Developing Stable Critical Materials and Microstructure for High-Flux and Efficient Hydrogen Production through Reversible Solid Oxide Cells

(Update on 2023 Research and Development)

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University of South Carolina

(DE-FE-0032111)

Present to 2024 FECM Spring Project Review Meeting, Pittsburgh, April 23-25, 2024

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Outline

- Process optimization of air electrode BYC-LSM barrier layer free (BLF) air electrode
- Button cell (1.5 cm^2) testing
- Planar 13 cm^2 cell making and testing
- ALD-SCT bilayer air electrode synthesis
- Multiphysics modeling
- Conclusion
- Ongoing work

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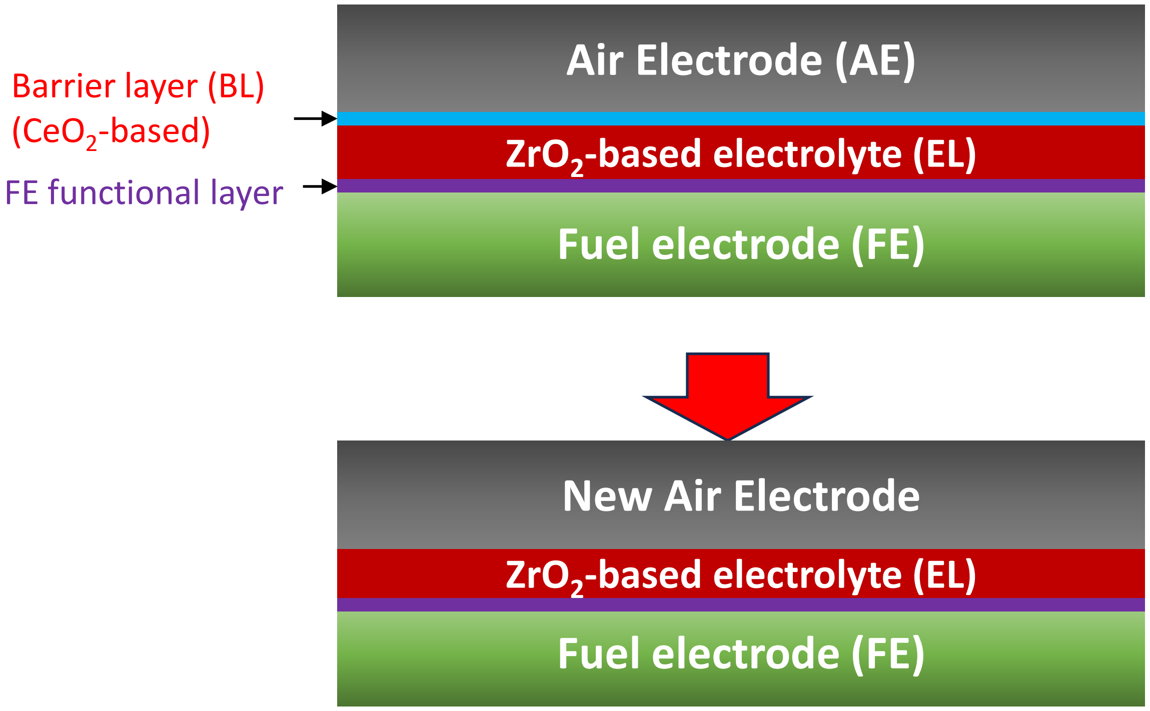
About Project

Project Goal

To develop reduced temperature (≤700°C) ZrO_2-based SOCs technology for high-efficiency and low-cost power and H_2 production.



Tasks

1. Engineering barrier layer free air electrode $(Bi_{0.75}Y_{0.25})_{0.93}Ce_{0.07}O_{2-\delta}$-$La_{0.8}Sr_{0.2}MnO_3$ (BYC-LSM) for 650°C SOCs (USC)
2. Developing ALD-SCT ($SrCo_{0.9}Ta_{0.1}O_{3-\delta}$) @LSCF-GDC bilayer AEs for 700°C SOCs (USC)
3. Developing porosity-graded fuel electrode (FE) substrates and cells (USC)
4. Validating the developed new materials/microstructure in small and large cells (PNNL)
5. Developing a coupled electro-chemo-mechano model (USC)

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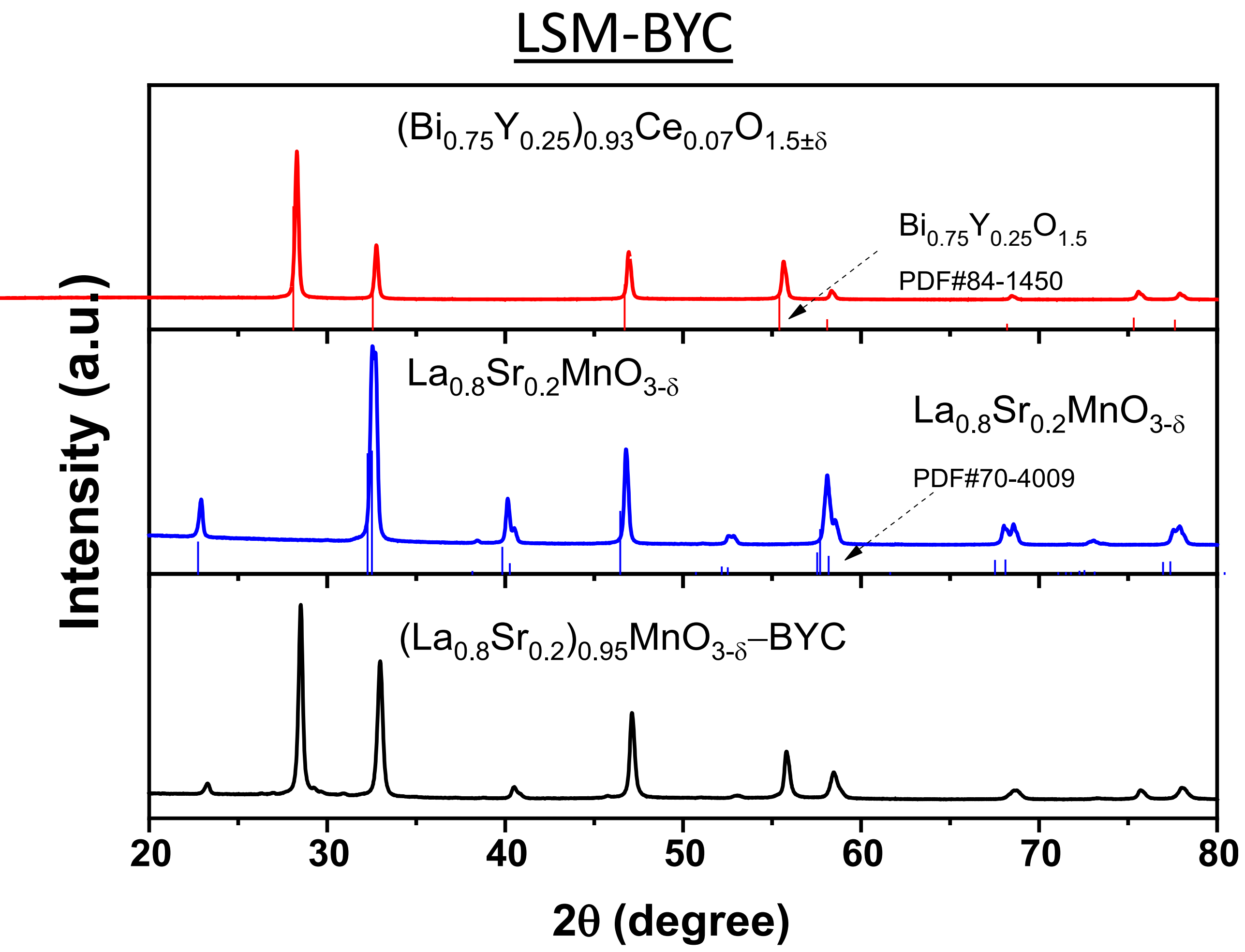
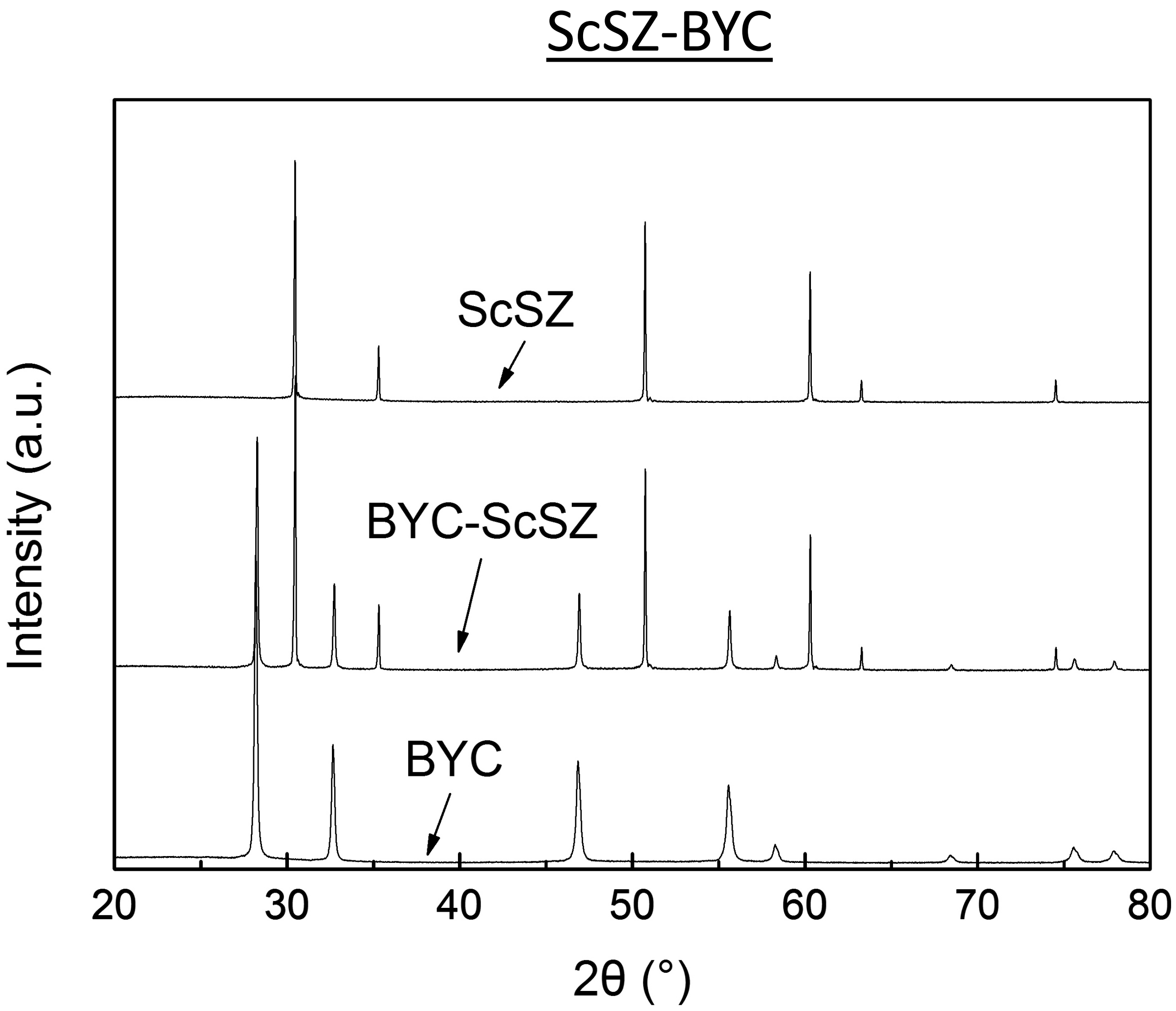
LSM-BYC-ZrO_2 Chemical Compatibility





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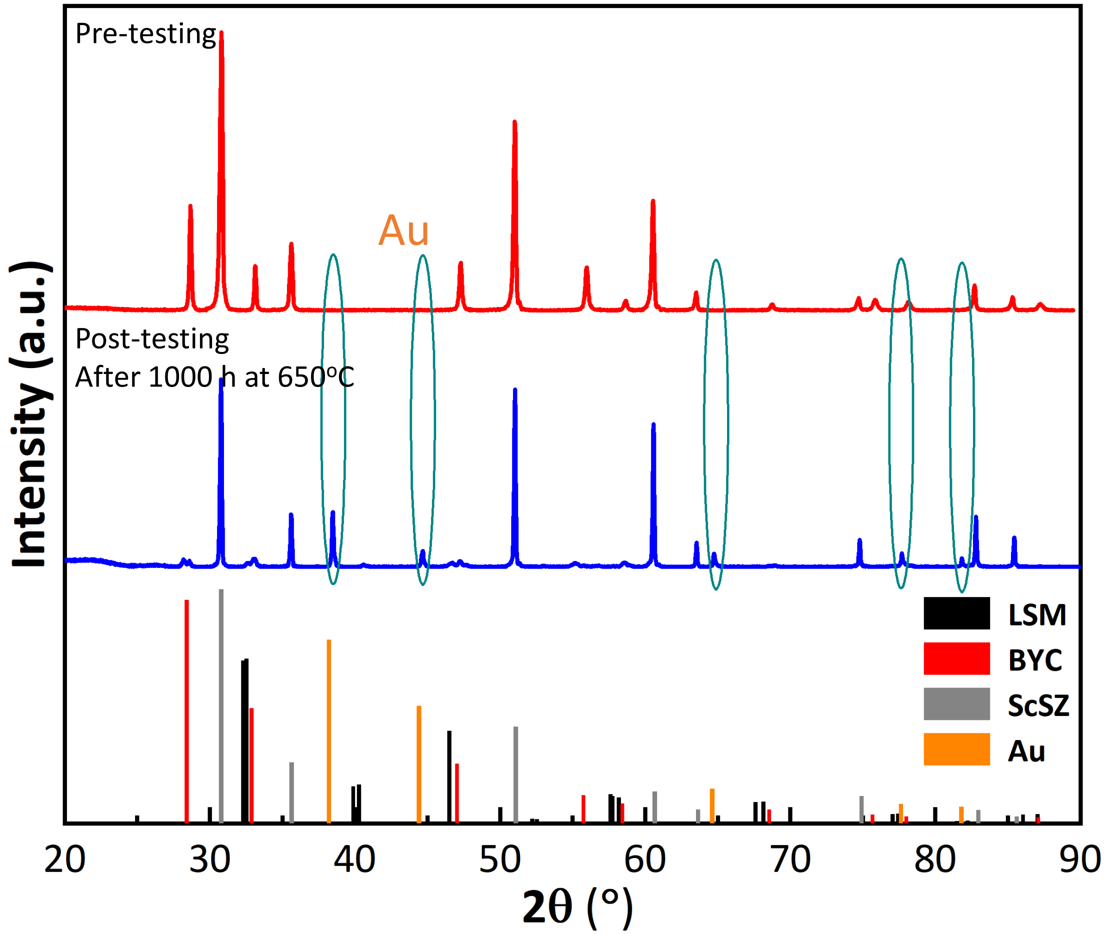
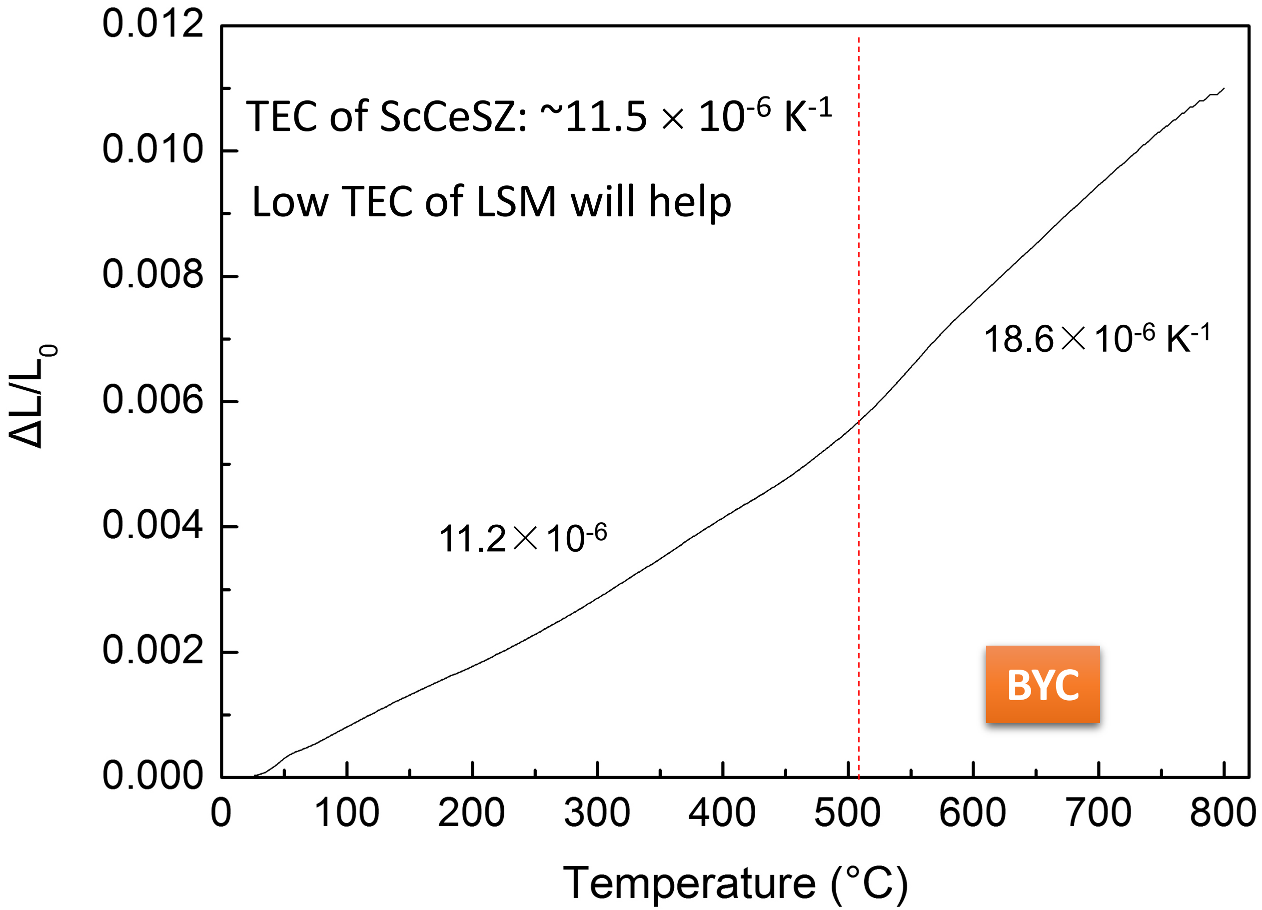
Phase/TEC Check Before and After Testing





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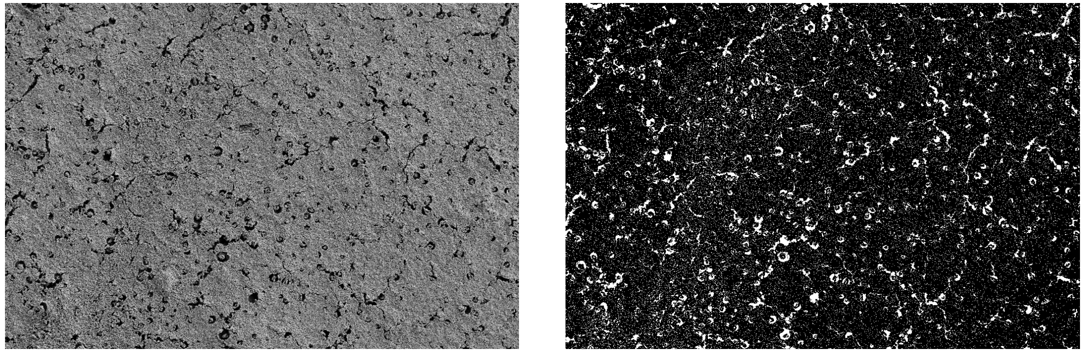
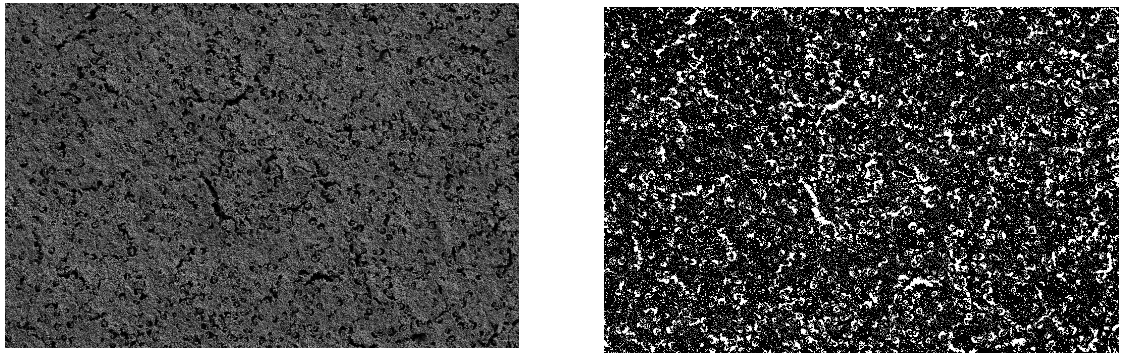
AE Optimization: Porosity by PMMA

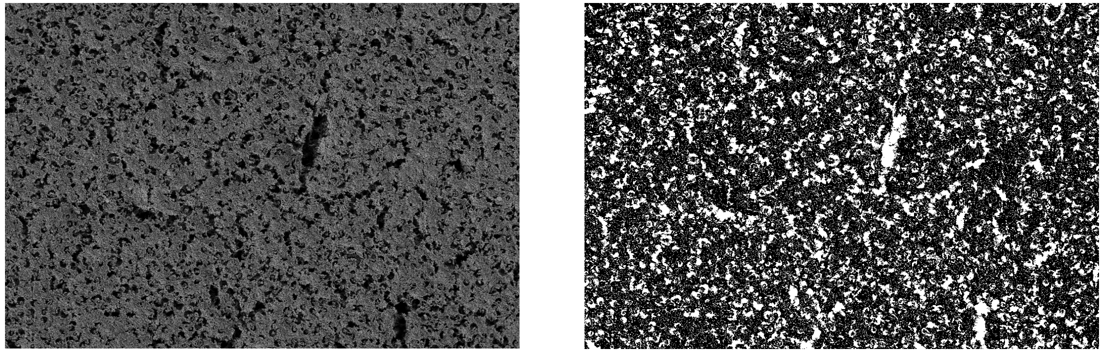


5 wt% pmma
19.5%

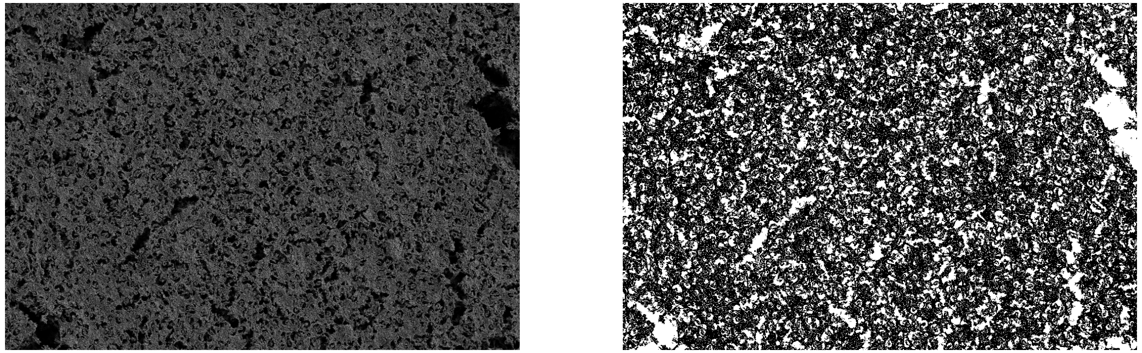


10 wt% pmma
43.5%

Fired at 800^{o}C



15 wt% pmma
57.3%



20 wt% pmma
66.8%

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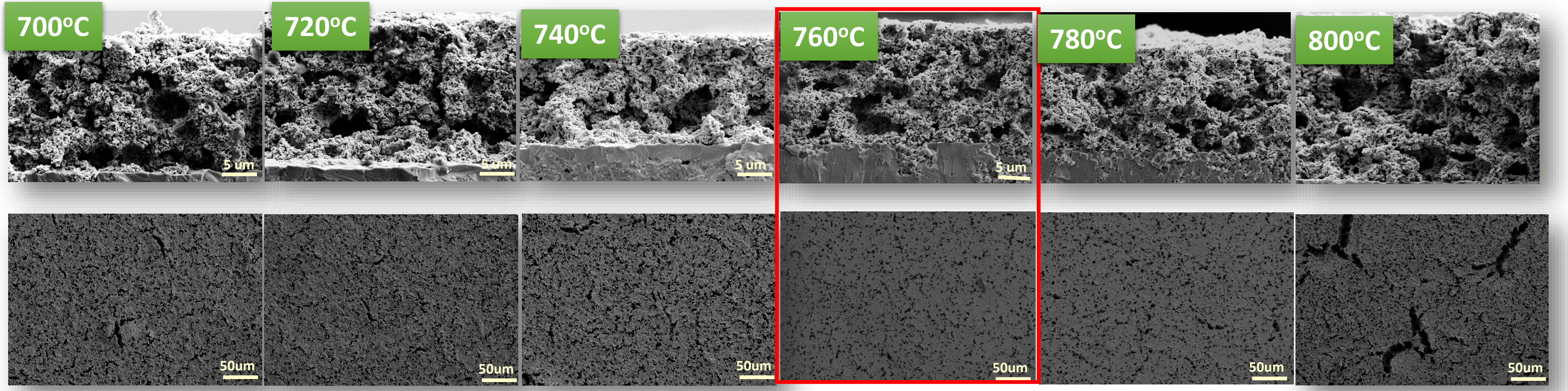
Calcining T Effect on Microstructure

Cross-section of BYC-10pmma sintering at 700, 720, 740, 760, 780, 800 ºC



Top view of BYC-10pmma sintering at 700, 720, 740, 760, 780, 800 ºC

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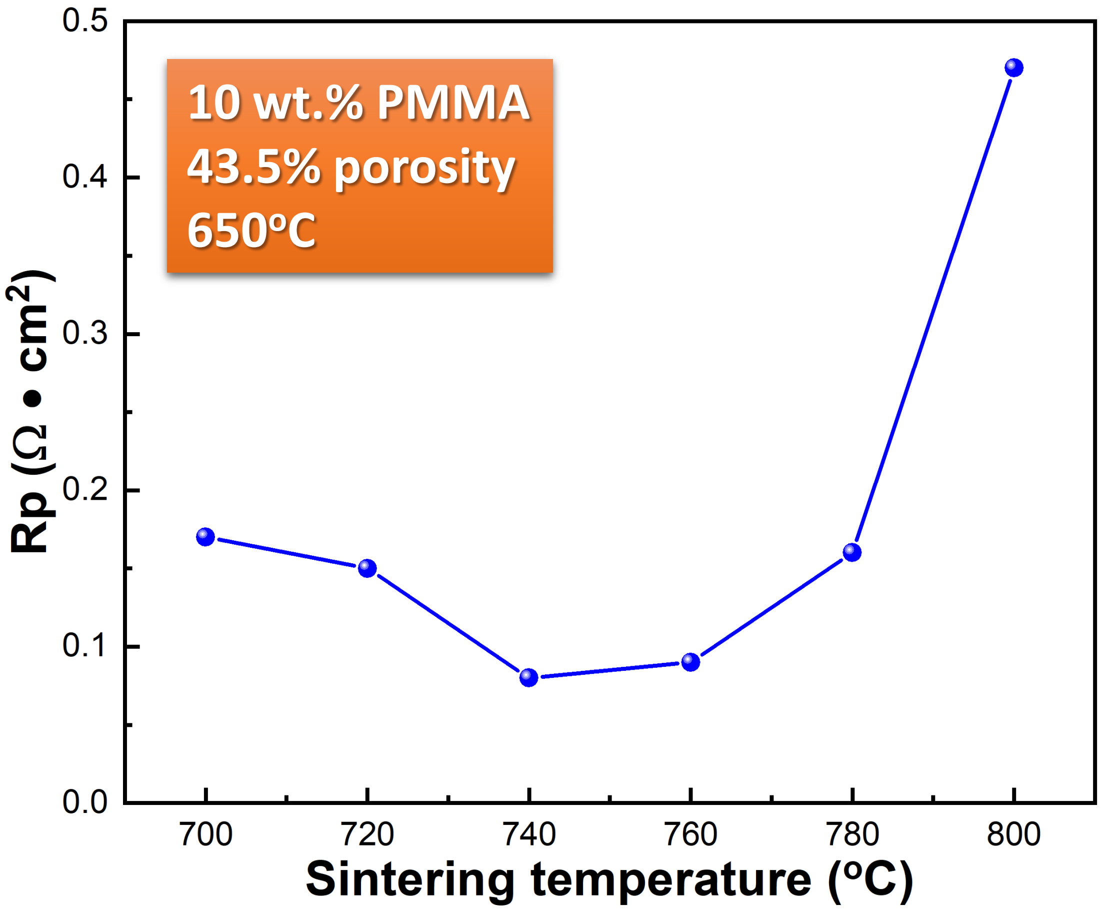
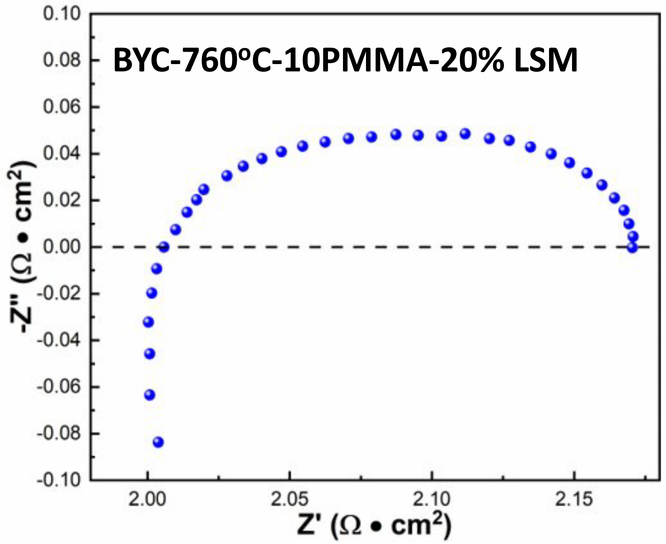
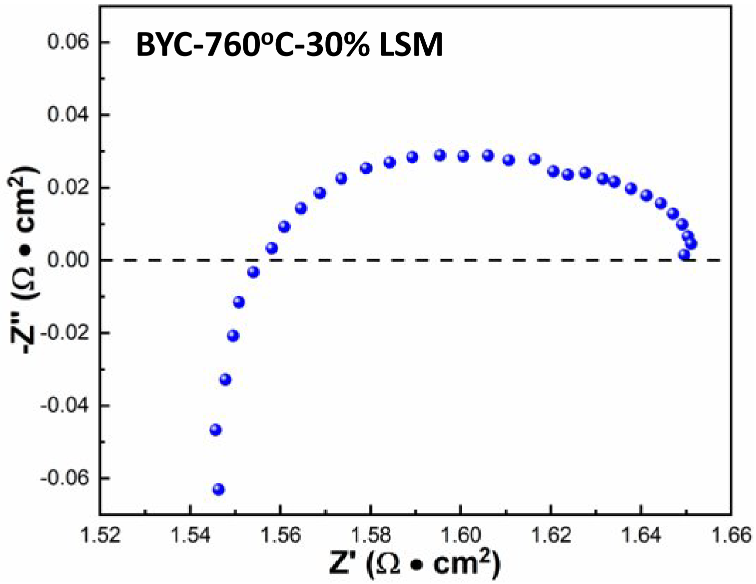
Calcining T Effect on R_P

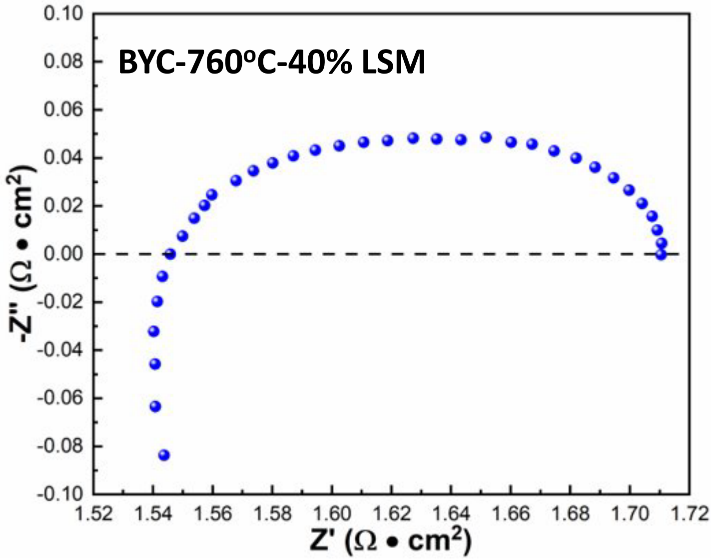


BYC skeleton	R_p (Ω cm^2)
10pmma-700 °C	0.17
10pmma-720 °C	0.15
10pmma-740 °C	**0.08**
10pmma-760 °C	0.09
10pmma-780 °C	0.16
10pmma-800 °C	0.47

LSM Loading Effect on R_P







LSM loading	R_p (Ω cm^2) at 650°C
20 wt%	0.17
30 wt%	0.08
40 wt%	0.15

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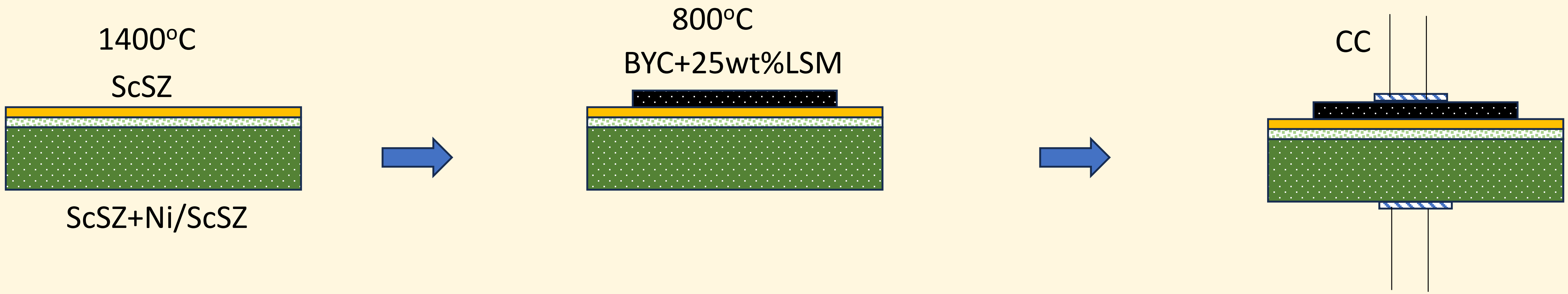
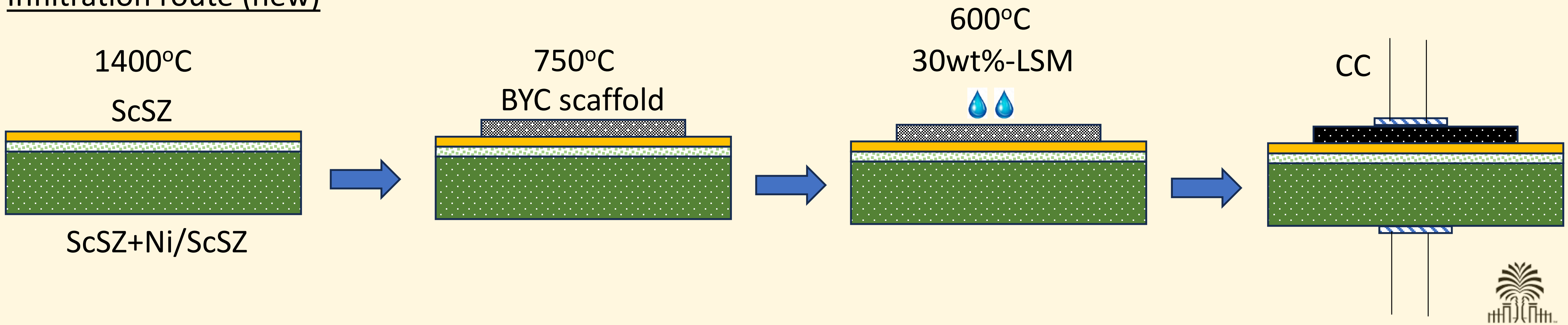
LSM-BYC Full Cell Fabrication

Screen printing route (baseline)



Infiltration route (new)



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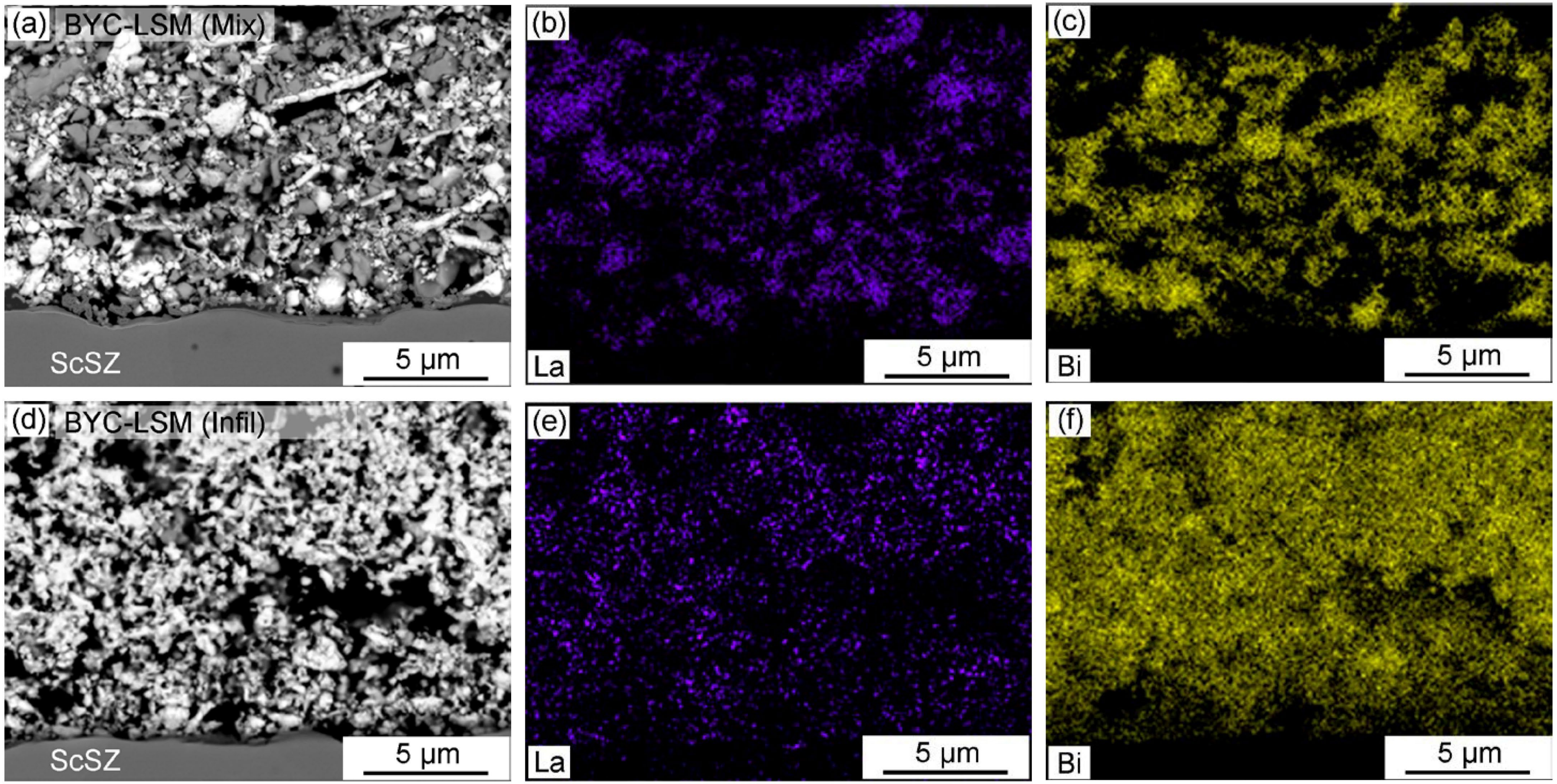
LSM-BYC Cell Cross-Section (Pre-Testing)

Screen printed

Infiltrated



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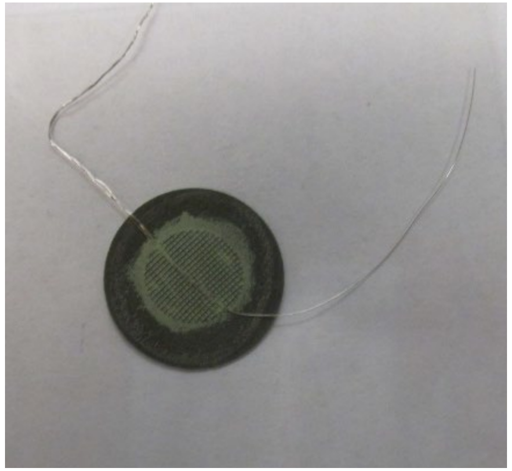
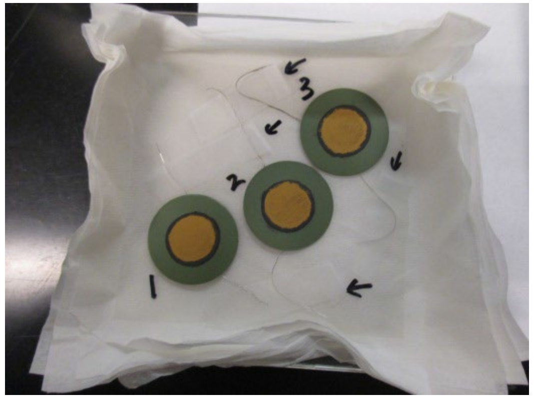
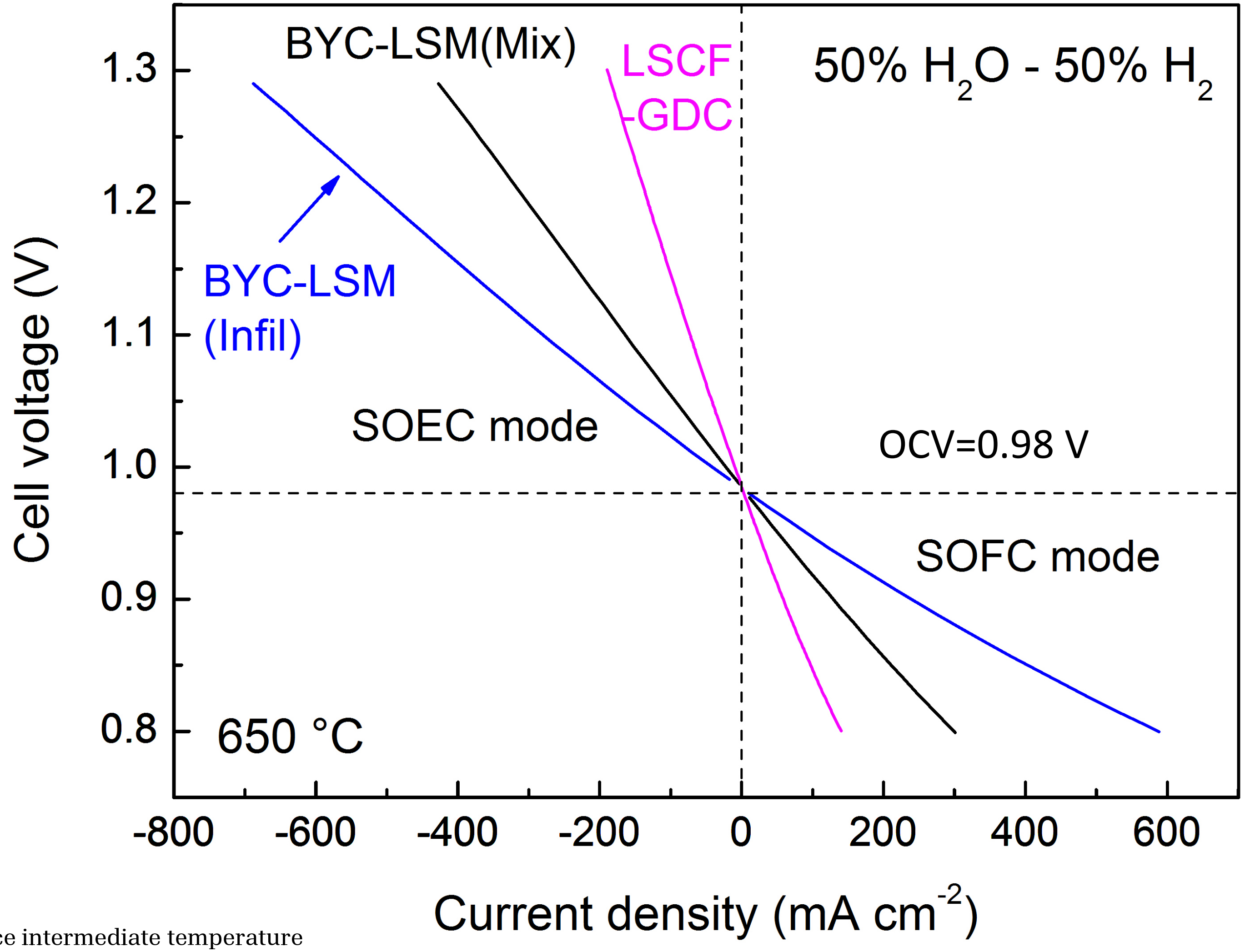
V-I Characteristic

1.5 cm^2 active area



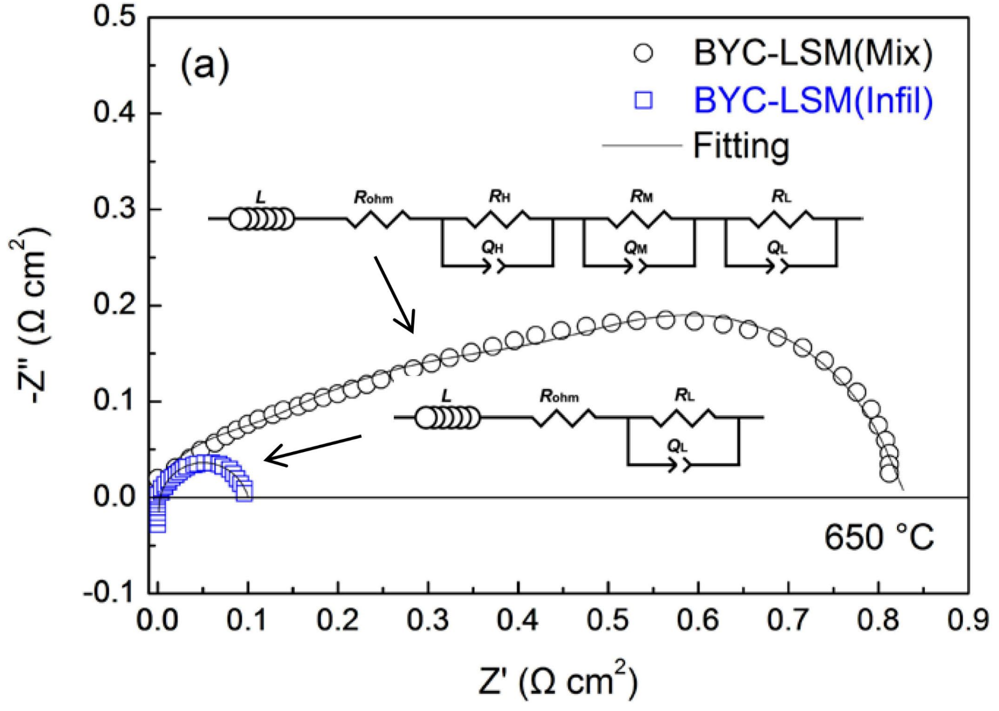




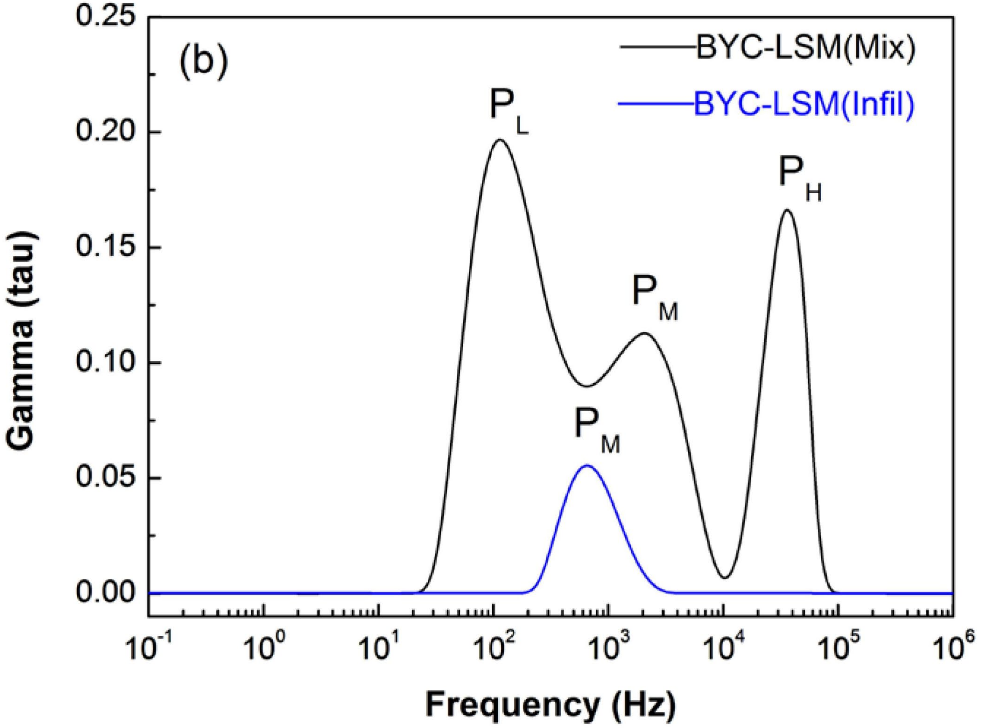
Kai Zhao, Olga A. Marina*, Kevin Huang*, etc. “A high-performance intermediate temperature reversible solid oxide cell with a new barrier layer free oxygen electrode”, **Applied Energy**, 2024, **361**, 122962. DOI: 10.1016/j.apenergy.2024.122962.

Air, LSM-BYC|ScSZ|ScSZ-Ni, 50%H_2O-H_2

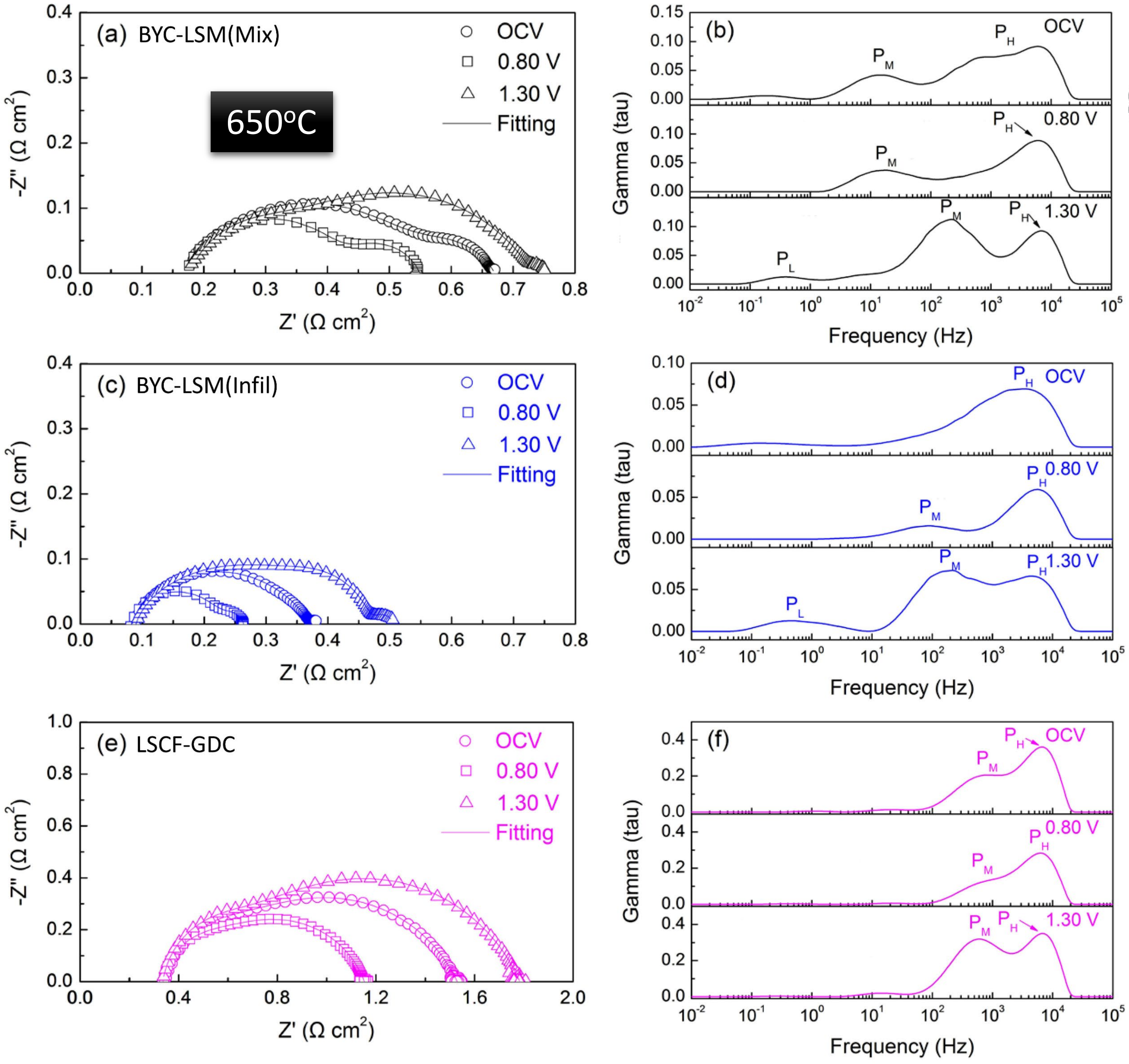
EIS Spectra



DRT profile



Air, AE|ScSZ|ScSZ-Ni, 50%H_2O-H_2



- **Lowest R_P at SOFC mode**
- **Highest R_P at SOEC mode**
- **Different DRT profile between the three AEs under OCV mode**

Comparison of Electrode ASRs at Different Feq Ranges

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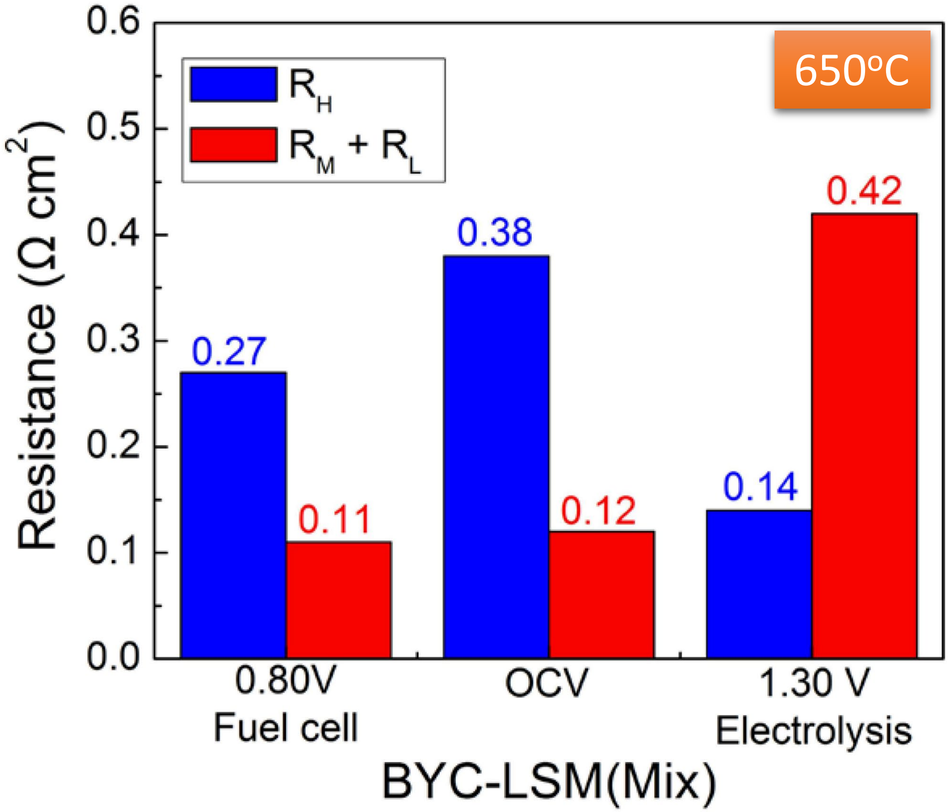

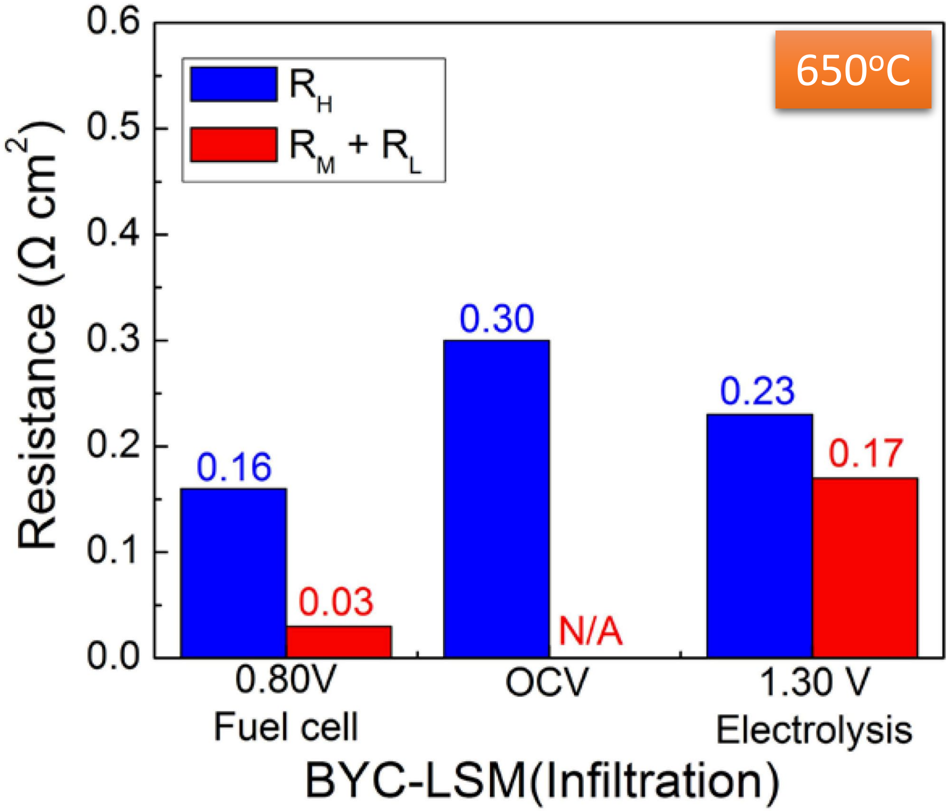

- Both samples dominated by high-f resistance. More impact in screen-printed sample
- Screen printed sample dominated by mid-low-f resistance under SOEC mode

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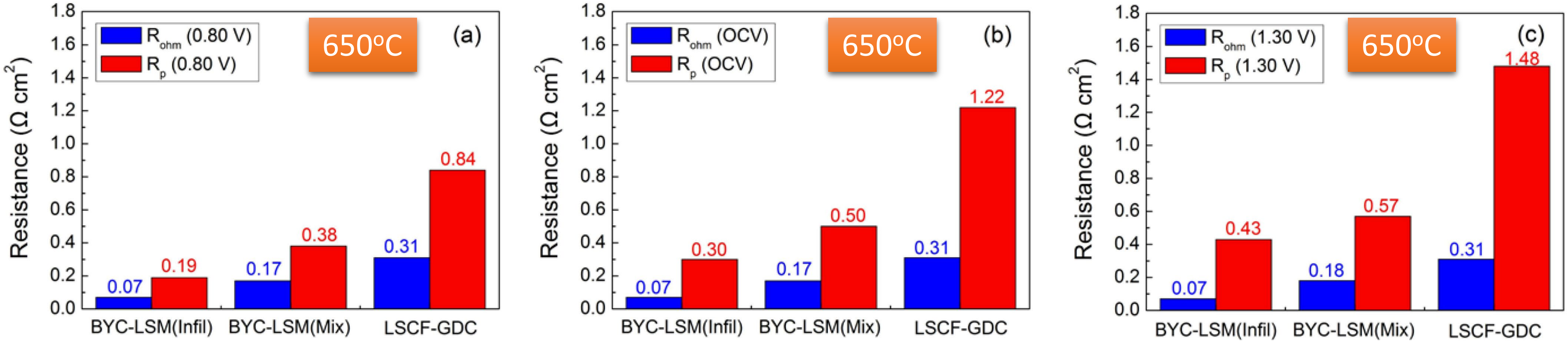
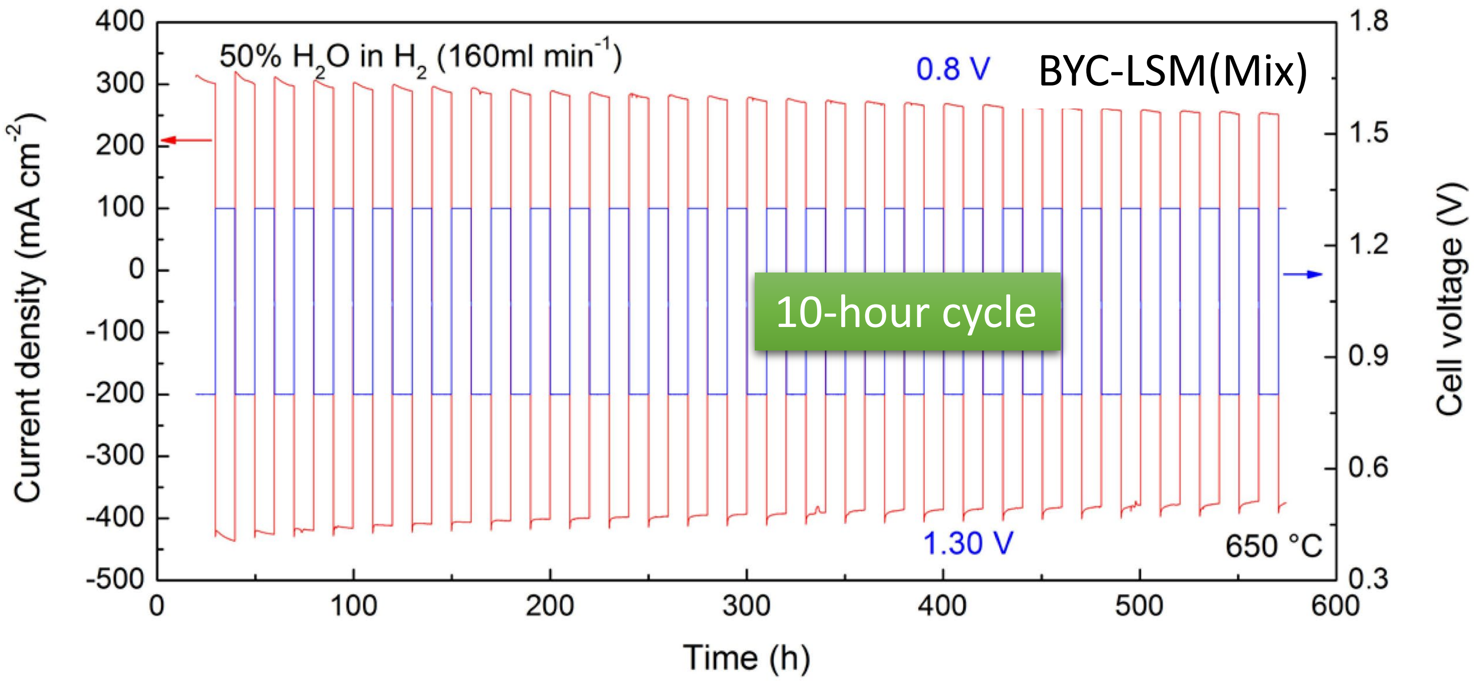
Comparison of Ohmic and Polarization ASRs of Different AEs

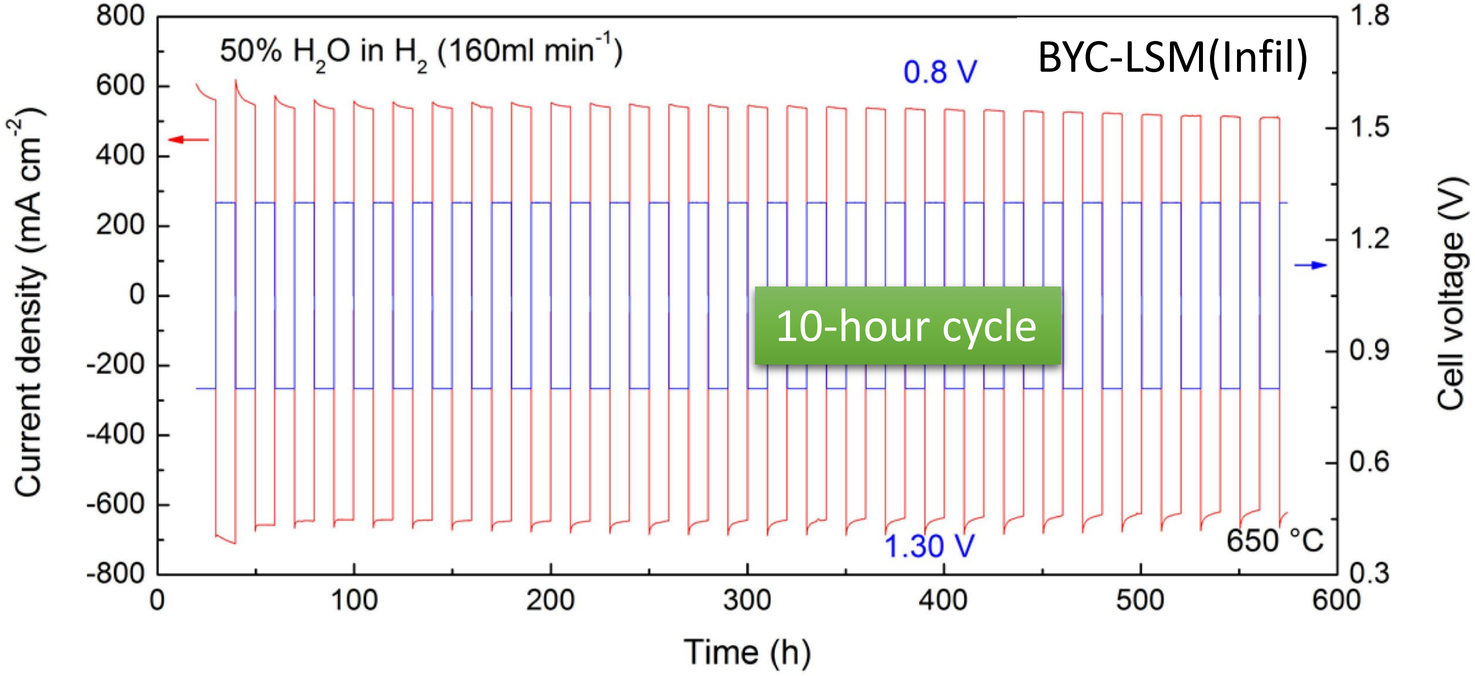
Single cells with different air electrodes



- **All three samples exhibited the similar R_O under different modes**
- **Infiltrated sample exhibited the lowest R_O and R_P among all three samples**
- **R_P under SOEC mode is higher than OCV and SOFC modes**

Long-term performance at 650^{o}C





EIS and DRT Comparisons at t=0 h and 550 h

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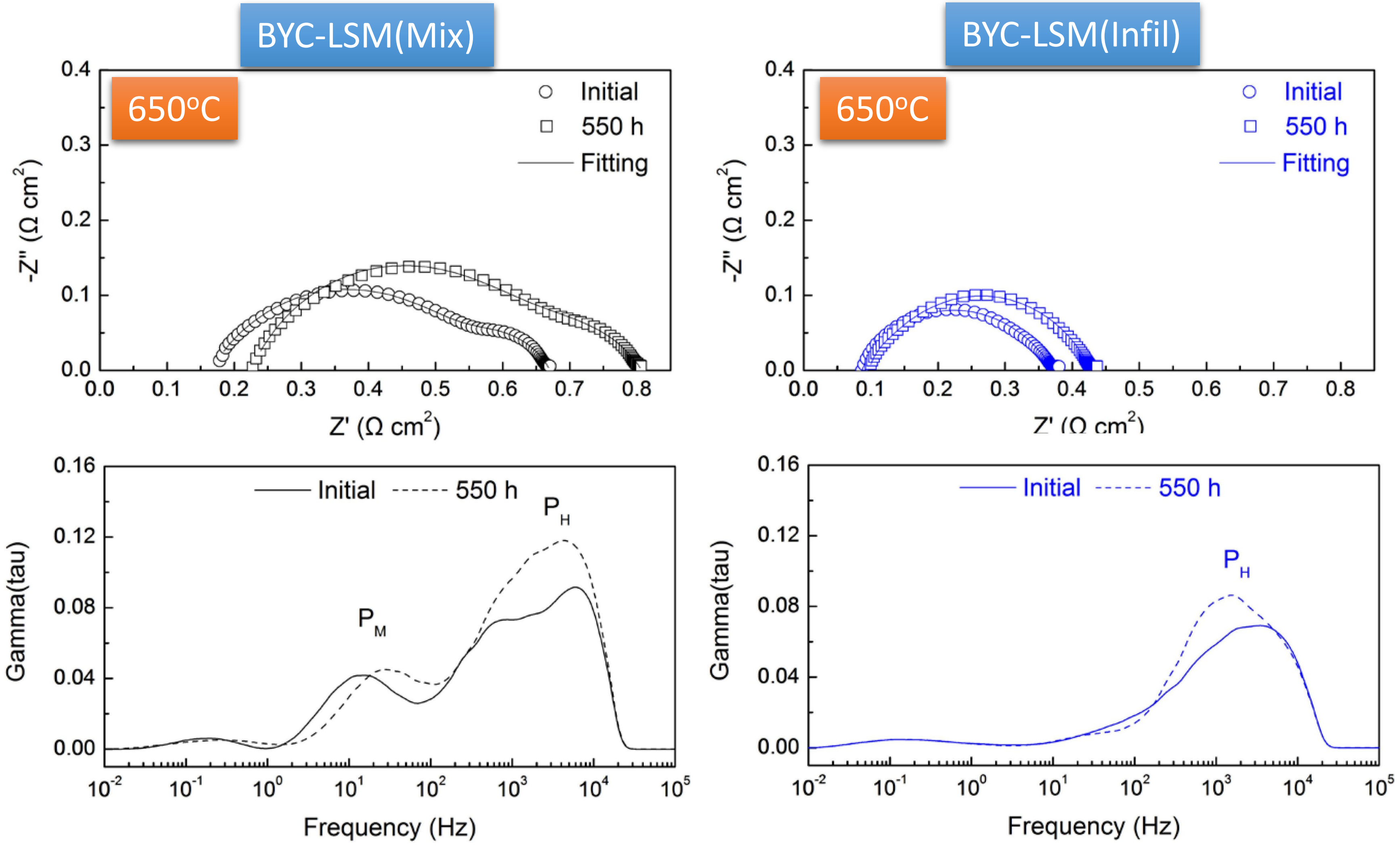

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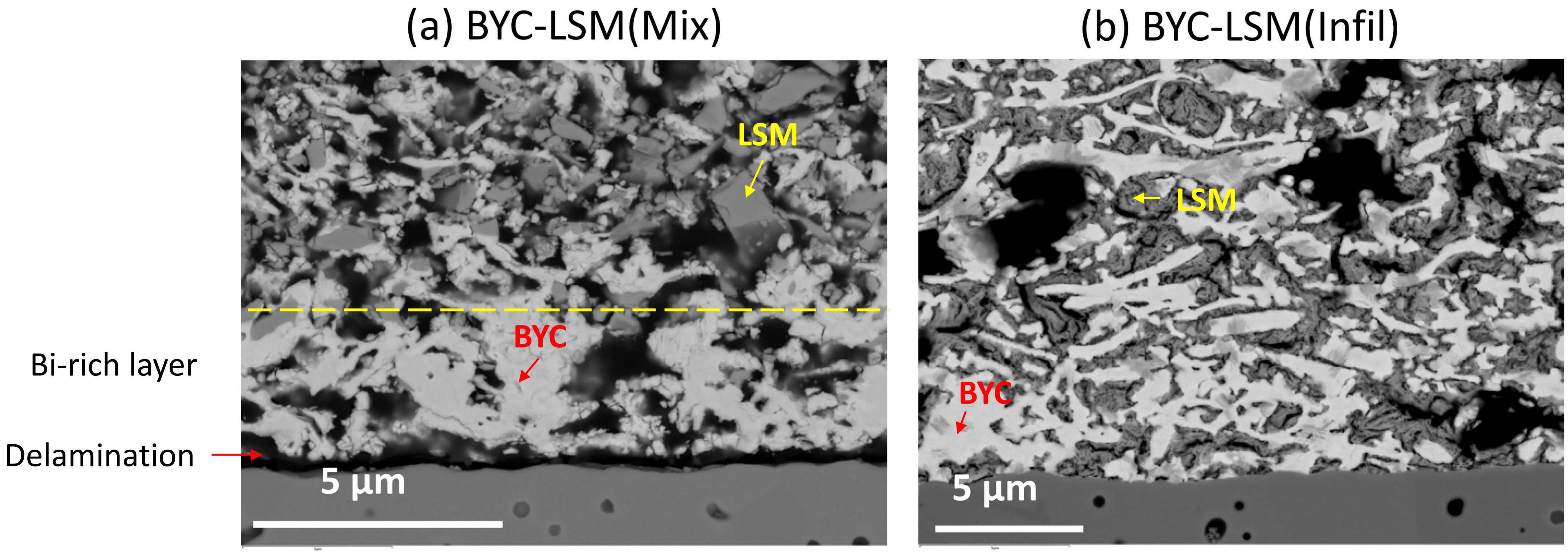
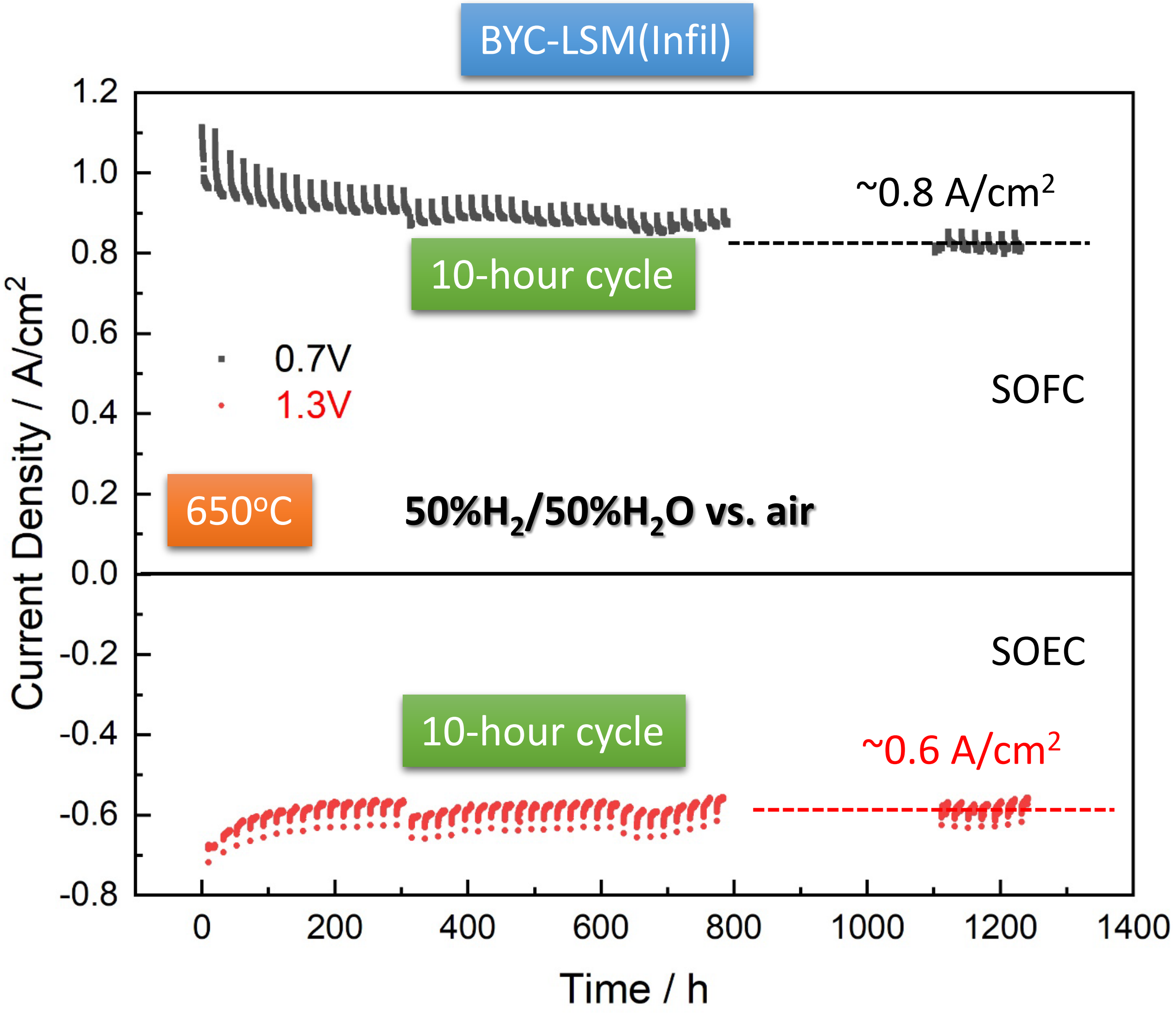
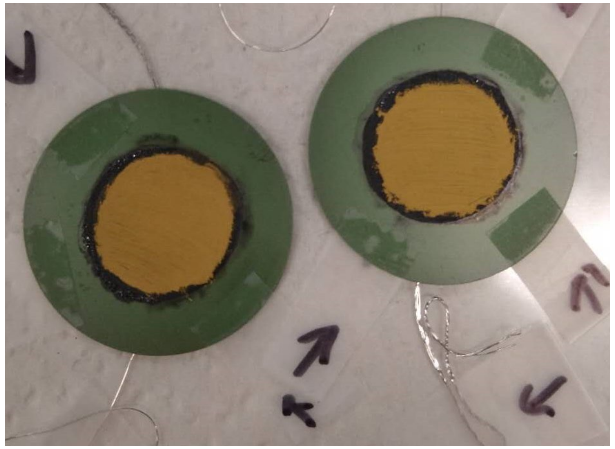
Microstructure Comparison after Testing



Independent Long-term Testing @INL

Idaho National Laboratory





A=1.5 cm^2

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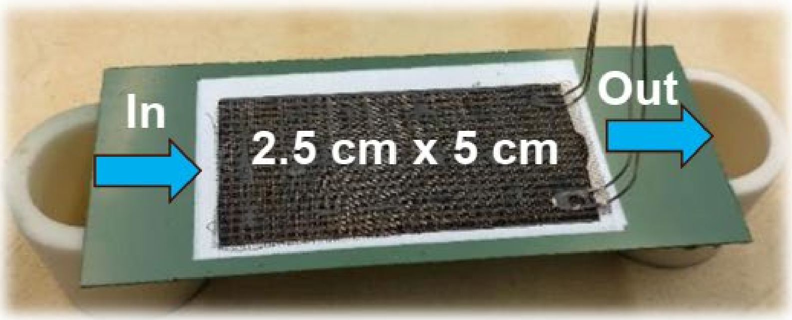
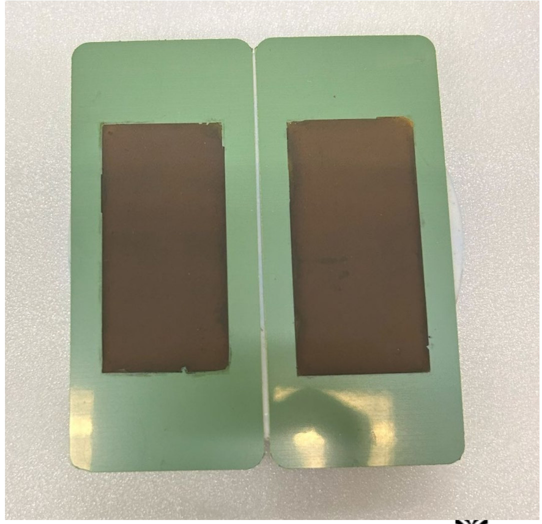
13 cm^2 Cell Making and Testing at PNNL

- 500 um Ni-YSZ electrode-supported cells
  - 2.5 cm x 5 cm (13 cm^2 active area)
- 8 um YSZ electrolyte
- 20 um Ni-YSZ active fuel electrode, Pt mesh contacts
- BYC-LSM oxygen, Au contacts
- Sealed and tested at 650°C

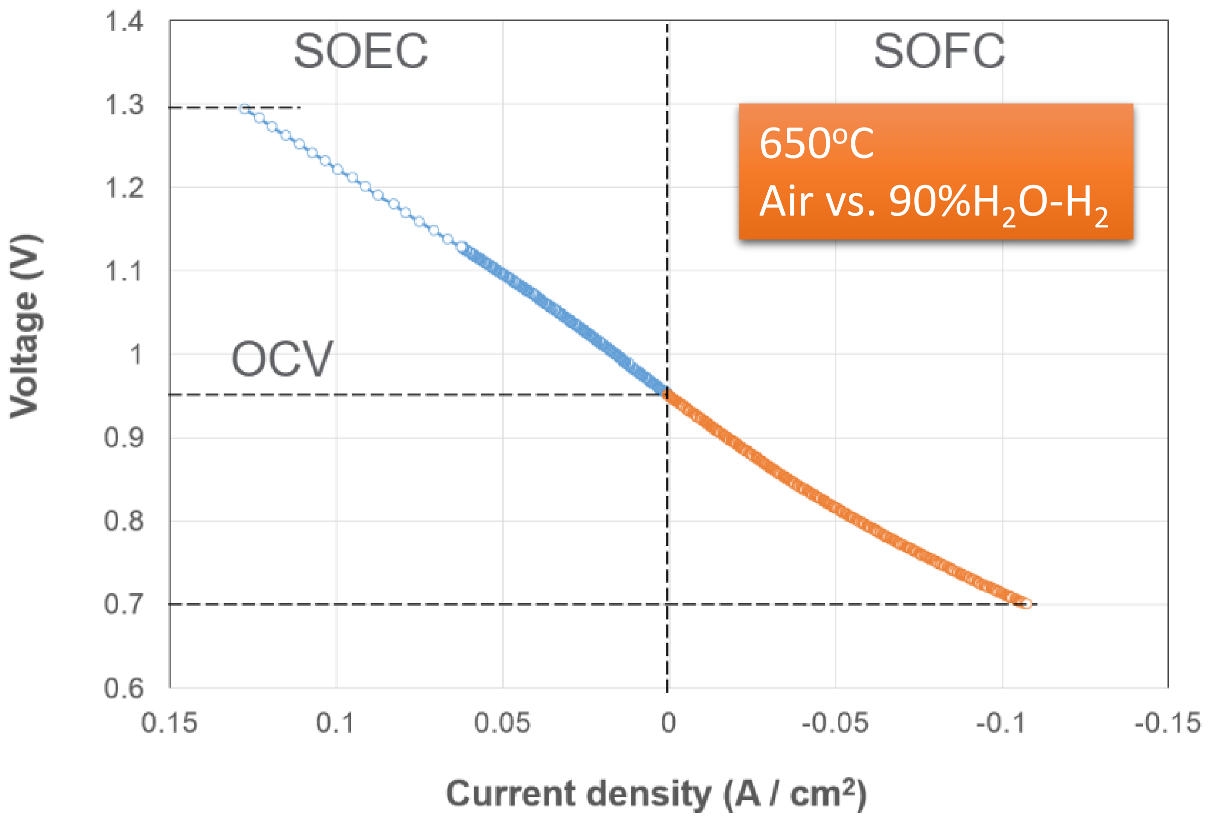


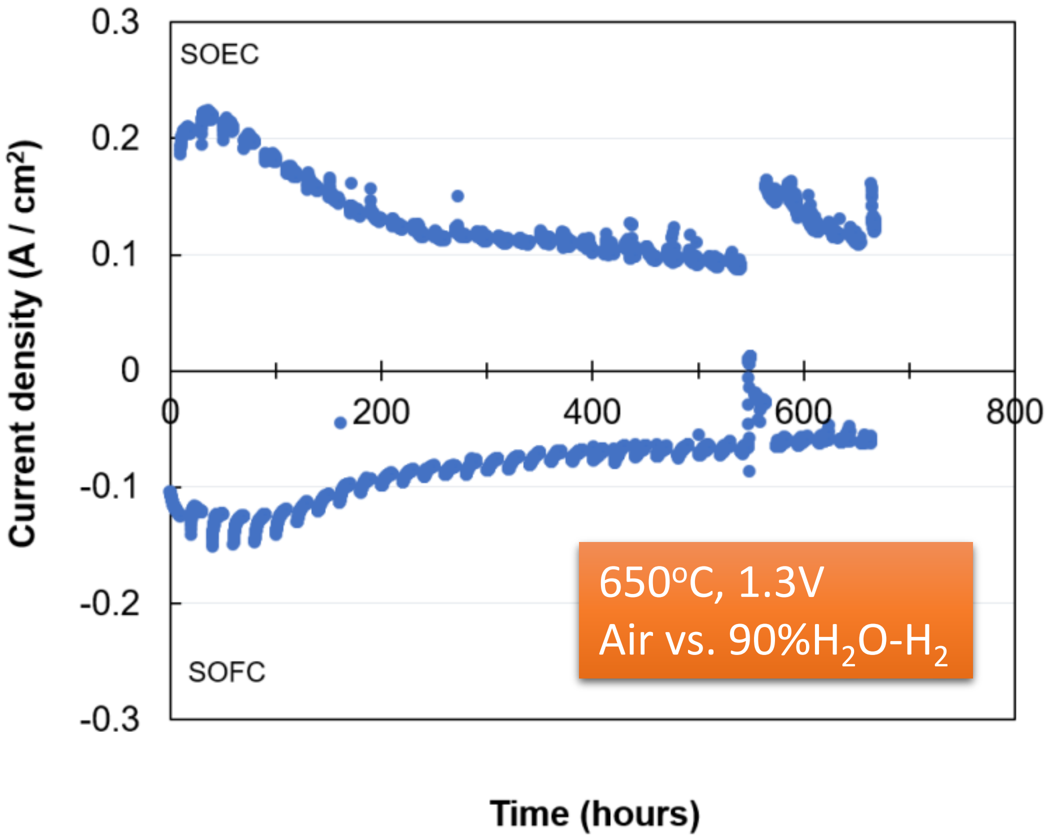
After BYC coating

After LSM infiltration



Performance of 13 cm^2 YSZ Cell

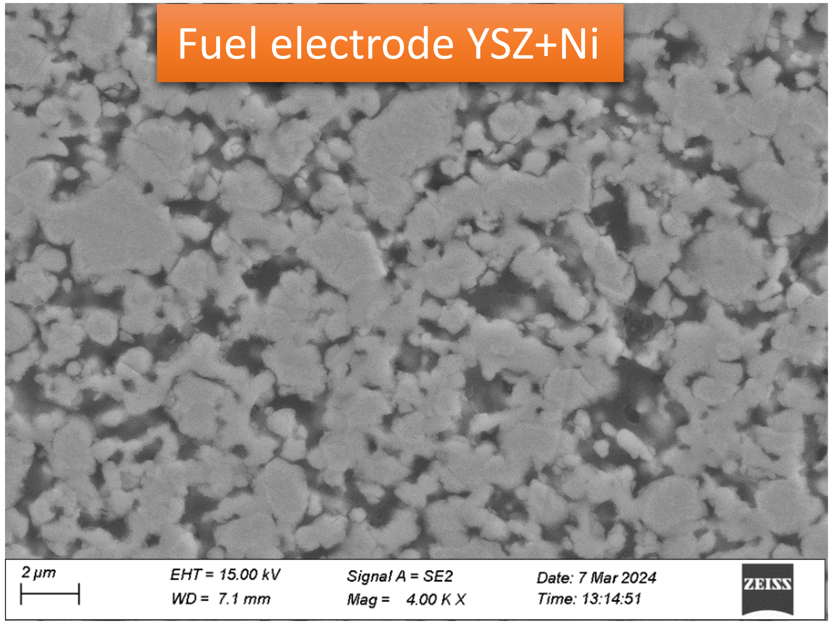


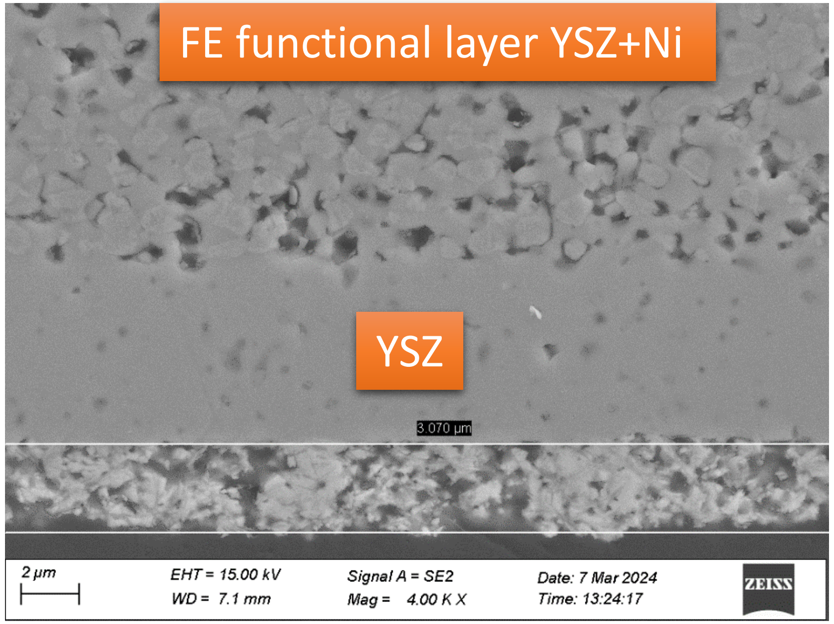


13 cm^2 Cell by PNNL (1st, USC#1-1)

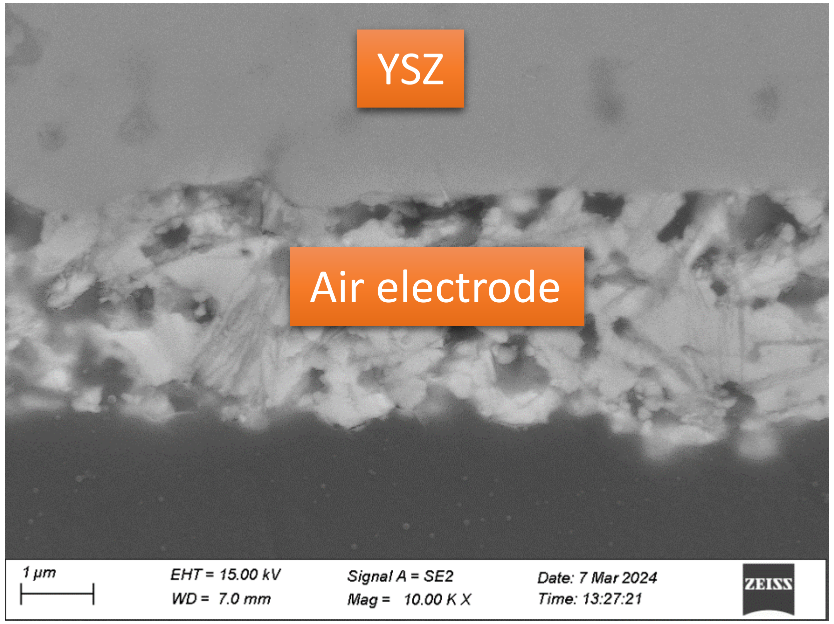
Pacific Northwest National Laboratory

2023-10-20_S7_c46
Rectangle cell with PNNL bilayer and USC's O-electrode
Sample ID: USC#1-1
Tested for 70 hours @ 1.3V, 50% steam, 650^{o}C + 50 hours @ 1.3V, 90% steam, 700C





FE functional layer might be too dense



The air electrode is too thin.

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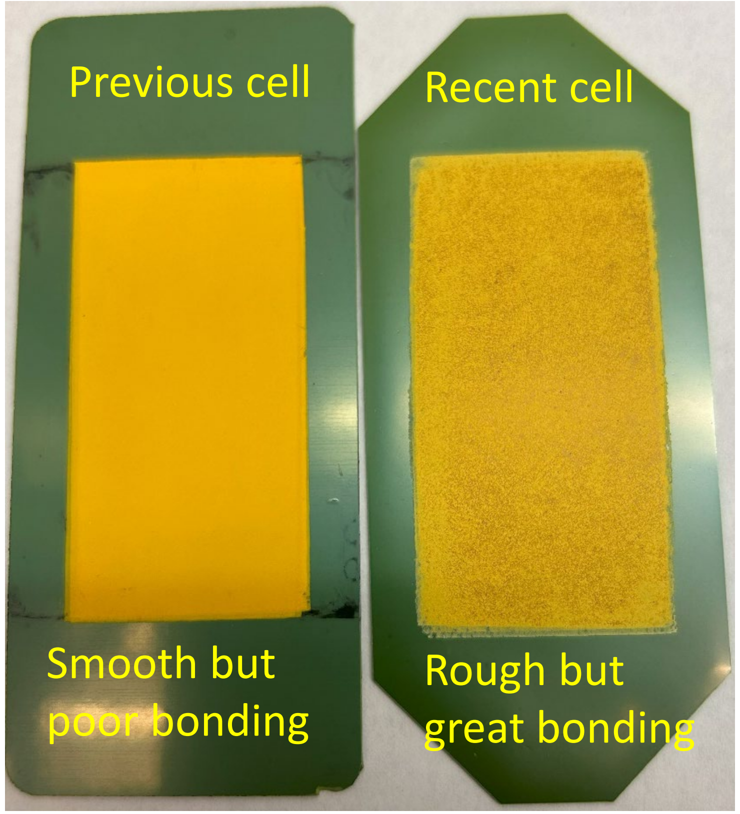
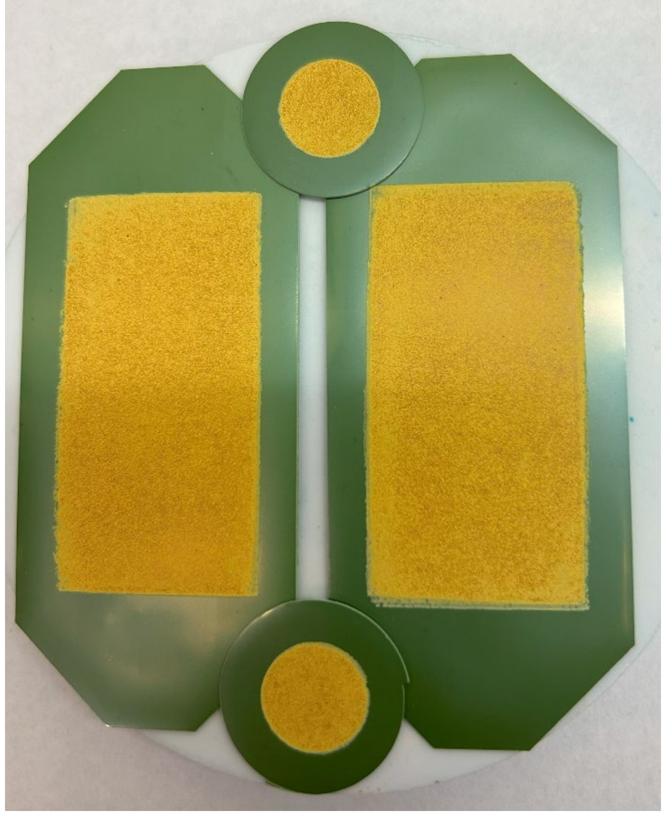
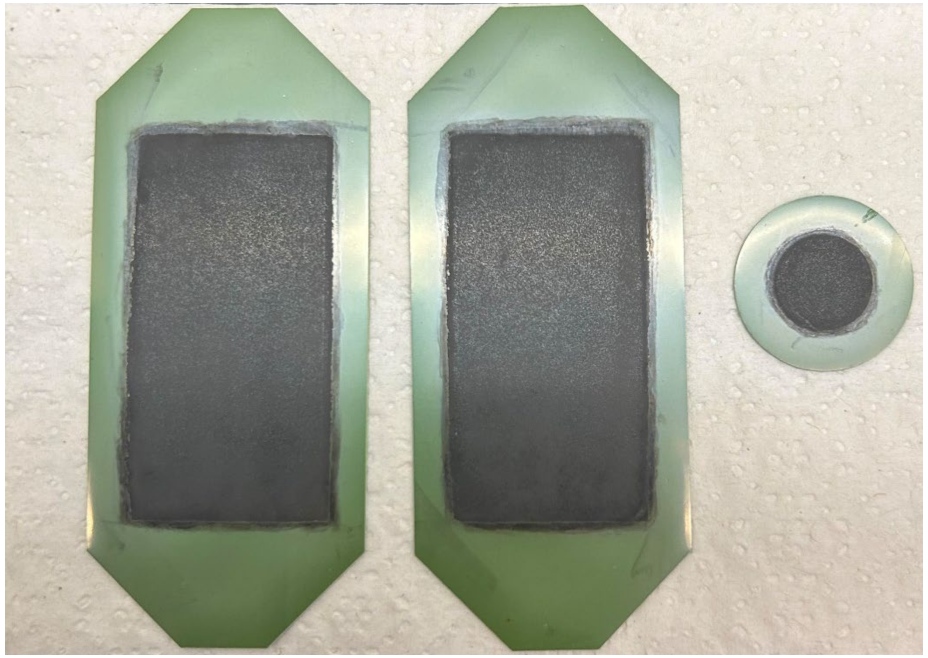
New 13 cm^2 Cell Making by PNNL





SCSZ Cells

~30 wt% LSM loading



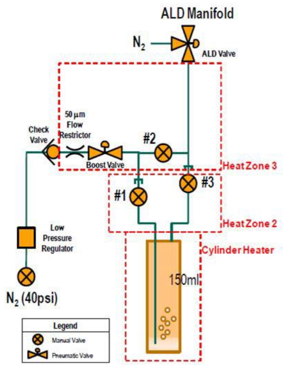
AE: BYC-LSM
EL: ScSZ
FE: ScSZ-NiO

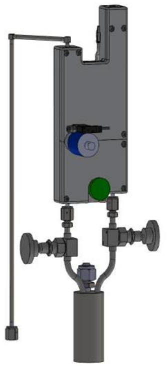
To be tested at PNNL in the next few weeks

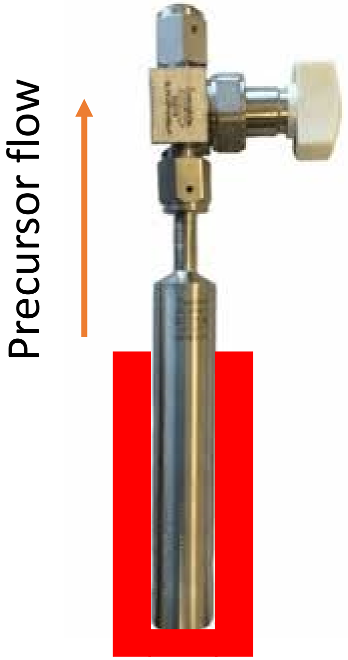
ALD-SCT Bilayer AE with Alternate Sr Precursor

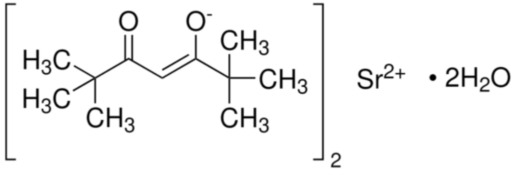
The previous Sr precursor:
Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)strontium hydrate [Sr(TMHD)$_2$]
The melting point is 200°C. The temperature limit for the heater is 190°C
Booster is needed, the supply is not stable

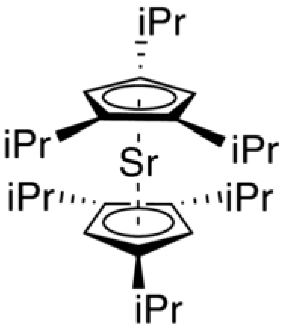
The new Sr precursor:
Bis(tri-isopropylcyclopentadienyl)strontium (Sr(iPr$_3$Cp)$_2$)
Gel-like at room temperature, the boiling point is 150°C
Reactive with H_2O.
High vapor pressure, only requires the regular cylinder.











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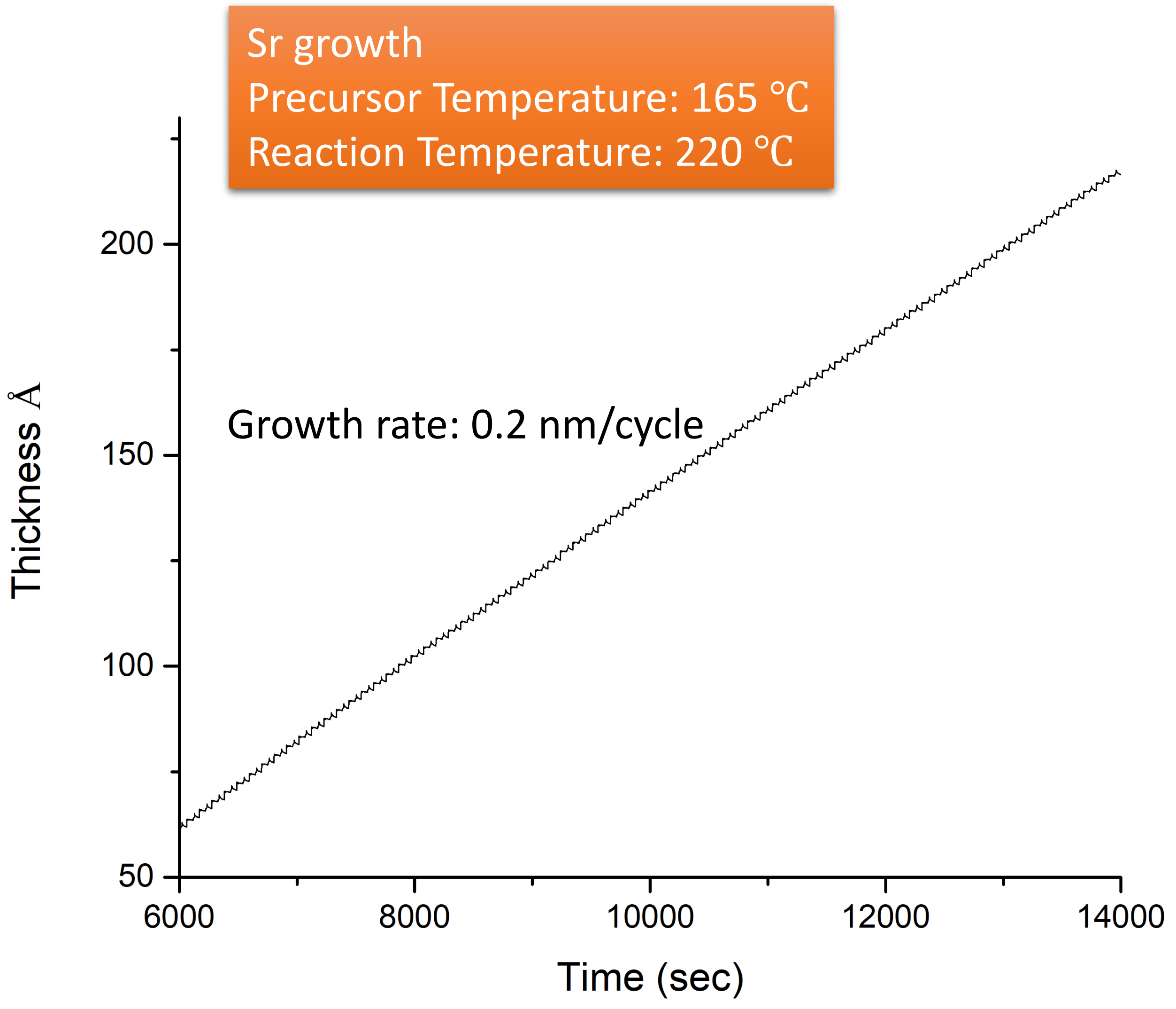
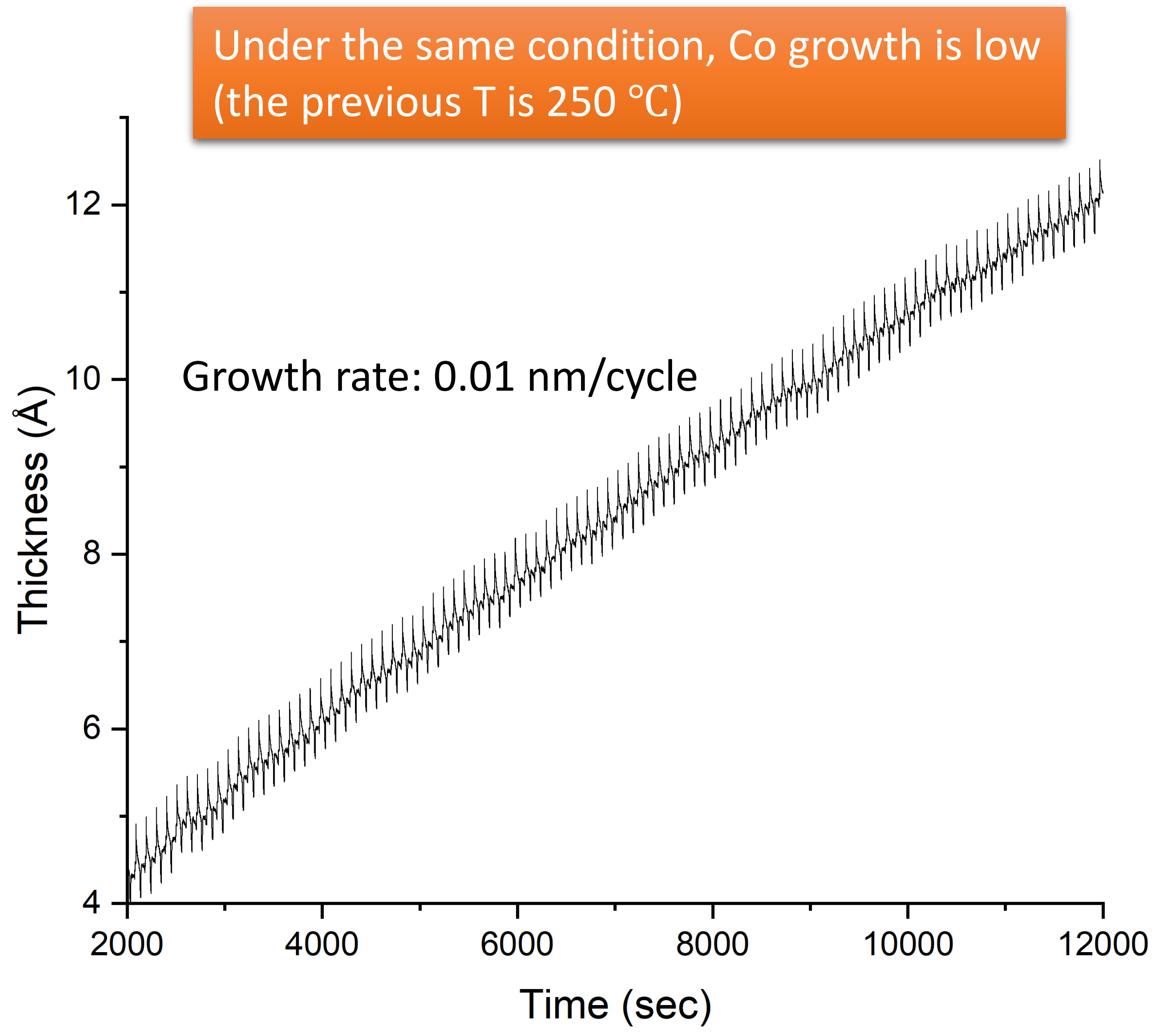
SrO Growth with $Sr(iPr_3Cp)_2$ and CoO_x Growth





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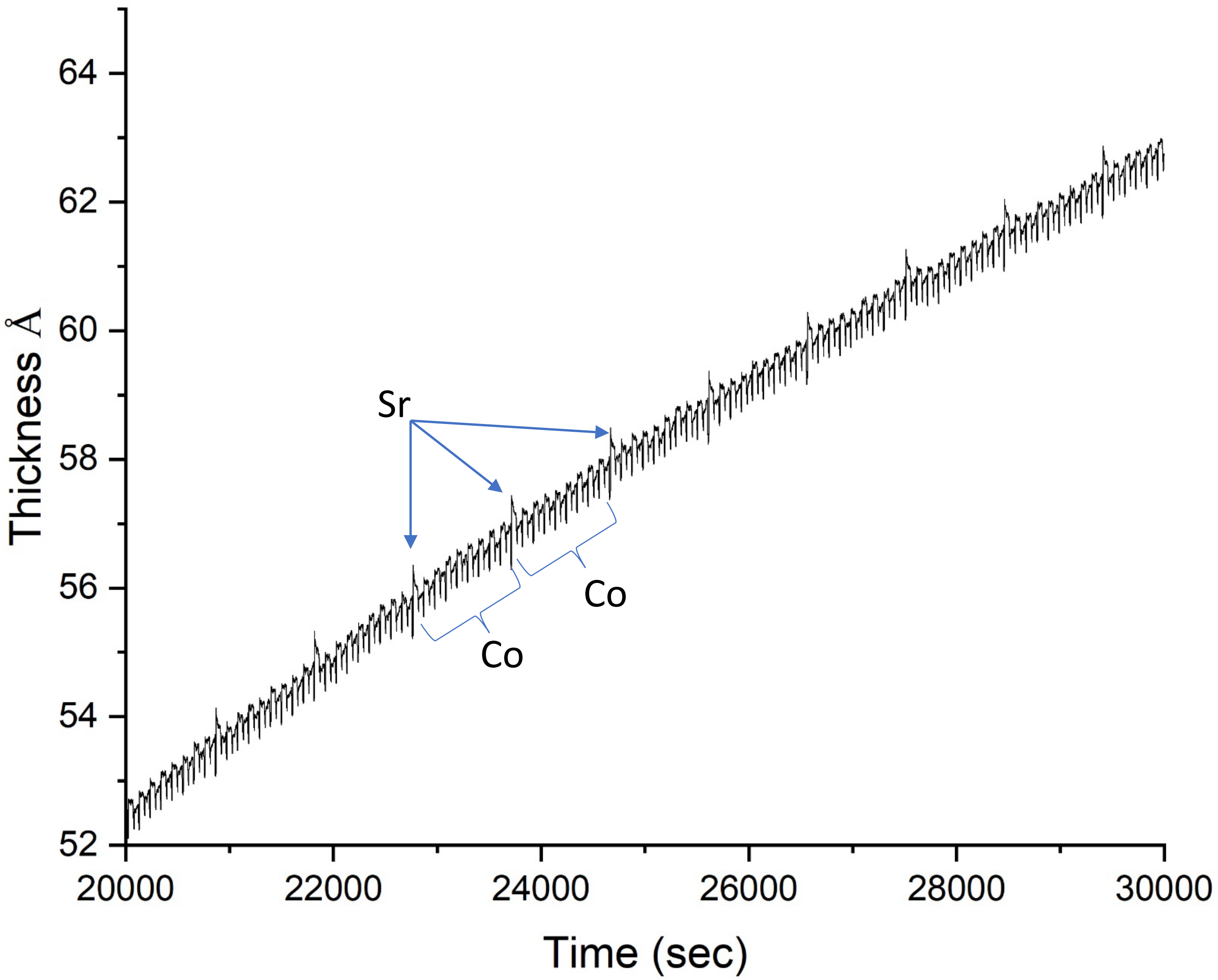
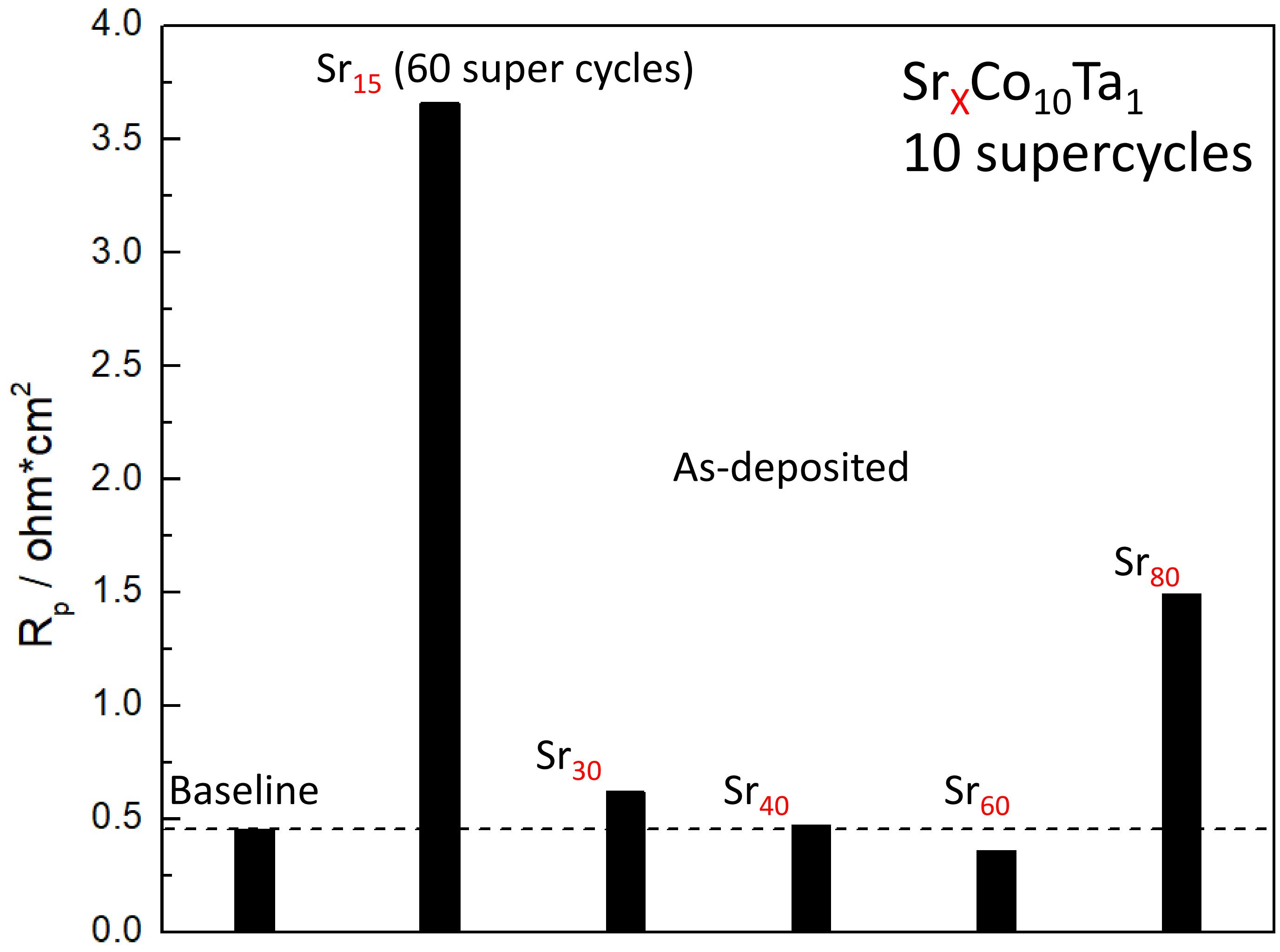
Co and Sr ALD Co-growth Supercycle

<u>Co-growth condition</u>
Growth temperature: 220 °C
Sr precursor temperature: 165 °C
Co precursor temperature 120 °C

Previously determined Sr growth rate: 0.2 nm/cycle
Previously determined Co growth rate: 0.01 nm/cycle
The cycle ratio of Sr and Co is 8:1



R_P of all ALD-SCT Samples



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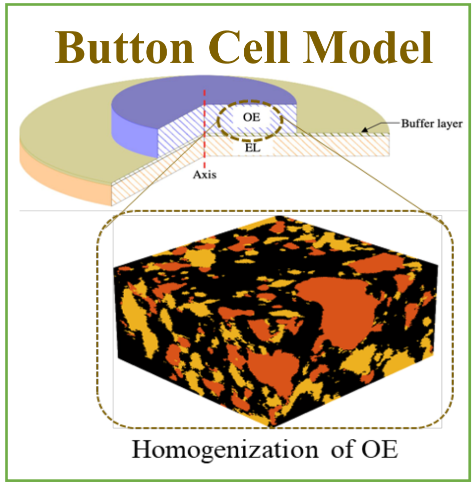
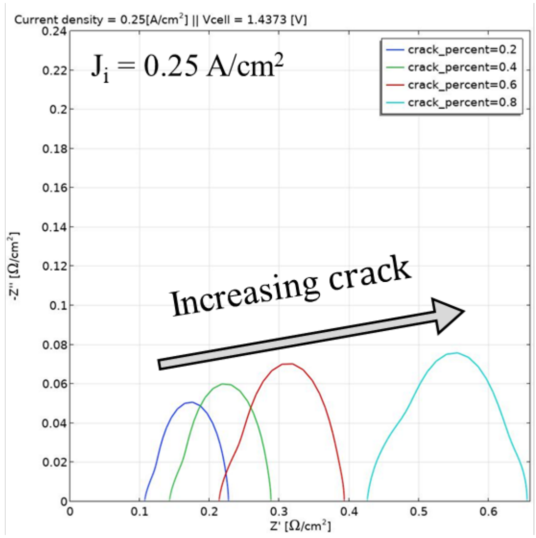
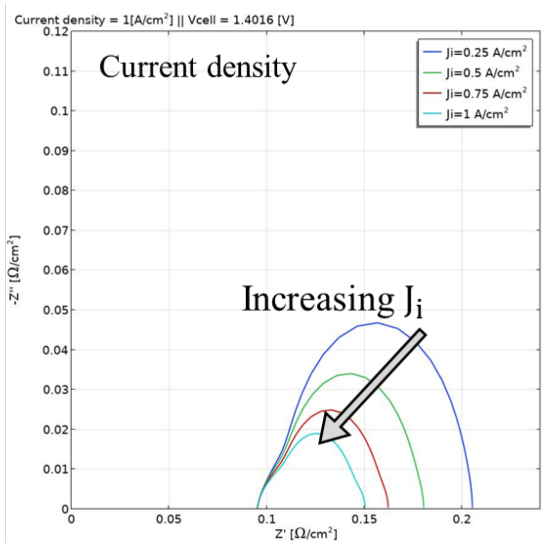
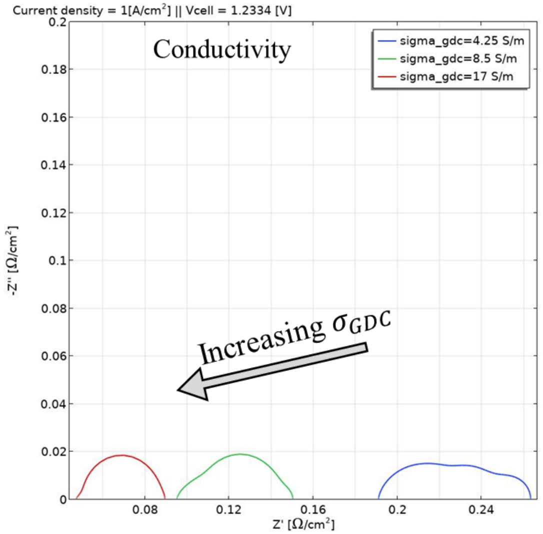
Modeling
Approaches

PHYSICS-BASED BUTTON CELL MODEL
EIS under OCV or DC bias

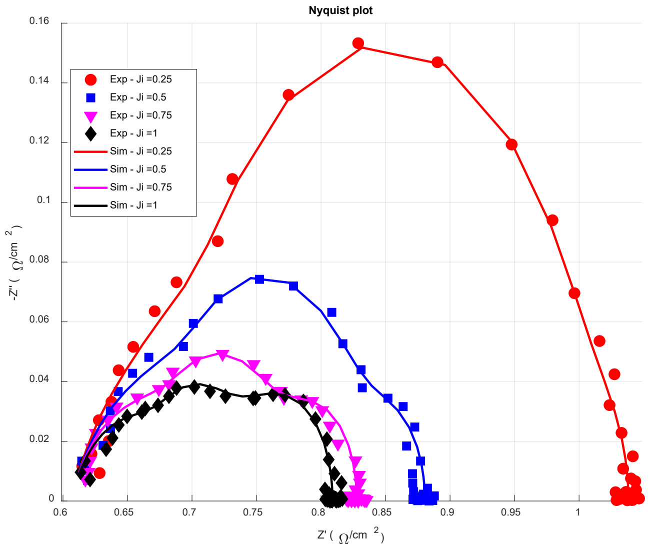








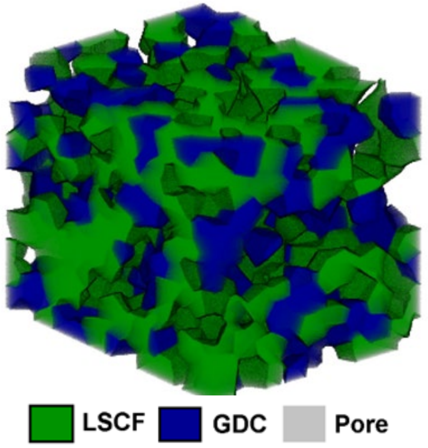
✓ **Synthetic EIS**



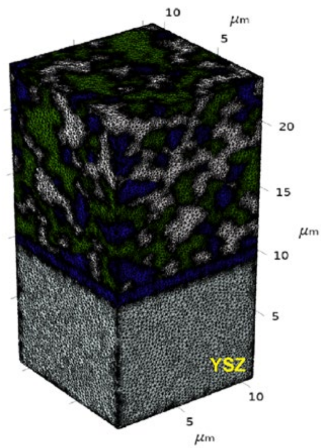
- Physics-based button cell model has been built to simulate EIS under OCV or DC bias, considering two transport pathways: 2PB vs 3PB.
- Parametric study, sensitivity and correlation analysis have been performed. The model could fit with synthetic EIS data well.

PHYSICS-BASED MICROSTRUCTURE MODEL

Modeling Approaches

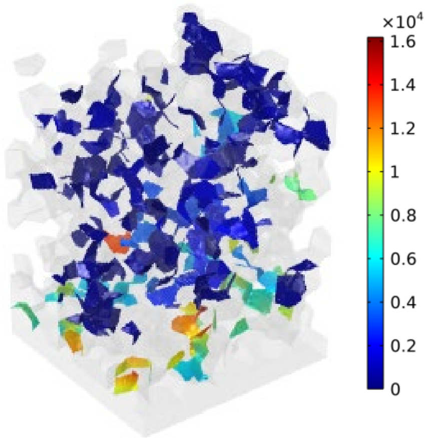


Synthetic structure from Dream.3D

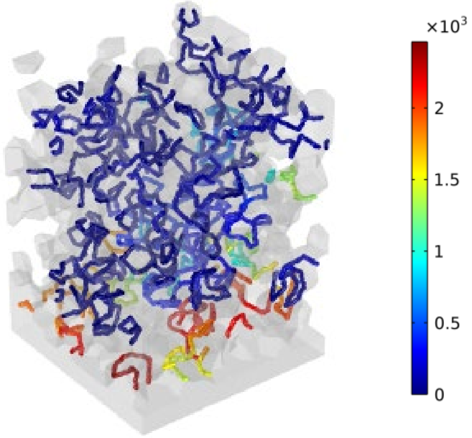


Mesh file from Iso2Mesh

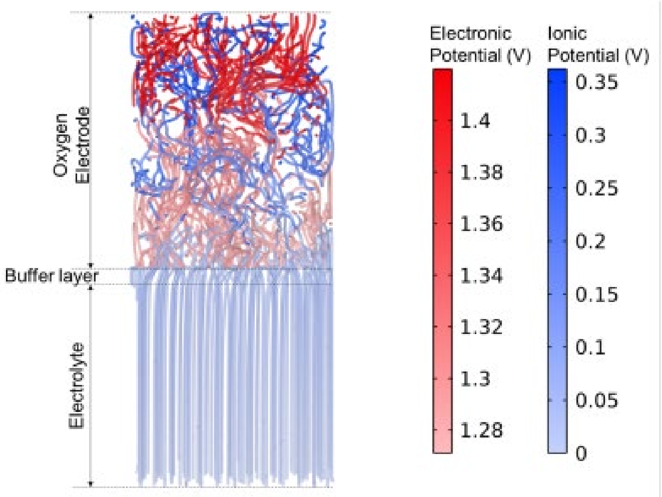
2PB



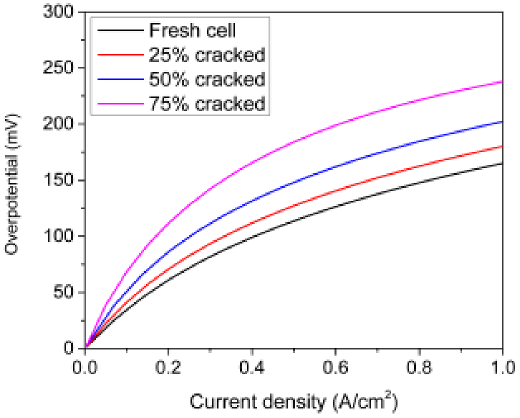
3PB



Electronic vs Ionic Current

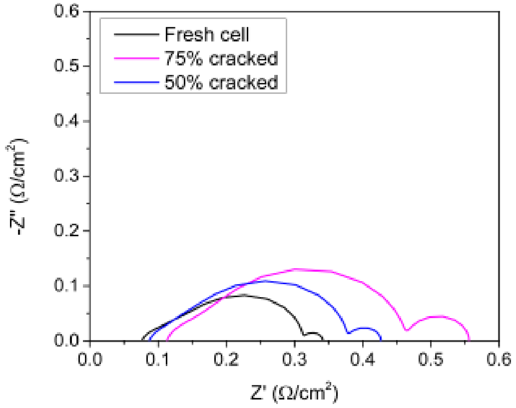


Overpotential

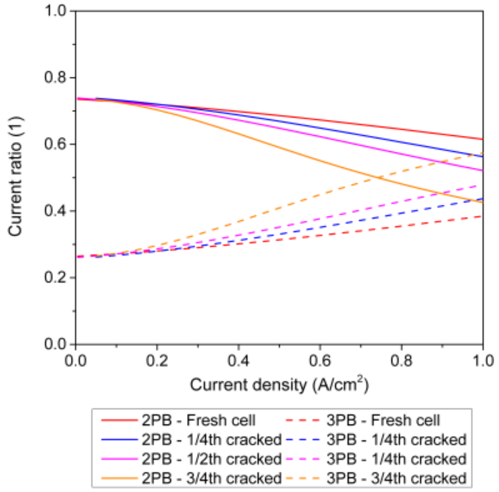


(a) I_0^{2PB}

EIS



Current Ratio 2PB/3PB



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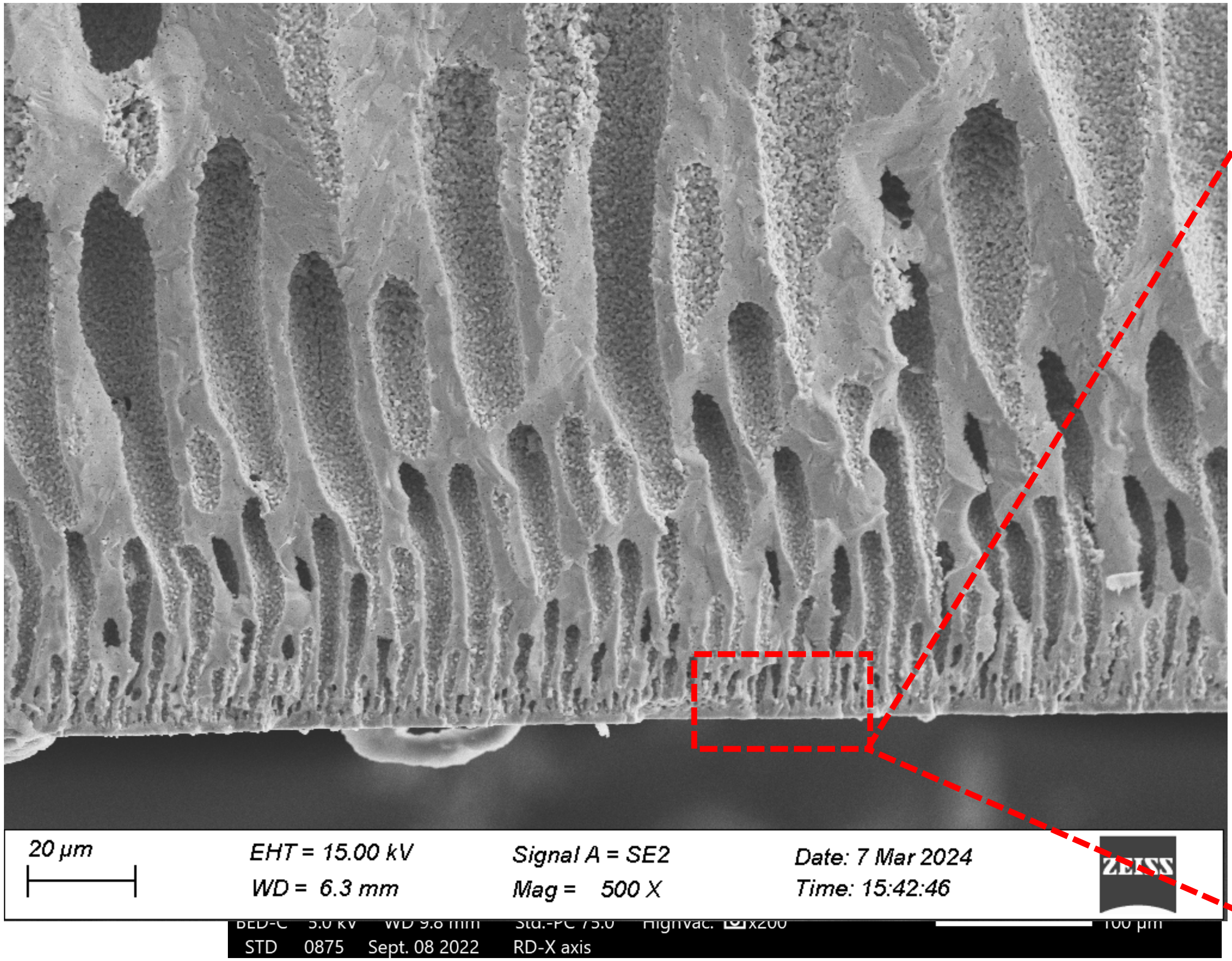
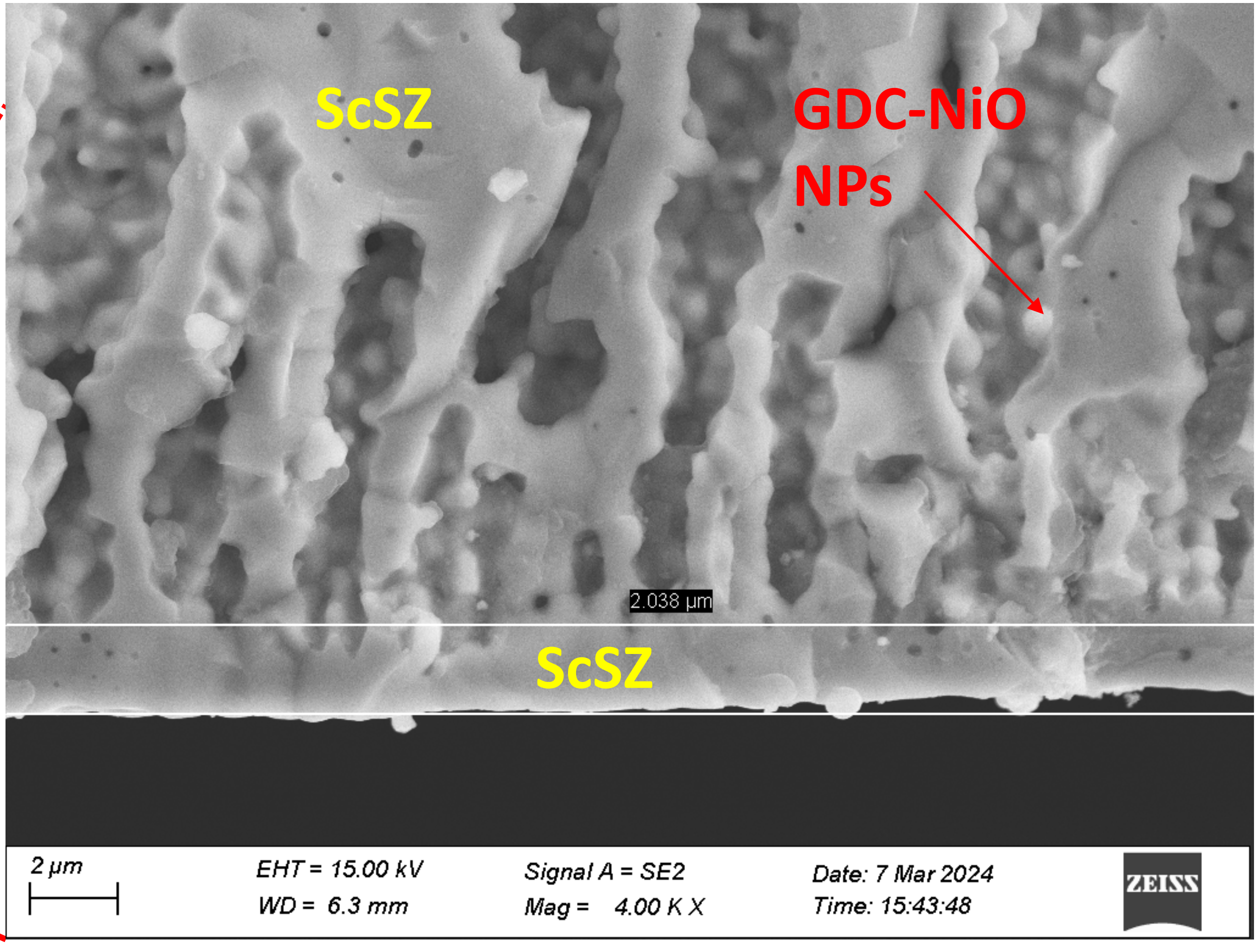
Ongoing Work - A New Cell Design





Phase inversion derived ScSZ+NiO substrate

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Summary

- Optimized process parameter for BYC-LSM AE. Achieved $R_p < 0.1\ \Omega \cdot cm^2$ at 650^oC
- Achieved excellent 650^oC full button cell performance at PNNL and INL
- Obtained initial performance of large cell performance at 650^oC
- Developed one ALD recipe for SCT supercycle
- Developed a Multiphysics model for AE delamination behavior

Ongoing

- Making the new 2 μm electrolyte cell
- Finalizing ALD-bilayer air electrode development
- Testing ScSZ-based BLF-AE 13 cm^2 cell testing at PNNL

Milestone Status

	Milestones	Task	Planned	Actual	Verification method
1	Update Project Management Plan	1.1	10/10/21	complete	PMP submitted to DOE
2	Submit initial Technology Maturation Plan	1.2	12/09/21	complete	TMP submitted to DOE
3	Demonstration of barrier-layer-free OE performance: Overpotential: $\leq$0.15V@$\pm$1A/cm^2@650^{o}C	2.2	03/31/23	complete	STEC and Report to DOE
4	Demonstration of ALD bilayer OE performance: Overpotential: $\leq$0.15V@$\pm$1A/cm^2@700^{o}C	3.2	06/30/2024	80%	STEC and Report to DOE
5	Demonstration of optimized PI process conditions to produce quality porosity-graded open-channel HEs	4.1	06/30/2023	complete	Report to DOE
6	Demonstration of button cell (1.5 cm^2) performance specified in the Success criteria	5.1	12/31/2022	100%	Cell testing and Report to DOE
7	Demonstration of large-area cell (13 cm^2) performance specified in the Success criteria	5.4	09/09/2024	50%	Cell testing and Report to DOE
8	A multiphysics model detailing OE failure mechanisms and modes	6.0	09/09/2023	100%	Report to DOE

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