Energy & Environmental Research Center (EERC)

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

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FY24 FECM Spring R&D Project Review
April 23, 2024

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ACKNOWLEDGMENTS AND DOE DISCLAIMER

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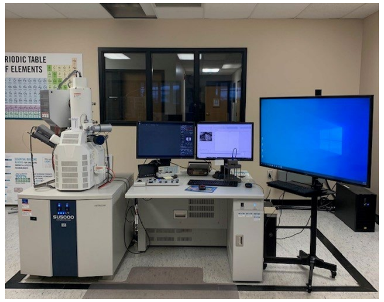
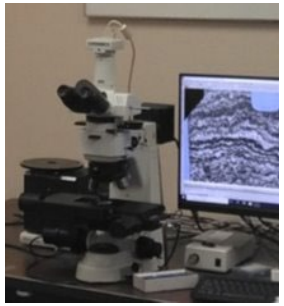
Project Objectives

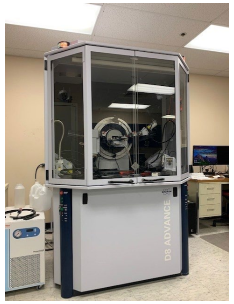
- Establish a SOFC Development and Demonstration Test Center at the EERC, enabling testing on coal and natural gas derived fuels.
- Provide fuel storage and delivery system to meet the need to evaluate SOFCs performance and long-term durability.
- Perform component- and system-level SOFC testing using variety of fuels.
- Multiyear project with two activities
  - Activity 1: Fabricate and Validate SOFC Test Facility
  - Activity 2: Component- and System-Level SOFC Testing to Support SOFC Program Activities

Project Schedule

Activity 2: Oct. 1, 2022 - April 31, 2024		2022			2023												2024			
		Q4			Q1			Q2			Q3			Q4			Q1			Q2
Tasks		Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
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) Postmortem analysis									■	■	■	■	■	■	■	■	■	■	
	2.2.2 Optimization of proton conducting electrolyte and cell development																			
	1) Conductivity, stability, and thermal property of electrolyte.	■	■	■	■	■	■	■	■											
	2) Evaluation of electrolyte durability								■	■	■	■	■	■	■					
	3) Post-mortem analysis								■	■	■	■	■	■	■					
	2.2.3 Establish the capability of SOFC cell processing and prepare button cells																			
	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 2.2 SOFC Component Testing

2.2.1 SOFC Performance and Durability Test Using Alternative Fuels

- Use commercially available SOFC cells.
- SOFC cell performance and durability using alternative fuels are comparable to baseline data.
  - Ammonia
  - Renewable natural gas
- Two types of SOFCs
  - Anode-supported cells
  - Electrolyte-supported cells

2.2.2 Development of Proton-Conducting Electrolyte

- Process development for higher densification
- Electrolyte characterization
  - Conductivity, XRD, SEM, TGA, DSC

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**
Day 1	450	0	1	0	12	2	0	100	85
Day 1	500	0	1	0	13	4	0	100	82
Day 1	600	0	0	0	17	19	0	100	63
Day 1 & 2	650	0	0	0	21	36	0	100	42
Day 2	**675**	**0**	**0**	**0**	**24**	**47**	**0**	**100**	**29**
Day 2	700	0	0	0	27	56	0	100	17
Day 2	750	0	0	0	31	70	0	101	-1

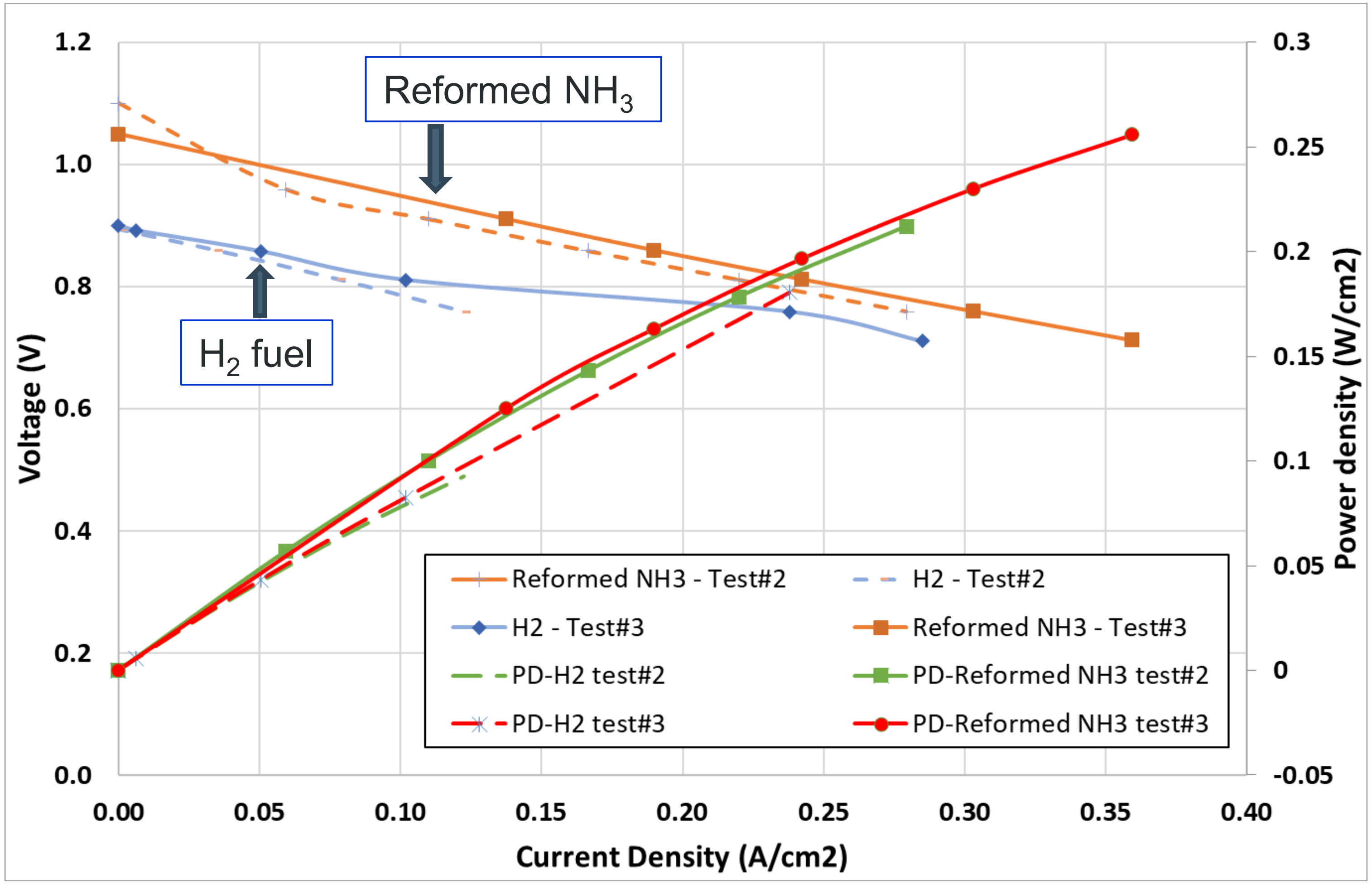
SOFC Testing – Cell Performance with Different Fuel Compositions

Three tests

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

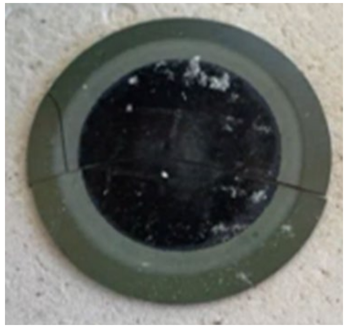
- Temperature – 675°C
- H_2 test
  - Fuel flow: 200 sccm
  - Airflow: 400 sccm
- Reformed NH_3 Test
  - Fuel Flow: 200 sccm
    - ♦ NH_3: 29%
    - ♦ H_2: 47%
    - ♦ N_2: 24%
  - Airflow – 400 sccm

- Cell V/I and P/I Curves with H_2 and Reformed NH_3 Fuel.
- Durability test failed due to unstable cell performance

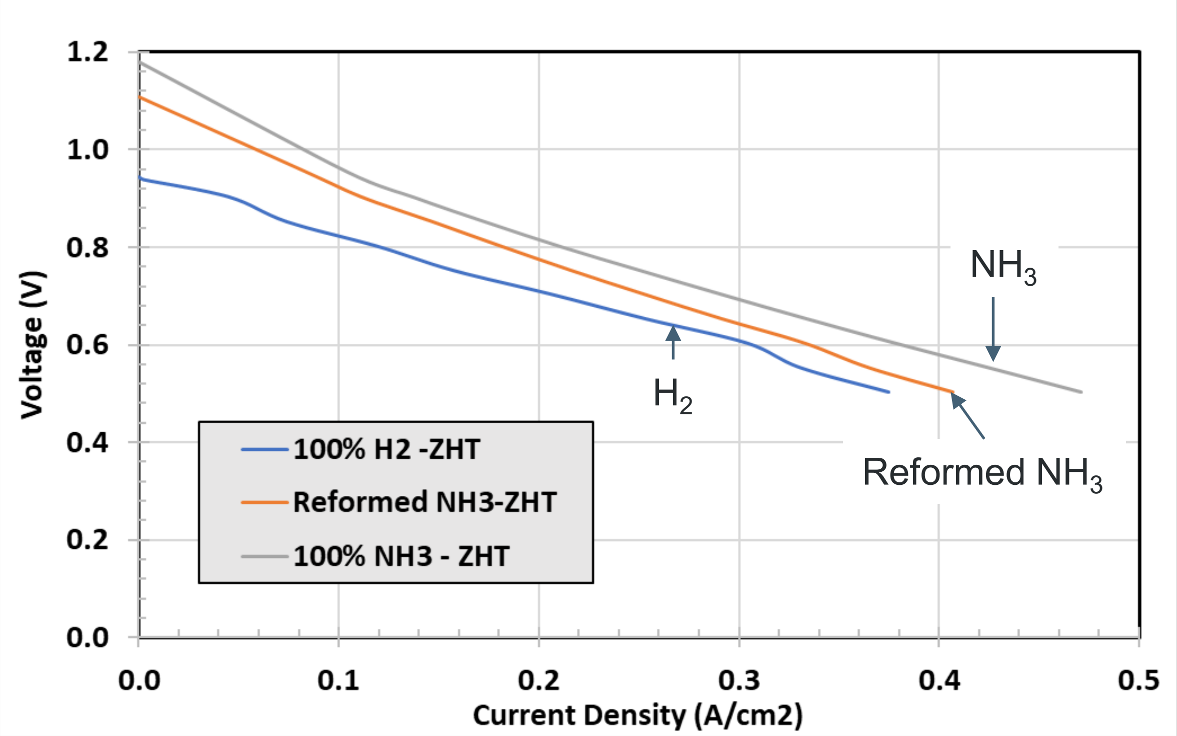


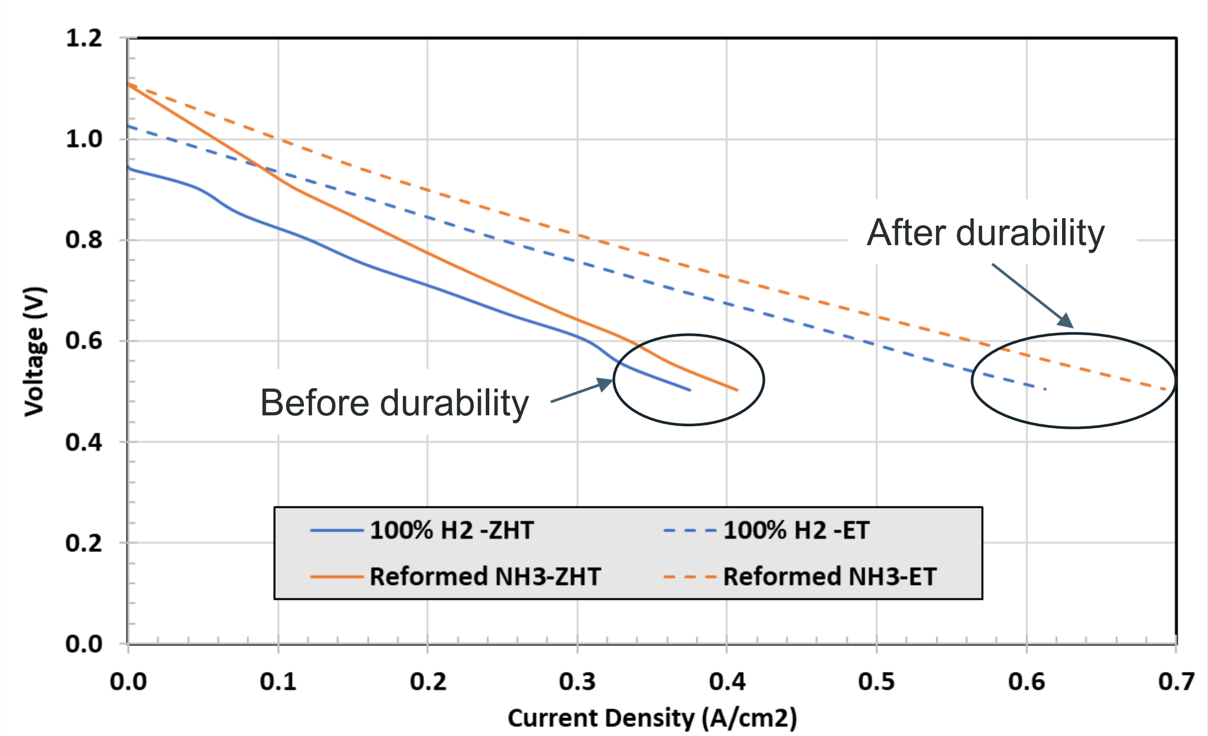
SOFC Testing using Modified Procedures

- Post-test inspection indicates cell cracking
- Cell installation procedures were modified to prevent cell damage.
- Cell was tested using improved procedures with H_2, reformed NH_3, and 100% NH_3
- SOFC shows improved performance after durability test



Anode –supported cell

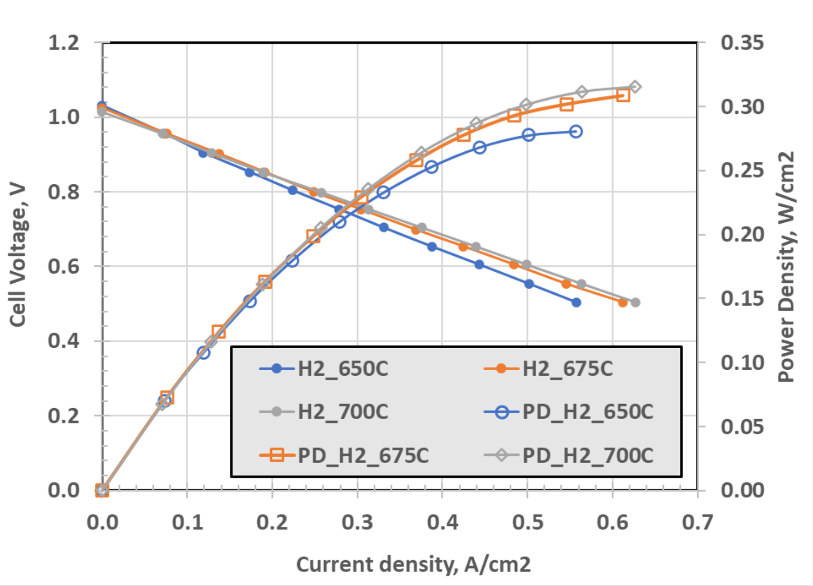




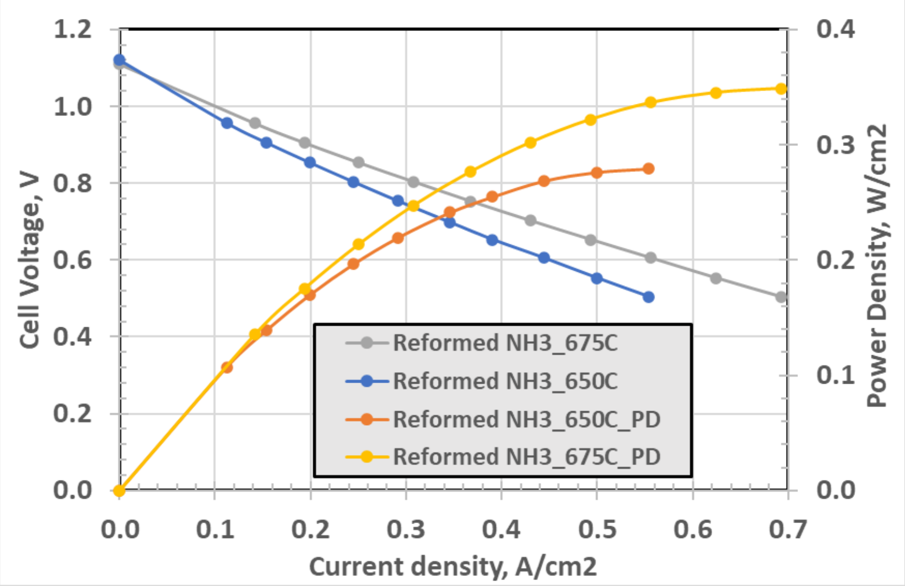
SOFC Testing using Improved Procedures

Temperature effect on SOFC performance

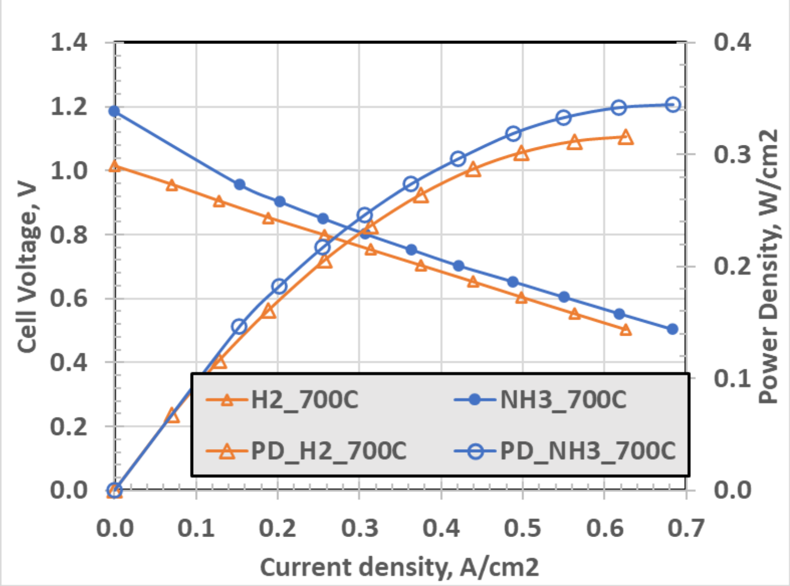
- V-I and PD-I were measured at different temperatures after ~130-hr durability test
  - Significant performance difference between 650°C and 675°C
- Cell shows better performance with NH_3 fuel than H_2 at 700°C



H_2



Reformed NH_3

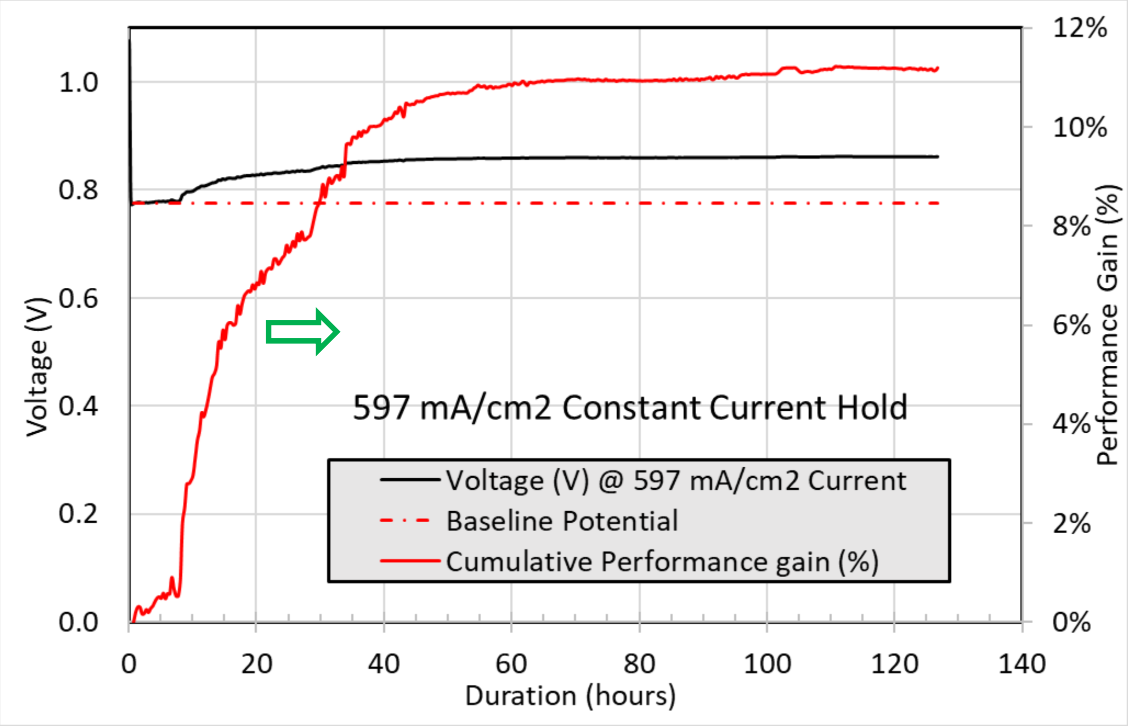


H_2 vs. NH_3

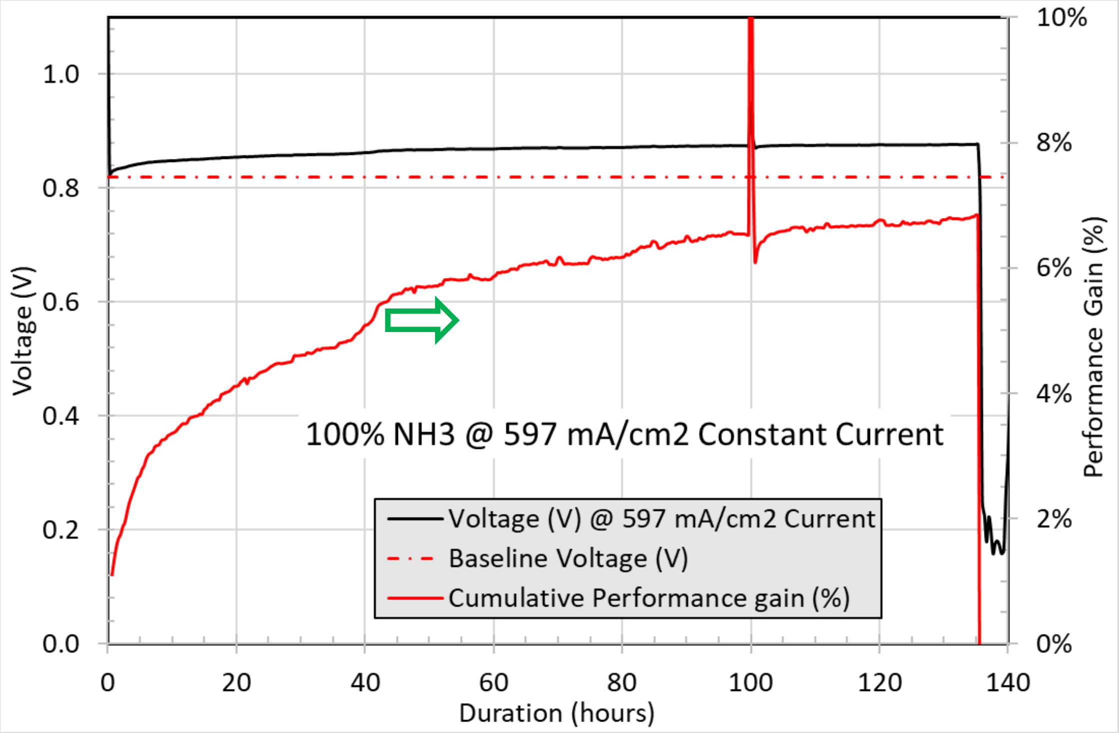
SOFC Durability Test Using Alternate Fuels

Durability at 675°C

- Durability test was conducted at 675°C using reformed NH_3 and NH_3 fuel, respectively
- Cell performance shows significant improvement versus time for both fuels



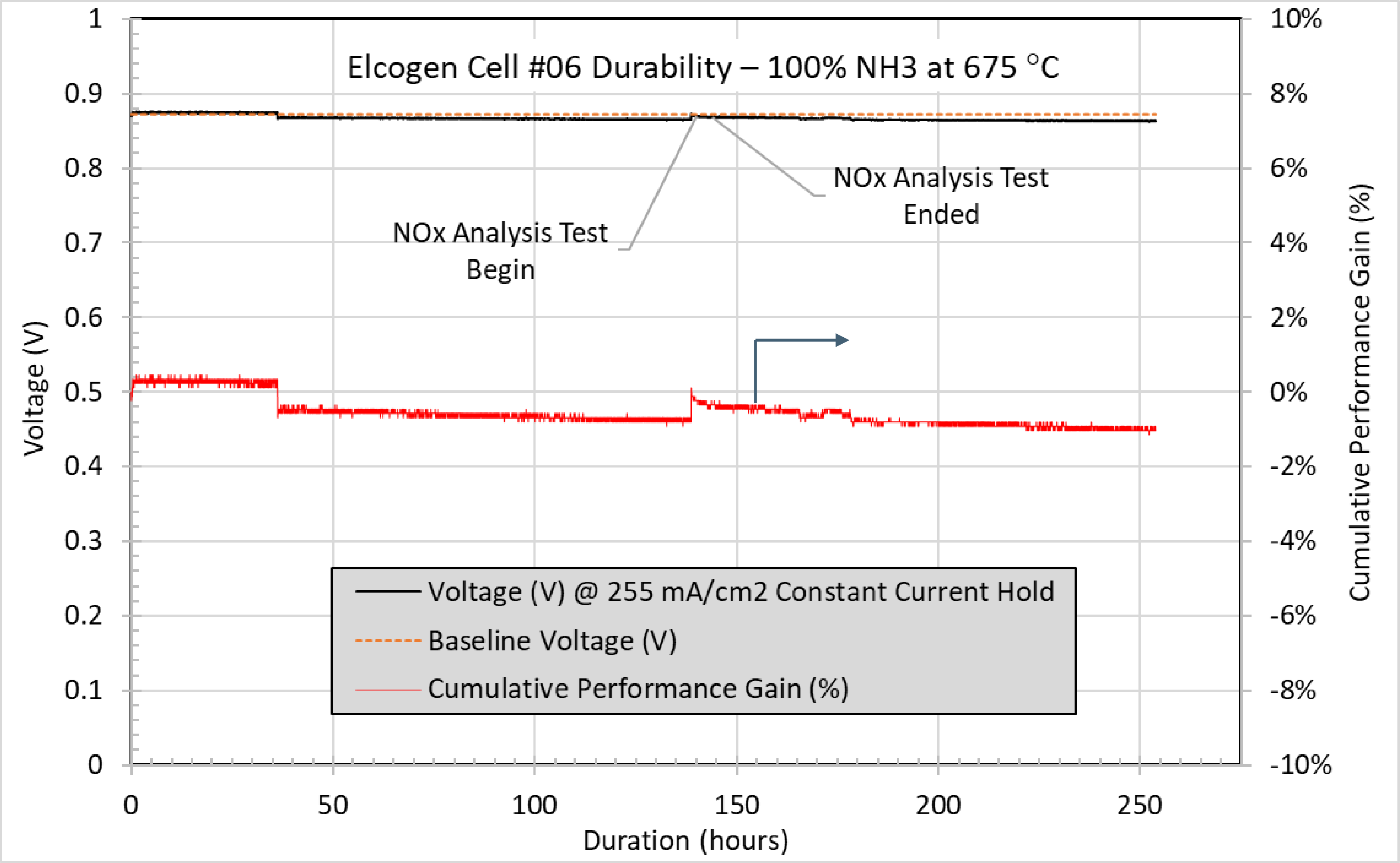
Reformed NH_3 fuel



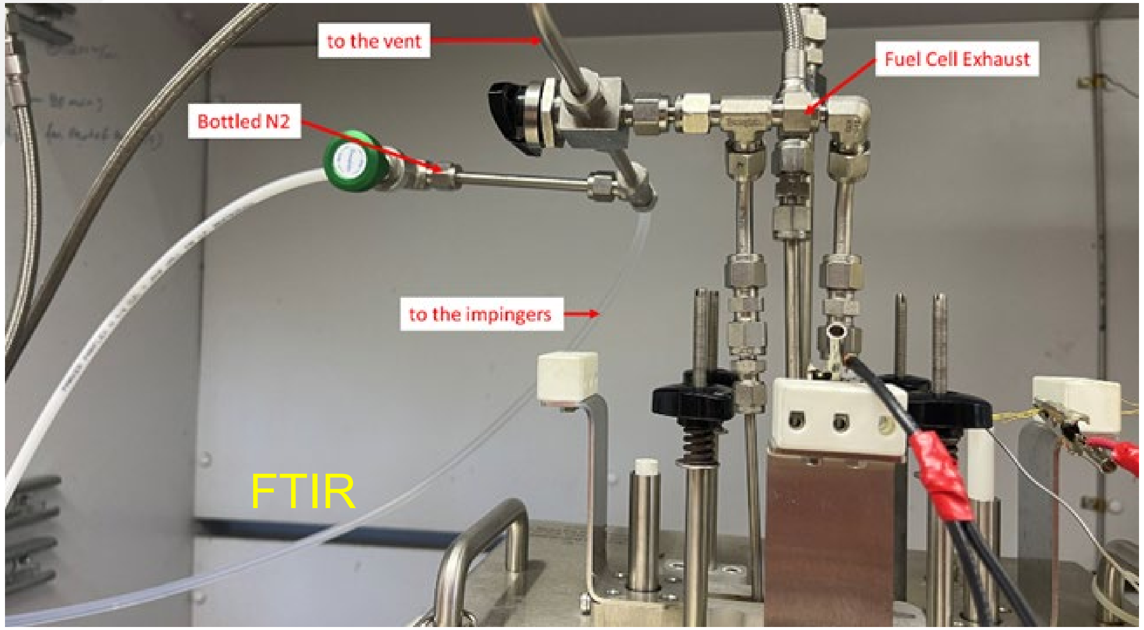
NH_3 fuel

Second Durability Test of Anode-Supported Button Cell

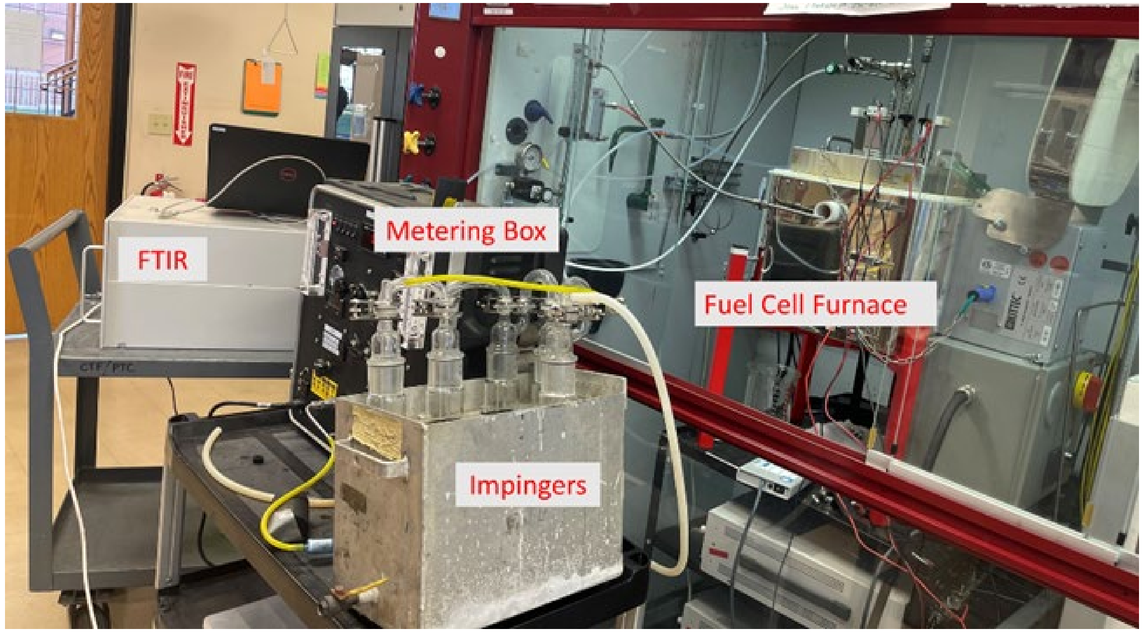
- Over 250 hours duration
  - 255 mA/cm^2
  - 100% NH_3 fuel
- Performed tail gas analysis
  - NOx formation
  - NH_3 decomposition
- 1% cumulative performance loss



Test Set-up for Tail Gas Collection and Analysis



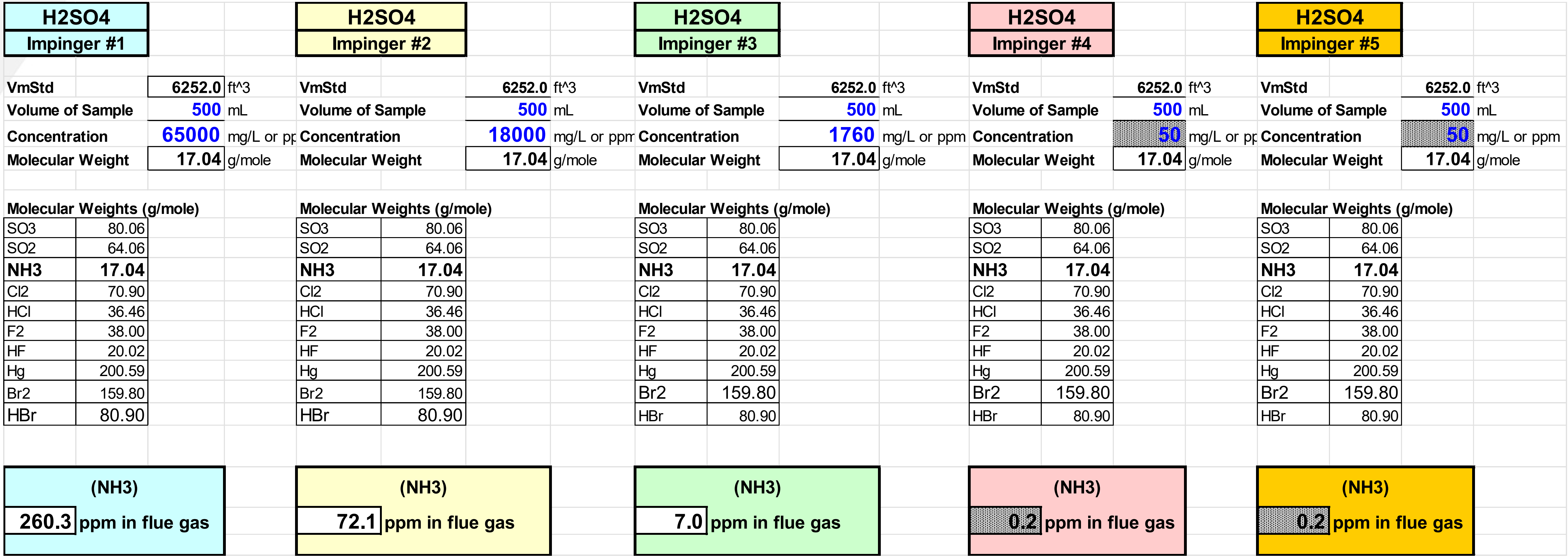
Fuel outlet pipeline of the testing stand for tail gas collection



FTIR and impinger set-up for NOx and NH_3 analysis of exhaust fuel

Tail Gas Analysis for NOx and Ammonia

- There is no presence of NOx in the exhaust fuel.
- Chemical analysis indicates 20.0% unconverted NH_3 in exhaust fuel (N_2-H_2-NH_3) excluding moisture



H2SO4
Impinger #1

VmStd	**6252.0**	ft^3
Volume of Sample	**500**	mL
Concentration	**65000**	mg/L or pp
Molecular Weight	**17.04**	g/mole

Molecular Weights (g/mole)

SO3	80.06
SO2	64.06
NH3	**17.04**
Cl2	70.90
HCl	36.46
F2	38.00
HF	20.02
Hg	200.59
Br2	159.80
HBr	80.90

(NH3)
260.3 **ppm in flue gas**

H2SO4
Impinger #2

VmStd	**6252.0**	ft^3
Volume of Sample	**500**	mL
Concentration	**18000**	mg/L or ppm
Molecular Weight	**17.04**	g/mole

Molecular Weights (g/mole)

SO3	80.06
SO2	64.06
NH3	**17.04**
Cl2	70.90
HCl	36.46
F2	38.00
HF	20.02
Hg	200.59
Br2	159.80
HBr	80.90

(NH3)
72.1 **ppm in flue gas**

H2SO4
Impinger #3

VmStd	**6252.0**	ft^3
Volume of Sample	**500**	mL
Concentration	**1760**	mg/L or ppm
Molecular Weight	**17.04**	g/mole

Molecular Weights (g/mole)

SO3	80.06
SO2	64.06
NH3	**17.04**
Cl2	70.90
HCl	36.46
F2	38.00
HF	20.02
Hg	200.59
Br2	159.80
HBr	80.90

(NH3)
7.0 **ppm in flue gas**

H2SO4
Impinger #4

VmStd	**6252.0**	ft^3
Volume of Sample	**500**	mL
Concentration	**50**	mg/L or pp
Molecular Weight	**17.04**	g/mole

Molecular Weights (g/mole)

SO3	80.06
SO2	64.06
NH3	**17.04**
Cl2	70.90
HCl	36.46
F2	38.00
HF	20.02
Hg	200.59
Br2	159.80
HBr	80.90

(NH3)
0.2 **ppm in flue gas**

H2SO4
Impinger #5

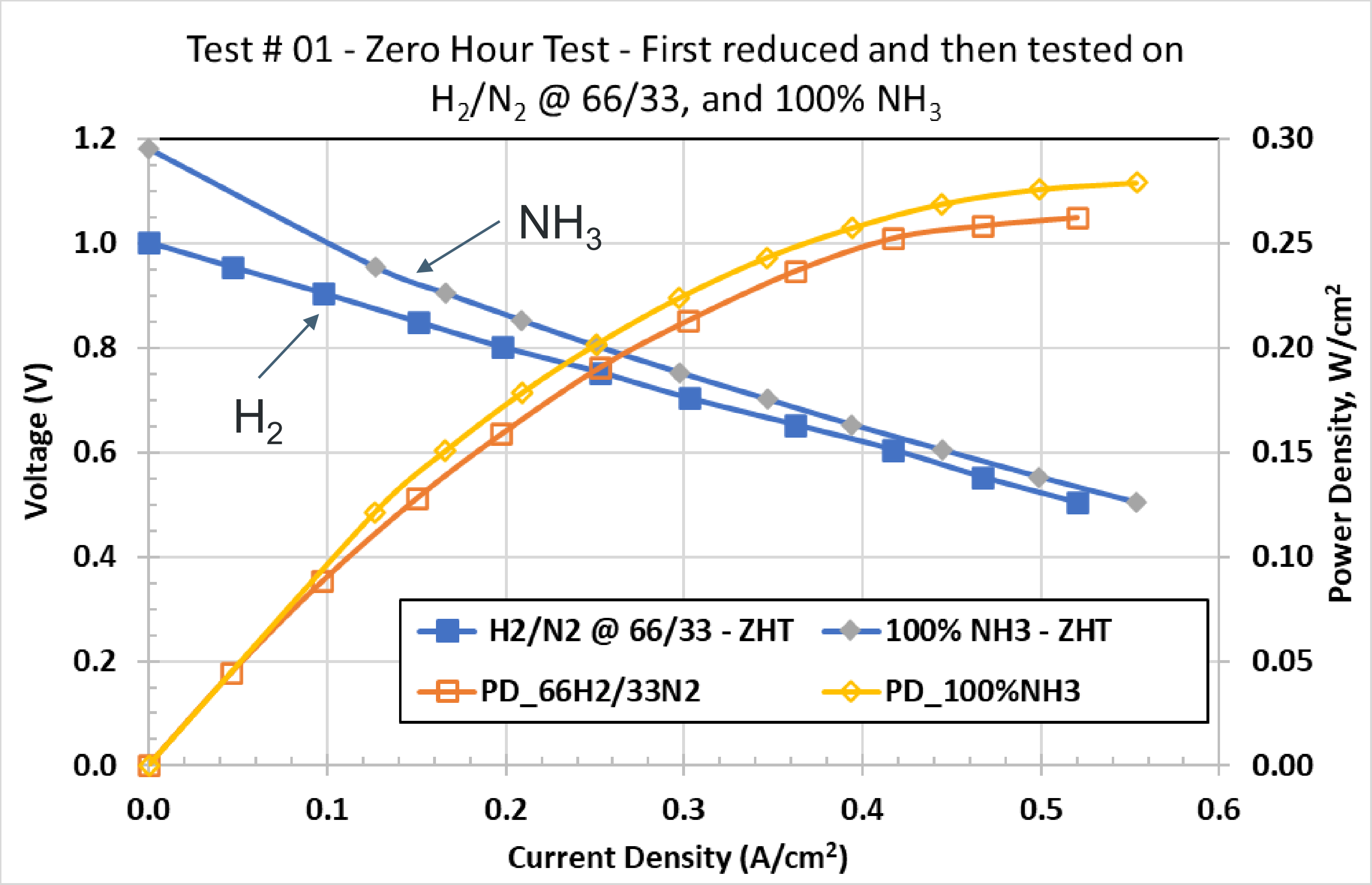
VmStd	**6252.0**	ft^3
Volume of Sample	**500**	mL
Concentration	**50**	mg/L or ppm
Molecular Weight	**17.04**	g/mole

Molecular Weights (g/mole)

SO3	80.06
SO2	64.06
NH3	**17.04**
Cl2	70.90
HCl	36.46
F2	38.00
HF	20.02
Hg	200.59
Br2	159.80
HBr	80.90

(NH3)
0.2 **ppm in flue gas**

Electrolyte-Supported Button Cell Testing

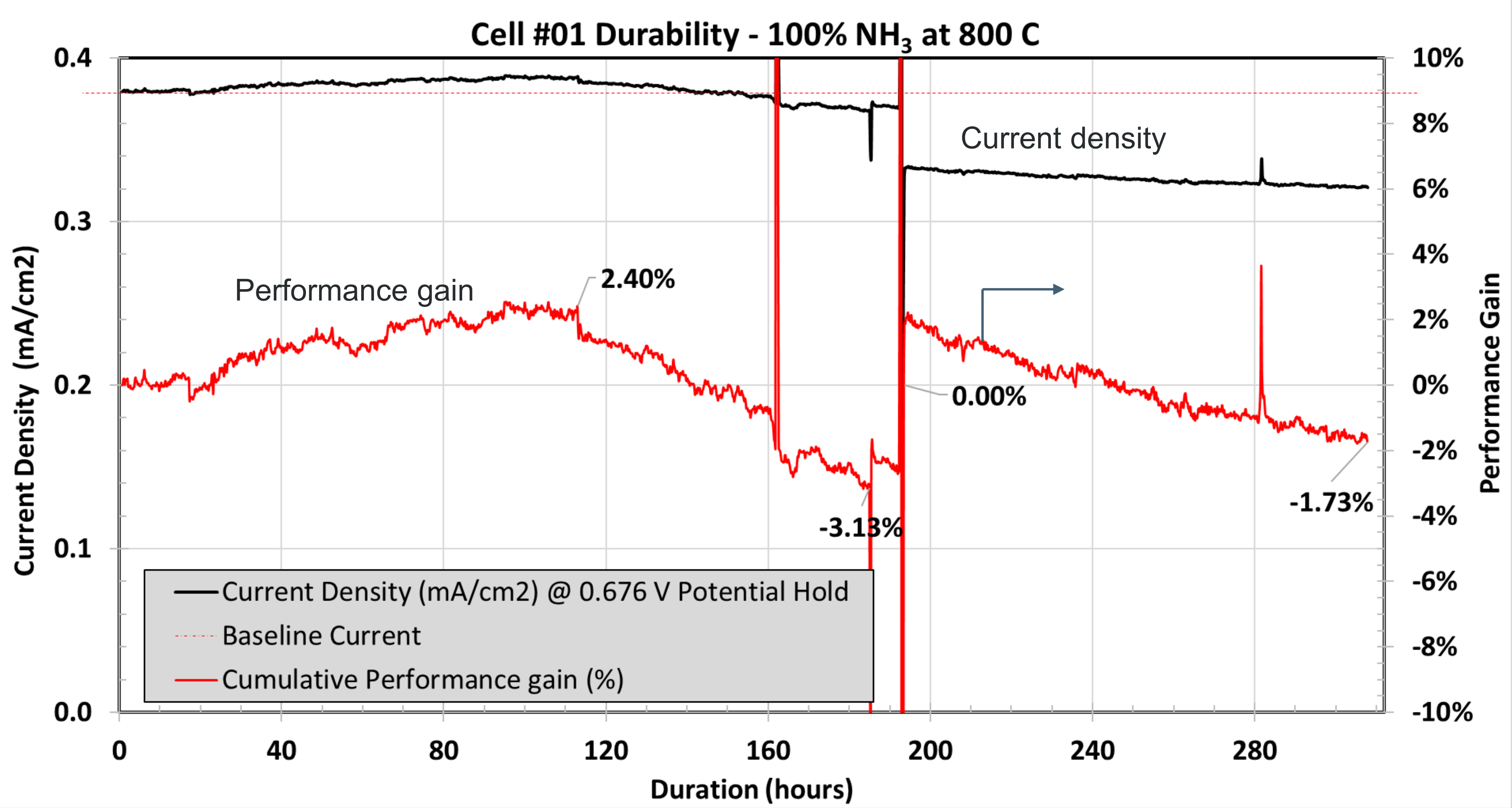


Cell OCV vs. gas flow

	Anode			Cathode	
	H2	N2	Total	Air	OCV
1	90	30	120	120	0.955
2	120	40	160	120	1.028
3	120	40	160	160	1.038
4	150	50	200	160	1.069
5	150	50	200	200	1.045
6	150	50	200	160	1.065
7	180	60	240	160	1.084
8	180	60	240	200	1.065
9	180	60	240	150	1.091

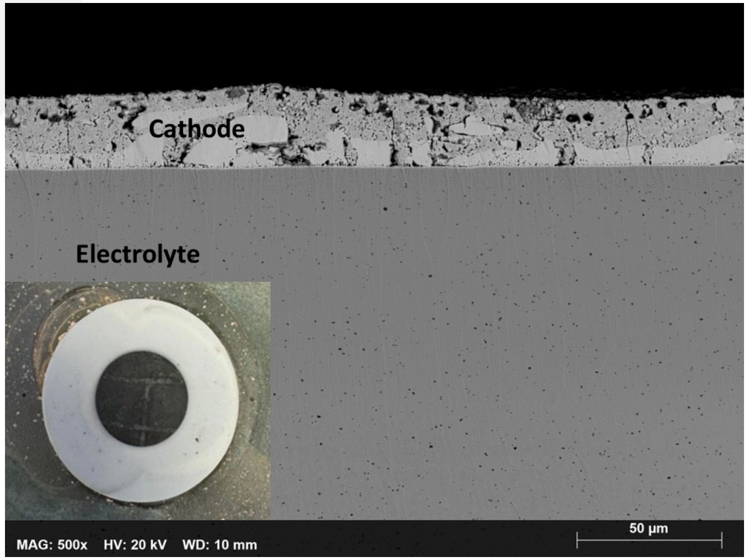
Separate button cell

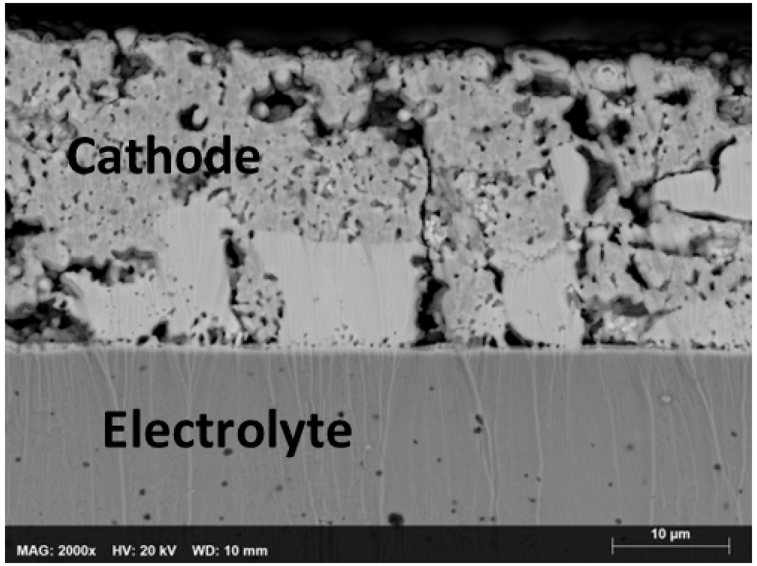
Durability of Electrolyte-Supported Button Cell with NH_3

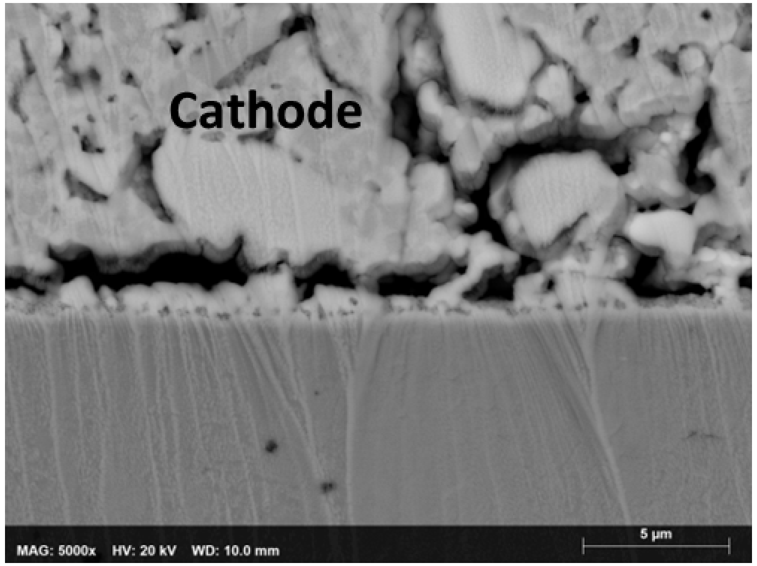


Post-Mortem Analysis

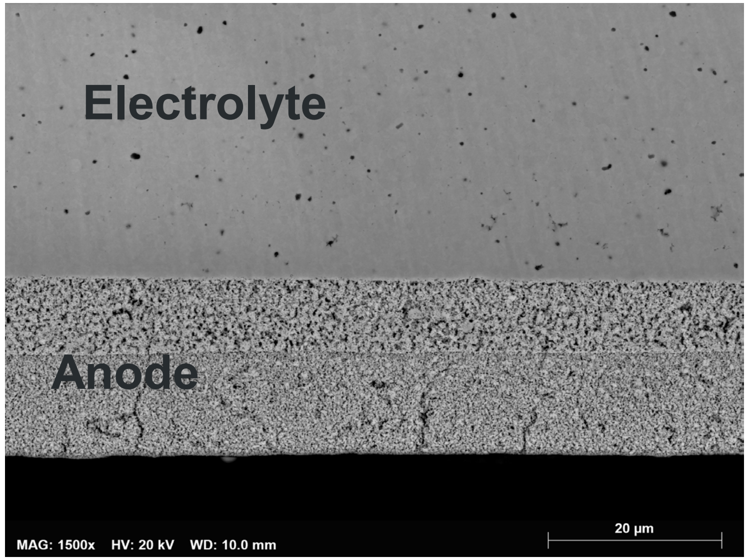
Cathode

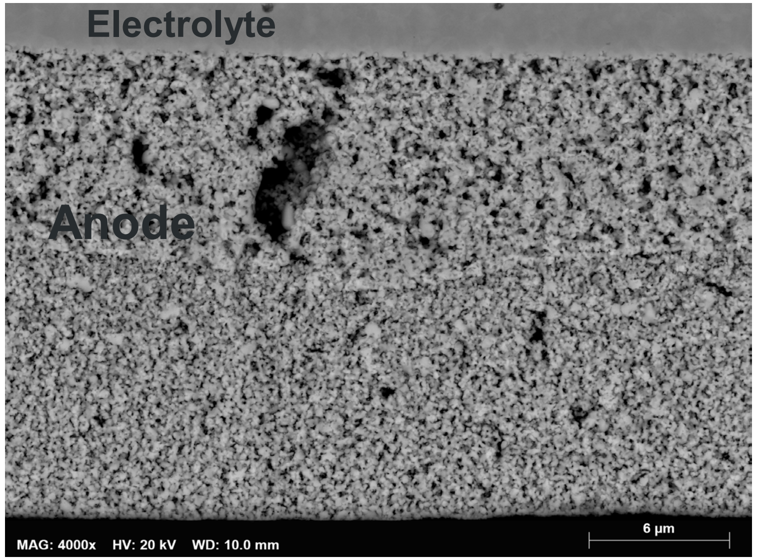


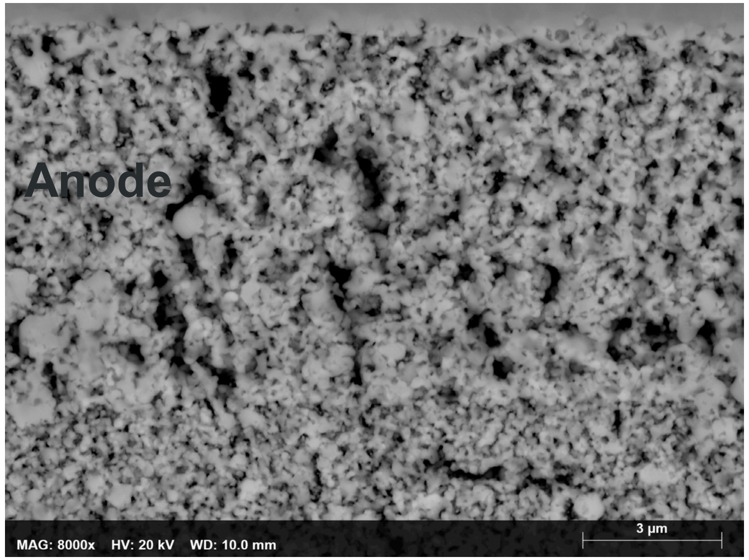




Anode







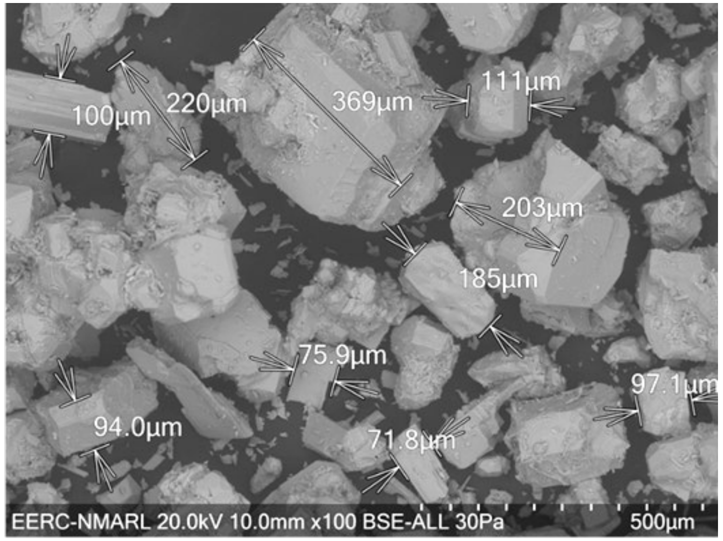
2.2.2 Proton conducting electrolyte and SOFC development

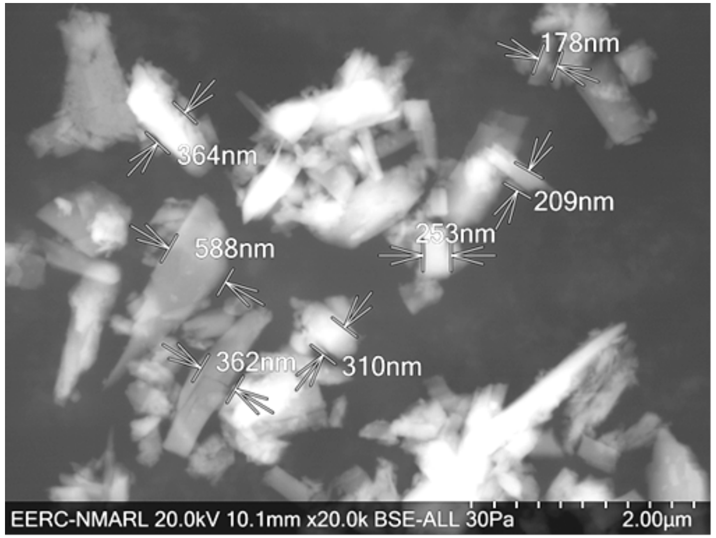
Cerium **U**ltra**P**hosphate Proton-Conducting Electrolyte – CeP_5O_{14} (**CUP**)
Brief Summary From Last Review

- **Electrolyte processing**
  - Performed CUP disk milling study
    - ♦ Dry vs. wet milling
  - Investigated the effect of pressing parameters on green density of CUP disk using heated die
  - Studied chemical stability of CUP powder
- **Electrolyte characterization**
  - CUP disk conductivity vs. processing
  - 0.027 S/cm conductivity was achieved at 225°C
  - XRD for phase identification
  - CUP thermal and chemical stability

CUP Powder Milling Study

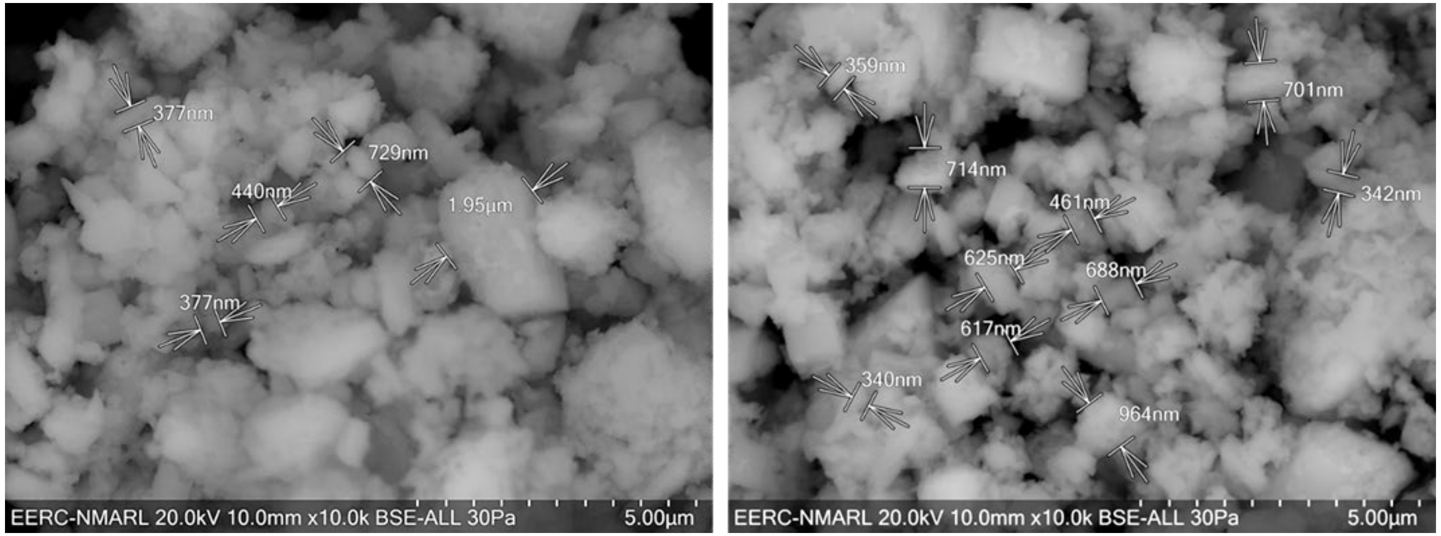
As-synthesized powder
- 70-350 μm





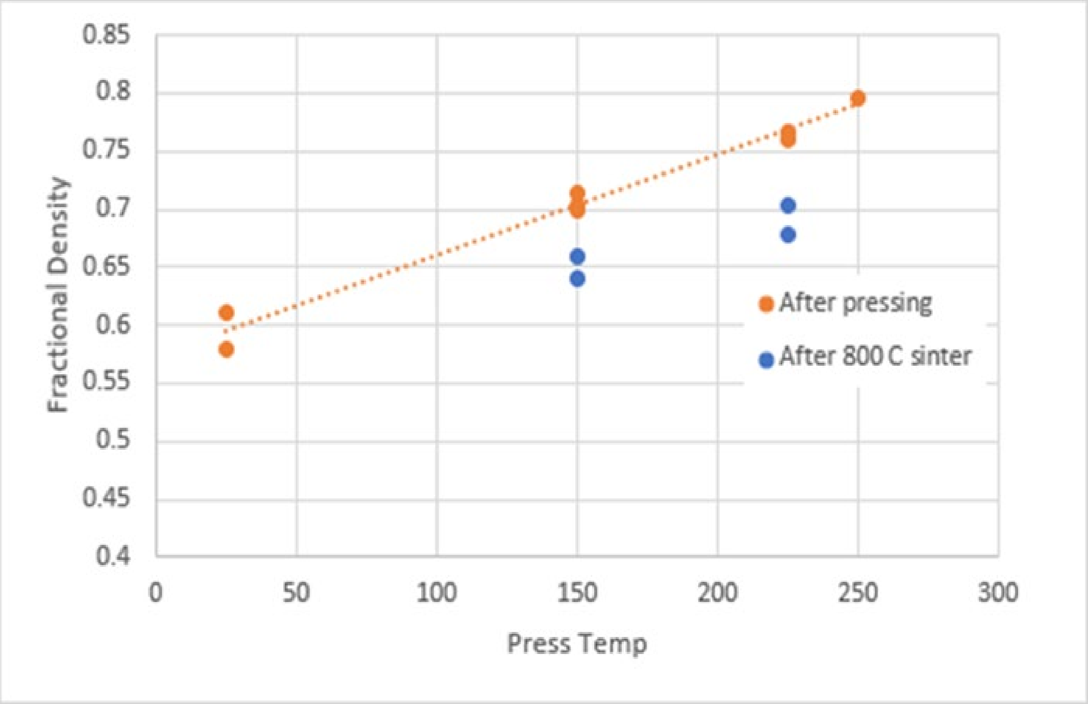
Wet-milled powder
- 0.2- 0.6 μm

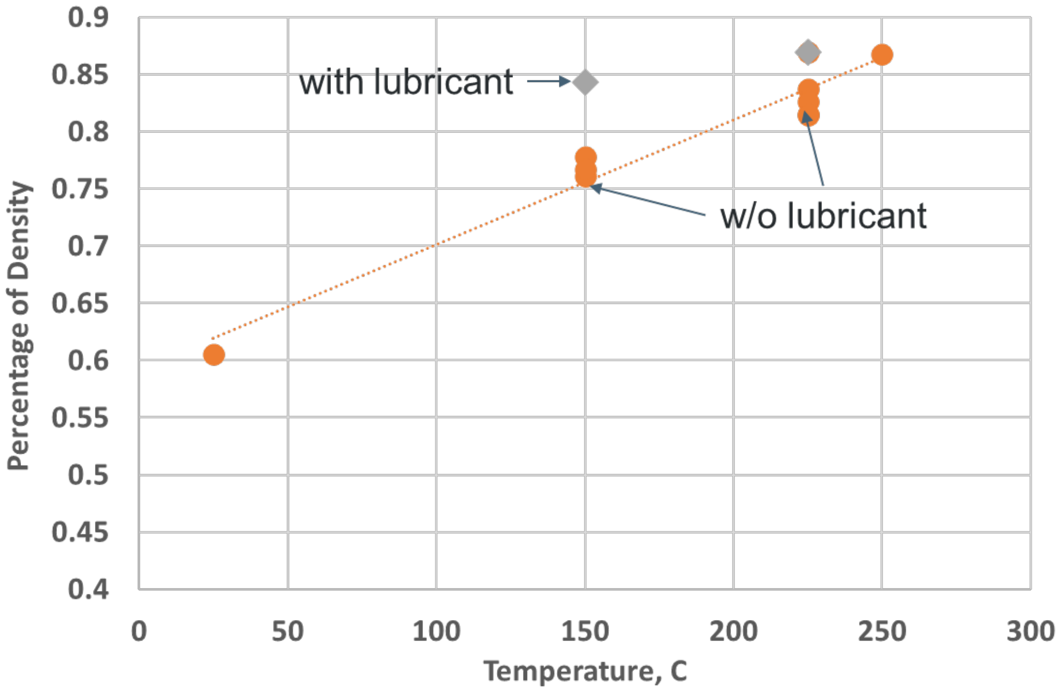
4-cycles of dry-milled
- 0.3-2 μm



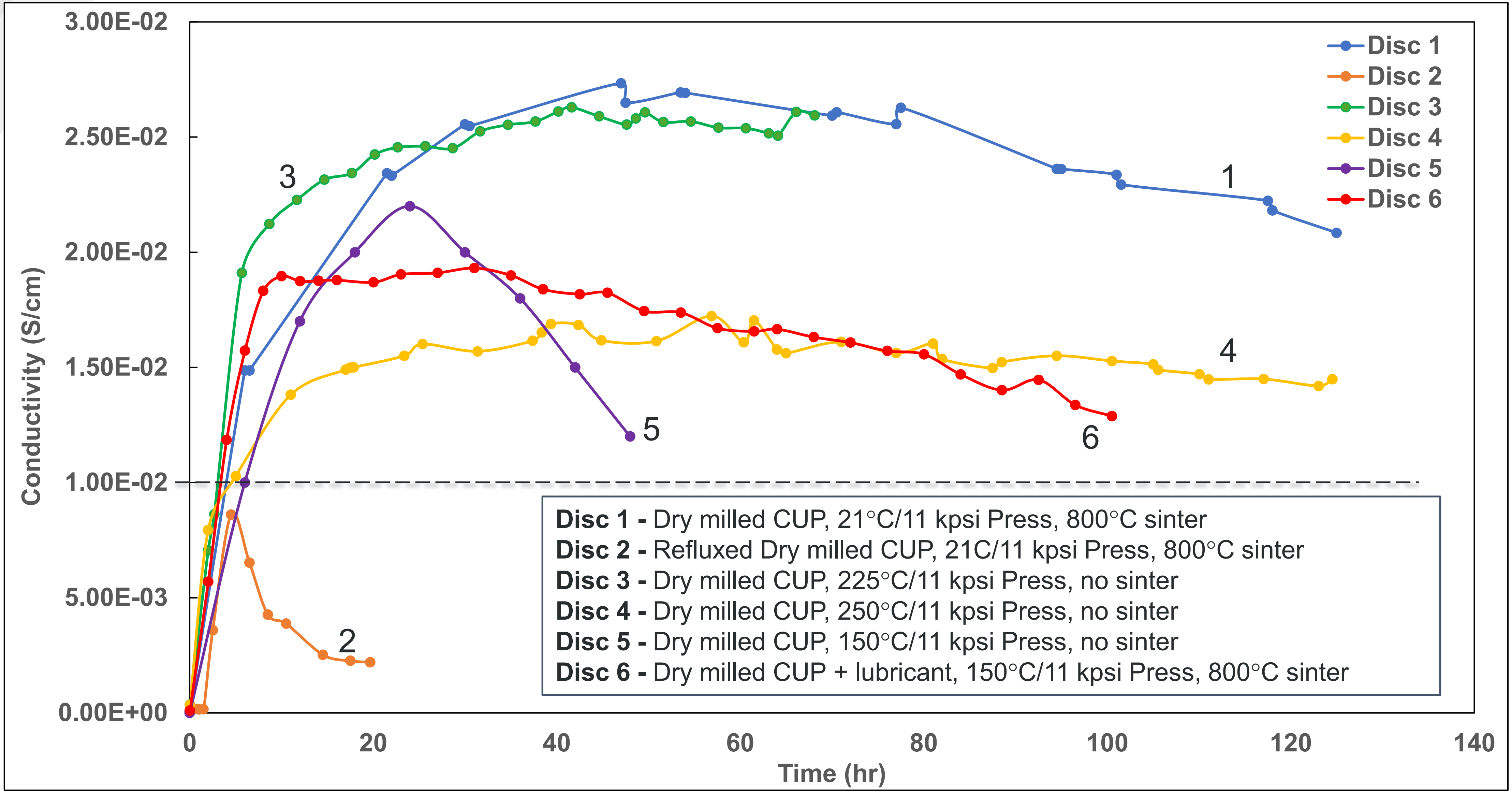
CUP Disk Green Density Optimization

- Standard procedures for CUP disk preparation – 11,00 psi at room temperature, followed by sintering at 800°C and ambient pressure.
- Pressed CUP disk at elevated temperatures, 150-250°C and 11,000 psi (with no 800°C sinter), showing green density improvement by up to 50%.
- Addition of lubricant (liquid to enable particle rearrangement under pressure) to CUP powder further improved green density, especially at lower temperatures





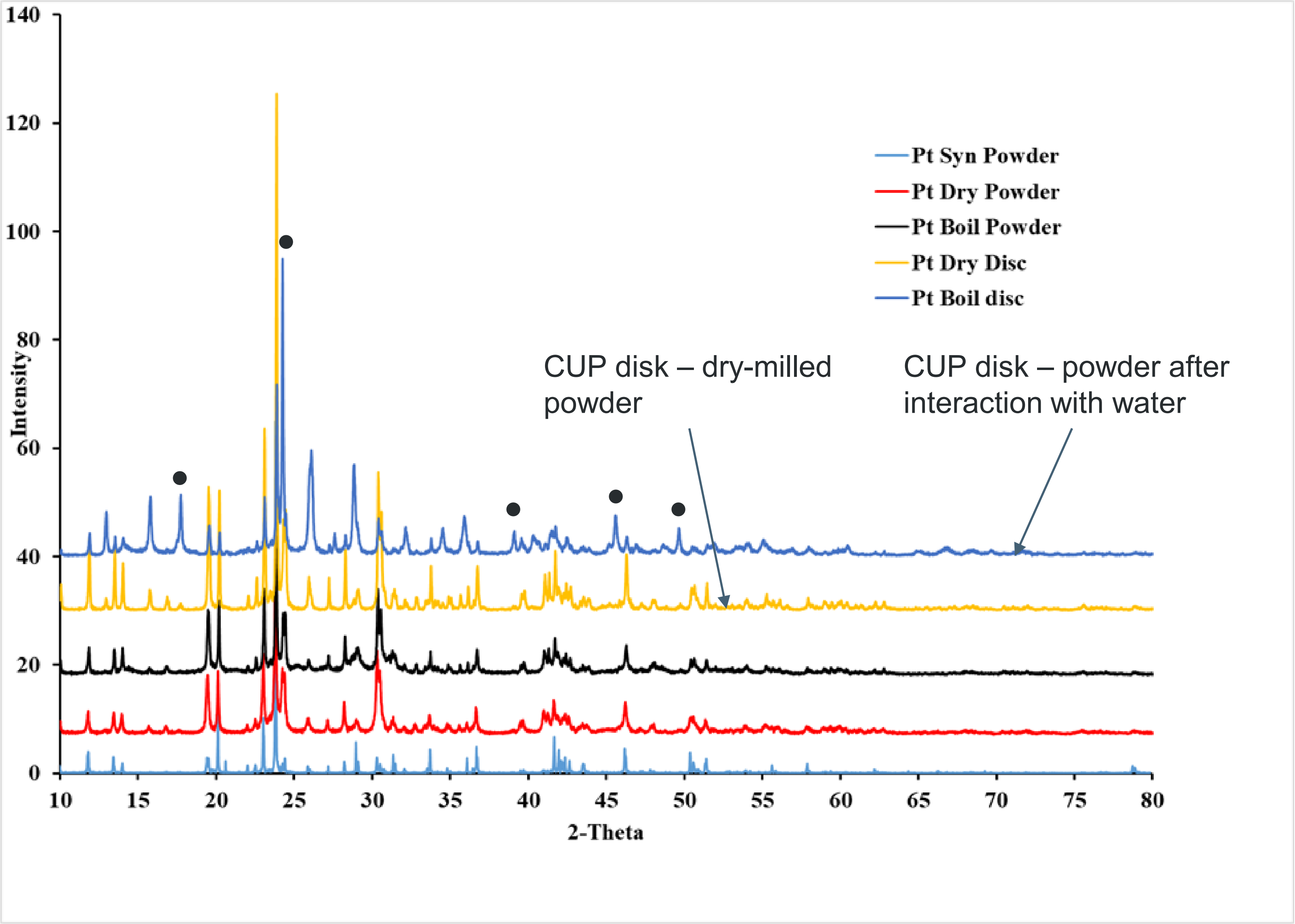
Summary of CUP Disk Conductivity



Disc 1 - Dry milled CUP, 21°C/11 kpsi Press, 800°C sinter
Disc 2 - Refluxed Dry milled CUP, 21C/11 kpsi Press, 800°C sinter
Disc 3 - Dry milled CUP, 225°C/11 kpsi Press, no sinter
Disc 4 - Dry milled CUP, 250°C/11 kpsi Press, no sinter
Disc 5 - Dry milled CUP, 150°C/11 kpsi Press, no sinter
Disc 6 - Dry milled CUP + lubricant, 150°C/11 kpsi Press, 800°C sinter

CUP Chemical Stability Investigation

- CUP chemical stability was investigated by interacting CUP powder with 100°C water
- CUP disk was made using interacted powder
- XRD indicates possible new phase formation



CUP disk – dry-milled powder

CUP disk – powder after interaction with water

CUP Powder Thermal Properties

No of milling cycles	Estimated particle size, µm	Atomic%			
		Ce	O	P	P/Ce
1	0.25-13	7	50	43	6.1
2	0.05-5	7	53	41	5.9
4	0.05-2	5	65	30	6.0
CeP_5O_{14}		5	70	25	5.0

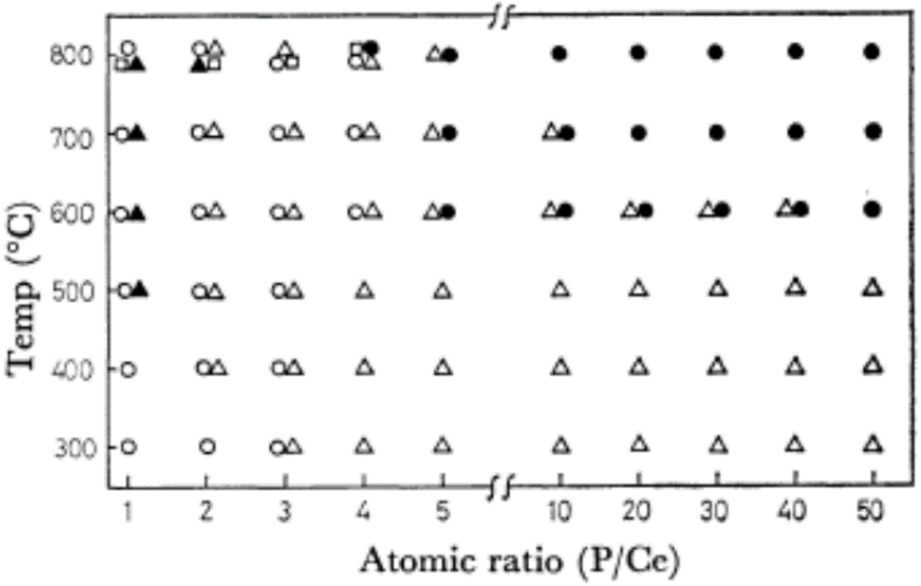
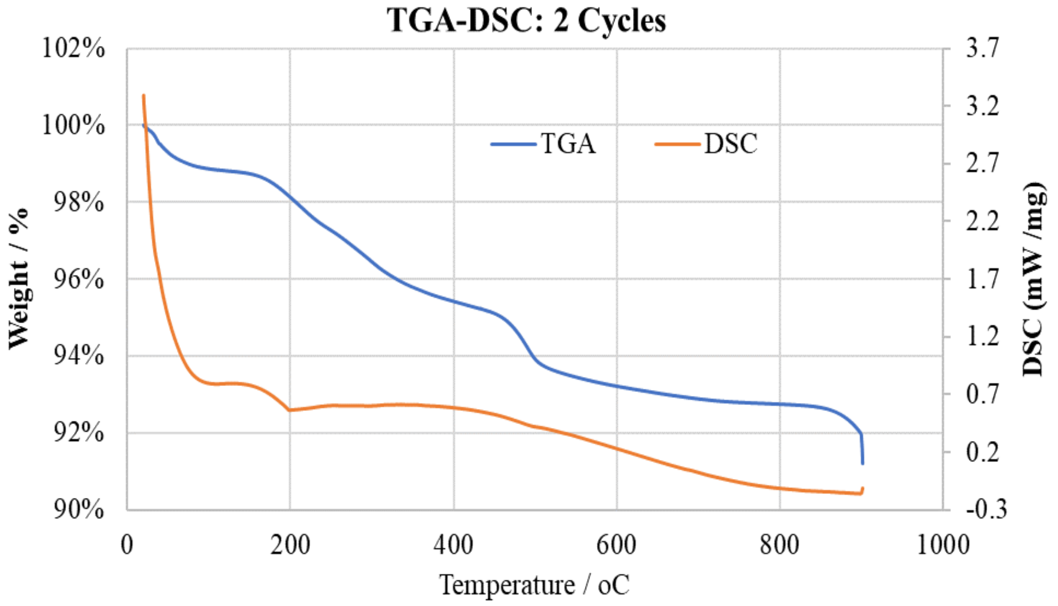
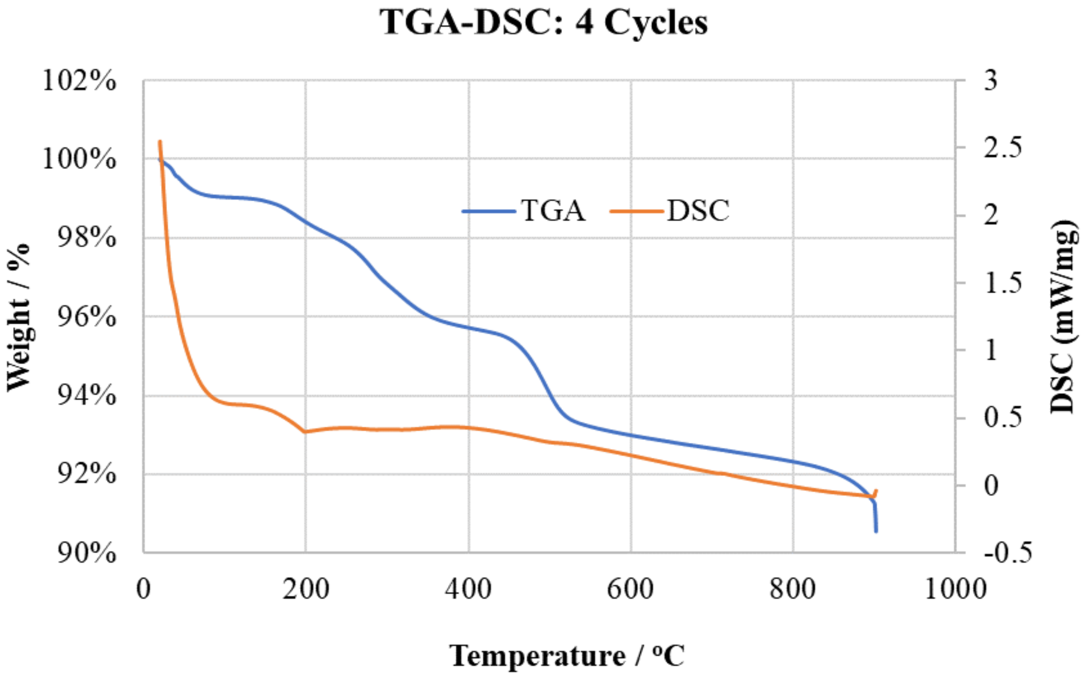


Fig. 5. Relationship of the species of cerium phosphates to heating temperature and atomic ratio. ▲: $CePO_4$, ○: CeP_2O_7, □: $Ce(PO_3)_3$, △: $Ce(PO_3)_4$, ●: CeP_5O_{14}.

M. Tsuhako, Bulletin Chem. Soc. Japan, 52(1979)1034





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 report was completed.

Summary

- SOFC suppliers were selected to support testing activities at EERC.
- Generated SOFC performance and short-term durability data using anode-supported cell and ammonia as fuel.
  - Performed tail gas analysis for NOx and NH_3 decomposition at SOFC operation conditions
- Initiated SOFC testing using electrolyte-supported cell and ammonia fuel.
- Conducted milling study to reduce particle size of CUP powder.
- Optimized processing parameters to improve CUP green density.
- Investigated CUP thermal and chemical stability using TGA/DSC and by interacting CUP powder with fluxed water at 100°C.
- Measured conductivity of CUP disks pressed at variety of conditions at 225°C and achieved max. conductivity of 0.027 S/cm.

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