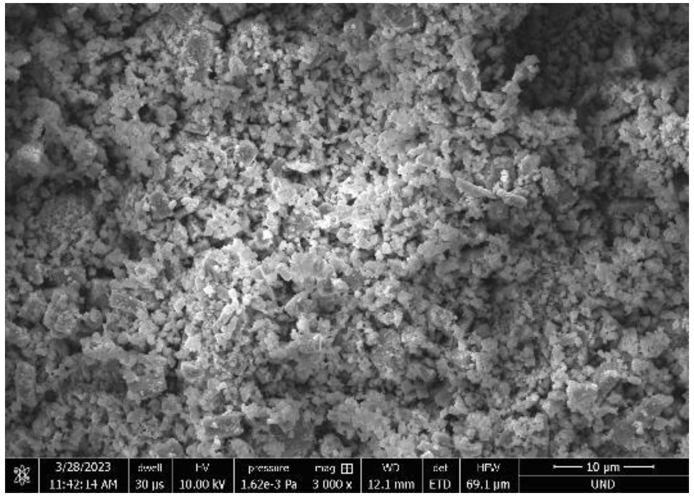
CUP Powder-Milling Study for Improved Densification

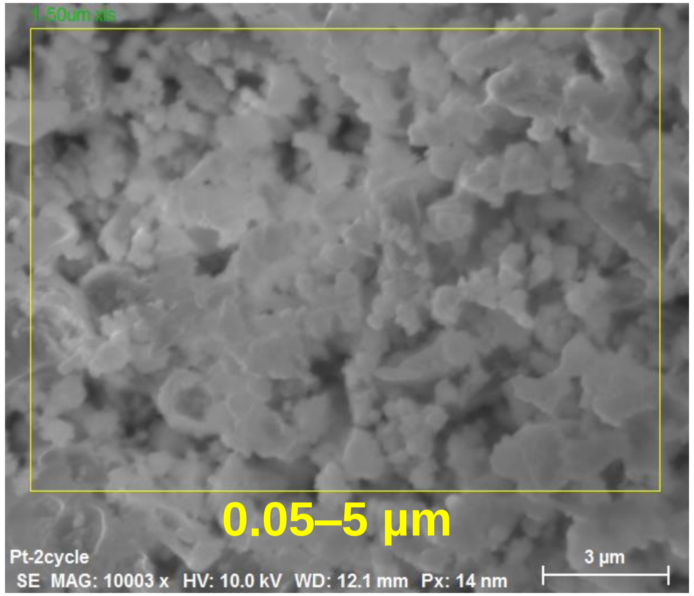
One Milling Cycle



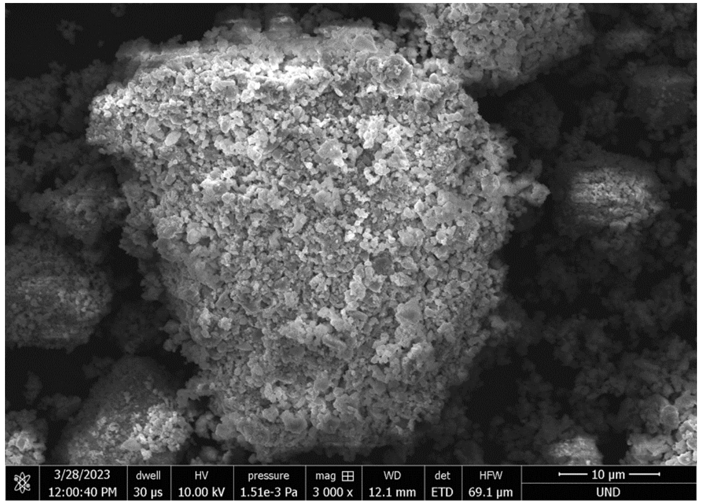


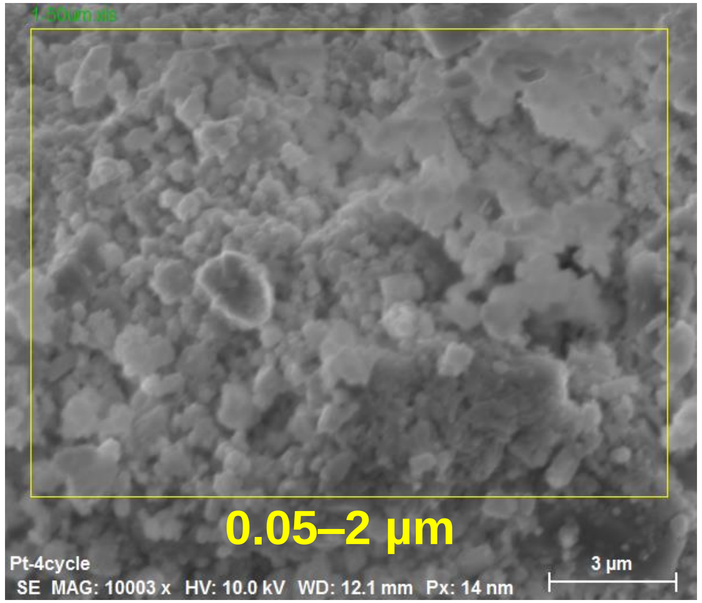
Two Milling Cycles





Four Milling Cycles





Tape-Casting Trial of CUP Green Tape

- CUP green tape can be made via tape-casting approach, tape thickness in the range of 120–280 µm.
- CUP powder with optimized milling cycle will be used for future tape-casting.

500 µm

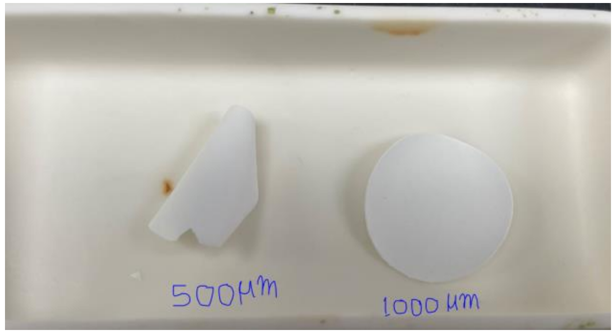
1000 µm

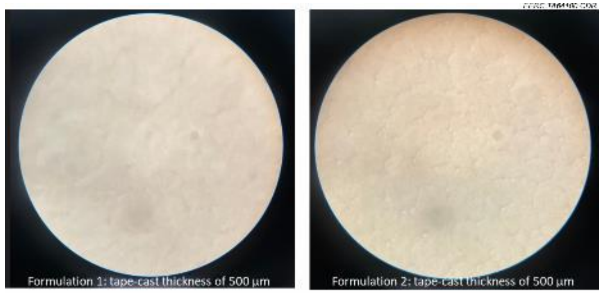
First Casting Trial

500 µm

1000 µm

Second Casting Trial





Fired CUP Tape

Doctor Blade Opening

Development of Protocols for Accelerated Stress Tests

- Completed literature review.
- Design principles of accelerated testing methodology for SOFC.
- AST methodology for SOFC anode material evaluation.
- AST methodology for both cathode and anode materials evaluation.
  - AST – elevated operating temperature
  - AST – high current density and low pO_2
  - AST – load cycle effect
- AST – accelerated cathode degradation by moisture.

Summary

- SOFC supplier was selected for SOFC testing using alternate fuel.
- Generated initial SOFC performance data using anode-supported cell and ammonia as fuel.
- Completed NH_3 decomposition tests from 450 ° to 750°C.
  - Full conversion of NH_3 to H_2 at 750°C.
  - Catalytic NH_3 conversion may be required low-temperature SOFC.
- Synthesized CUP powder and measured proton conductivity at 200°–300ºC, showing steady degradation in 100-hr duration test.
- CUP shows stable phase during processing and phase change during conductivity testing.
- Conducted milling study to reduce particle size of CUP powder and improve densification.
- Initial tape-casting trial is promising for CUP green tape fabrication.

Next Step

Alternative Fuels Testing

- Continue durability test using NH_3 fuel to identify potential degradation mechanism, and develop mitigation approach.
- Select supplier for renewable natural gas and initiate SOFC performance testing.

Proton-Conducting Electrolyte

- Understand the effect of milling cycles/PSD on CUP electrolyte processing and densification.
- Optimize CUP tape-casting and sintering profile to obtain low-porosity and high conductivity of ≥0.02 S/cm electrolyte at 200°–300°C.
- Better understand CUP electrolyte chemical stability and mechanical property at relevant conditions.
- Prepare P-SOFC button cell for electrochemical testing and meet performance target.

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