Summary of SOFC Development at Redox Power Systems for FE0027897 & FE0031656

3/2/2022

U.S. Department of Energy, National Energy Technology Laboratory's (NETL) Solid Oxide Fuel Cell (SOFC) Project Review Meeting

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Redox Power Systems

Updates for FE0027897 & FE031656

1. **FE0027897:** *Red-ox robust SOFC stacks for affordable, reliable distributed generation power systems*
   - Background (ceramic anode cell with a GDC electrolyte)
   - Red-Ox cycling impact on material conductivity and cell OCV & Power
   - Challenges balancing cell size, strength, and power density

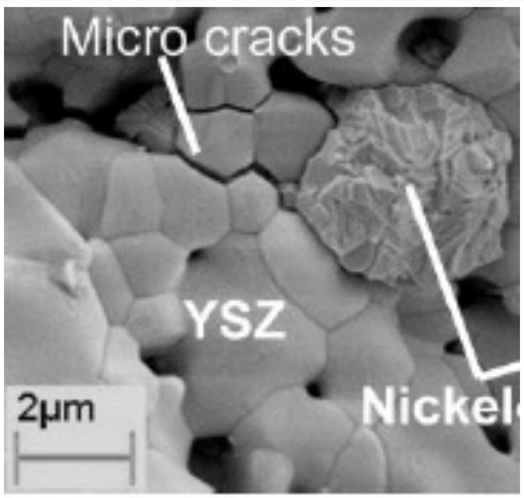
2. **FE0031656:** *Sputtered thin films for very high power, efficient, and low-cost commercial SOFCs*
   - Background (electron-blocking layer for GDC electrolyte SOFCs)
   - Problems/solutions for achieving high OCV
   - Problems/solutions for achieving low ASR

FE0027897 Red-Ox Robust Stacks

Red-ox cycles can be expected during long-term fuel cell operation

- Interruptions in fuel supply
- Impact of small seal leaks over the long-term
- Transient SOFC operation
  - System shutdown
  - Very high fuel utilization events (e.g., extreme load following)

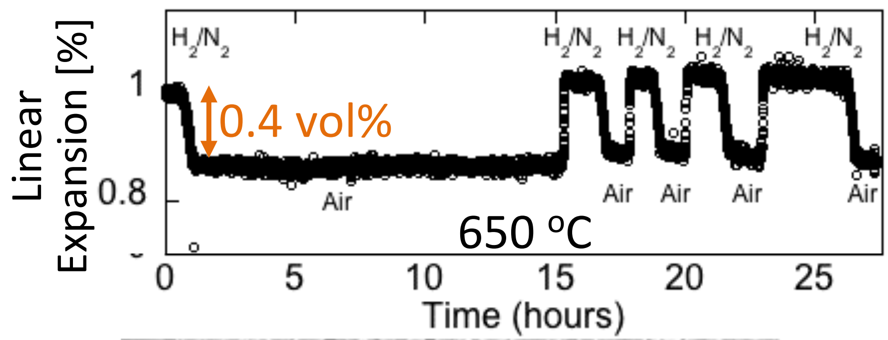
Ni-cermet anodes prone to mechanical failure during redox cycling

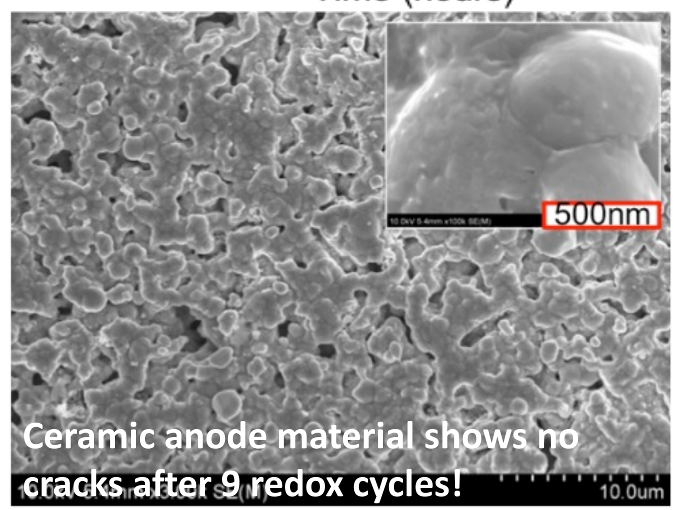


Journal of Power Sources 195 (2010) 5452–5467

~69 vol% expansion of Ni → NiO

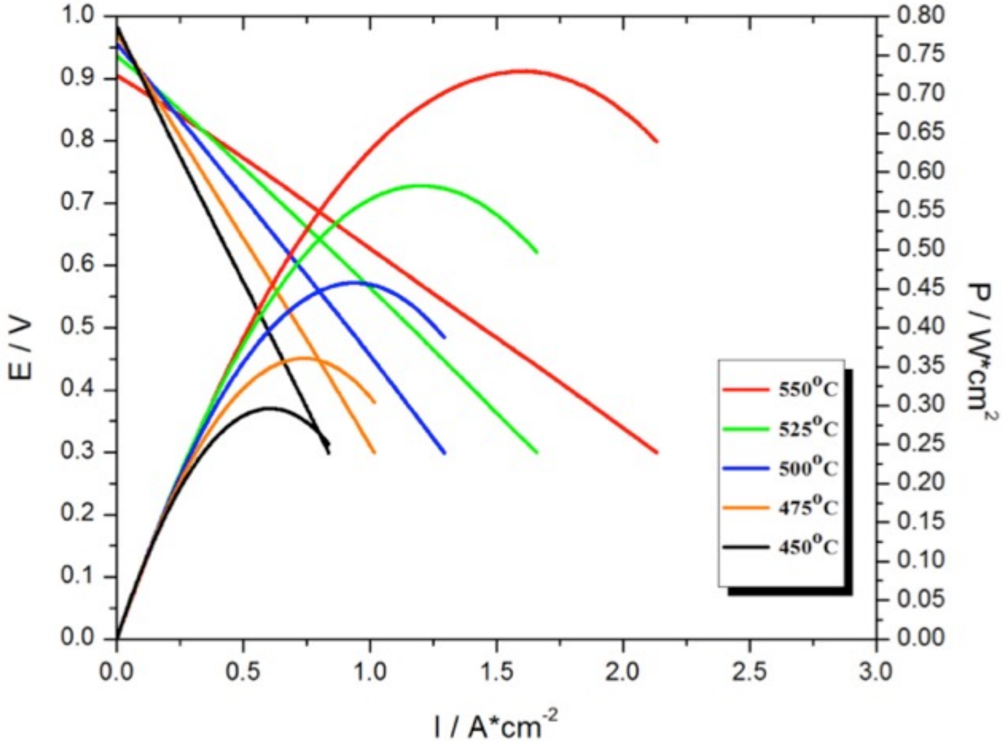
Solution:
Ceramic anode → small Δoxygen = small dimensional change (0.4 vol%)



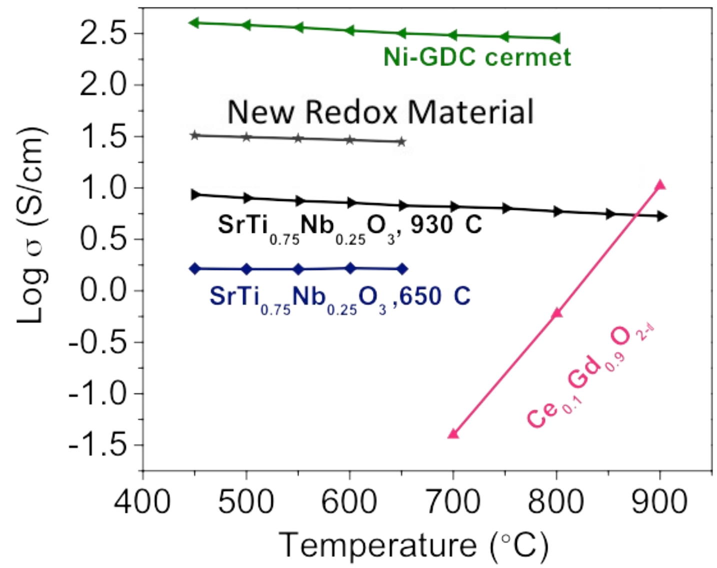


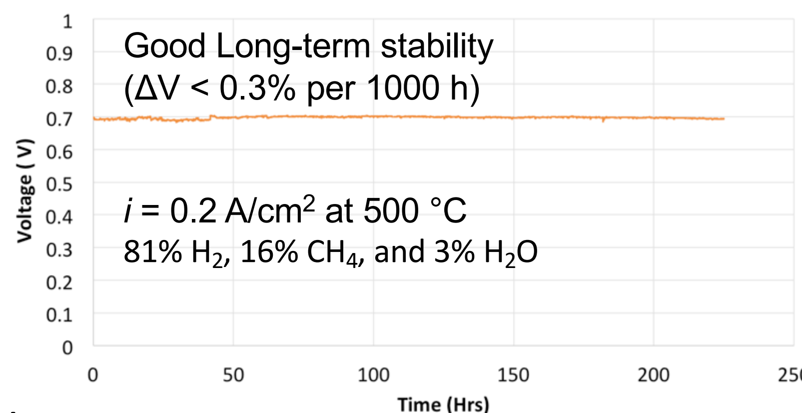
All-Ceramic Anode Performance

Button cell data



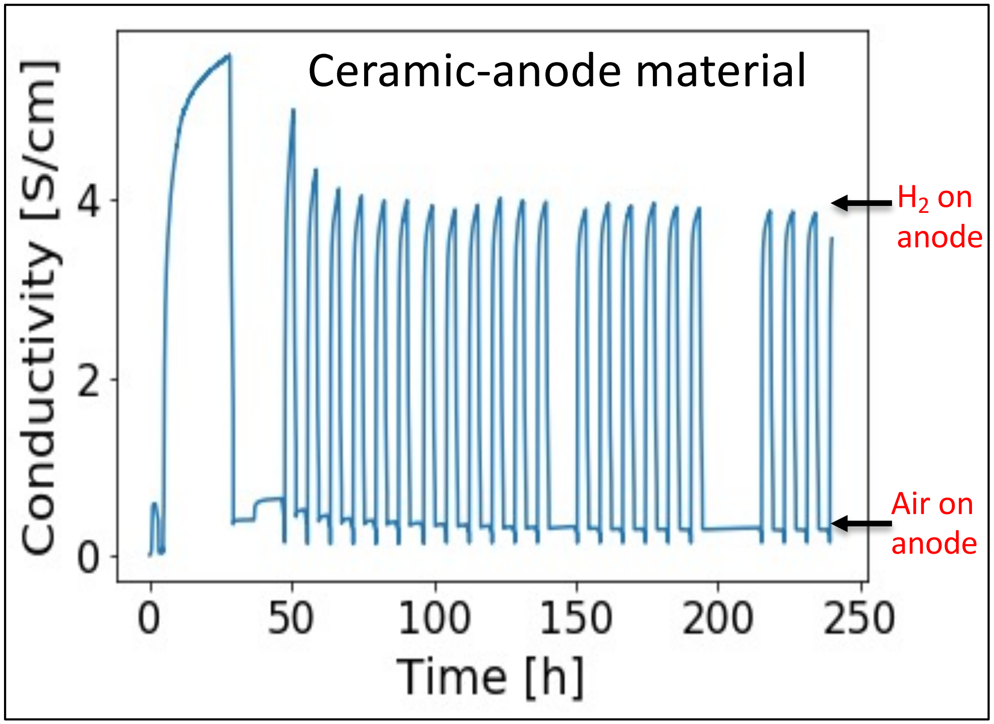
Anode electrical conductivity

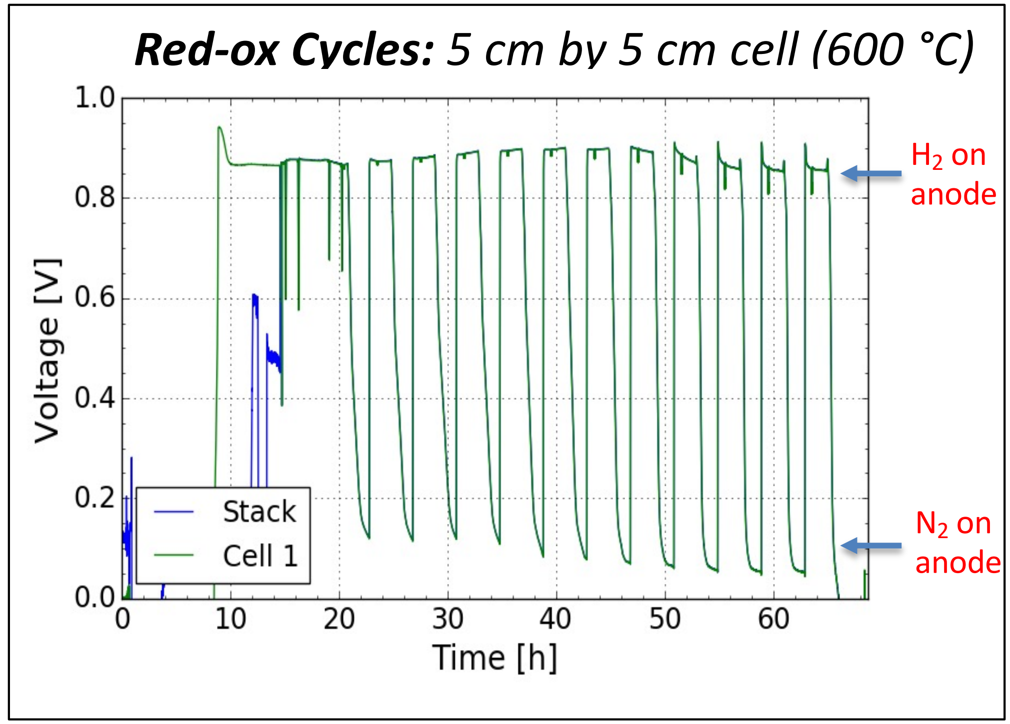




- High power densities
  - ~0.75 W/cm^2 @ 550°C
  - ~0.3 W/cm^2 @ 450 °C
- Reasonably high (acceptable) electronic conductivity
- Conductivity and electrochemical activity further boosted using anode infiltration

Red-Ox Cycling

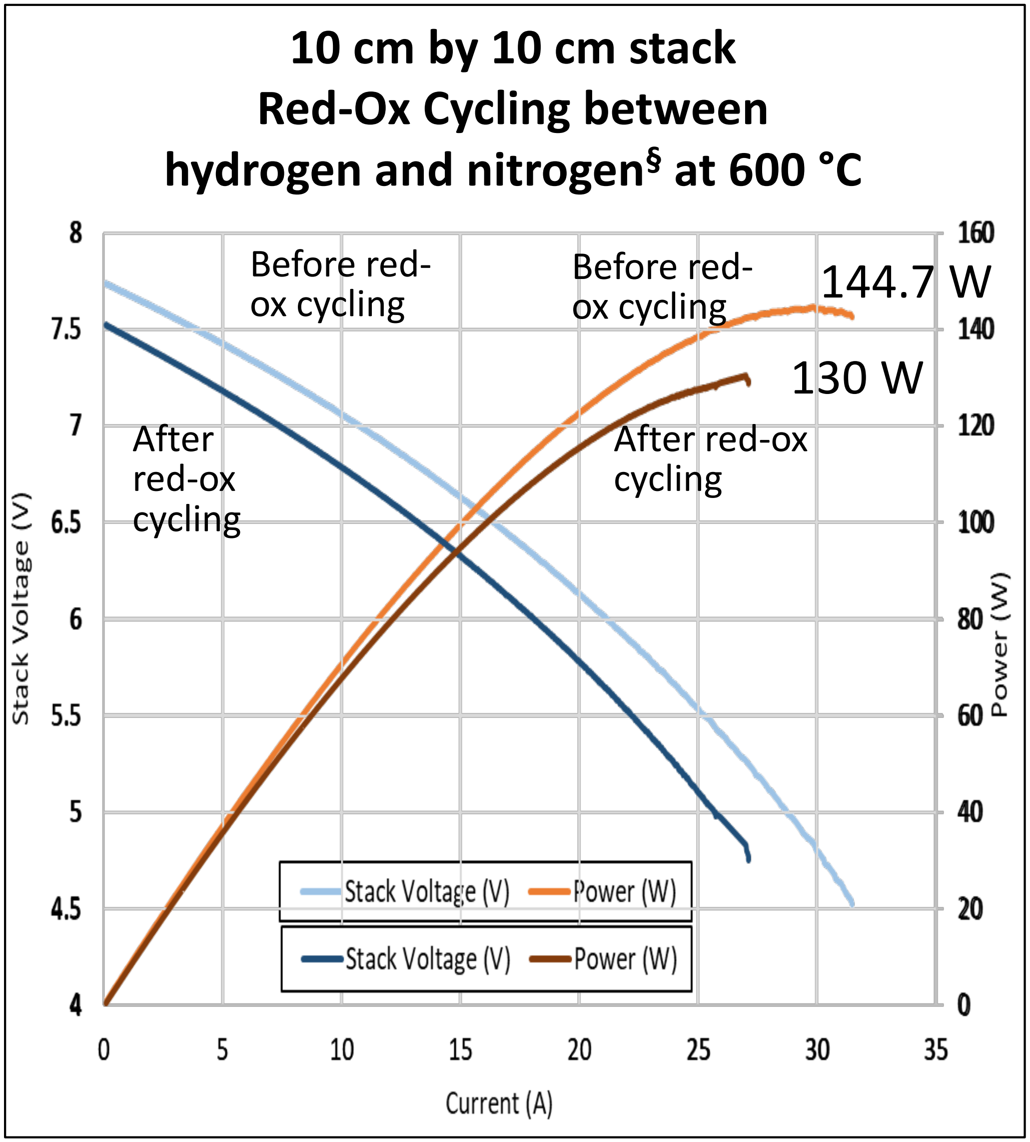




- Reduction-Oxidation cycles for ceramic anode material
- Single chamber environment, switching between H_2 and air (flush with N_2 first)

- Open Circuit Voltage during for 5 cm by 5 cm for 11 Red-Ox cycles (switching between H_2 and N_2)
- Industrial grade N_2 has some oxygen
- This was done primarily due to the test setup configuration and no difference was observed from when air is used instead of N_2

Red-Ox Cycling of Stack



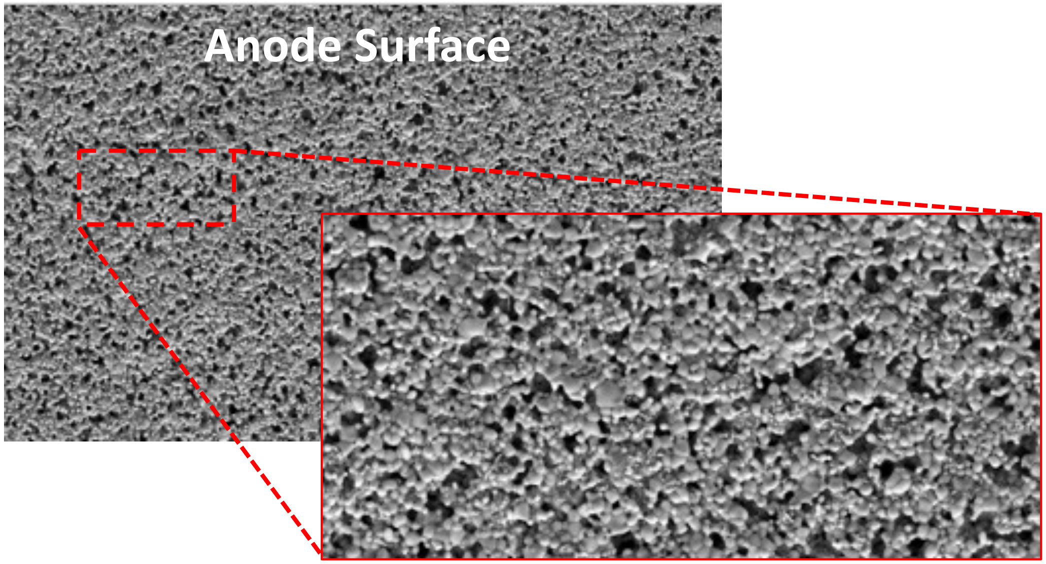
§ Industrial grade N_2 has some oxygen

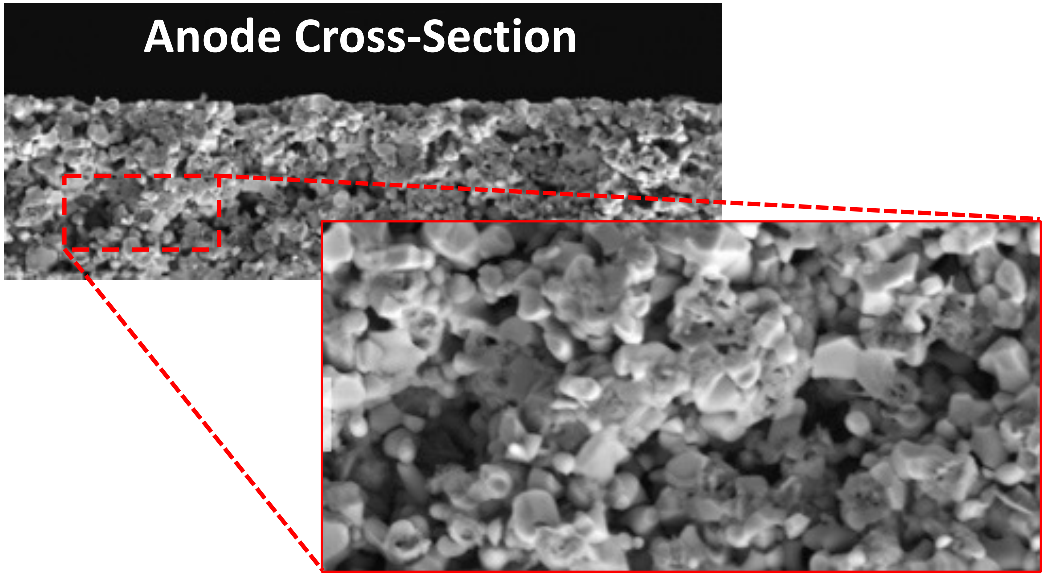
- Small performance drop after red-ox cycling
  - Possible small difference in operating temperature (thermal equilibrium not reached between cycles)
  - The ceramic anode may exhibit an initial decrease in conductivity after first cycle, followed by no changes (previous slide)
  - May also have been due to general long-term stability issues with large format cells
- Discovered problems with ceramic anode delamination during long-term operation in high humidity conditions experienced in large format cell operation and not observed in button cells
- Problem not in the ceramic-anode material itself (confirmed in 30% H_2O, balance H_2)
- Evidence that part of problem is due in part to bonding strength between layers
- To eliminate delamination, we explored modifications to the ceramic-anode configuration and processing conditions

Competing Challenges for Ceramic-Anode SOFC

- Strength issues for large format cell
- Cell must be flat to prevent stress concentrators during stack assembly and operation
- Porosity must remain high for catalyst infiltration
- Shrinkage mismatch is challenging and normal methods for characterization (e.g., dilatometry) cannot always be relied upon to guide design and processing optimization
- Balance between pore-former size/amount, composite anode composition, layer thickness, and sintering process

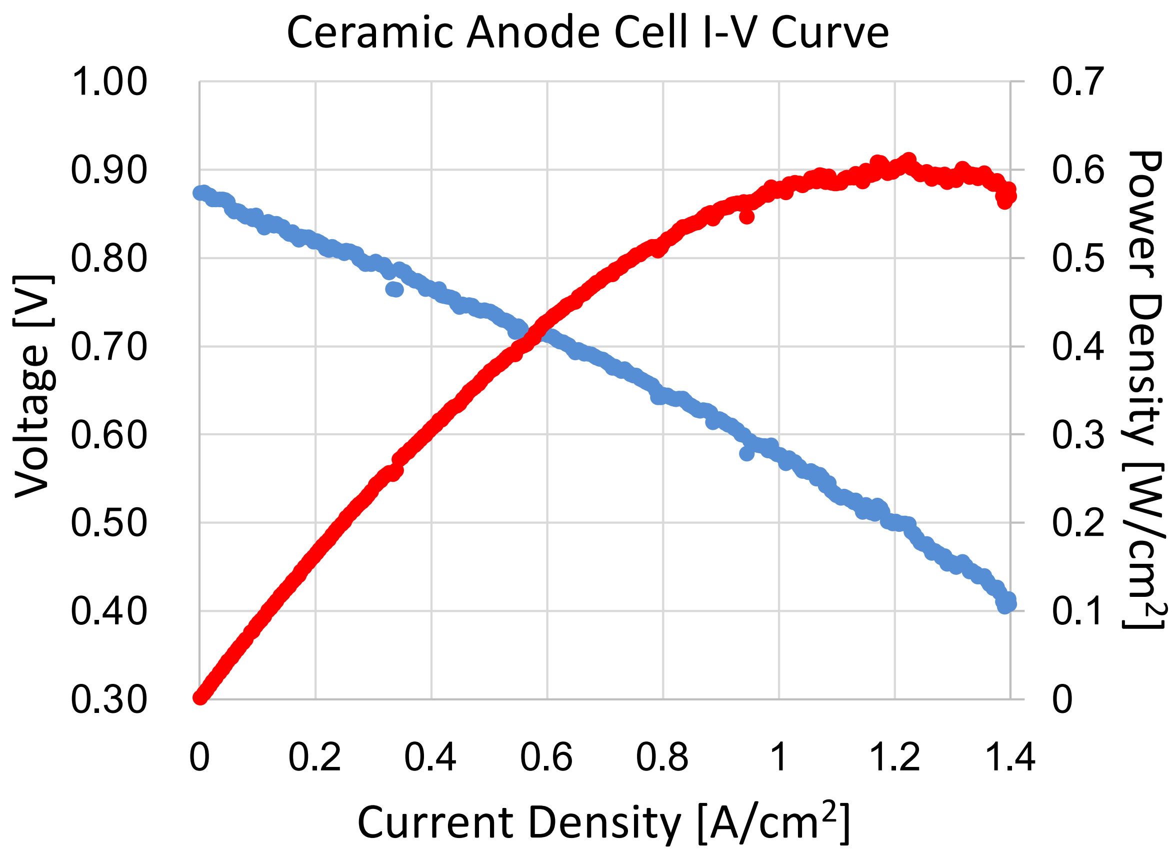
Red-Ox Cycling: Improved Ceramic-Anode Config.





- Red-Ox cycle conditions
  - The sample was heated to 600 °C in air, held for 3 hours; reducing gas (3% H_2 / 97% N_2) was introduced and held for 3 hours; air was re-introduced
- 10 red-ox cycles
- After 10 red-ox cycles, no cracks are observed in anode surface or cross-section
- No delamination of any layers, or any other mechanical problem

Improved Ceramic-Anode Config. Performance

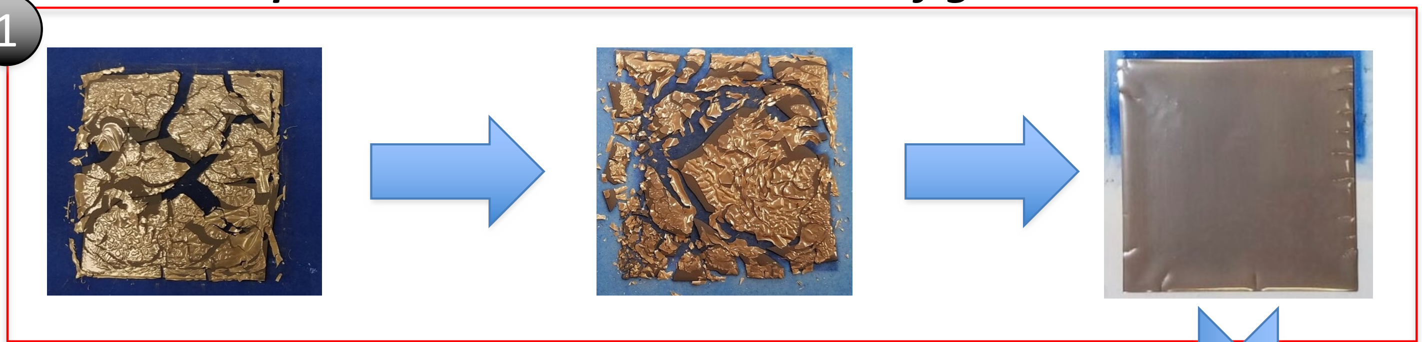


- 4 cm by 4 cm cell tested at 600 °C
- Better electrochemical performance compared to the original ceramic-anode configuration of the same size
  - > 5% increase in open circuit voltage
  - >35% increase in power density
  - Additional improvements possible

Cell Size & Batch Size Scaleup

Improved ceramic-anode cell config.

1



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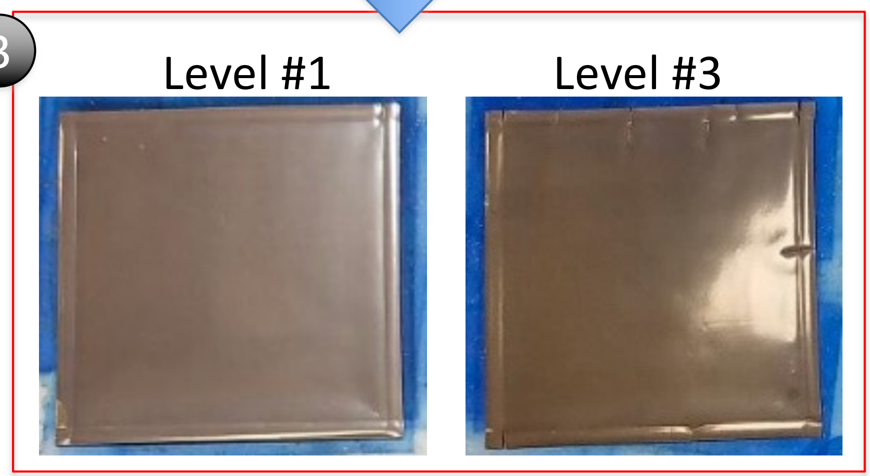
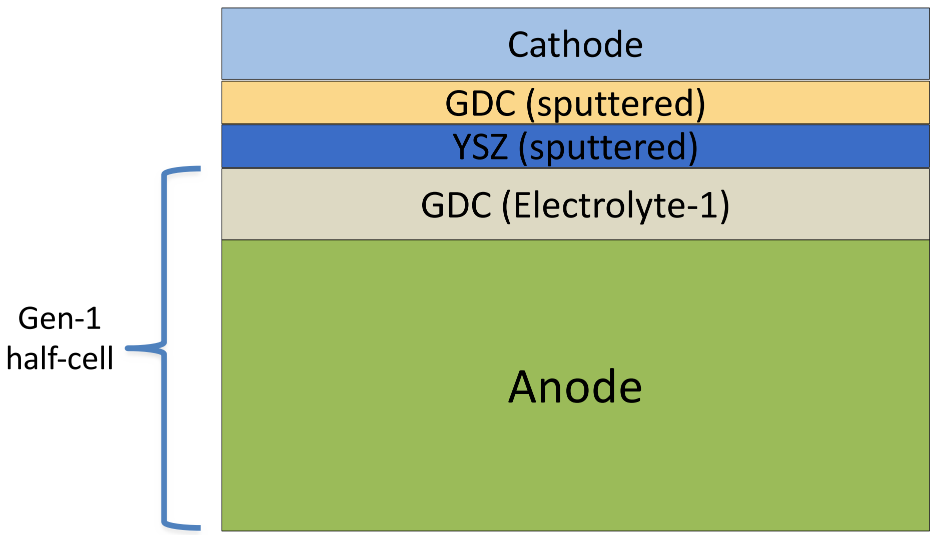
3

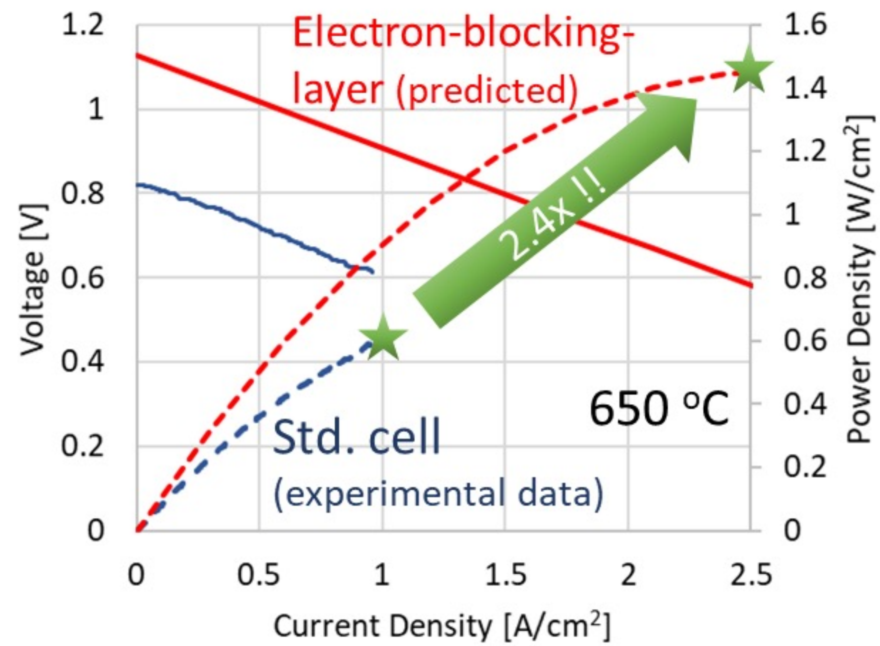


1. Composition optimization to prevent delamination (5 cm by 5 cm and 10 cm by 10 cm)
2. Fine tune composition / firing profile to reduce edge cracks
3. Optimize furnace temperature uniformity, tape caster thickness variation to increase yield in multi-level (4+) batch firing

FE0031656: Sputtered Thin Film SOFCs



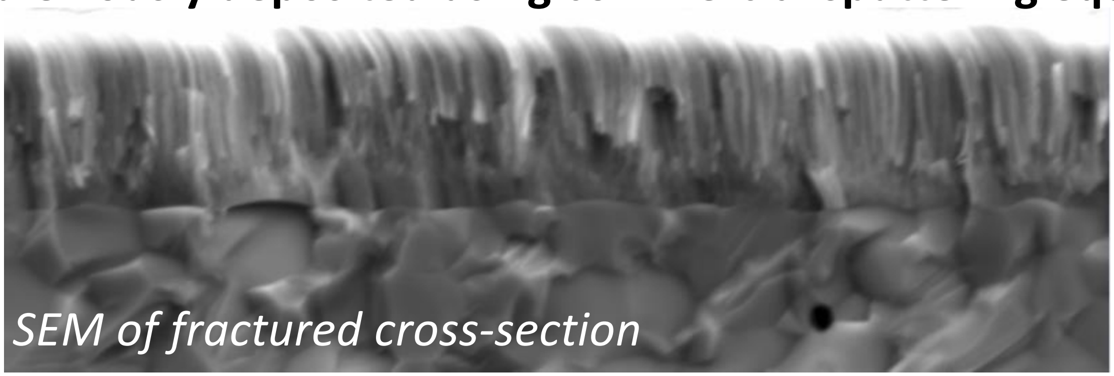
Note: *Layers are not shown to scale*



- Thin electron-blocking layer expected to increase Redox Gen-1 Ni-cermet cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria-based Electrolyte-1 → as much as ~40% increase in open circuit voltage is possible
- Very thin, dense electron-blocking layer adds negligible resistance
- Takes advantage of high-performance Redox Gen-1 cell platform
- Potential for even more power using Redox Gen-2 cell platform with porous, infiltrated anode (3.2 W/cm^2 at 650°C)

GDC Buffer Layer Deposition

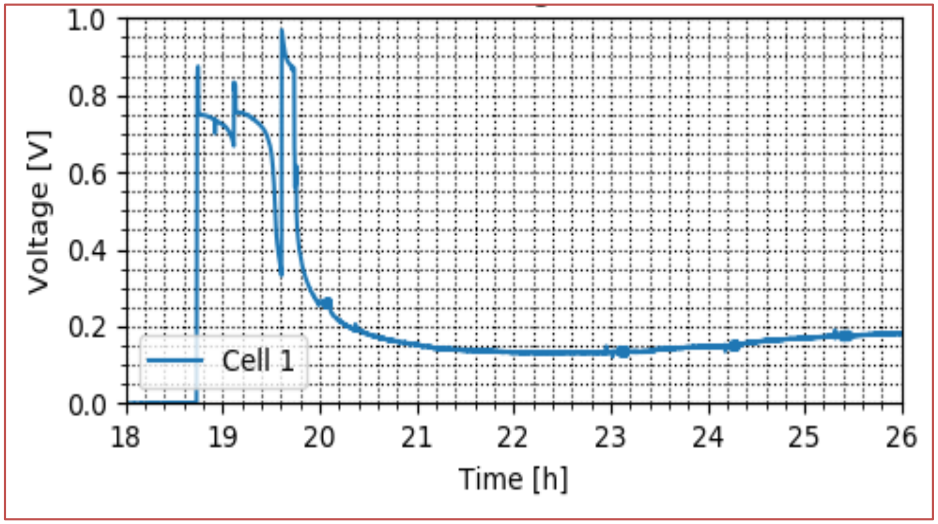
GDC deposited on Gen-1 SOFC sample with YSZ layer previously deposited using commercial sputtering equipment



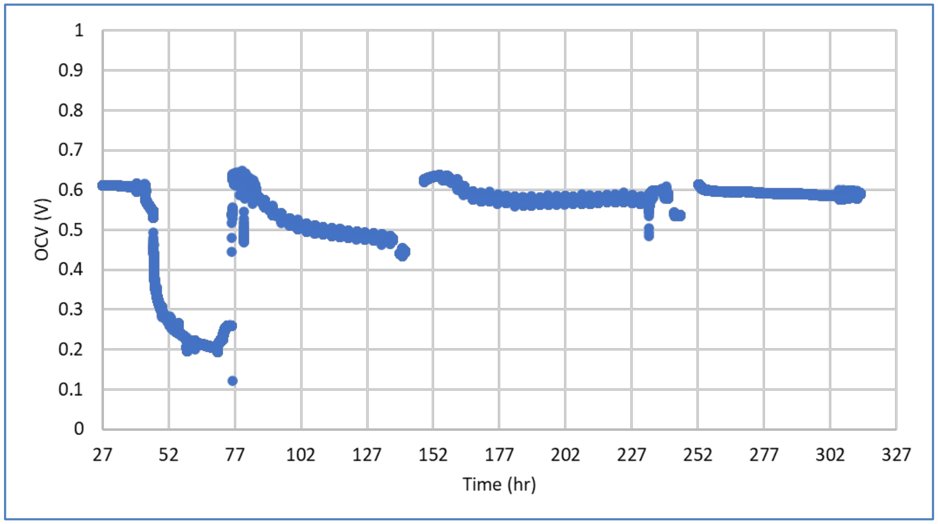
SEM of fractured cross-section

- Successful deposition of GDC buffer layer with over 1 μm/hour deposition rate on lab-scale system
- Required development of pre-sputter parameters and improvement of deposition conditions (e.g., Ar and O_2 pressure and sputtering power)
- GDC film deposition subsequently optimized on commercial equipment to ensure dense, robust film with greater uniformity in larger size cells and faster deposition rates

Initial Cell Tests: Difficulties Achieving Target OCV



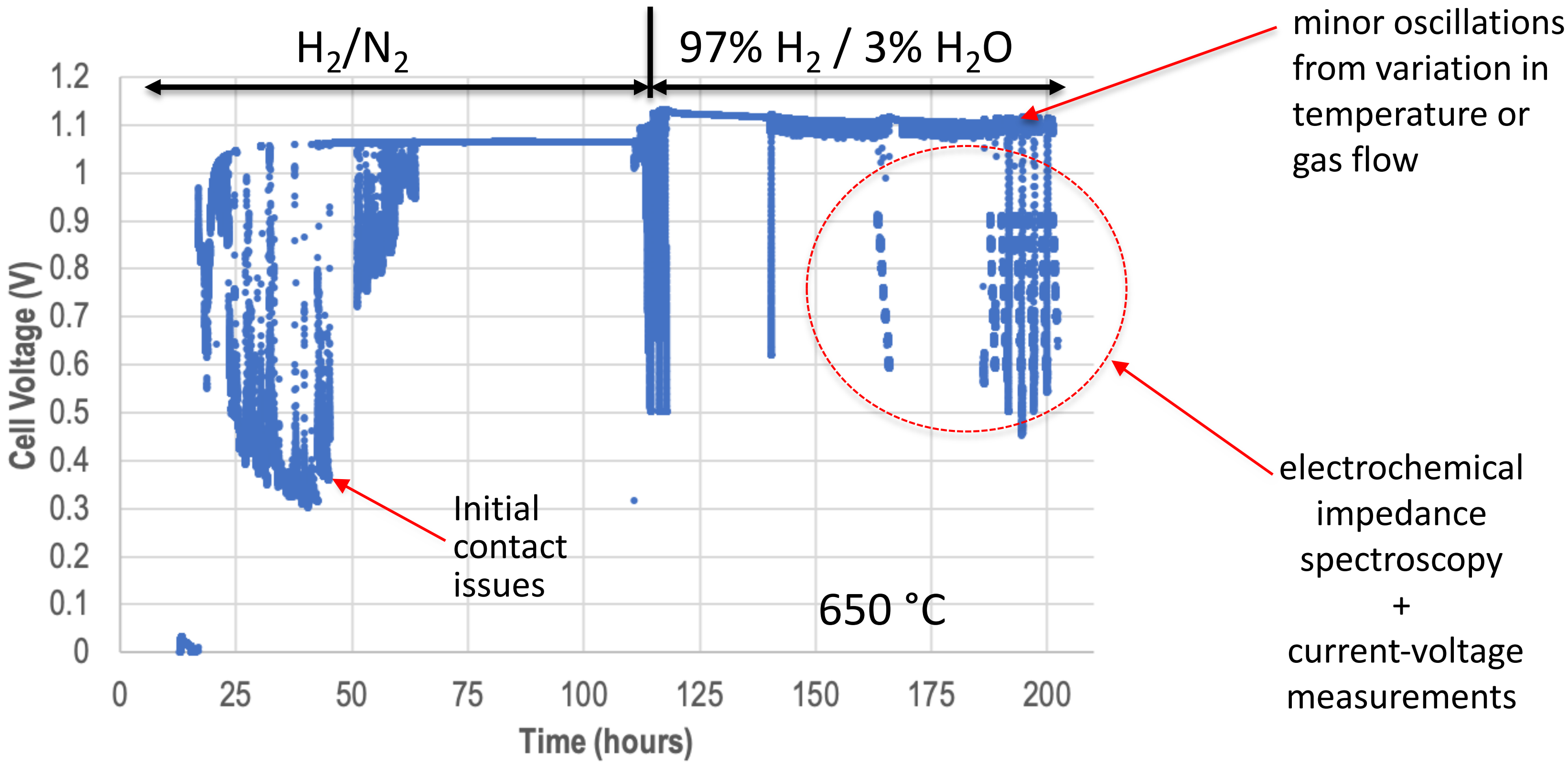
Cell 1
4 cm by 4 cm



Cell 2
4 cm by 4 cm

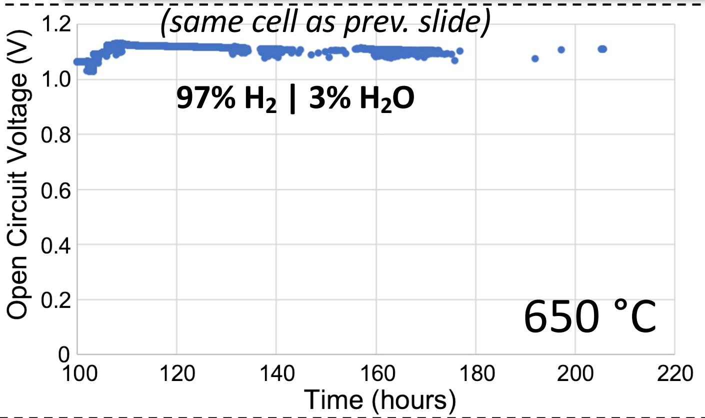
- Two types of issues were observed during initial tests
  - Stability Issues
    - Typically observed higher OCV initially, followed by rapid voltage drop to low values (e.g., Cell 1)
  - Lower OCV or similar OCV as standard, non-sputtered cells (same GDC electrolyte thickness)
    - Typically observed to have considerably lower OCV (e.g., Cell 2)

Achieving ≥ 1V Open Circuit Voltage



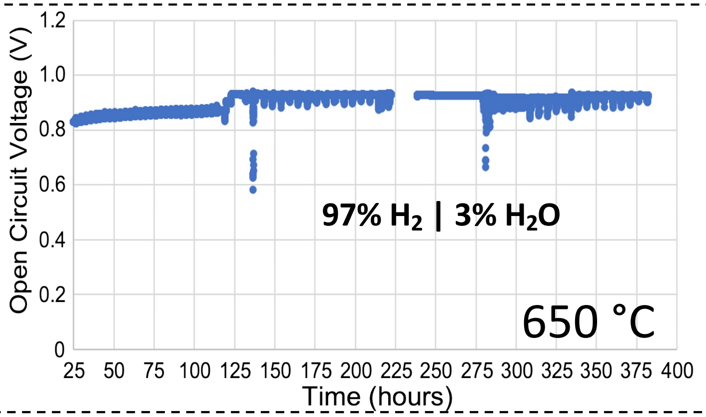
- Optimized sputtering conditions and post-sputter processing conditions
- 2 cm by 2 cm (sputtered YSZ & GDC) cell tested with stainless steel stack components
- Gas chromatography of the exhaust streams verified good sealing
- Theoretical OCV is 1.135V at 650 °C with 97% H_2 / 3% H_2O at the anode and air at the cathode
- Therefore, the observed OCV was 99.6% of theoretical OCV, confirming an effective electron-blocking layer on the GDC electrolyte
- The OCV is stable and represents a > 30% increase over the baseline (same GDC electrolyte thickness)

Processing Improvements for Repeatable High OCV



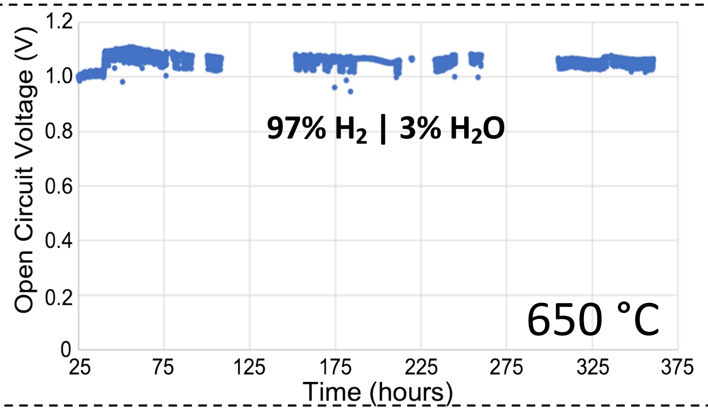
2 cm by 2 cm

- Type **A** sputtered layers*
- OCV: 1.13 V
- Stable for > 100 hours before scheduled shutdown



4 cm by 4 cm

- Type **B** sputtered layers*
- OCV: 0.95 V
- Stable for ~400 hours before scheduled shutdown

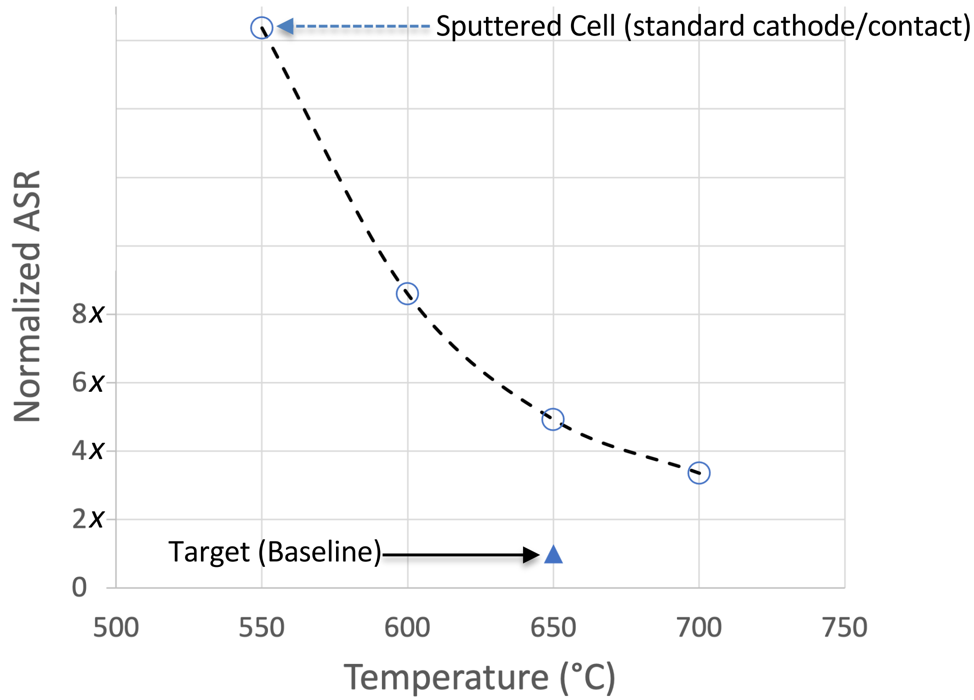


4 cm by 4 cm

- Type **C** sputtered layers*
- OCV: 1.10 V
- Stable for ~400 hours before scheduled shutdown

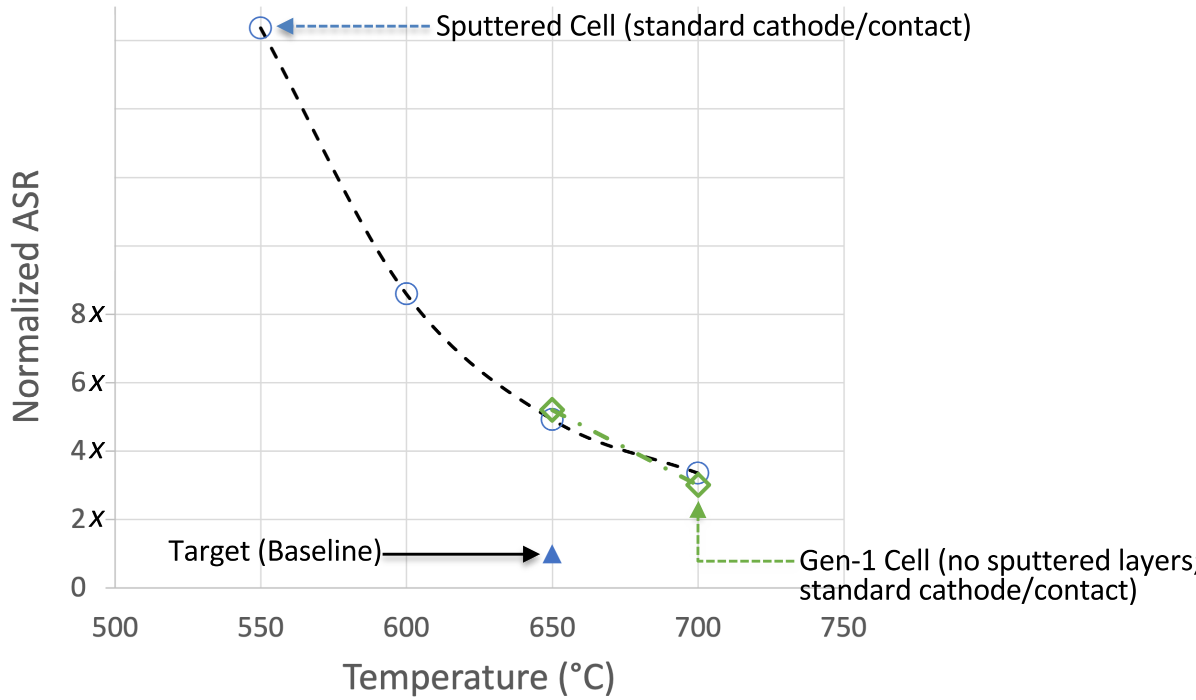
*made using production sputtering equipment

Higher Than Anticipated ASR



- Sputtered cell tested between 550 °C and 700 °C
- *High OCV:* ~1.13 V
- ASR of sputtered cell at 650 °C is about 5X higher at 650 °C than the target ASR (Redox Gen-1, non-sputtered)
- ASR did not change at 33% O_2 or 55% O_2 (mixed with air) or flow rate, suggesting the cathode is not the problem

Higher Than Anticipated ASR

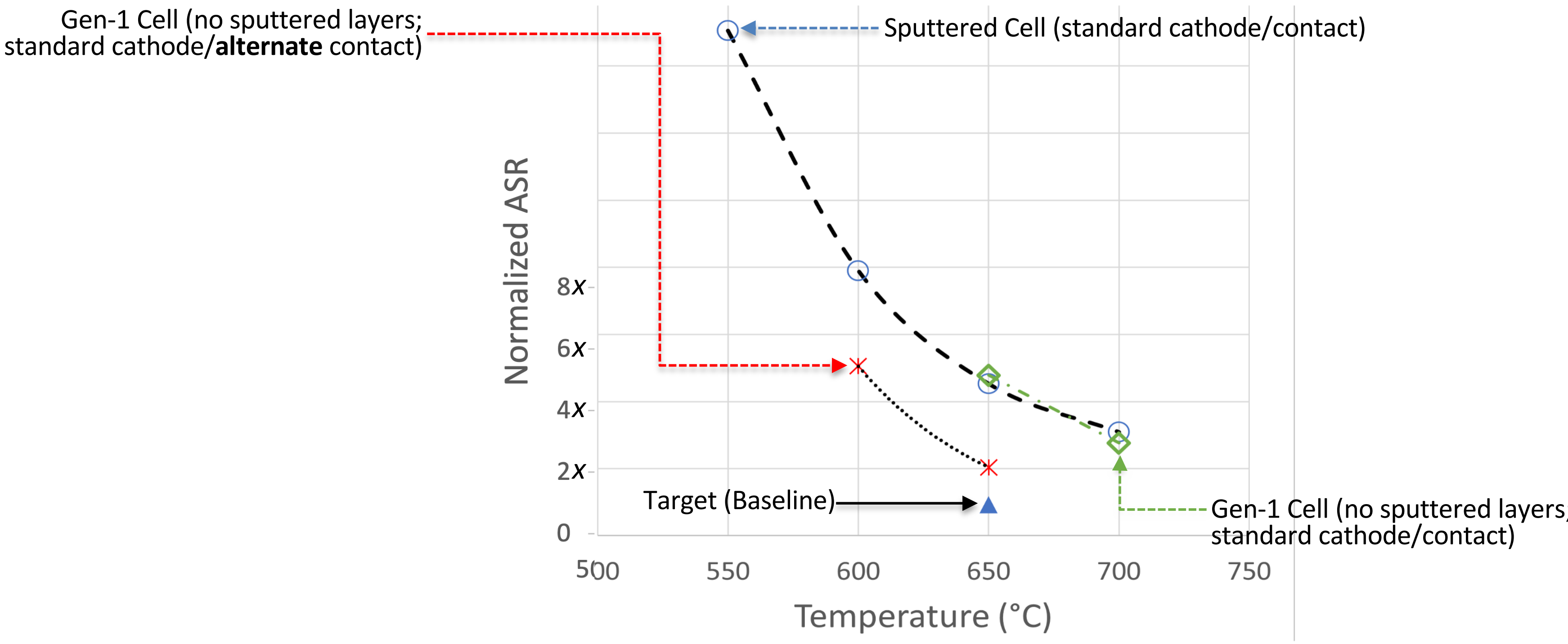


- Regular (non-sputtered) Gen-1 cell with same cathode/contact processing as sputtered cell
- Same ASR for the two cells at 650 °C and 700 °C
- Confirms the higher ASR is very likely due to cathode/contact processing

Contact Adhesion Issues

- We conducted several studies looking at cathode and contact adhesion at the various processing conditions used with sputtered cells
- Cathode/contact adhesion was found to be poor
- Adhesion of cathode (directly on GDC, without contact) was found to be sufficient
- Adhesion of standard contact (directly on GDC) was found to be poor
  - We therefore looked at some alternate contact materials
  - Several of the alternate contacts were found to have "good" adhesion
  - Adhesion remained "good" for the cathode/alternate contact

Higher Than Anticipated ASR



- Standard Gen-1 cell (no sputtered layers) with standard cathode + alternate contact ("good" adhesion)
- Much lower ASR: ~2x the target ASR at 650 °C
- This result combined with adhesion test results provide strong evidence that the high ASR is due to the contact

Next Steps for Sputtered Cells

- Repeat test with standard (non-sputtered cell)
  - fresh cathode paste to verify results
  - Standard contact & alternate contact
  - Use gold or silver contact
- Once the cathode and an alternate contact are found to match the target ASR, prepare additional sputtered cells
- Test these sputtered cells using the same procedures as the latest tests at several temperatures

Summary of FE0027897 & FE0031656

- FE0027897: Red-Ox Robust SOFCs
  - Red-Ox stability demonstrated
  - Improved performance demonstrated
  - Future room for improvement to balance strength and performance at large format cell size

- FE0031656: High-Power Thin-Film SOFCs
  - Optimized sputtering conditions to achieve dense YSZ electron-blocking layer and dense GDC buffer layer
  - Overcame low OCV issues and repeatably achieved theoretical OCV at 650 °C using target cell size
  - Demonstrated that the cathode contact is the cause for high ASR and that there is a path for reaching the target ASR with the sputtered cells

Acknowledgements

NETL program manager: Jason Montgomery

- **DE-FE0027897**
- **DE-FE0031656**