Low Cost, Large Area SOEC Stack for H_2 and Chemicals

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Develop and Build an Efficient 5 kW Solid Oxide Electrolyzer and Demonstrate Operation under Simulated, but Commercially Relevant Conditions

- Develop and build an efficient SOEC and demonstrate operation under simulated, but commercially relevant conditions
- Design electrode cassette modules that include a large 300 cm^2 active area cell, a metal frame and channels for gas flow.
- Develop and employ optimized materials to provide the best possible combination of performance, lifetime and cost.

R&D to Reduce Stack Cost and Improve Durability

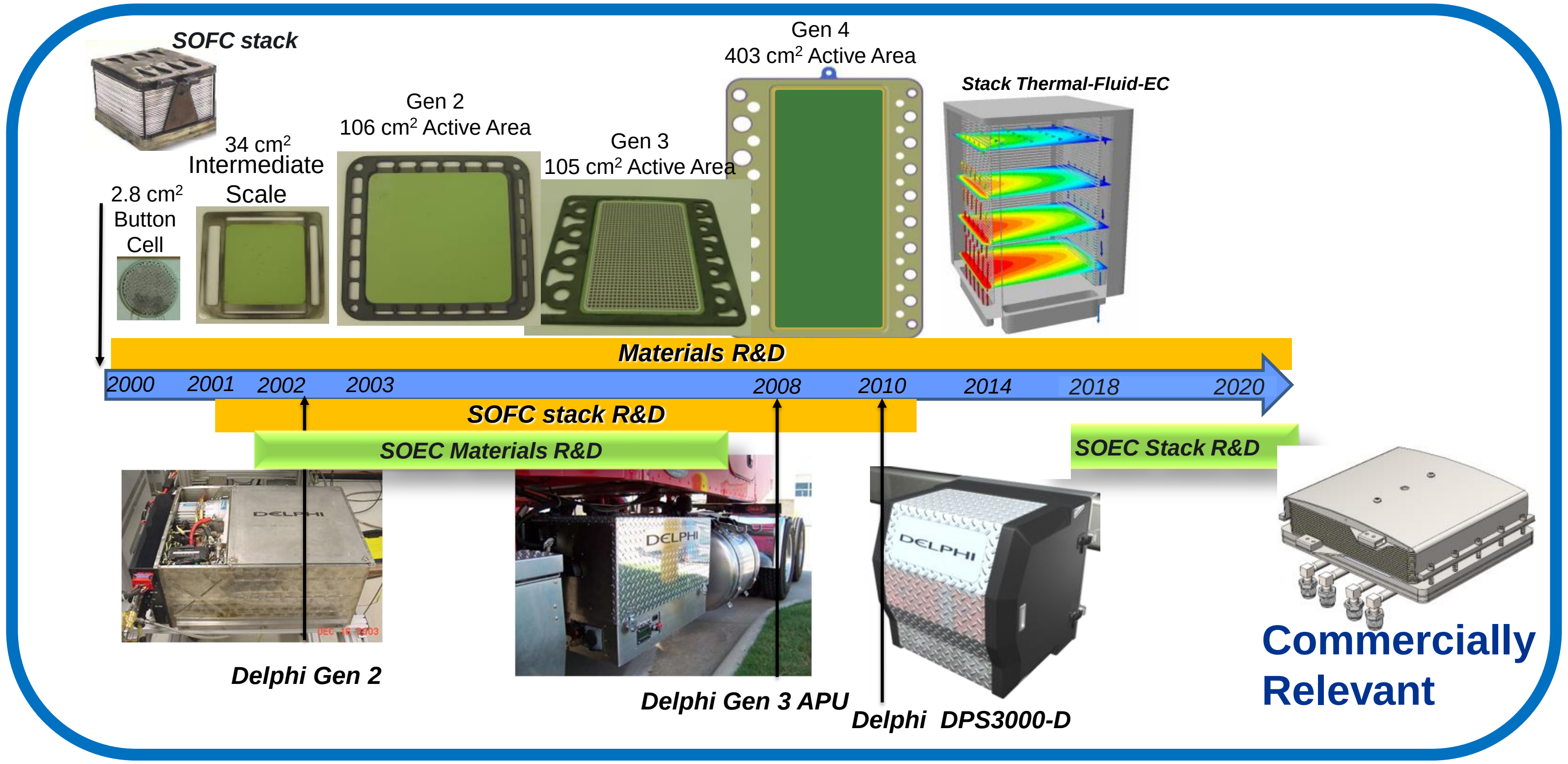
Technical Barriers and Gaps

HTE stack performance and durability remains understudied due to industry proprietary R&D:

- Stack durability is rarely reported
- Cost at scale is not known
- Commercially relevant repeat units are not available

DOE Targets

HTE Electrolyzer Stack Goals by 2025	
Capital Cost	\$100/kW
Electrical Efficiency (LHV)	98% at 1.5 A/cm^2
Lifetime	60,000 hr



PNNL has established cells/stacks fabricating and modeling capabilities and expertise from multiple DOE SOFC R&D programs and private investments

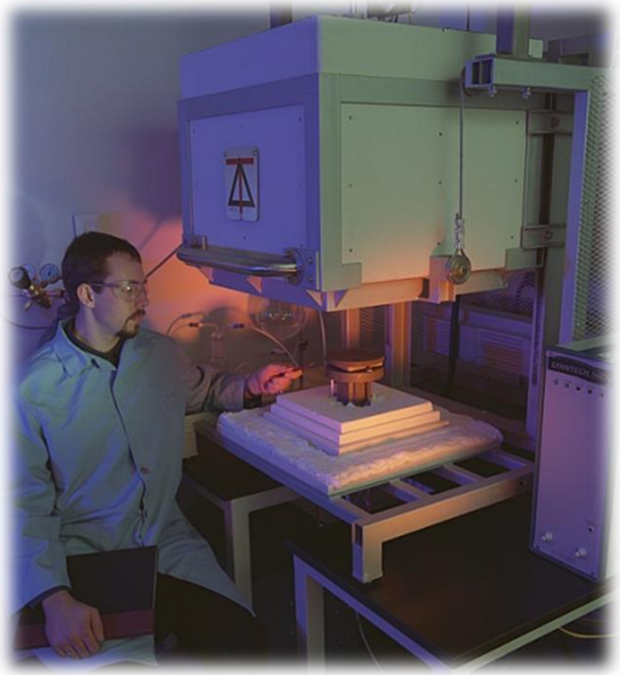
PNNL Testing Approach: Button Cells, Full Size Cells, and Stacks

High throughput button cell testing (~70 cells)

active area is 2-4 cm^2

- Materials screening
- I-V and EIS measurements
- pH_2O=1-99%; impurities

Larger size planar cell testing (2+6)



with and without metal IC

active area is 16 cm^2

- Relevant steam utilizations
- High currents
- Temperature gradients
- Interconnect

H2NEW
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1-5 kW short stack testing (3 platforms)

active area 300 cm^2

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- Components
- Seals
- Steam delivery and utilization
- Heat management
- Durability

Solid Oxide Cell Manufacturing

Powder Synthesis and Processing

Fabrication Techniques

- Tape casting, screen printing, compression molding, injection molding, isostatic and uniaxial pressing, slip casting, laser cutting, roll lamination

Thin Film Techniques

- Spin coating, PVD, ALD,PLD, slurry and solution coating, ultrasonic spray coating

Sintering in air and environment upto 1500°C

Seals and Protective Coating

Glycine – nitrate powder synthesis

8 ft long tape caster

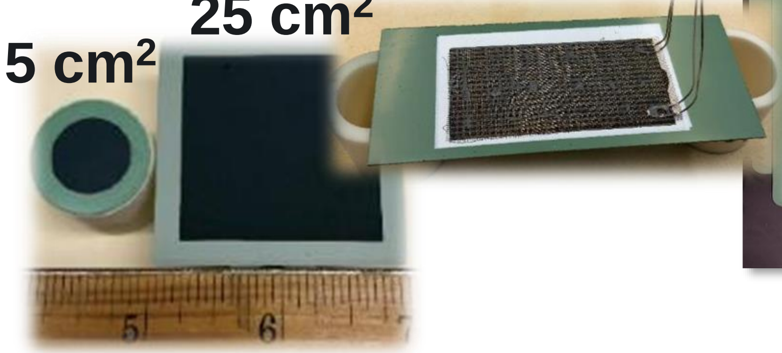
Vacuum sealer

High Temperature Furnaces

Hot roll laminator

Screen Printer

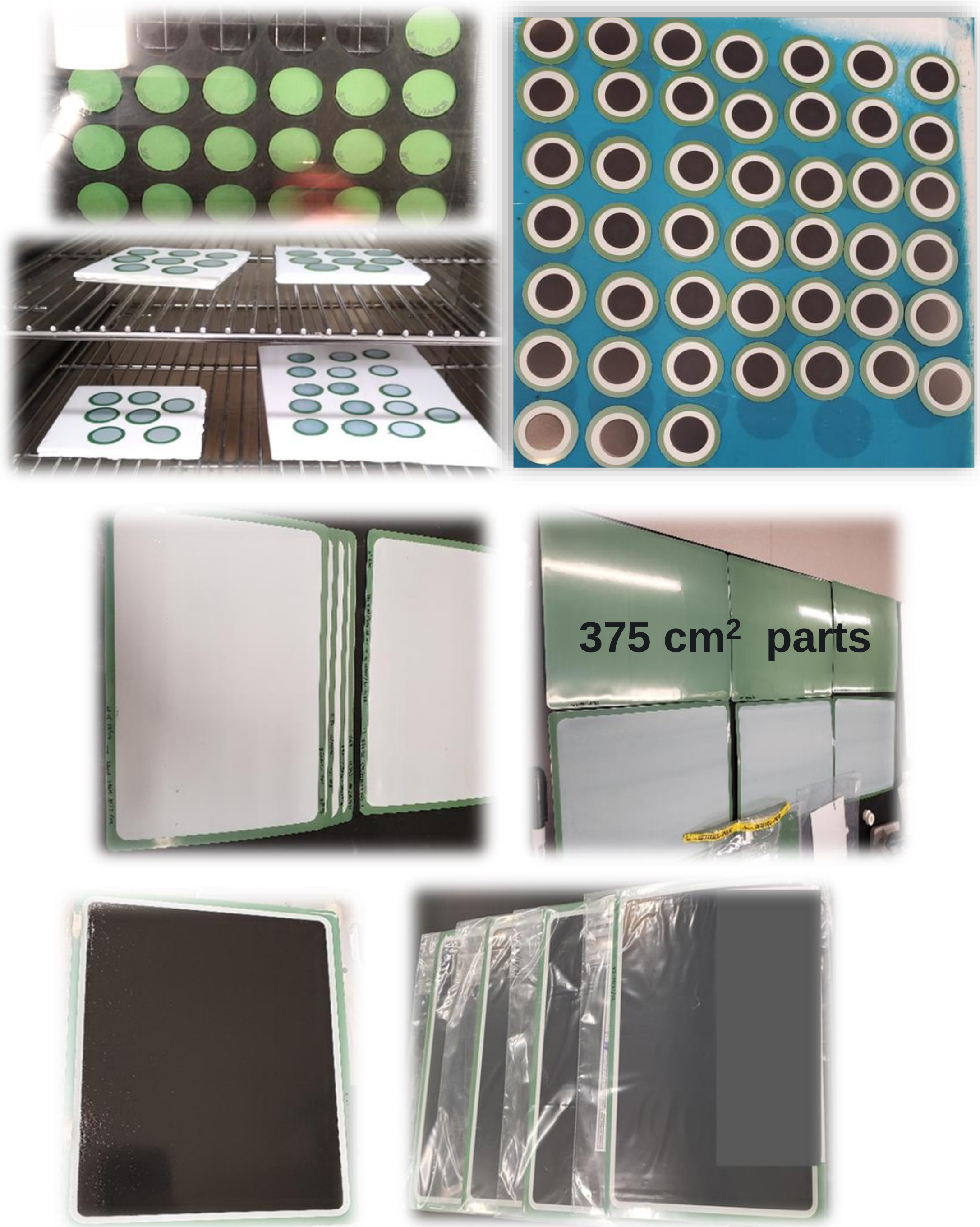
5 cm²   25 cm²   25 cm²



375 cm²

Laser Cutter

Cell Production of Different Sizes Established

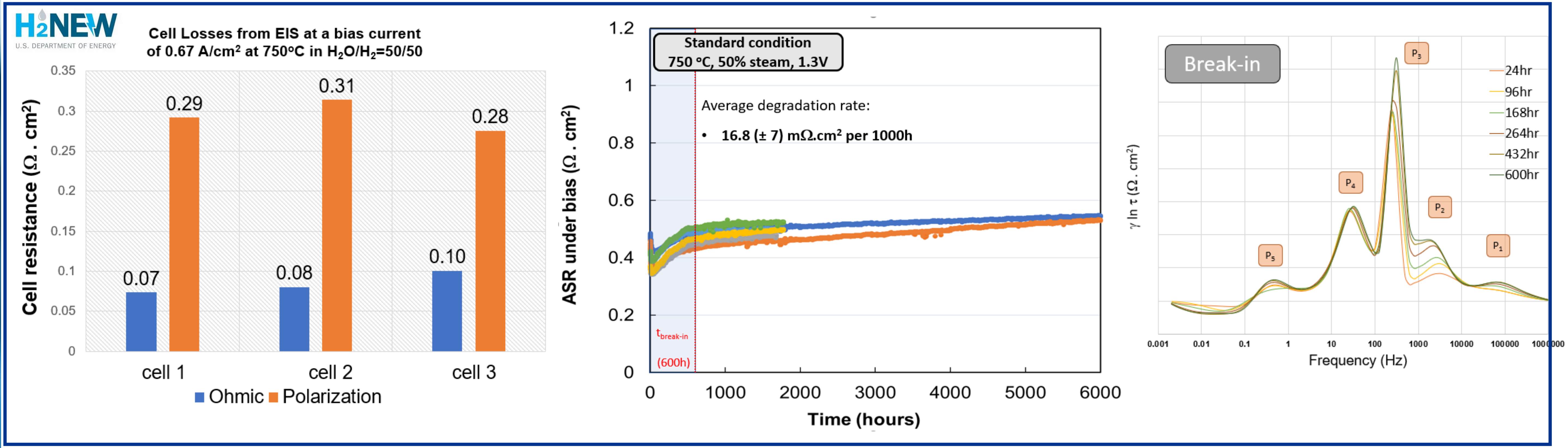


PNNL produces cells for H2NEW

U.S. DEPARTMENT OF ENERGY

- ❑ Ni-YSZ electrode-supported planar cells have been selected as standard reference cells
- ❑ Successfully produced large cells to reduce stack part count, the number of interfaces in stack, and cost
- ❑ Decreased YSZ thickness to reduce firing steps, cost, and improve the performance
- ❑ Developed a batch fabrication process to minimize the variance between separate cells
- ❑ Initiated the development of QA/QC procedures
- ❑ Initiated electrode microstructure optimization to improve performance and durability

Baseline Performance Obtained at 750ºC at 1.3 Volt in 50% Steam Using Multiple Repeats for 6,000 hours

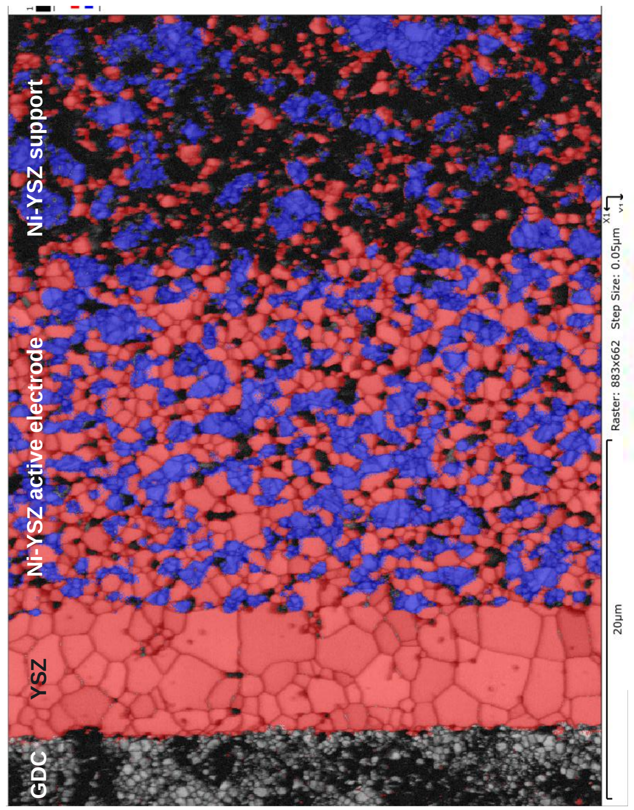


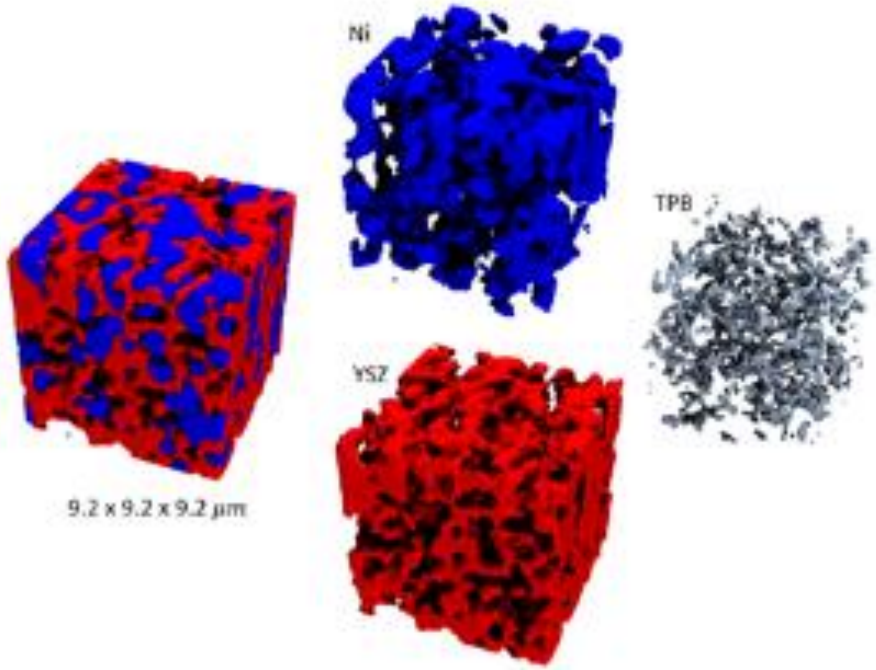
- Demonstrated in house reproducibility
- Demonstrated cell stability; average degradation rate is below 17 ohm·cm^2 per 1,000 hours
- Detailed EIS and DRT analyses attributed degradation during break-in period to two processes in 1 kHz–10kHz and 100 Hz–1 kHz frequency ranges, likely associated with diffusion phenomena in the oxygen electrode

Probing for Degradation Mechanisms: Post-Test Cell and Component Characterization by SEM/EDS, EBSD, STEM, APT

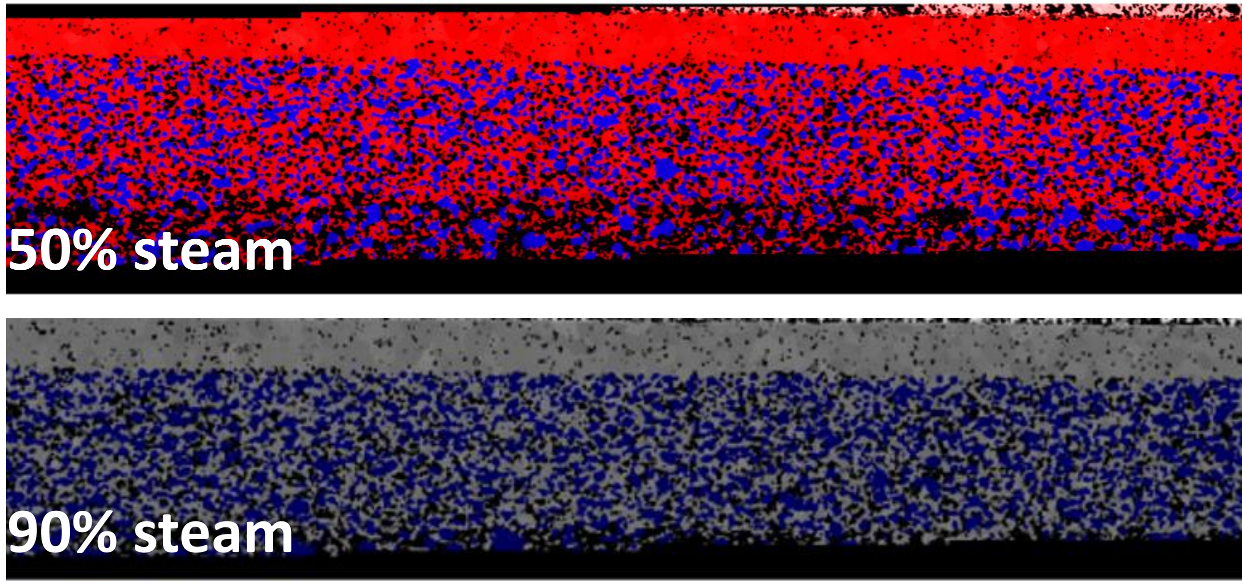
Hydrogen Electrode

No Ni coarsening or migration after 3,000 hours at 1.3V at 750 and 800ºC





Triple-phase boundary determination using PNNL modeling tools

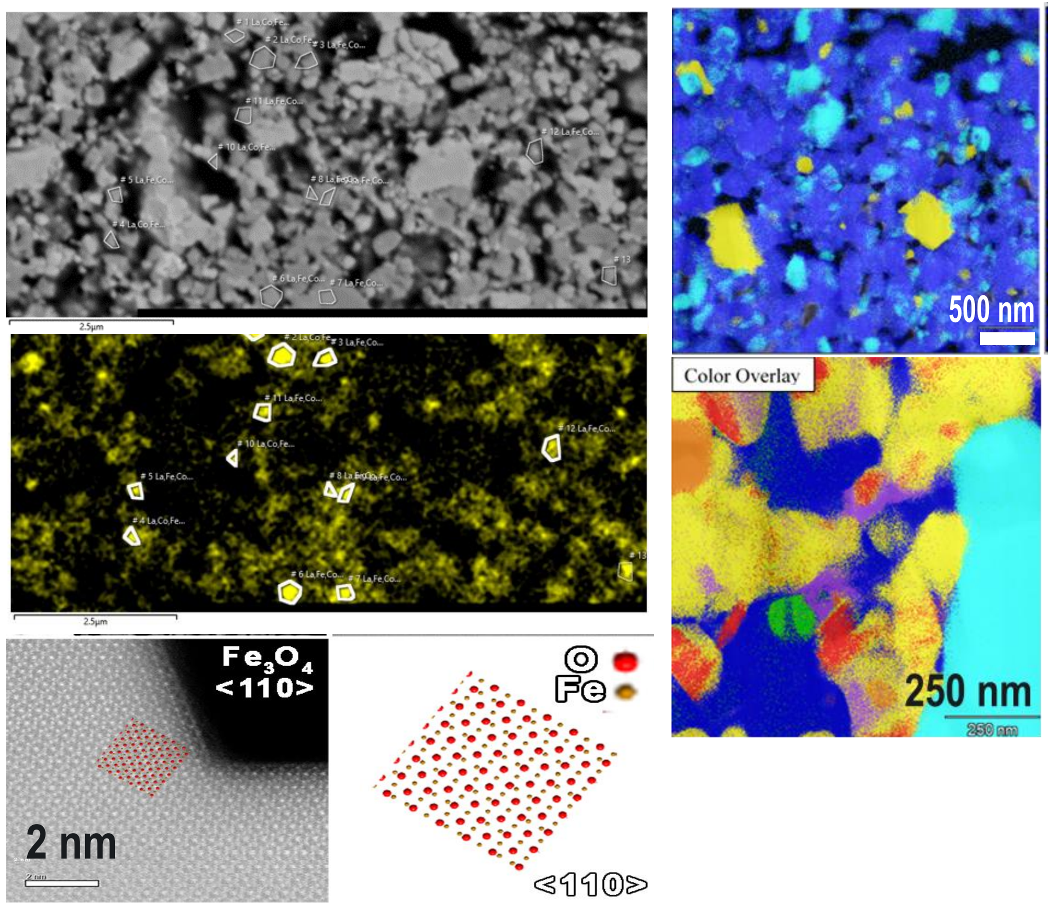


Probing for Degradation Mechanisms:

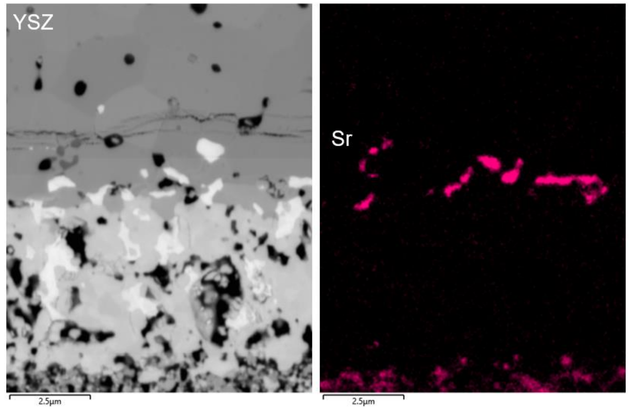
Post-Test Cell and Component Characterization by SEM/EDS, EBSD, STEM, APT

Oxygen Electrode

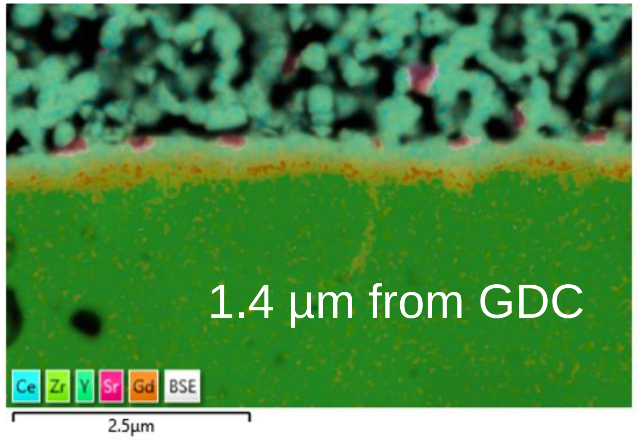
Co inconsistency



Sr migration

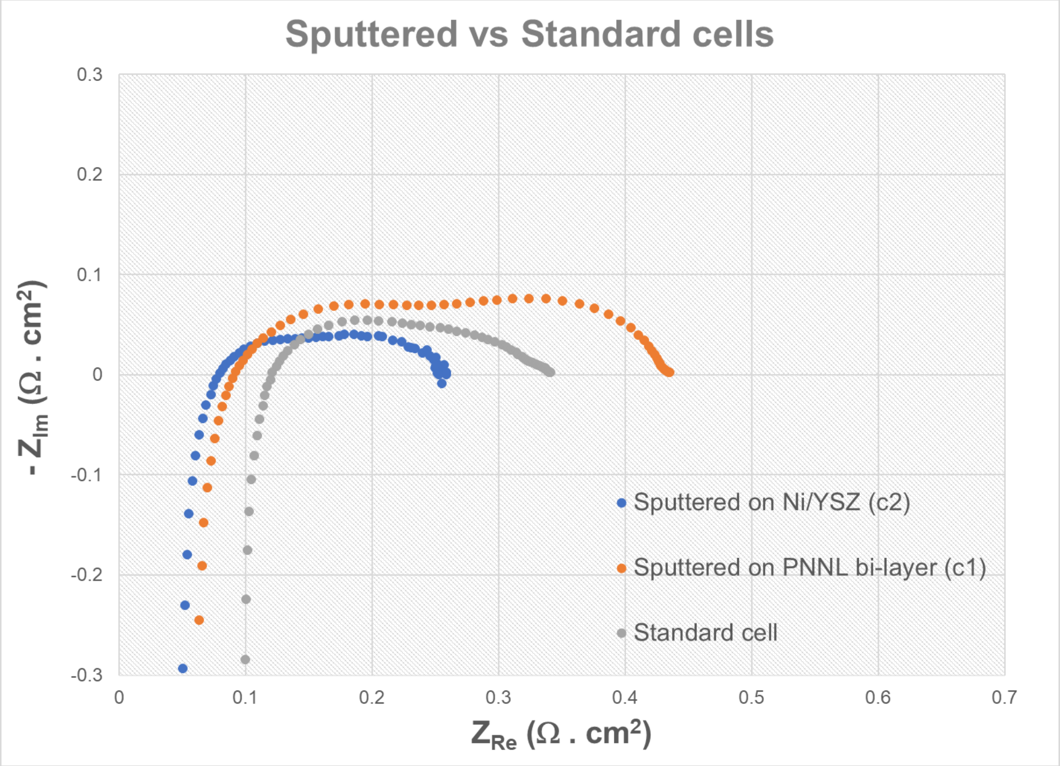


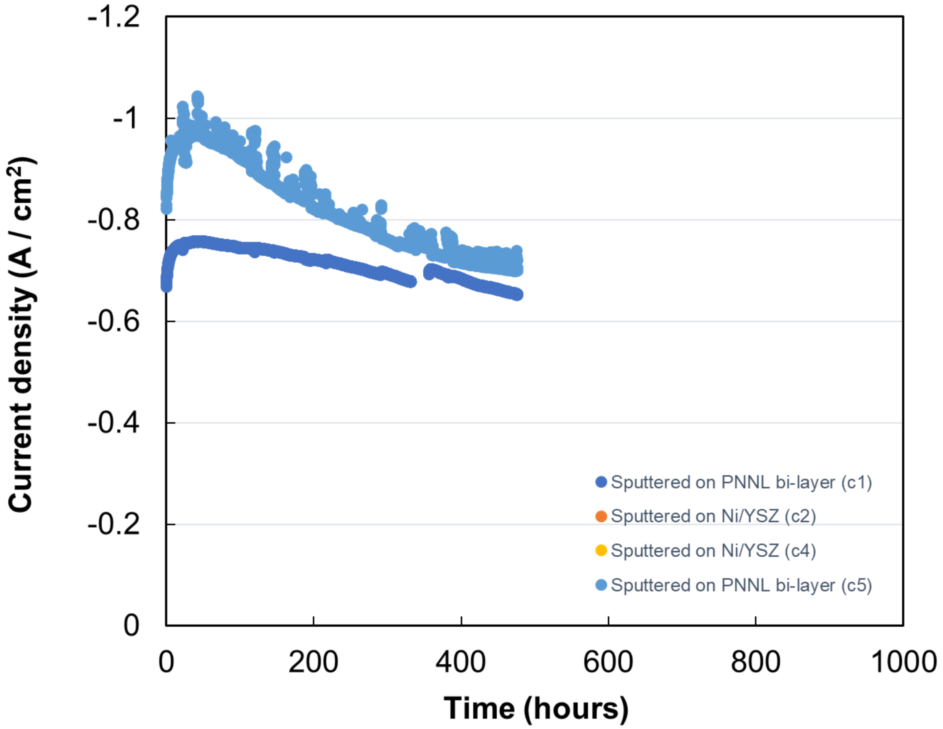
Gd diffusion into YSZ

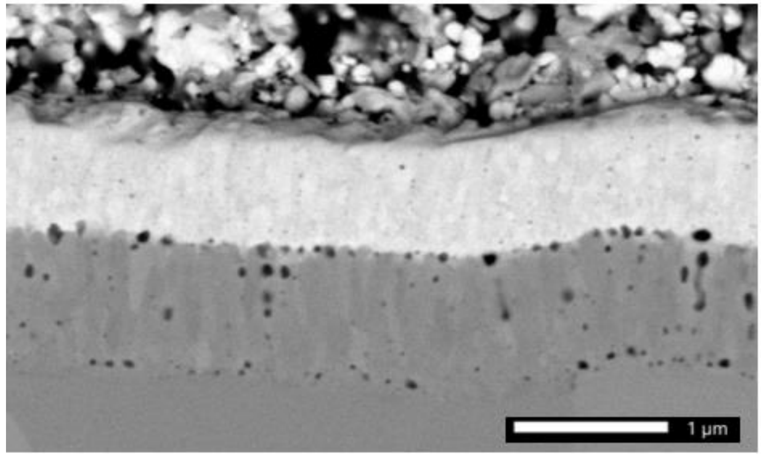


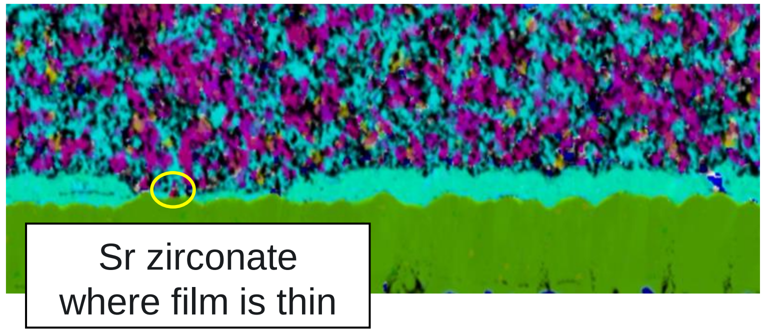
Fe,Co composition becomes richer in Fe; needs more statistics to confirm

Thin Film Deposition of GDC and YSZ









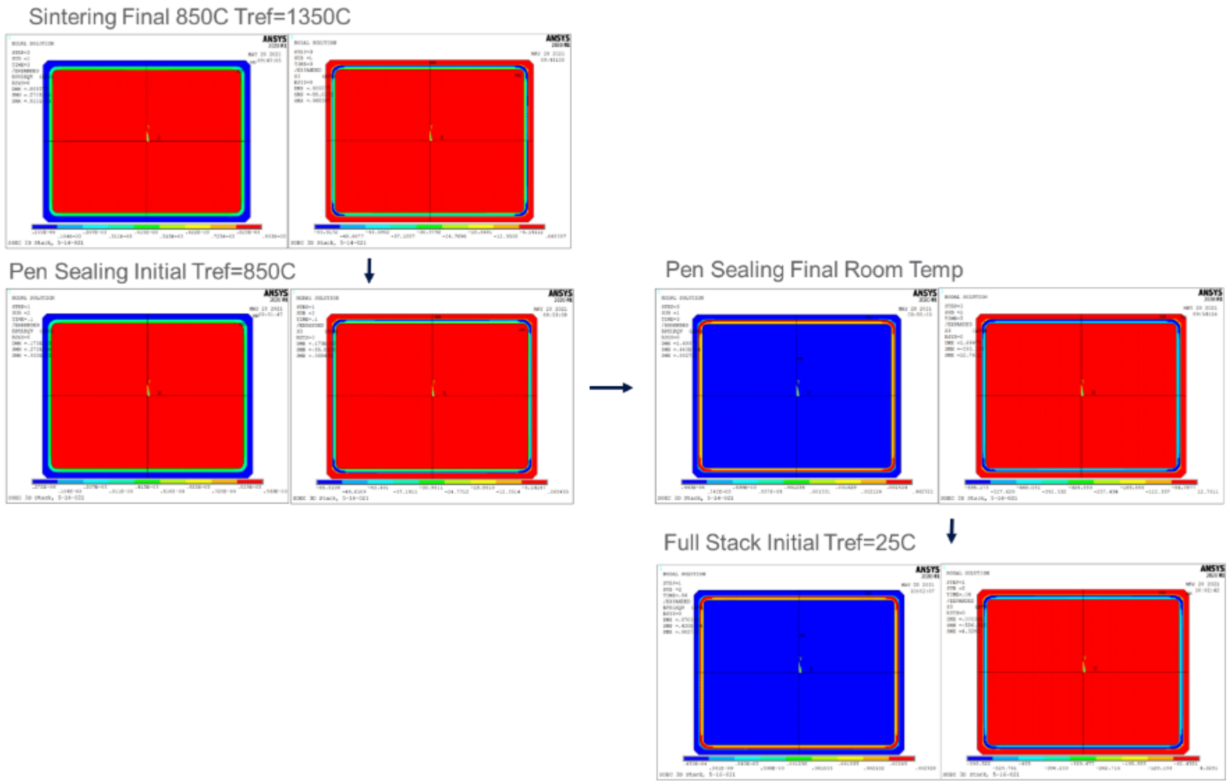
- Tested cells with and without pre-sintered YSZ electrolyte after YSZ and GDC sputtering
- Ohmic losses were reduced with sputtered GDC
- Observing more degradation that needs to be understood
- Not $SrZrO_3$ related

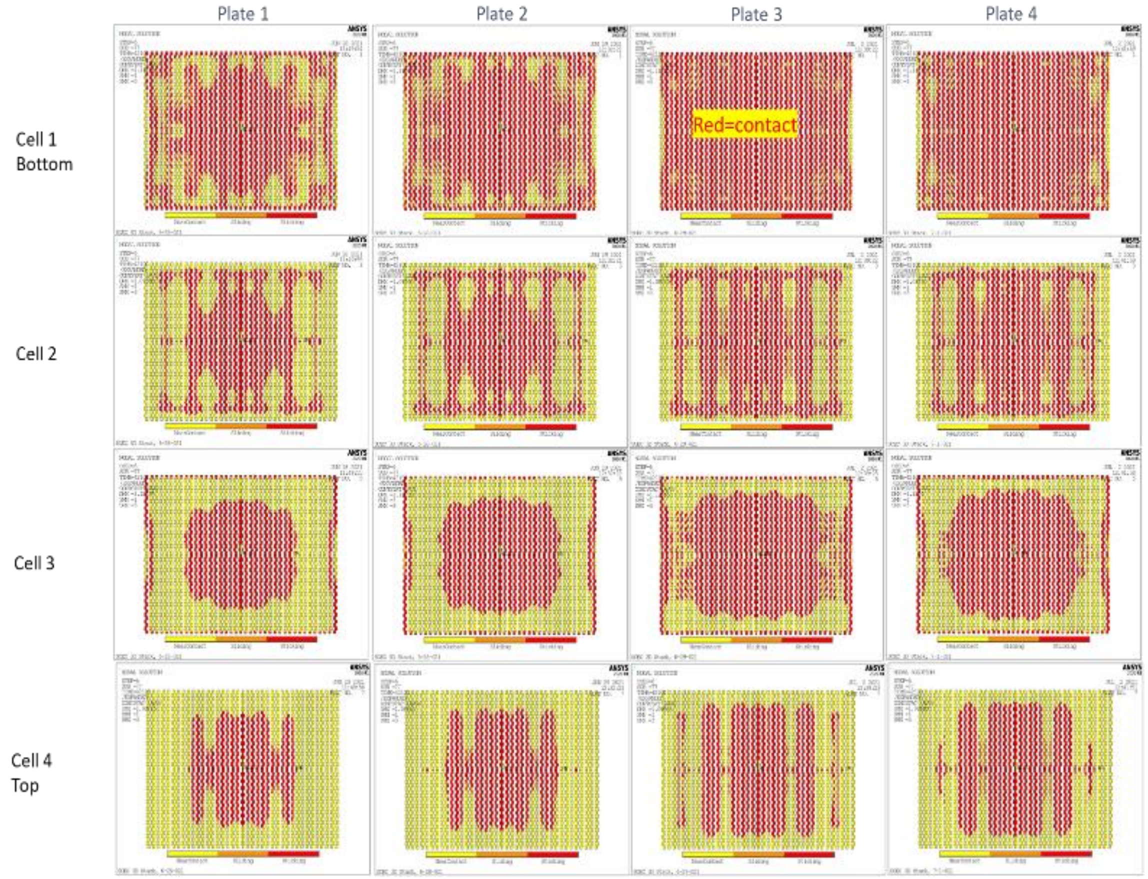
Assembled and Tested 14 SOEC Stacks Using 300 cm^2 Active Area Cells

- Successfully produced multiple well-sealed cassettes with large 300 cm^2 active area electrode-supported SOEC cells
- Fabricated all other components
- Applied protective coatings to the metal parts and metallic interconnects to prevent corrosion and chromium volatility
- Assembled and tested 14 short stacks of different sizes, ranging from 250 W (1 cell) to 1 kW (4 cells)
    - Optimized cell fabrication and sizing procedures to match the metal window frames
    - Optimized welding and sealing steps
    - Improved air side contacts
    - Addressed cassettes shorting

1 kW SOEC stack with 300 cm^2 active area cells

Used Predictive Modeling to Address the Initial Stress State in the PEN from Sintering and Sealing

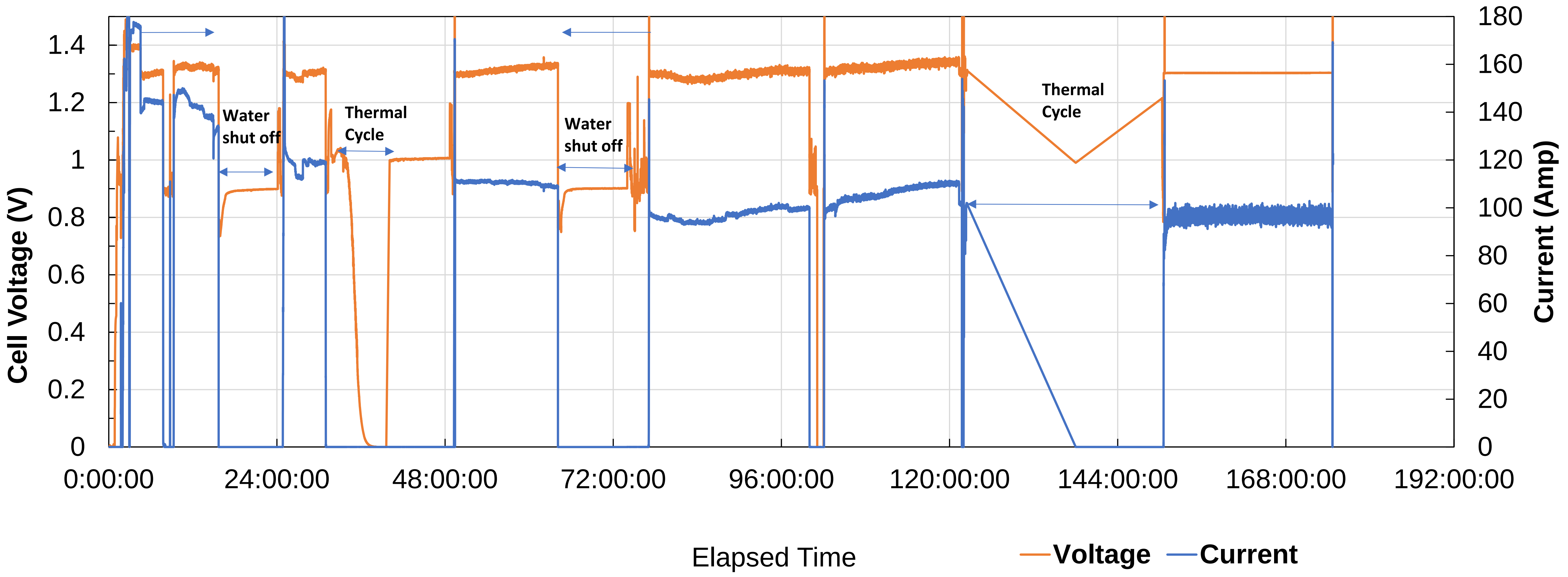




- ANSYS Initial State process employed
- Assessed principal stresses in anode, electrolyte, and cathode H_2 side stack seal
- Identified elastic strains from the elements in the PEN after running simulations of PEN sintering and PEN sealing

- Predict/ID key processing windows & tolerance: tested different plates, thicknesses, weights to obtain the best contacts while keeping the weight down

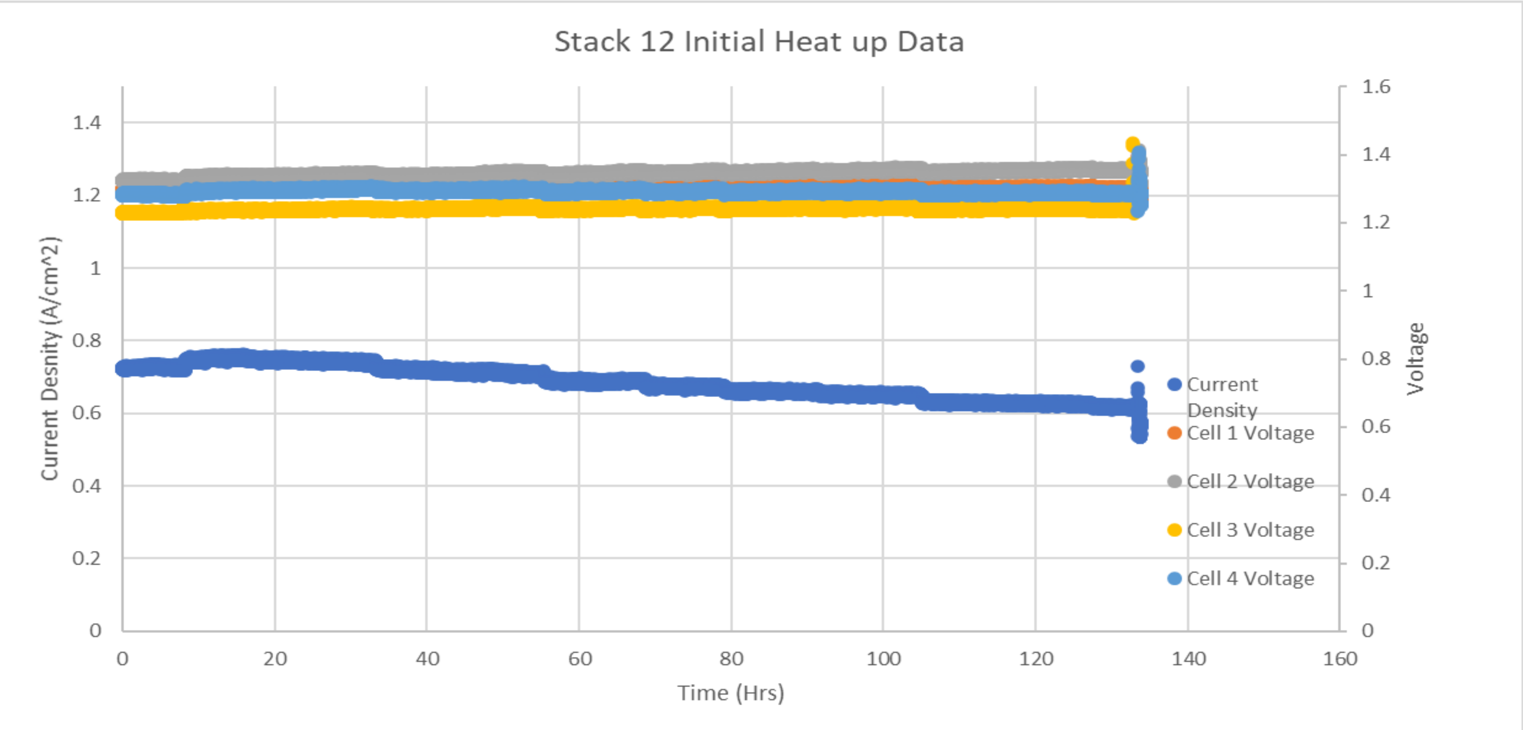
Demonstrated Several Full Thermal Cycles

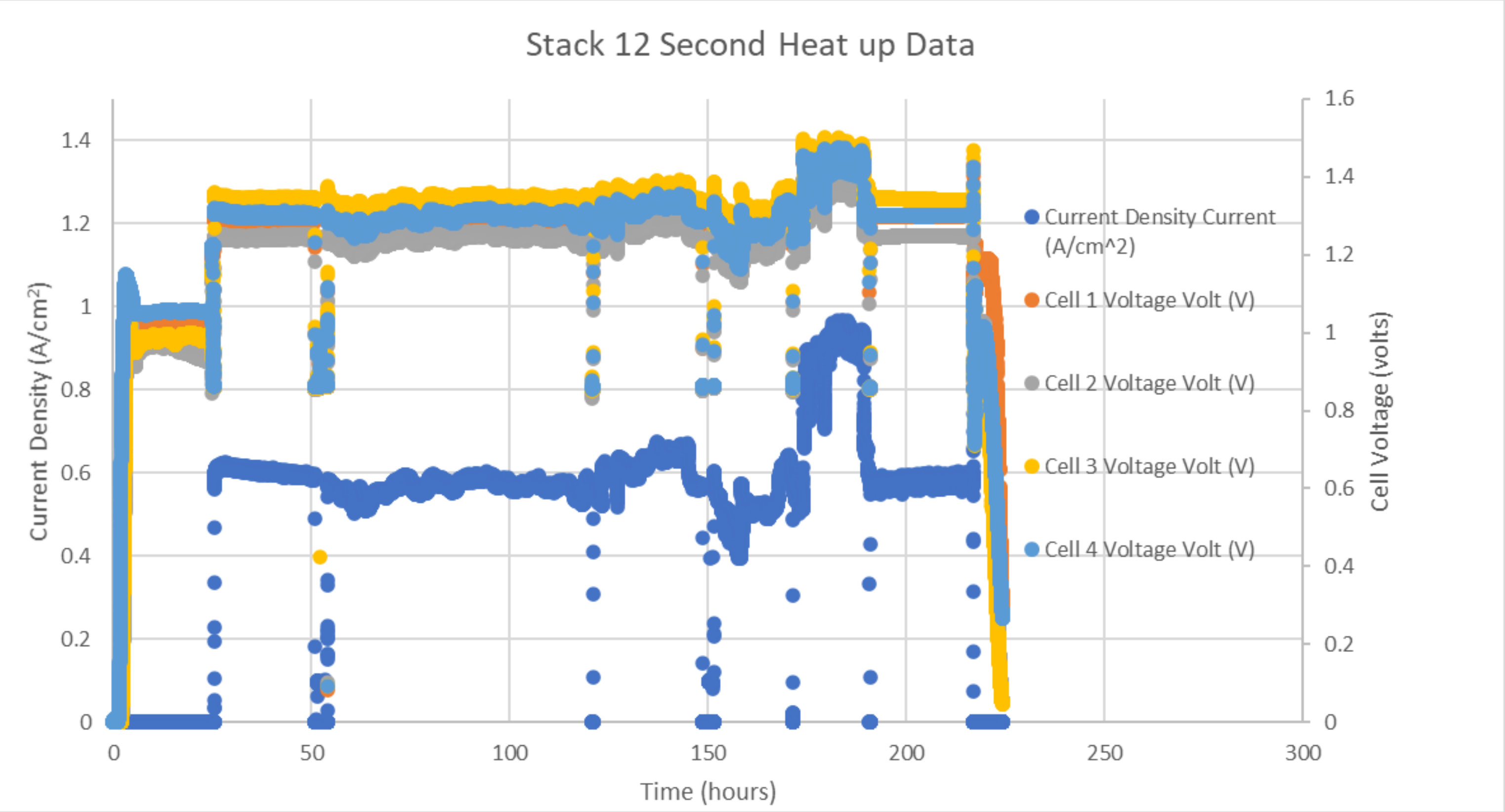


Single Repeat Unit Stack
200-250 W in 80% Steam at 750°C
Leak rate below the detection limit, hermetic seals
OCV=0.893 V, constant throughout the test

Stack 12 Results

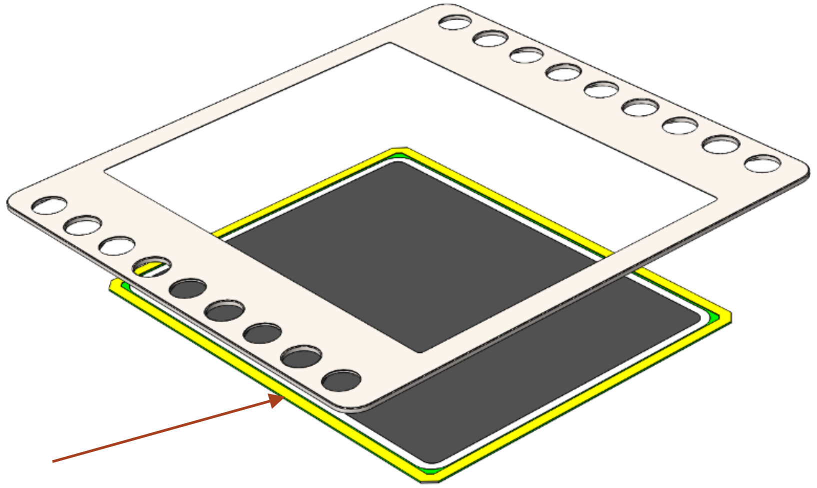
- Good initial performance with some initial degradation with time.
  - 90% steam and ~ 50% steam utilization
- Total run time of about 350 hours
- Successfully thermally cycled
- Developed a short between cell 3 and 4 shortly after the third thermal cycle



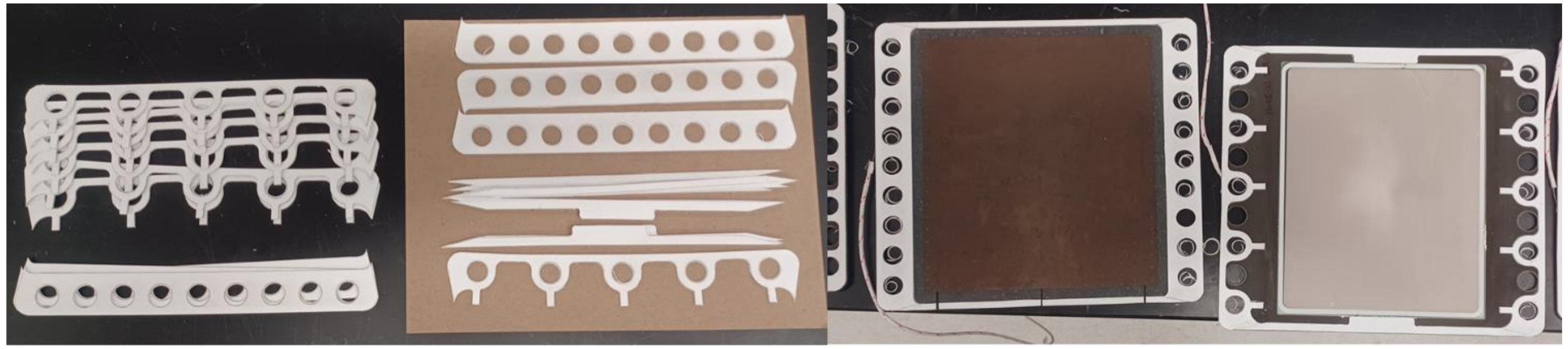


Sealing Procedure Improvements

- Issue: low yield after the cell-to-window-frame sealing procedure; about 50% failure rate
- Improvements: replaced dispensed glass by tape casting and improved load uniformity on the cell; yield is now very close to 100%; assemble is easier
- Made many changes to prevent shorting



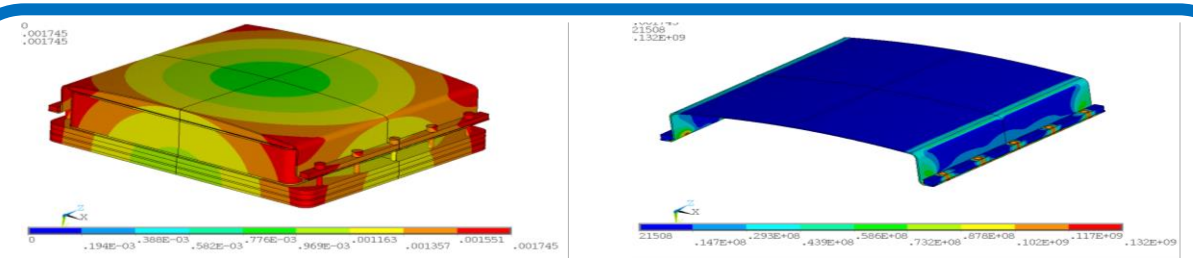
Cell to window frame seal



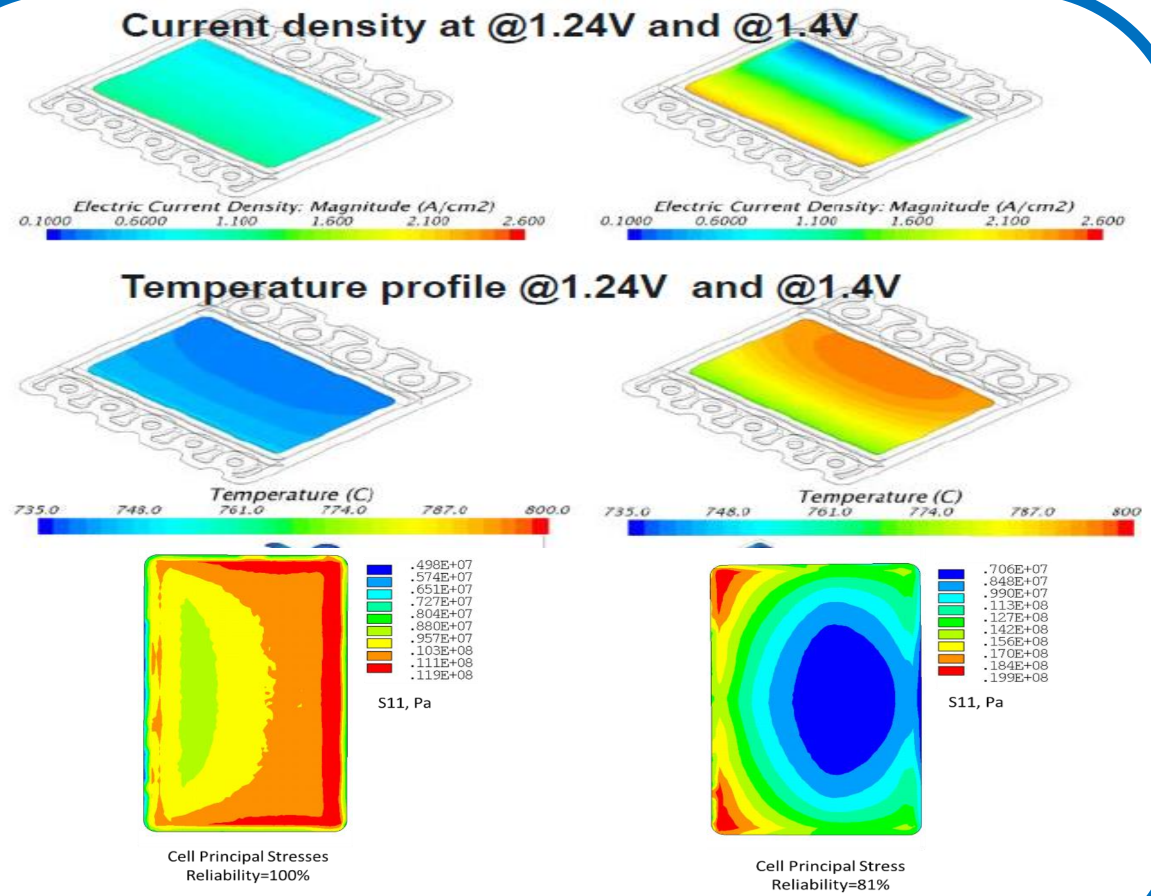
Tape cast seals

Stack Structural Integrity and Reliability Analysis Predicts Low Failure Probability

- Designed stack components and validated the design using thermomechanical analysis for structural integrity to predict stack and enclosure level displacements, stresses and investigate any CTE mismatch issues
- Optimized the meshing process of computational grids to reduce the computation time
- The reliability analysis mapped potential failure probabilities concentrated locally to specific areas of the cell depending on operating voltages and operating conditions



Stack overall displacements (in-plane max ~1mm) | **High local stresses in casing (near bolt holes)**

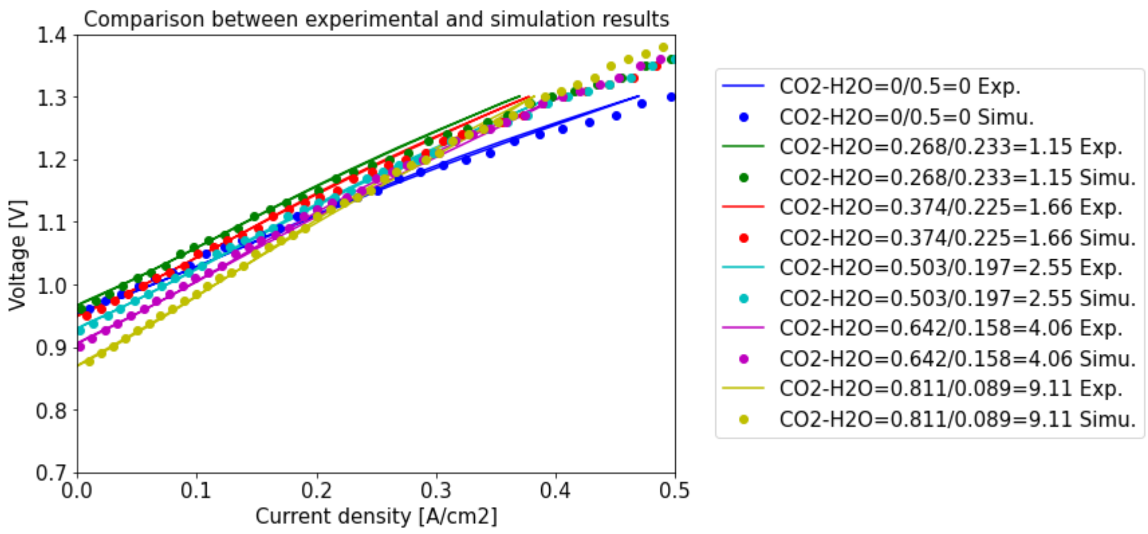


Cell temperature profile | **Principal stress distribution**

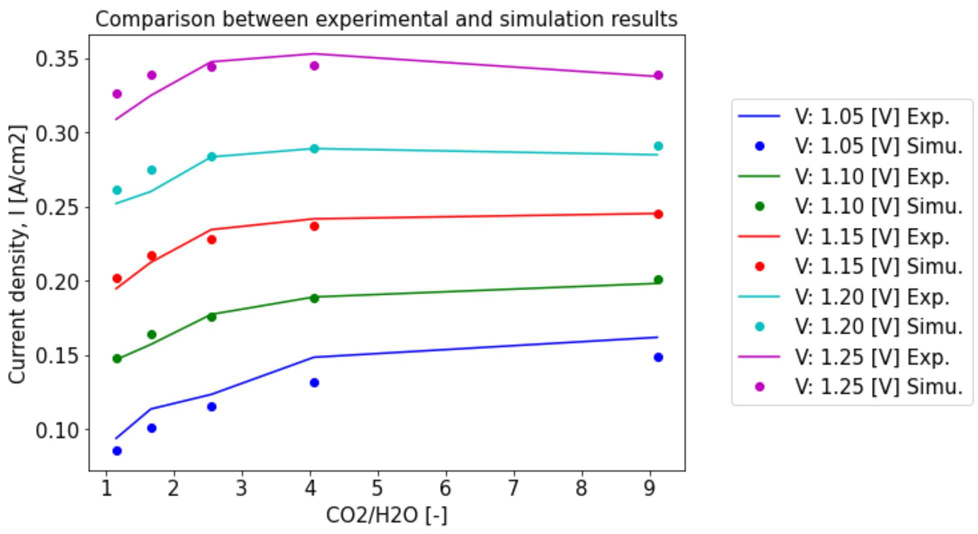
J. Bao et al, J. Electrochem. Soc. 2022, 169, 054523

Investigation of Solid Oxide Co-electrolyzer Performance with Deep Neural Network

- The PNNL developed multi-physics solver (SOFC-MP[1][2]) for SOFC has been upgraded to support solving co-electrolysis in 2D and 3D scheme.
- The solver predicts the co-electrolysis performance matching the experimental measurement for button cell at various cell operating conditions.



Voltage - current density relationships for six fuel compositions



Current density versus CO_2/H_2O ratio at five cell voltages

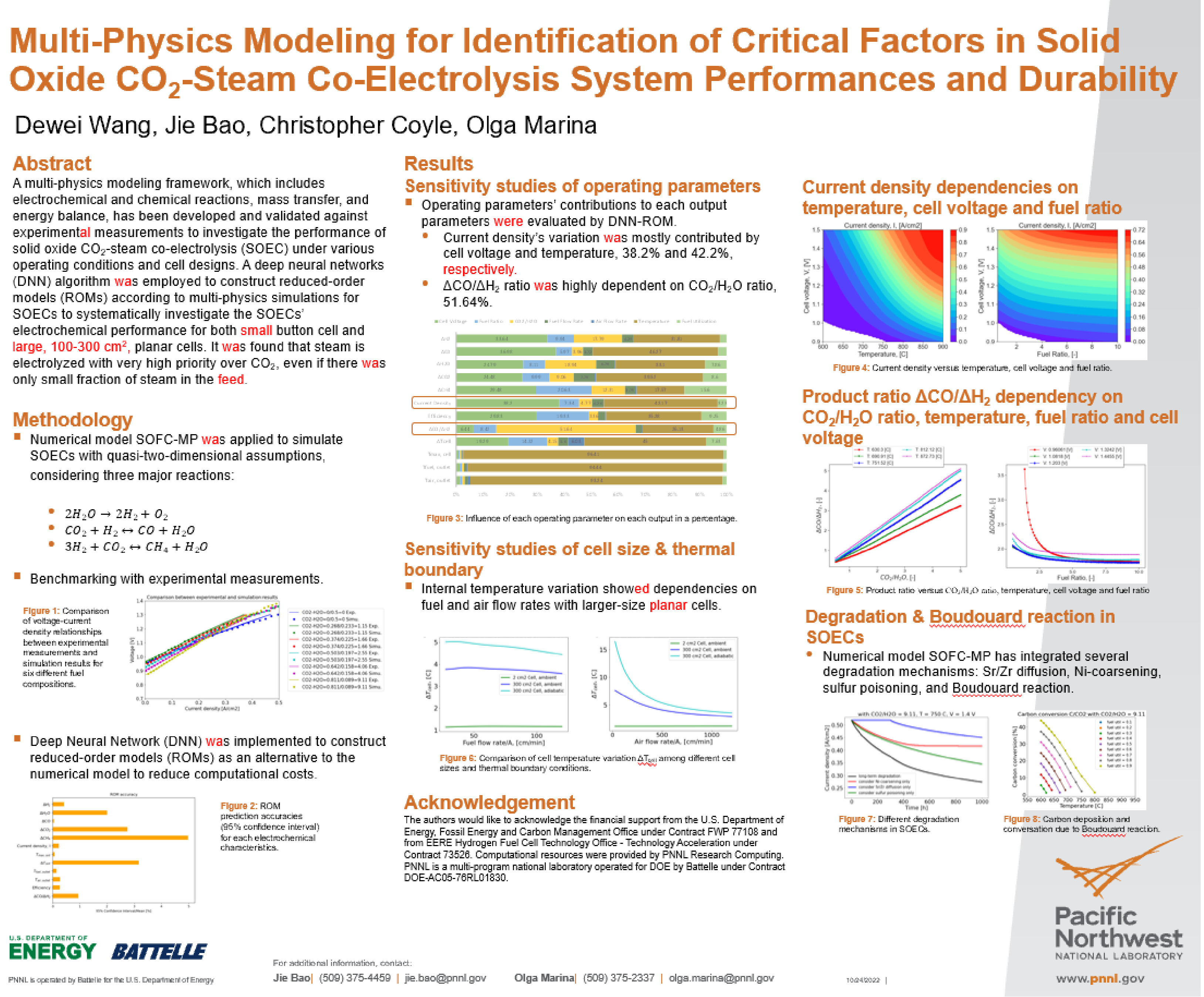
[1]: Lai, K., et al., Journal of Power Sources, 2011. 196(6): p. 3204-3222
[2]: Pan, W., et al., Journal of Power Sources, 2013. 232: p. 139-151.

Bao et al., in preparation

Investigation of Solid Oxide Co-electrolyzer Performance with Deep Neural Network

Bao et al., POSTER SESSION

- SOFC-MP is applied to explore the performance of co-electrolyzer at different cell operating conditions with 5000 simulation cases, 300 cm^2 planar cells
- The deep neural network (DNN) is applied to construct the reduced order model (ROM)
- The DNN based ROM provides higher prediction accuracy than the conventional regression approaches
- DNN-ROM helps on understanding the response of the cell performance to the operating conditions



Multi-Physics Modeling for Identification of Critical Factors in Solid Oxide CO_2-Steam Co-Electrolysis System Performances and Durability

Dewei Wang, Jie Bao, Christopher Coyle, Olga Marina

Abstract

A multi-physics modeling framework, which includes electrochemical and chemical reactions, mass transfer, and energy balance, has been developed and validated against experimental measurements to investigate the performance of solid oxide CO_2-steam co-electrolysis (SOEC) under various operating conditions and cell designs. A deep neural networks (DNN) algorithm was employed to construct reduced-order models (ROMs) according to multi-physics simulations for SOECs to systematically investigate the SOECs' electrochemical performance for both small button cell and large, 100-300 cm^2, planar cells. It was found that steam is electrolyzed with very high priority over CO_2, even if there was only small fraction of steam in the feed.

Methodology

- Numerical model SOFC-MP was applied to simulate SOECs with quasi-two-dimensional assumptions, considering three major reactions:
  - $2H_2O \rightarrow 2H_2 + O_2$
  - $CO_2 + H_2 \leftrightarrow CO + H_2O$
  - $3H_2 + CO_2 \leftrightarrow CH_4 + H_2O$
- Benchmarking with experimental measurements.

Figure 1: Comparison of voltage-current density relationships between experimental measurements and simulation results for six different fuel compositions.

- Deep Neural Network (DNN) was implemented to construct reduced-order models (ROMs) as an alternative to the numerical model to reduce computational costs.

Figure 2: ROM prediction accuracies (95% confidence interval) for each electrochemical characteristics.

Results

Sensitivity studies of operating parameters

- Operating parameters' contributions to each output parameters were evaluated by DNN-ROM.
  - Current density's variation was mostly contributed by cell voltage and temperature, 38.2% and 42.2%, respectively.
  - $\Delta CO/\Delta H_2$ ratio was highly dependent on CO_2/H_2O ratio, 51.64%.

Figure 3: Influence of each operating parameter on each output in a percentage.

Sensitivity studies of cell size & thermal boundary

- Internal temperature variation showed dependencies on fuel and air flow rates with larger-size planar cells.

Figure 6: Comparison of cell temperature variation ΔT_{cell} among different cell sizes and thermal boundary conditions.

Acknowledgement

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Current density dependencies on temperature, cell voltage and fuel ratio

Figure 4: Current density versus temperature, cell voltage and fuel ratio.

Product ratio $\Delta CO/\Delta H_2$ dependency on CO_2/H_2O ratio, temperature, fuel ratio and cell voltage

Figure 5: Product ratio versus CO_2/H_2O ratio, temperature, cell voltage and fuel ratio

Degradation & Boudouard reaction in SOECs

- Numerical model SOFC-MP has integrated several degradation mechanisms: Sr/Zr diffusion, Ni-coarsening, sulfur poisoning, and Boudouard reaction.

Figure 7: Different degradation mechanisms in SOECs.

Figure 8: Carbon deposition and conversation due to Boudouard reaction.

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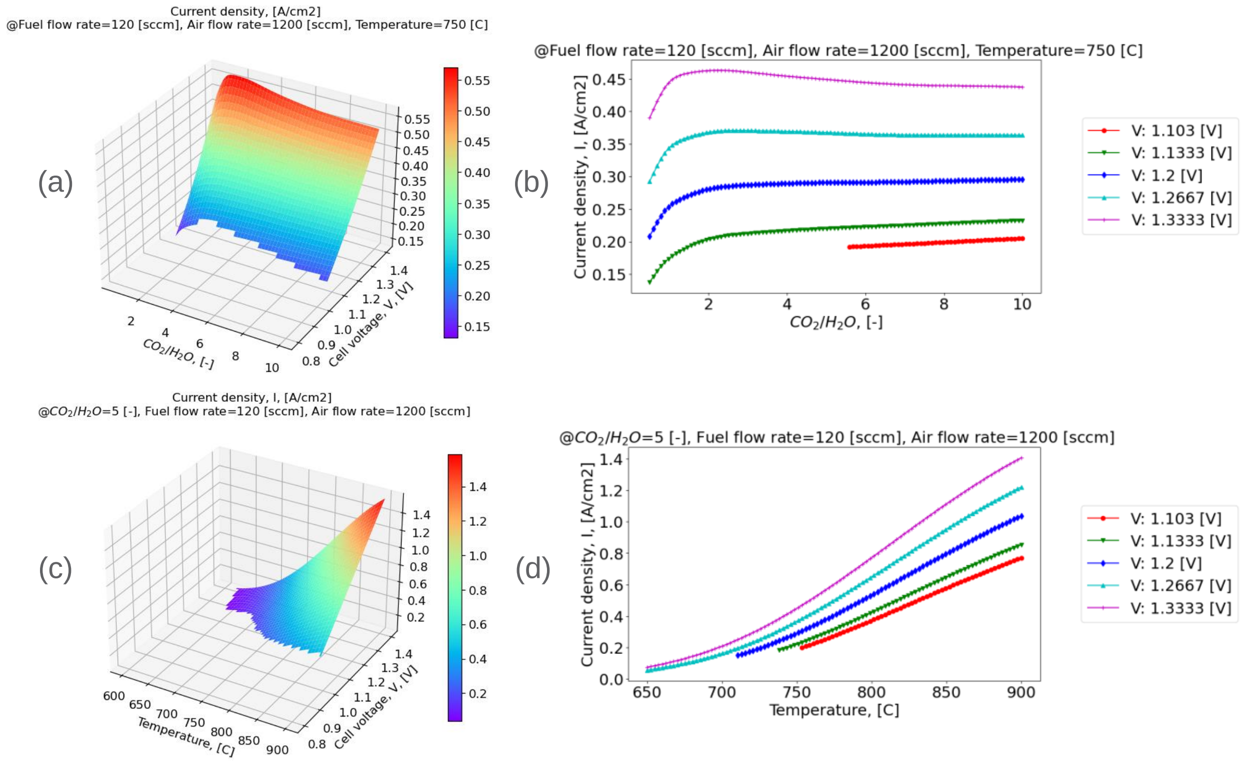
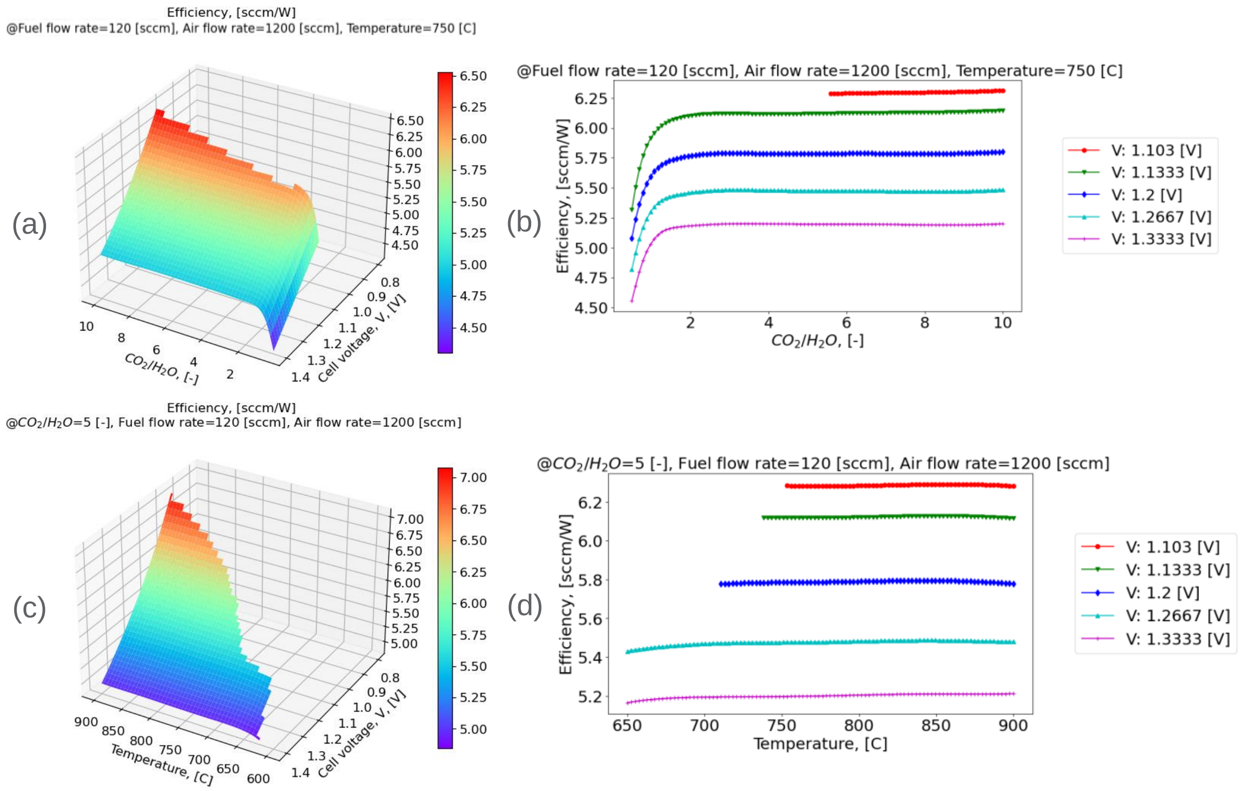
Investigation of Solid Oxide Co-electrolyzer Performance with Deep Neural Network

- DNN-ROM helps on understanding the response of the cell performance to the operating conditions



Current density variations at fuel flow/air rate of 120 and 1200 sccm. (a) versus CO_2/H_2O ratio and cell voltage at temperature of 750 ℃; (b) versus CO_2/H_2O ratio at different voltages at temperature of 750 ℃; (c) versus temperature and cell voltage with CO_2/H_2O ratio of 5; (d) versus temperature at different voltages with CO_2/H_2O ratio of 5.



System efficiency variations at fuel/air flow rates of 120 and 1200 sccm. (a) versus CO_2/H_2O ratio and cell voltage at temperature of 750 ℃; (b) versus CO_2/H_2O ratio at different voltages at temperature of 750 ℃; (c) versus temperature and cell voltage with CO_2/H_2O ratio of 5; (d) versus temperature at different voltages with CO_2/H_2O ratio of 5.

Summary

- Assembled and tested multiple short stacks using 300 cm^2 cells
  - Successfully established stack repeat unit fabrication process
  - Established baseline performance of 1 kW stack in 80% steam at 750^oC to understand impact of stack fabrication on performance and life
  - Thermally cycled SOEC stack with large cells
  - Obtained EIS data of a 1 kW stack and separate cells at 50-80% steam utilization.

5th Annual AWS Benchmarking Workshop to Engage Technology Experts

- **LTE** – Kathy Ayers, Nel
- **HTE** – Olga Marina, PNNL
- **PEC** – CX Xiang, Caltech
- **STCH** – Ellen Stechel, ASU

- Protocol development for bench-scale, sub-scale and higher levels
- Face-to-face discussions about protocols
- Effective comparison of results
- Leverage international efforts to increase harmony across the field
- Wide community engagement
- Identify Round Robin verification sites
- Understand needs of the community

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