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

(DE-FE-0032111)

Prof. Kevin Huang

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University of South Carolina

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*Present to the 23rd SOFC Review Meeting, Pittsburgh, October 25-27, 2022*

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# About Project

## Project Goal

- To advance reduced temperature ($\leq 700^oC$) $ZrO_2$-based SOCs technology for high-efficiency and low-cost power and $H_2$ production.
- Tasks:
  1. Developing barrier layer free oxygen electrode (BLF-OE) for SOCs operation at $\leq 650^oC$
  2. Developing ALD-SCT ($SrCo_{0.9}Ta_{0.1}O_{3-\delta}$)@LSCf-GDC bilayer OEs for SOCs operation at $\leq 700^oC$
  3. Developing porosity-graded hydrogen electrode (HE) substrate
  4. Validating the developed new materials/ microstructure in small and large cells
  5. Developing coupled electro-chemo-mechano model

## About Team

- University of South Carolina (Lead): Tasks 1, 2, 3, 5
  - Prof. Kevin Huang
  - Prof. Frank Chen
- Pacific Northwest National Laboratory (Subcontractor): Task 4
  - Dr. Olga Marina

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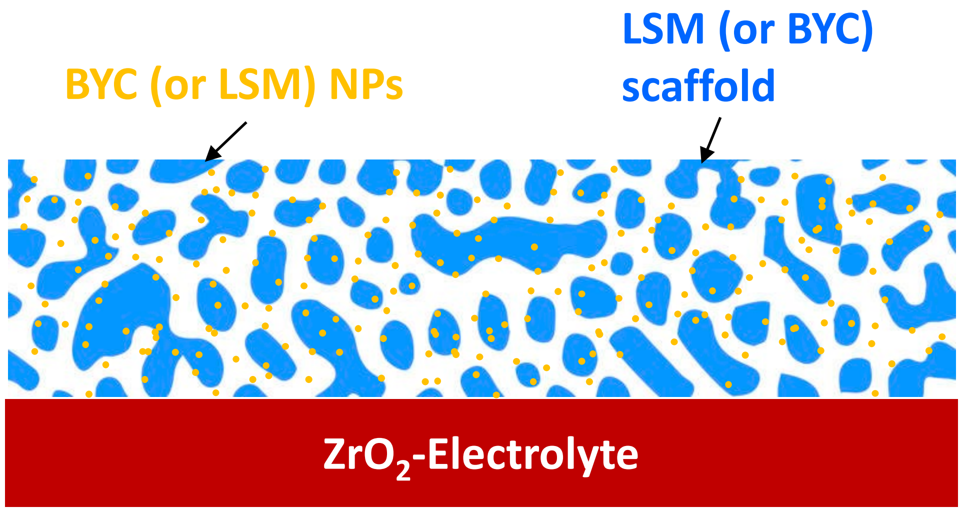
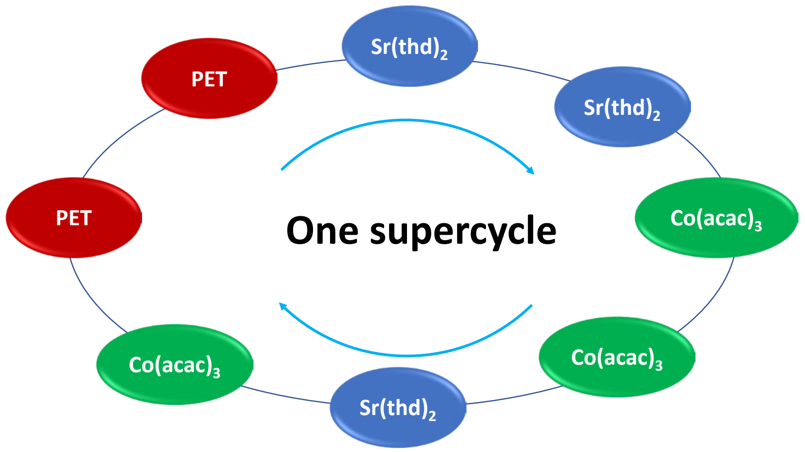
# Tasks

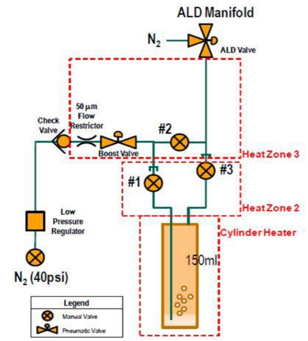
### Task-1: Developing High-Performance BLF-OE

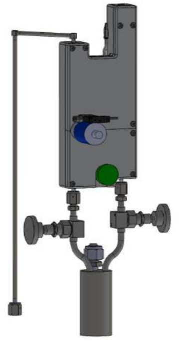



### Task 2: ALD Supercycle to Fabricate SCT overcoat on LSCF-GDC



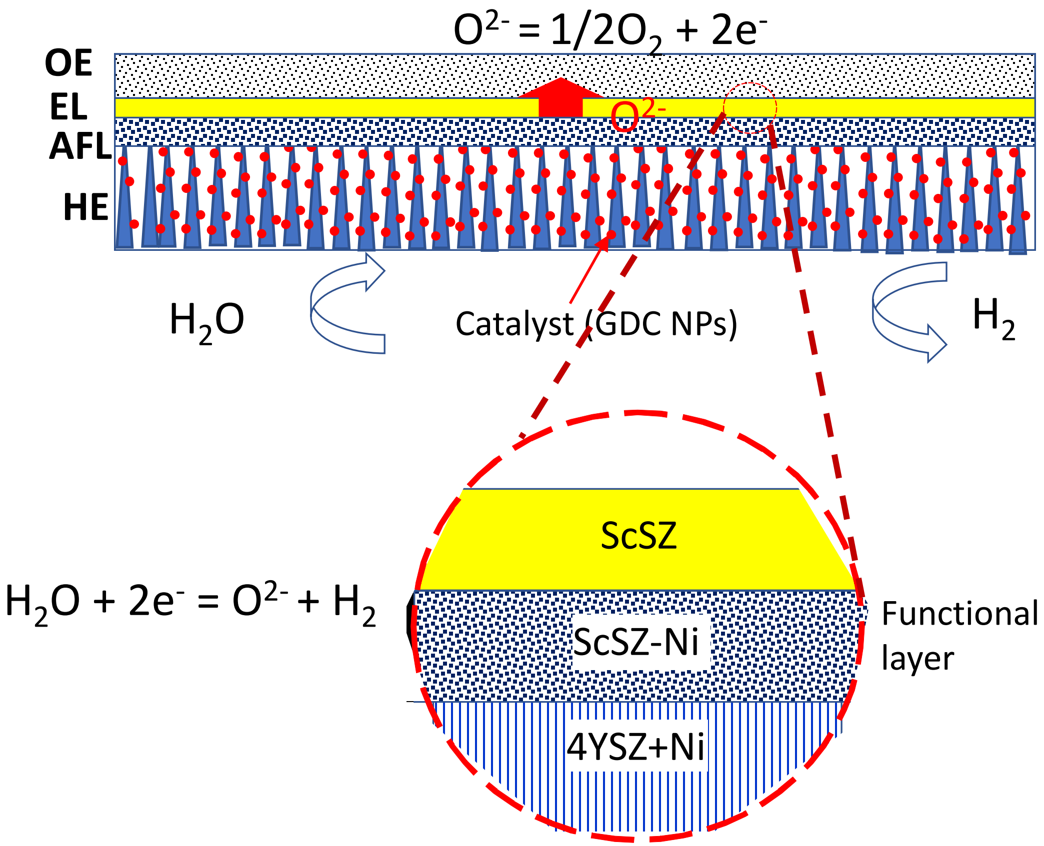




# Tasks

## Task-3: Fabricating Open Structured HE Substrate by Phase Inversion Method




## Task-4: Independent Cells Testing at PNNL

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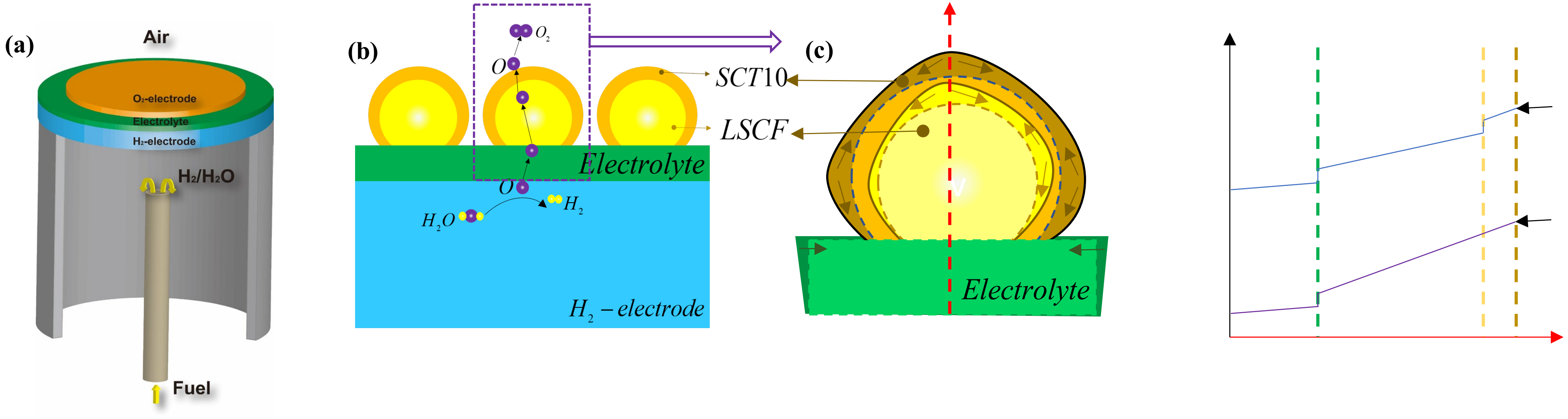
# Task-5: Developing Electro-Chemo-Mechano-Model at OE/Electrolyte Interface




- Electrical current vs. lattice O-stoichiometry of OE
- Lattice O-stoichiometry vs. chemical stress
- Chemical stress vs. mechanical stress

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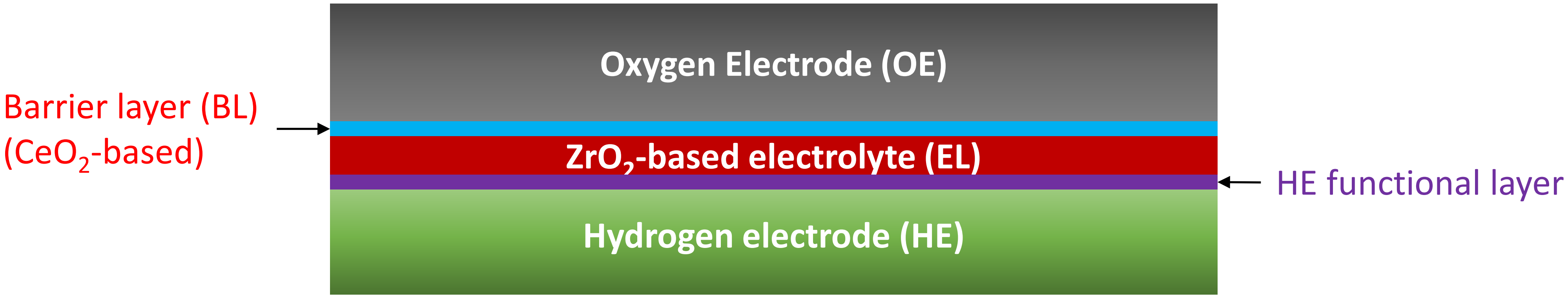
# Functional Layers in $ZrO_2$-based SOCs




Functionality of BL: to prevent interaction between OE and $ZrO_2$-ELs
It accounts for ~10-20% performance loss

# Potential Impacts of Removing Barrier Layer from SOCs

Simplifying SOCs processing by reducing one firing step

Avoiding chemical reactions between $CeO_2$ and $ZrO_2$

Lowering ohmic resistance

Improving cell performance

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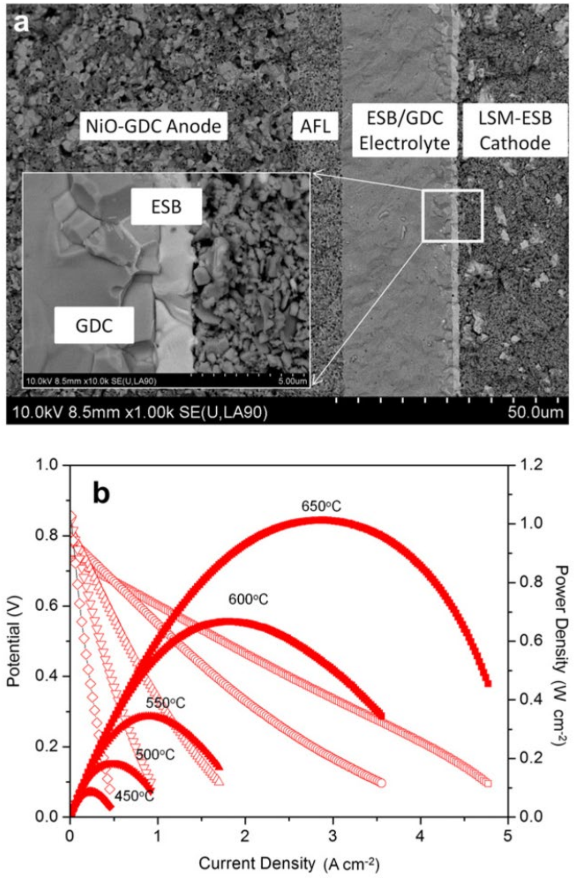
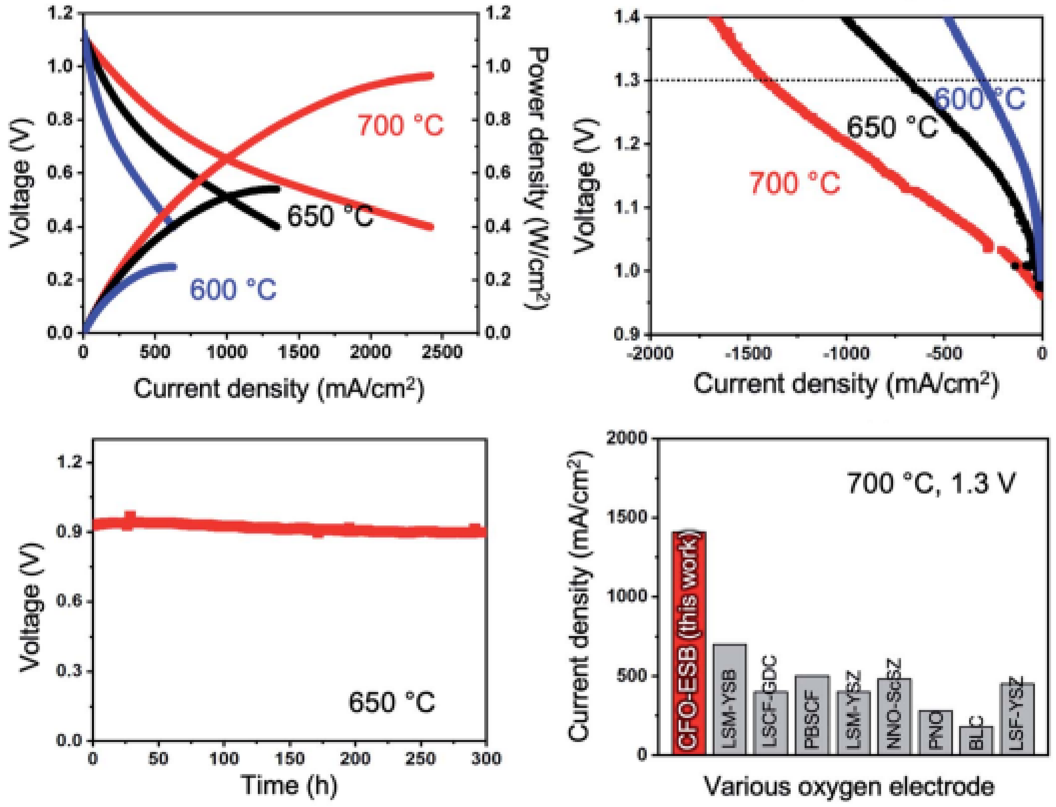
# First and Latest Reported BLF-OEs

**NiO-GDC/AFL/ESB-GDC/LSM-ESB/LSM+ESB**




K.T. Lee, E. Wachsman, et al. Journal of Power Sources 220 (2012) 324-330

**$CoFe_2O_4$-$Er_{0.4}Bi_{1.6}O_3$/YSZ/YSZ-Ni**




Kim, et al., J. Mater. Chem. A, 2022, 10, 2045

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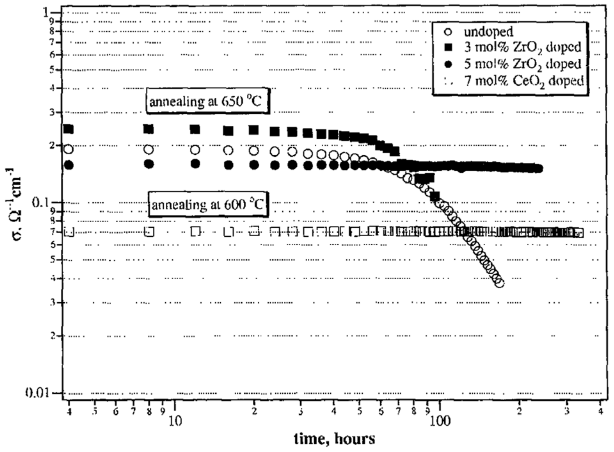
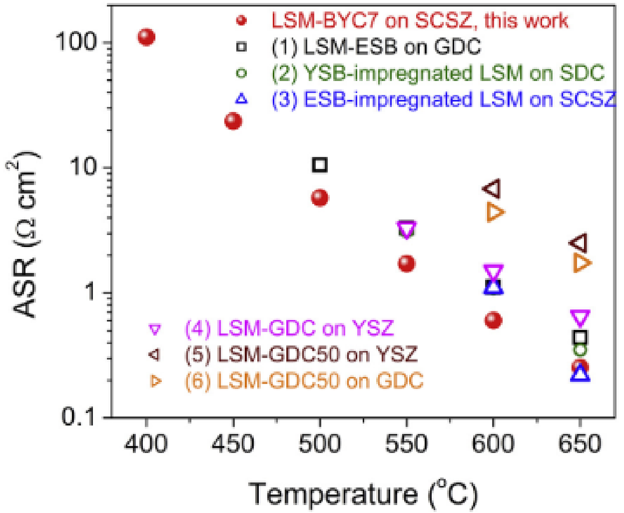
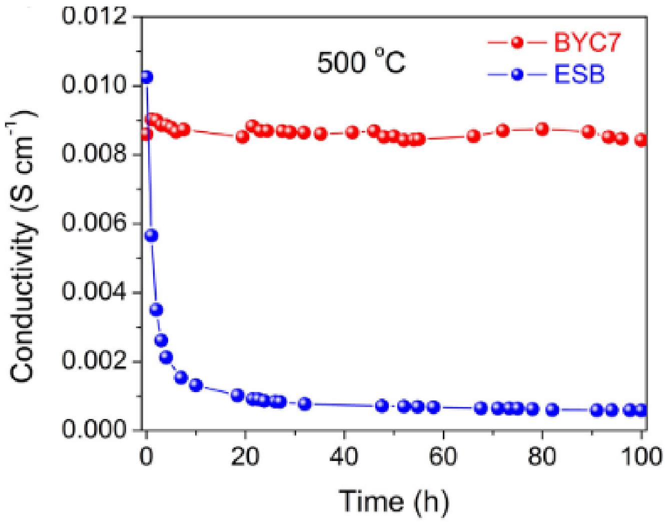
# Our Early Work on BLF-OEs: LSM-BYC

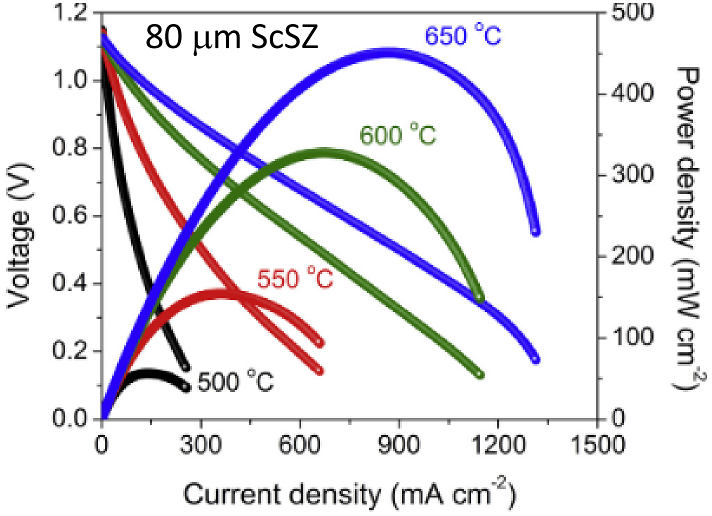
BYC7: $(Bi_{0.75}Y_{0.25})_{0.93}Ce_{0.07}O_{2-\delta}$
LSM: $La_{0.8}Sr_{0.2}MnO_3$




K. Huang and J.B. Goodenough, *Solid State Ionics*, **89** (1996) 17-24.




C. Zhang, K. Huang, *J. Power Sources*, **342** (2017) 419-426

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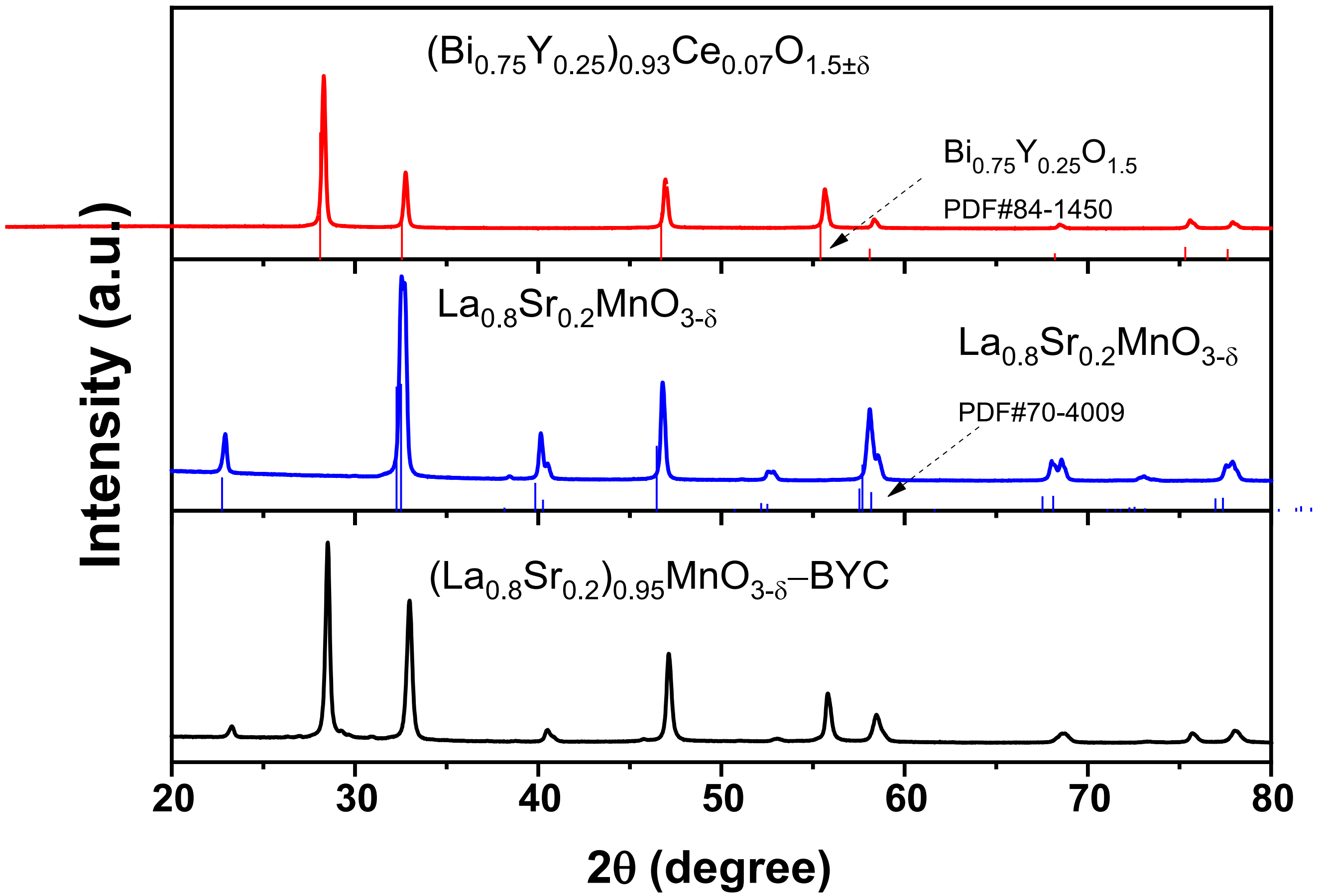
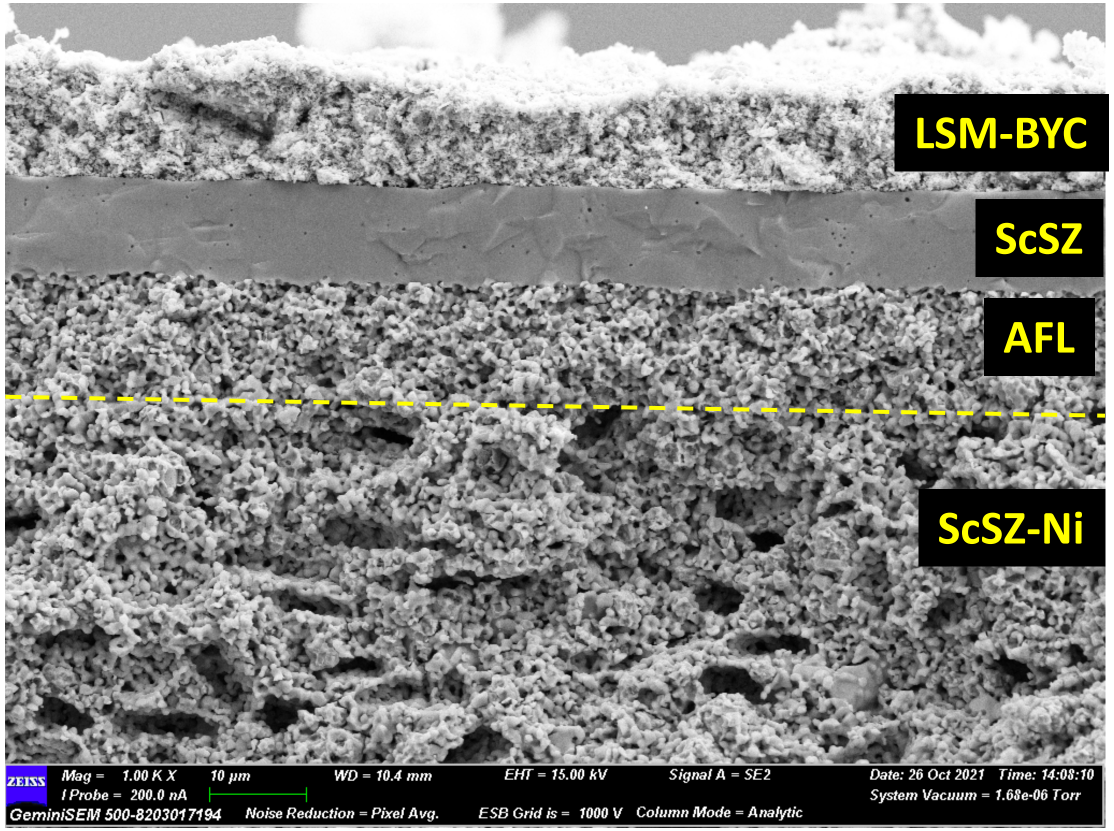
# LSM-BYC Phase and Cell Microstructure

“One-Pot” wet-chemical method




Y. Zhang and K. Huang, *J. Electrochem. Soc.*, 2022, **169**, 034516.

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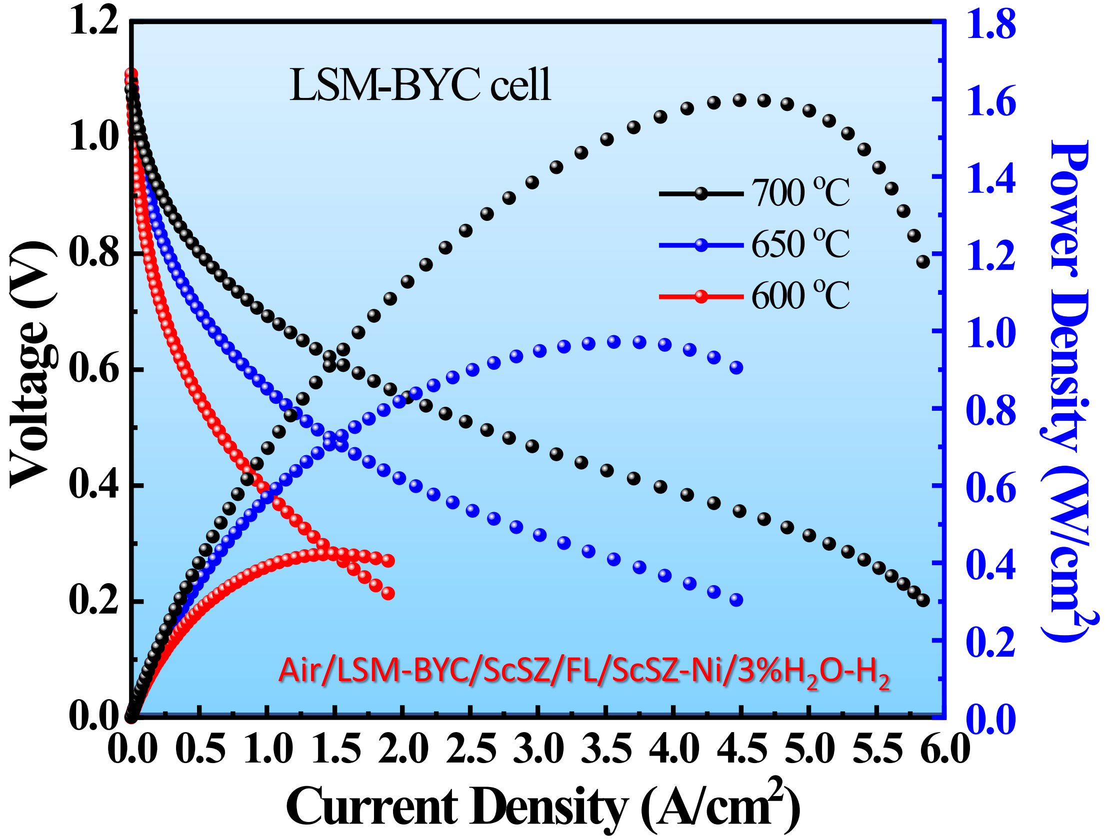
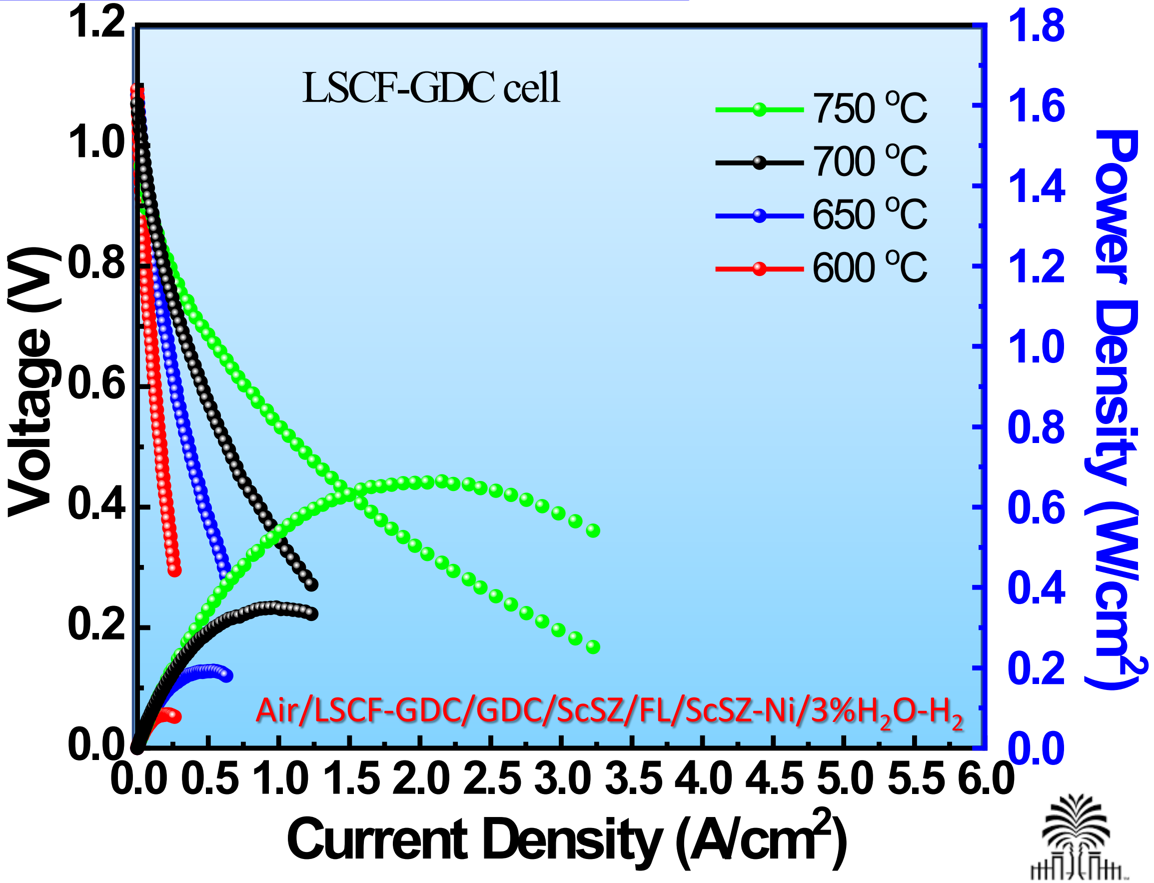
# Typical SOFC Performance of LSM-BYC Cell

HE substrate: 300 µm ScSZ-Ni; HE functional layer: 10 µm ScSZ-Ni; 10 µm SSZ electrolyte; 25 µm screen-printed LSM-BYC OE

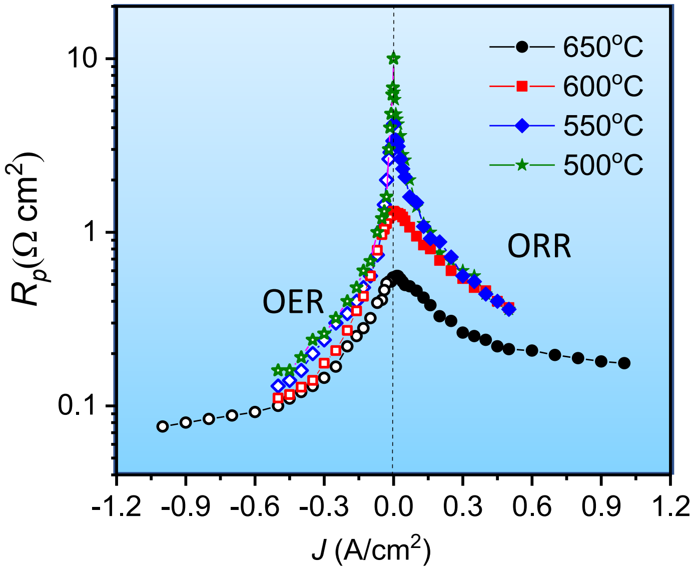


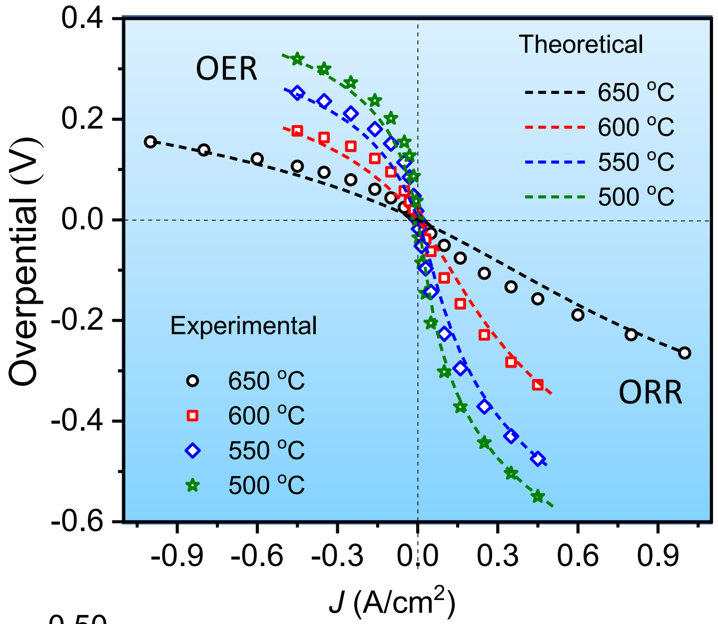



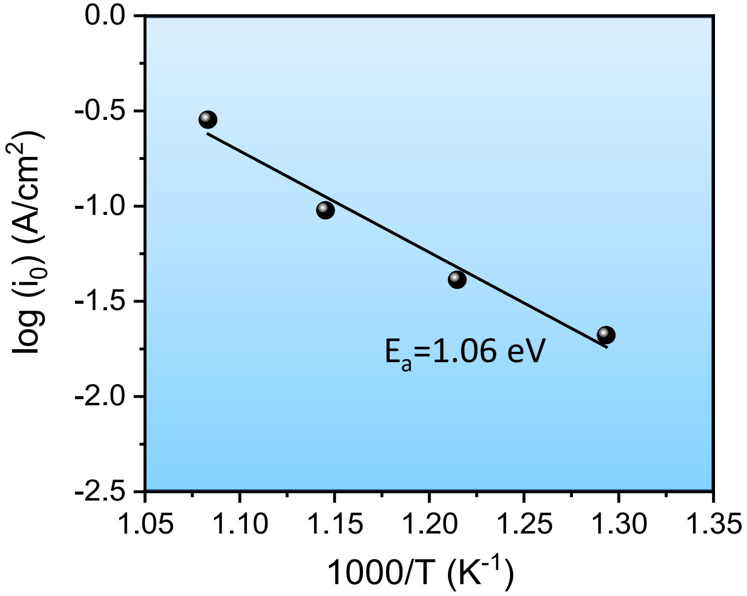

Zhang and Huang, *J. Electrochem. Soc.*, 2022, **169**, 034516.

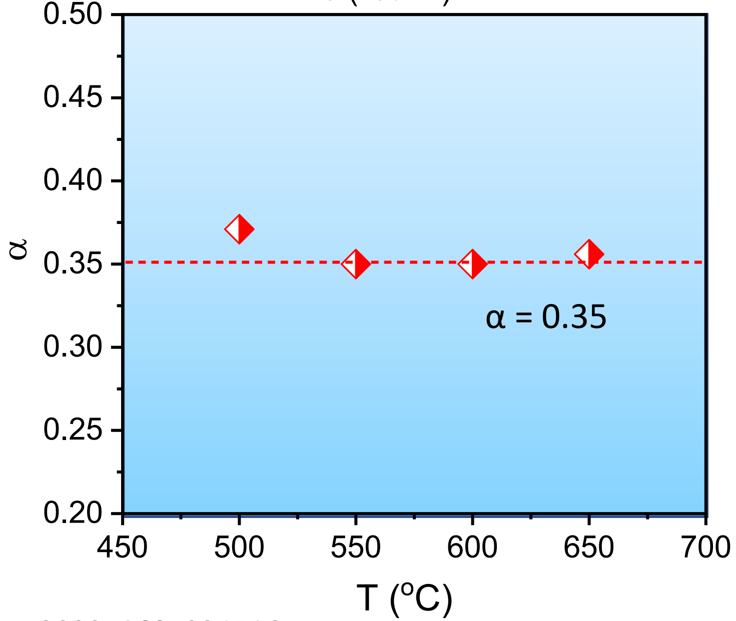
# $R_p$ and η of SP-BLF-OE

Measured by STEC method



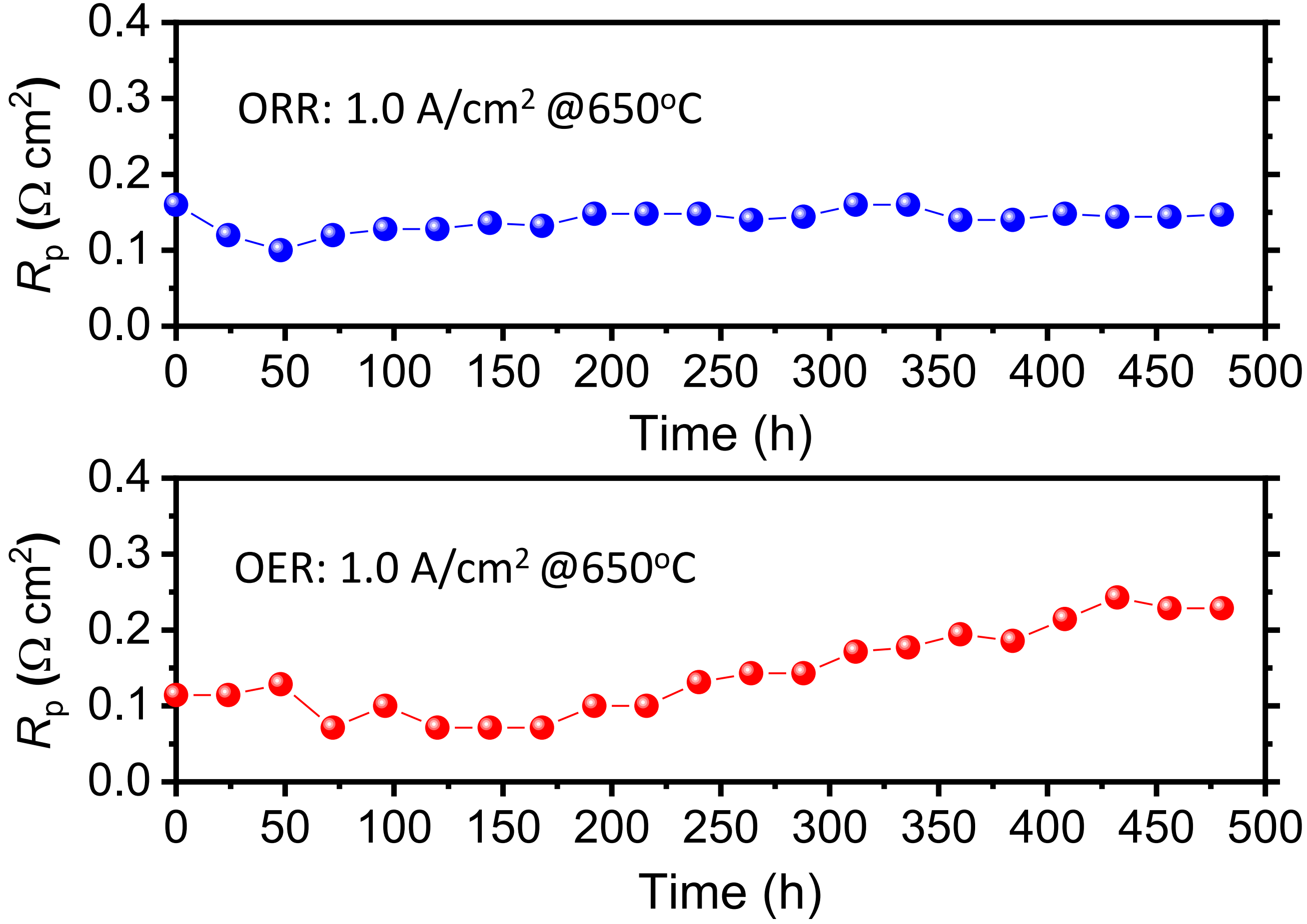



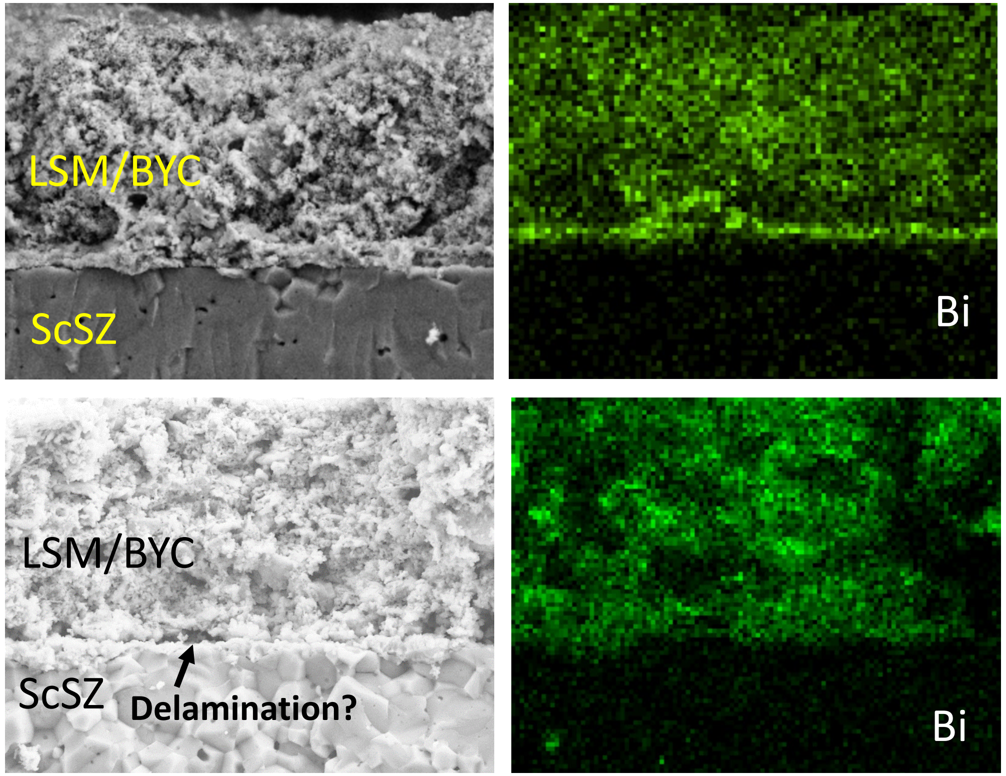




Zhang and Huang, *J. Electrochem. Soc.*, 2022, **169**, 034516.

# $R_p$ Stability under ORR and OER Modes of BLF-OE

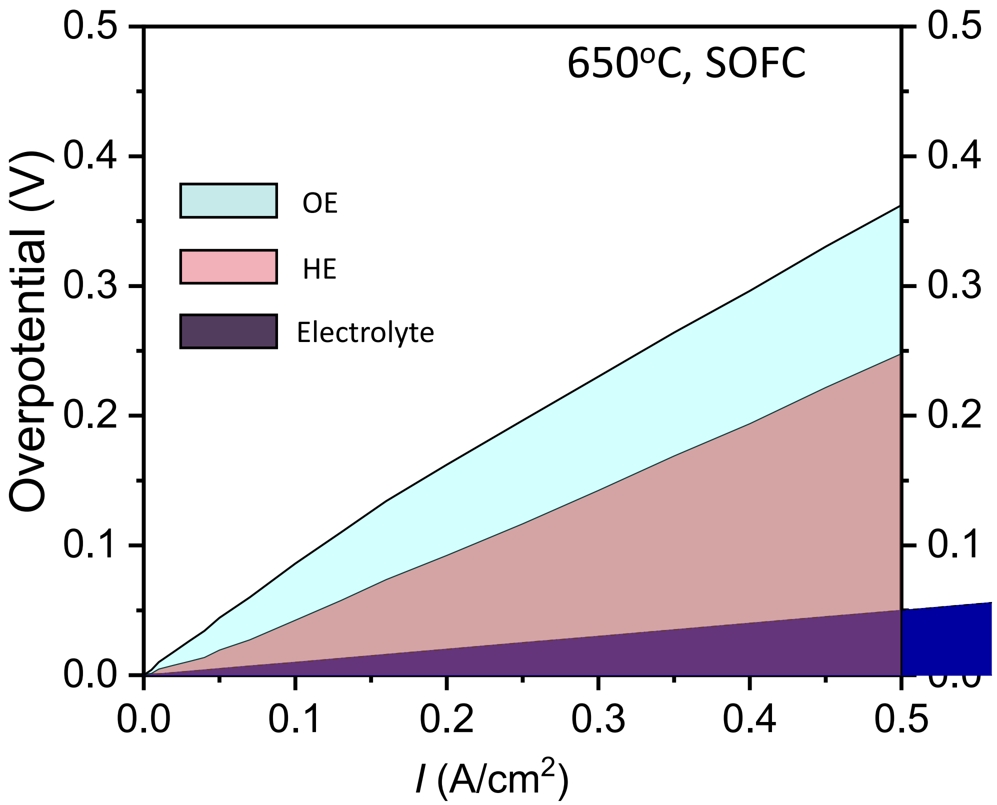
SP-LSM-BYC/ScSZ/LSM-BYC after constant j=±1A/cm² treatment

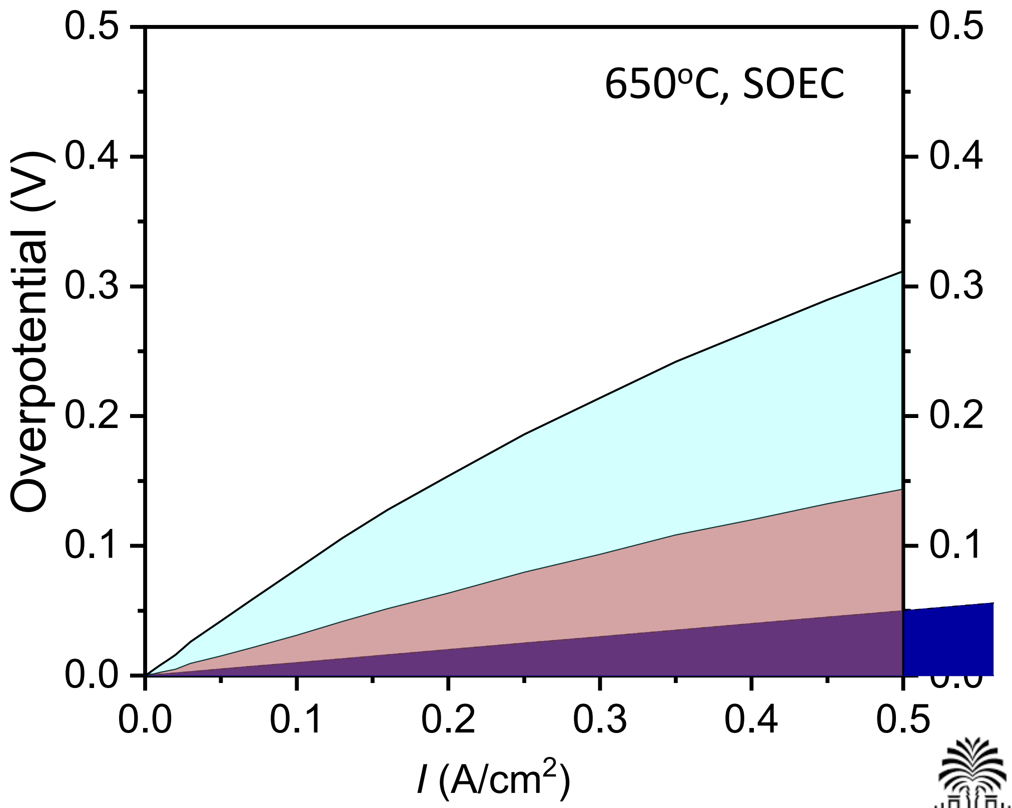


# Overpotential Distributions in a Single SOC

**Air/LSM-BYC/ScSZ/FL/HE/30%$H_2O$-$H_2$**

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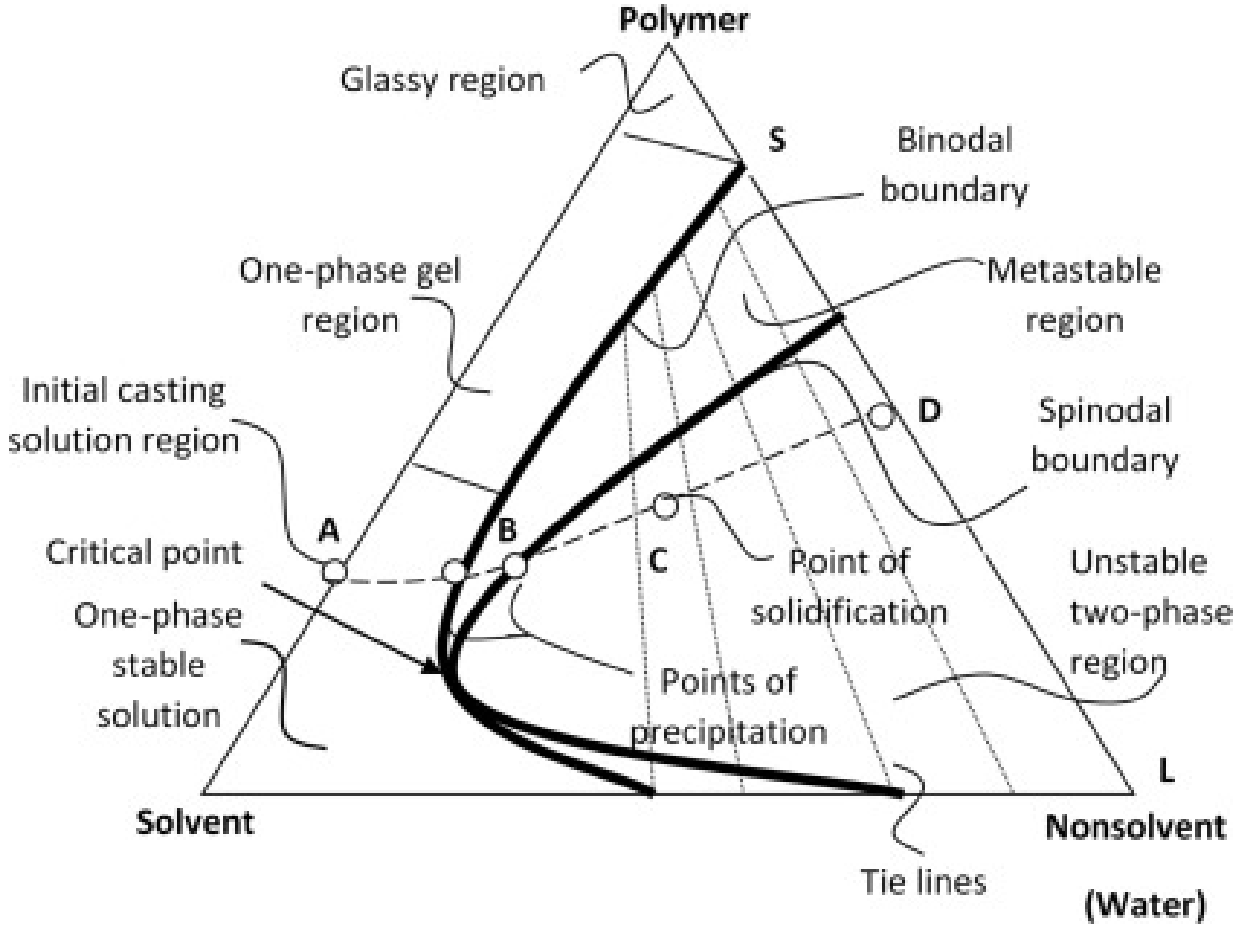
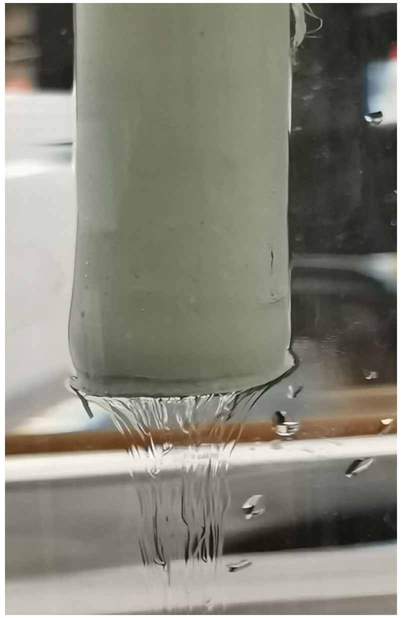
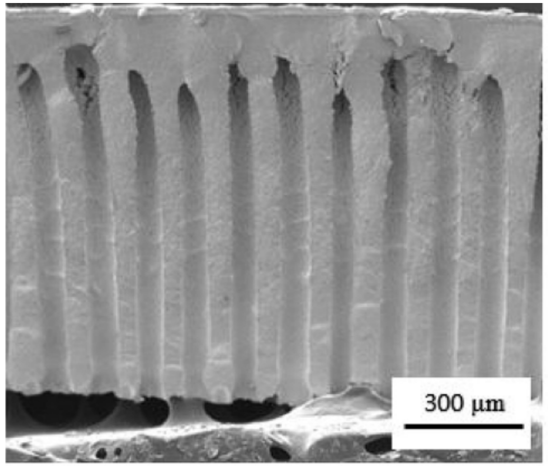
# Phase Inversion Process: Working Principle






Jaydevsinh M. Gohil, Rikarani R. Choudhury, in [Nanoscale Materials in Water Purification](), 2019

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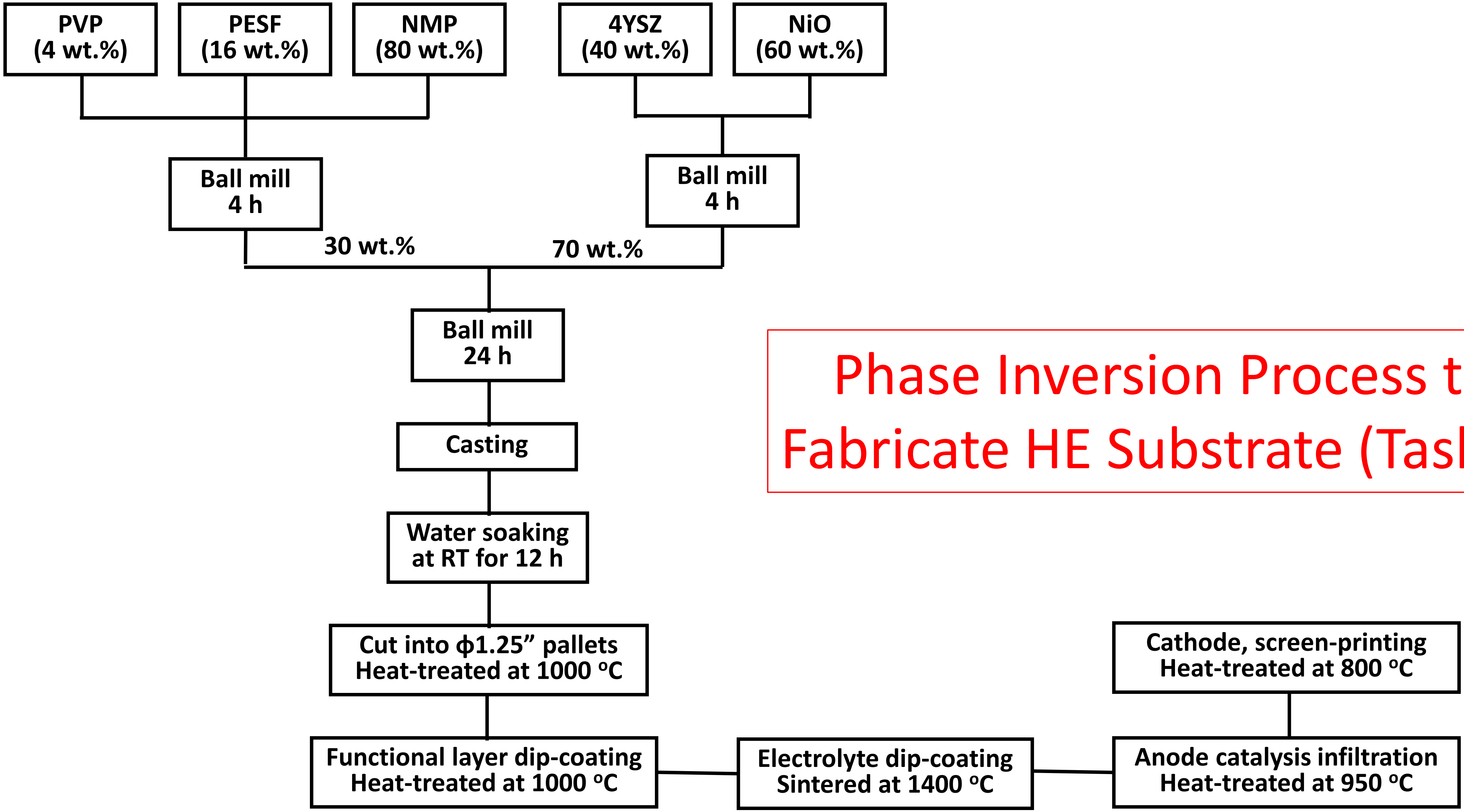
# Phase Inversion Process to Fabricate HE Substrate (Task 3)

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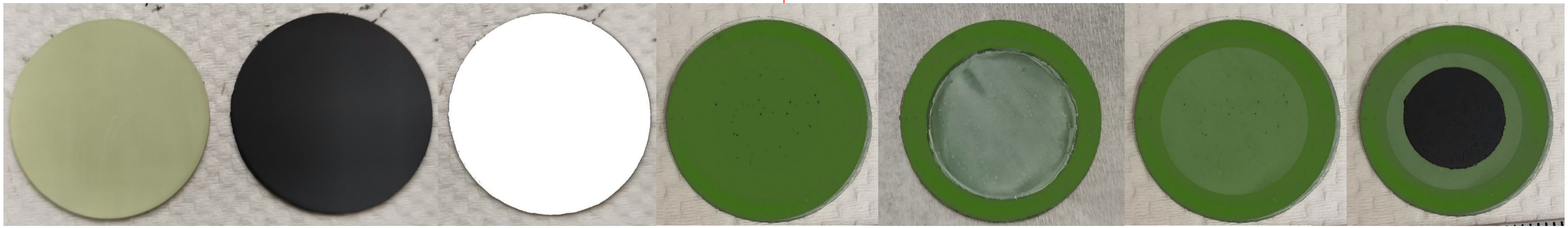
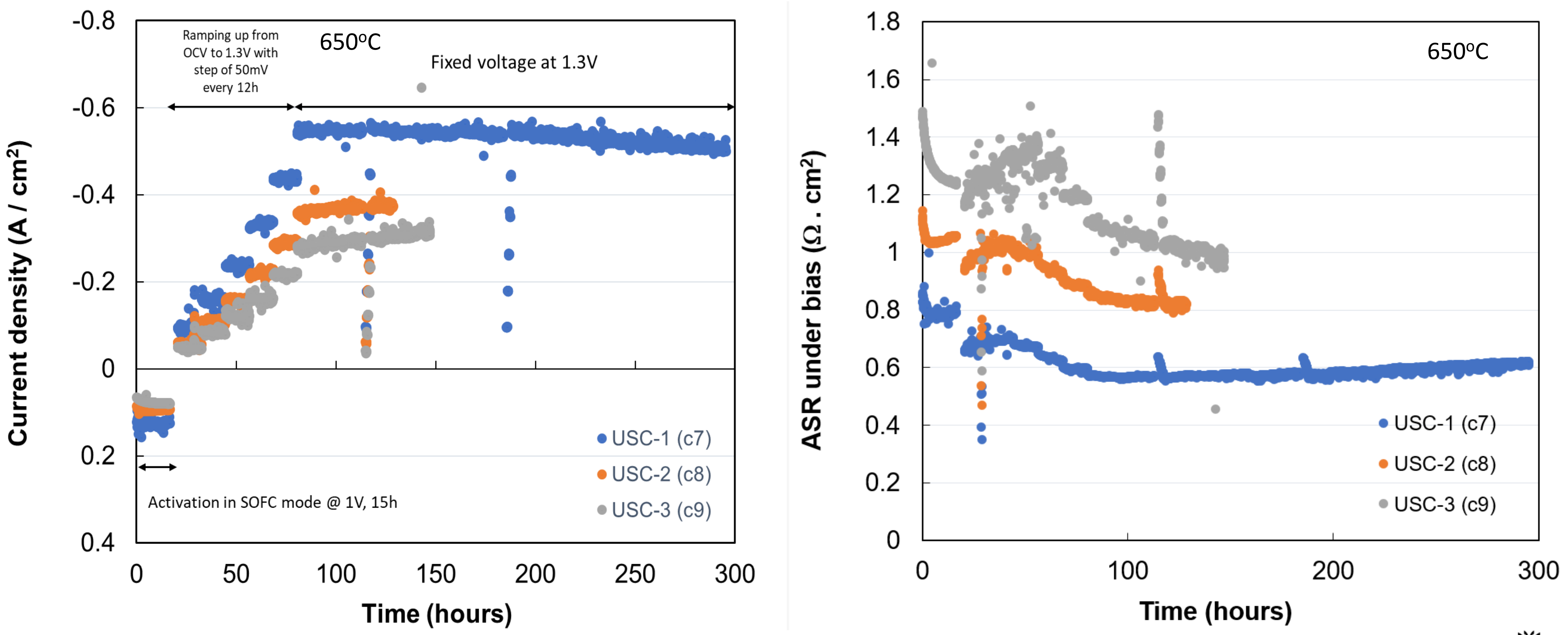
# $\phi$1.25” Phase Inversion Cell at Different Stages

For BLF cells

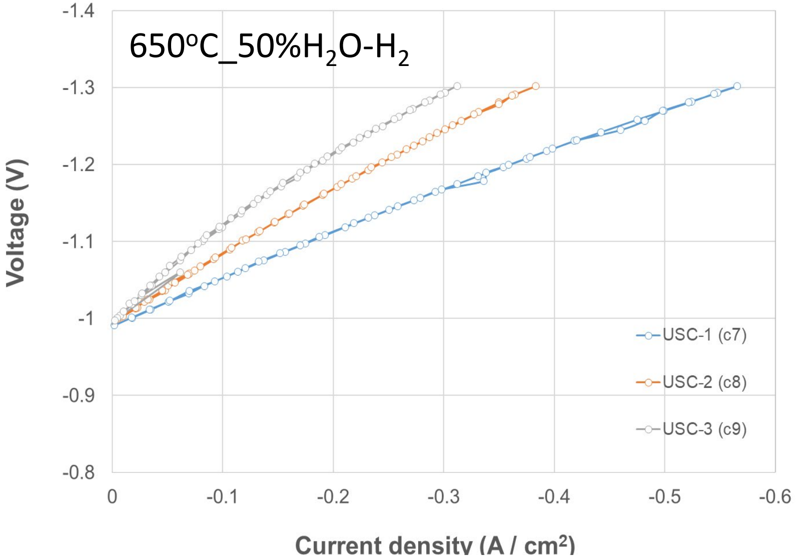


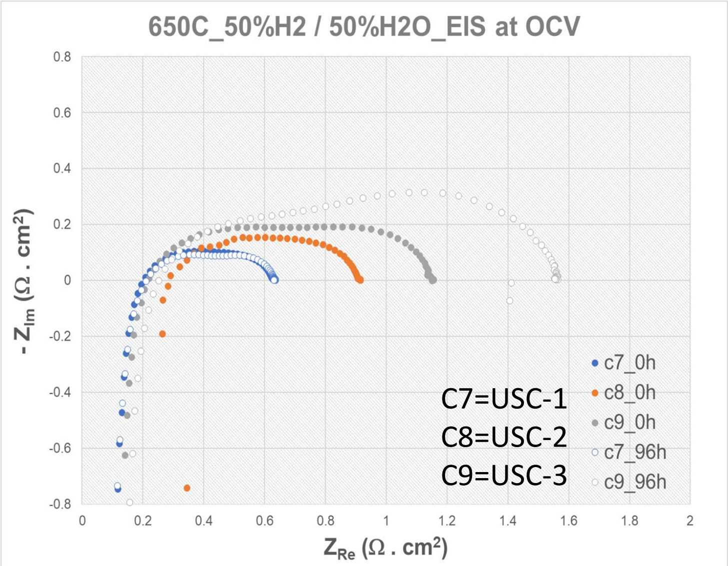
After PI | After AFL | After EL | After EL sintering | After GDC BL deposition | After GDC BL sintering | After OE

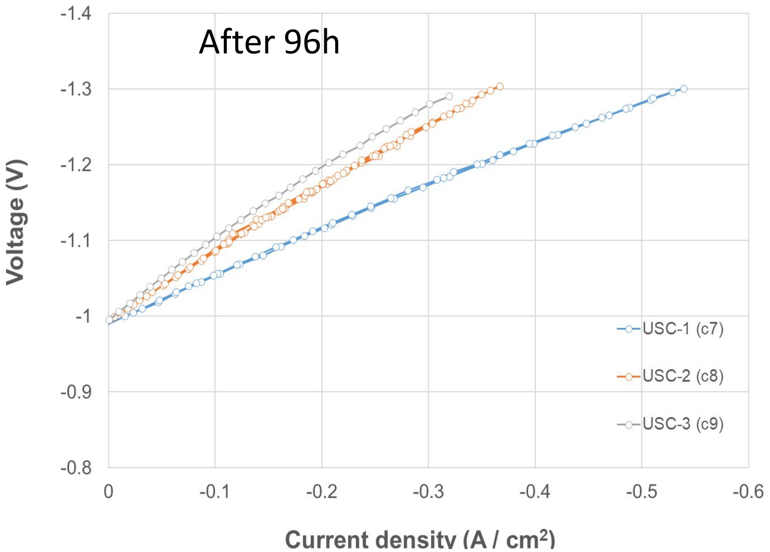
# SOEC Performance Testing at PNNL

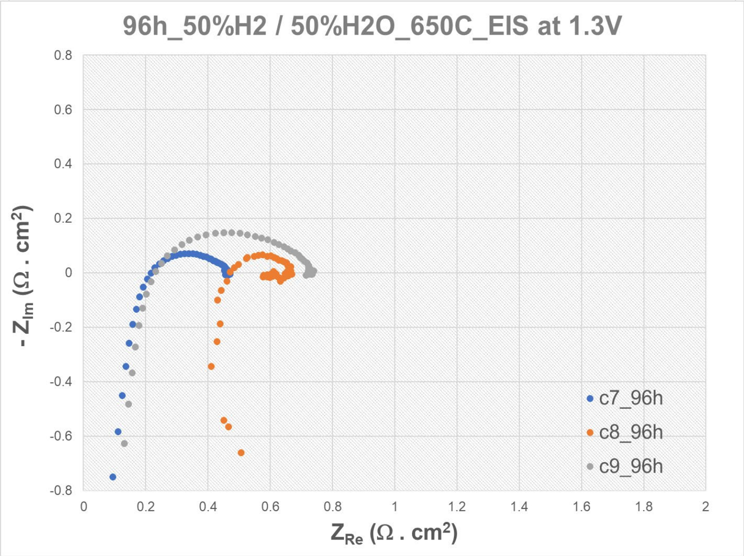


# SOEC Performance Testing at PNNL

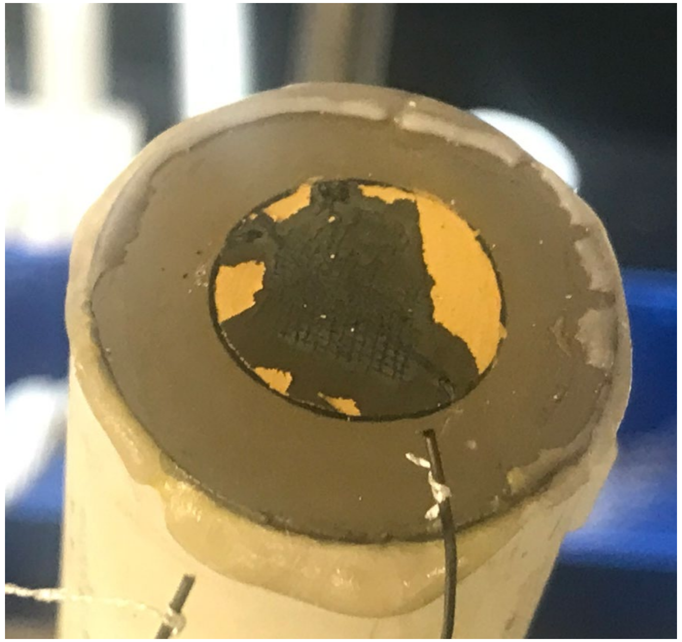


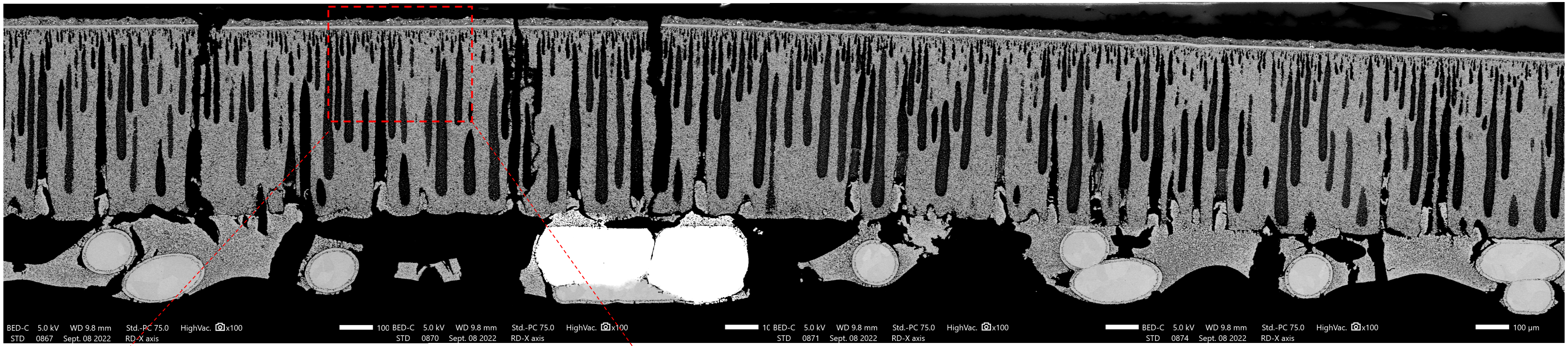



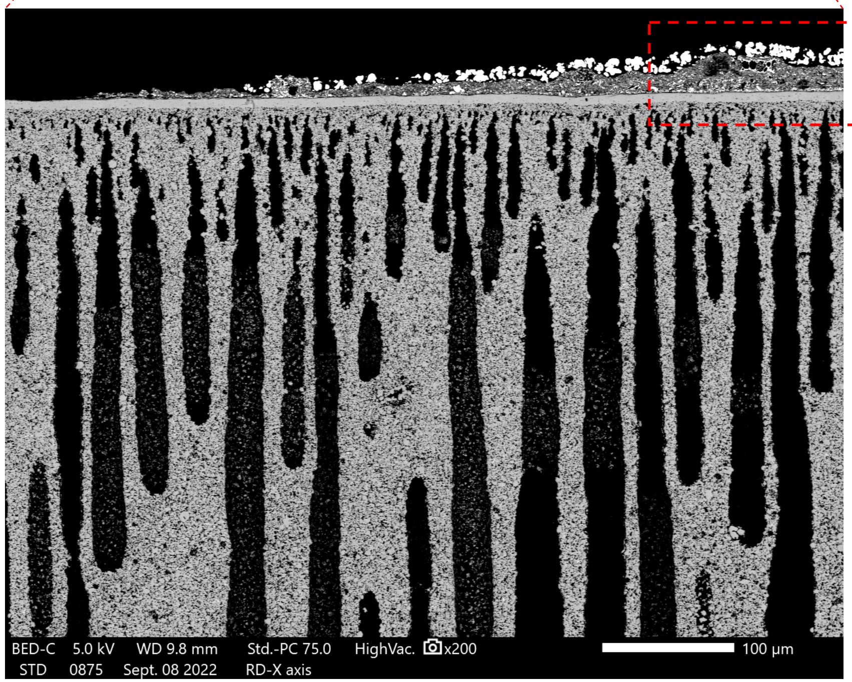



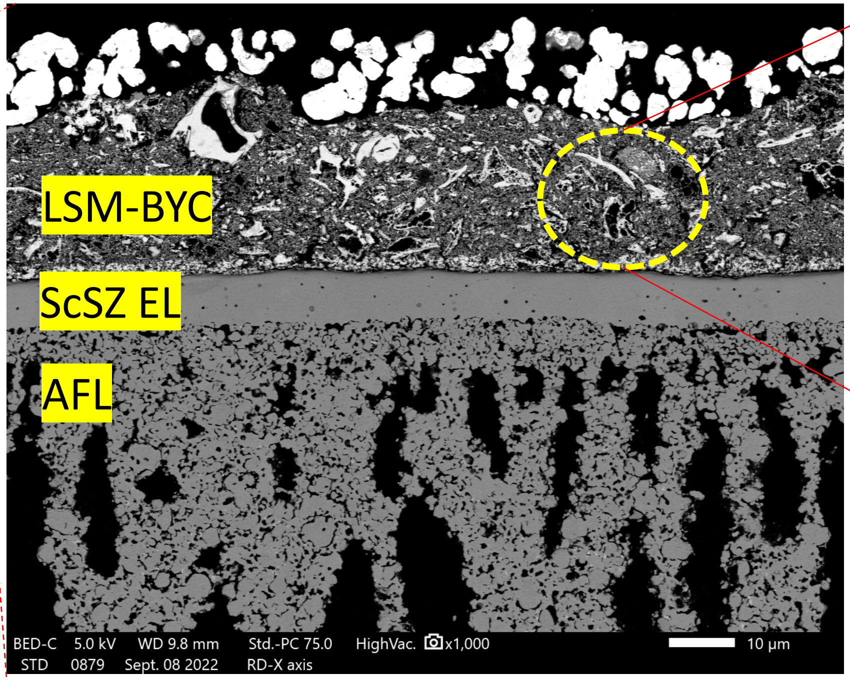
# Separation of Current Collector from OE

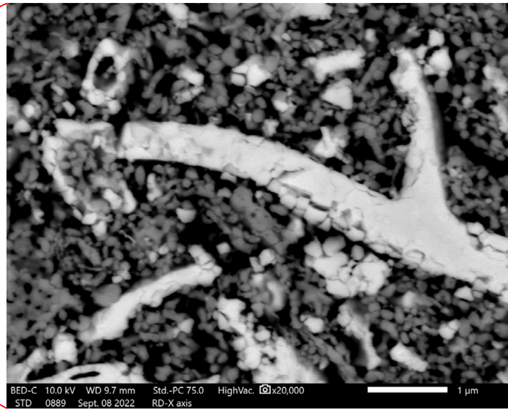


# Post-test Microstructural and Composition Analysis (USC#1)

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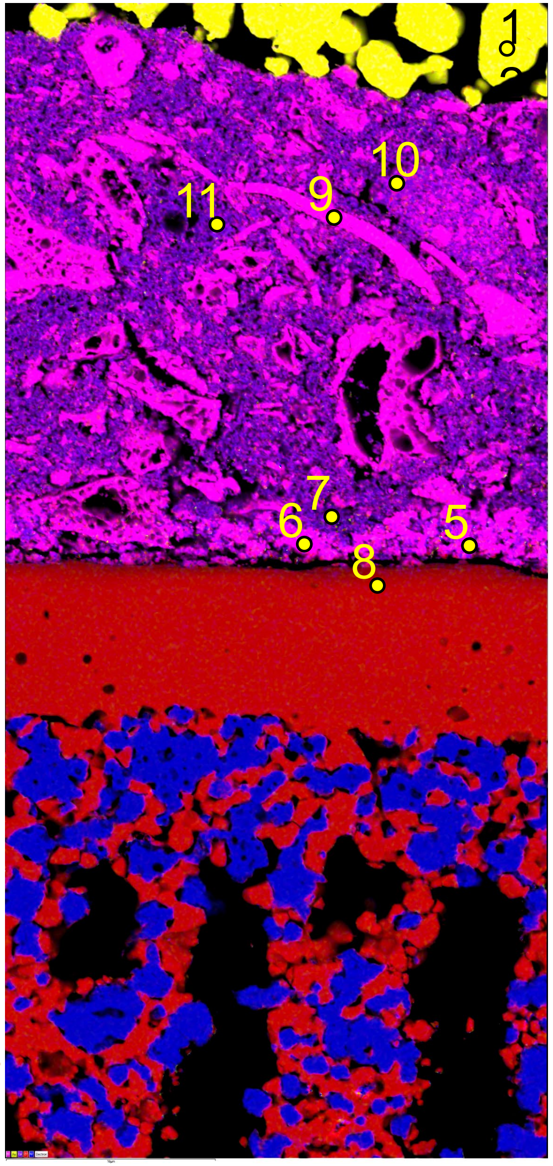
## Cell#1




| 5 | Atomic % |
|---|---|
| O | 59.75 |
| Bi | 18.37 |
| La | 11.01 |
| Ce | 4.36 |
| Zr | 3.24 |
| Y | 2.53 |
| Sc | 0.74 |
| Total | 100.00 |

| 6 | Atomic % |
|---|---|
| O | 62.70 |
| Bi | 15.36 |
| Y | 6.90 |
| La | 6.06 |
| Ce | 4.31 |
| Zr | 3.63 |
| Sc | 0.74 |
| Sr | 0.29 |
| Total | 100.00 |

| 7 | Atomic % |
|---|---|
| La | 48.52 |
| O | 33.19 |
| Sr | 5.36 |
| Zr | 4.83 |
| Bi | 4.25 |
| Si | 1.62 |
| Al | 1.36 |
| Mn | 0.51 |

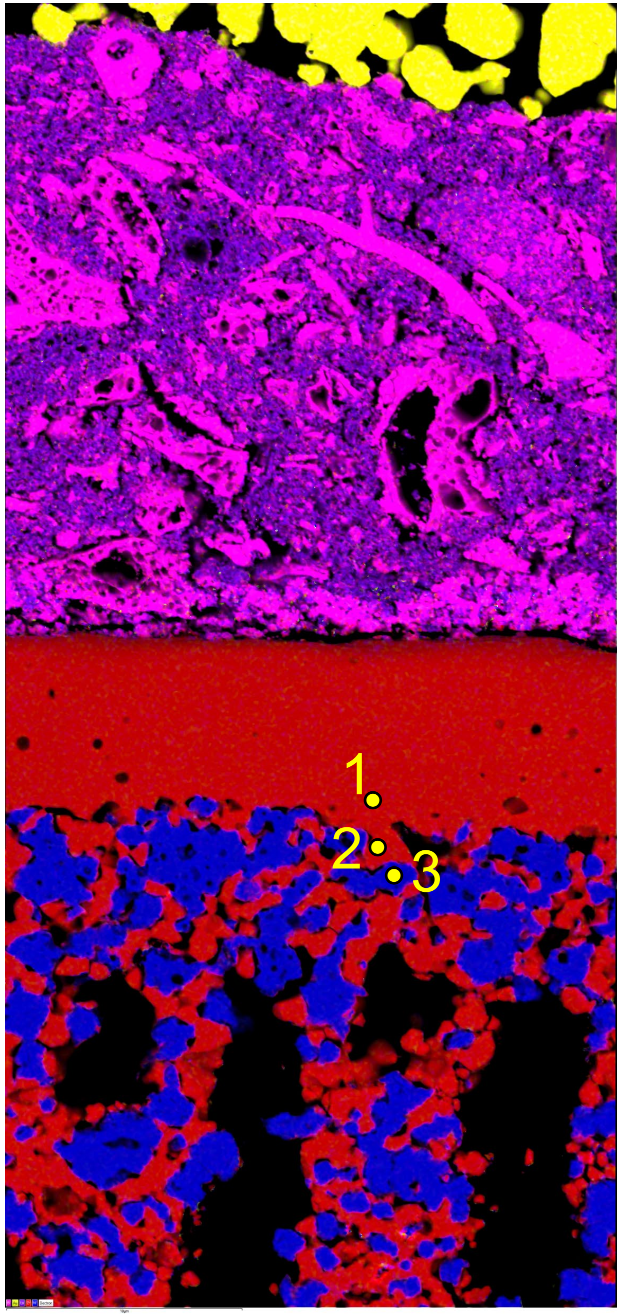
| 8 | Atomic % |
|---|---|
| O | 66.33 |
| Zr | 27.02 |
| Sc | 4.68 |
| Bi | 0.80 |

| 9 | Atomic % |
|---|---|
| O | 59.77 |
| Bi | 25.98 |
| Y | 10.04 |
| Ce | 4.21 |
| Total | 100.00 |

| 10 | Atomic % |
|---|---|
| O | 58.00 |
| Mn | 20.00 |
| La | 12.75 |
| Y | 3.49 |
| Bi | 2.95 |
| Sr | 2.81 |
| Total | 100.00 |

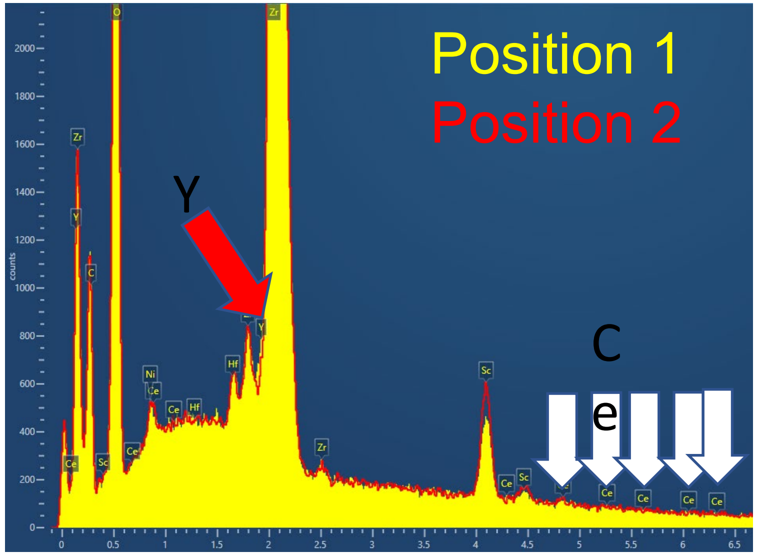
| 11 | Atomic % |
|---|---|
| O | 55.92 |
| La | 21.43 |
| Mn | 15.69 |
| Sr | 3.58 |
| Bi | 3.38 |
| Total | 100.00 |

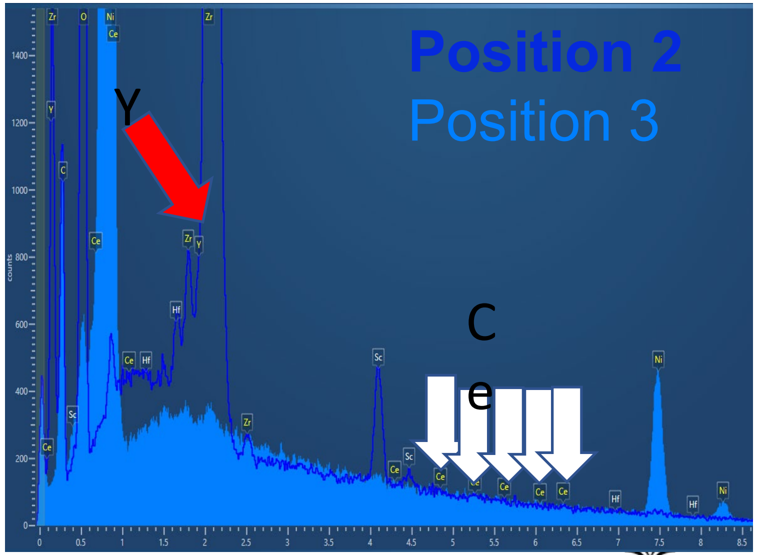
| 12 | Atomic % |
|---|---|
| Au | 96.85 |
| Ag | 3.15 |
| Total | 100.00 |




**Cell#1**

| 1 | Atomic % | 2 | Atomic % | 3 | Atomic % |
|---|---|---|---|---|---|
| O | 63.74 | O | 63.35 | Ni | 95.24 |
| Zr | 30.94 | Zr | 30.30 | Ce | 2.46 |
| Sc | 3.13 | Sc | 4.25 | O | 1.82 |
| Ni | 0.67 | Ce | 1.03 | Zr | 0.36 |
| Y | 0.61 | Ni | 0.62 | Y | 0.12 |
| Ce | 0.48 | Hf | 0.43 | Total | 100.00 |
| Hf | 0.43 | Y | 0.00 | | |
| Total | 100.00 | Total | 100.00 | | |

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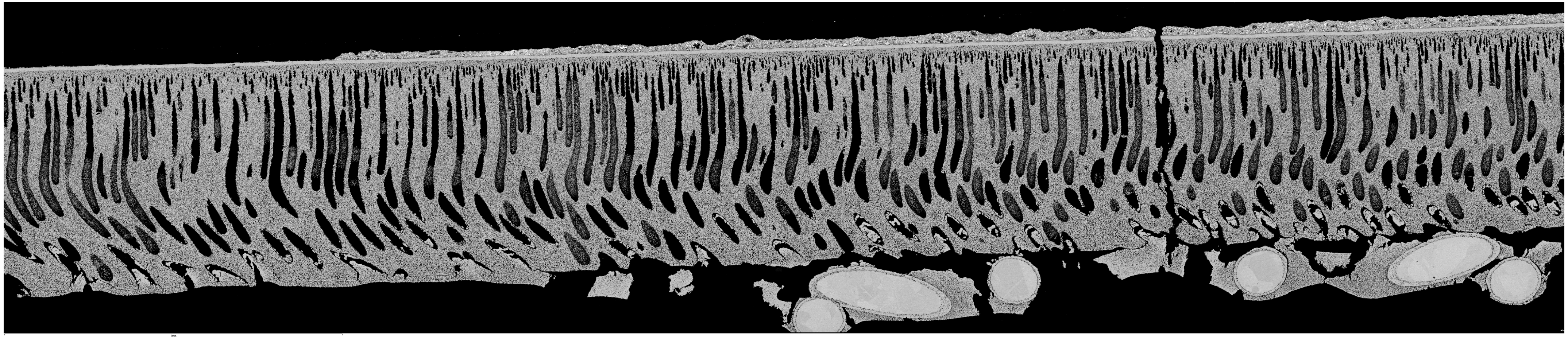
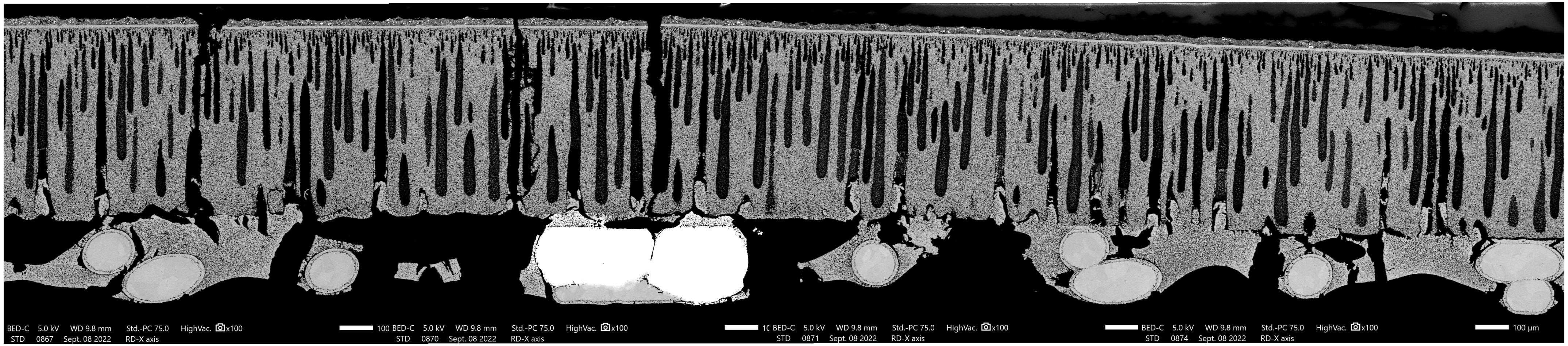
# Comparing Cell 1 and Cell 3

221361 EXP 2022_06_22_N2 c9 USC#3 (lowest performance)



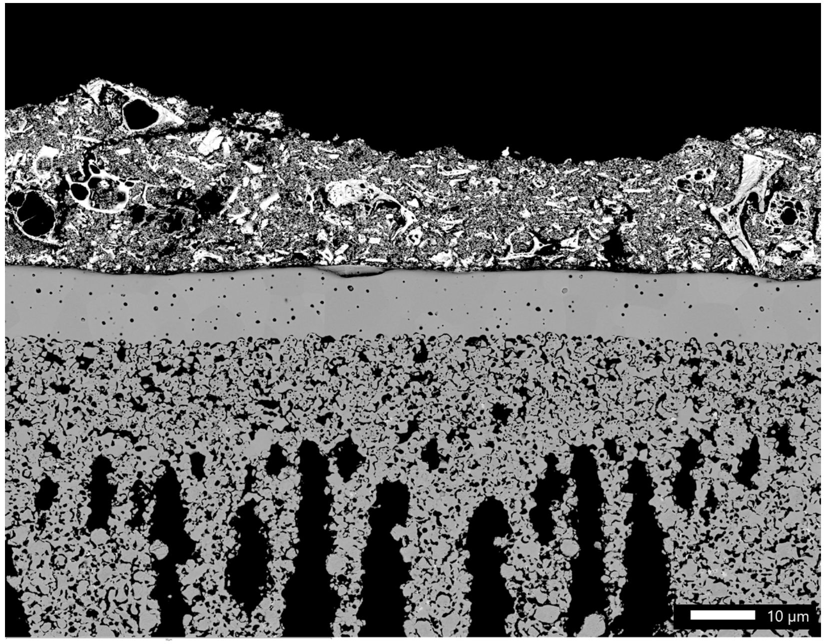
Cell has deformed pillar-like columnar structure

221361 EXP 2022_06_22_N2 c7 USC#1 (highest performance)



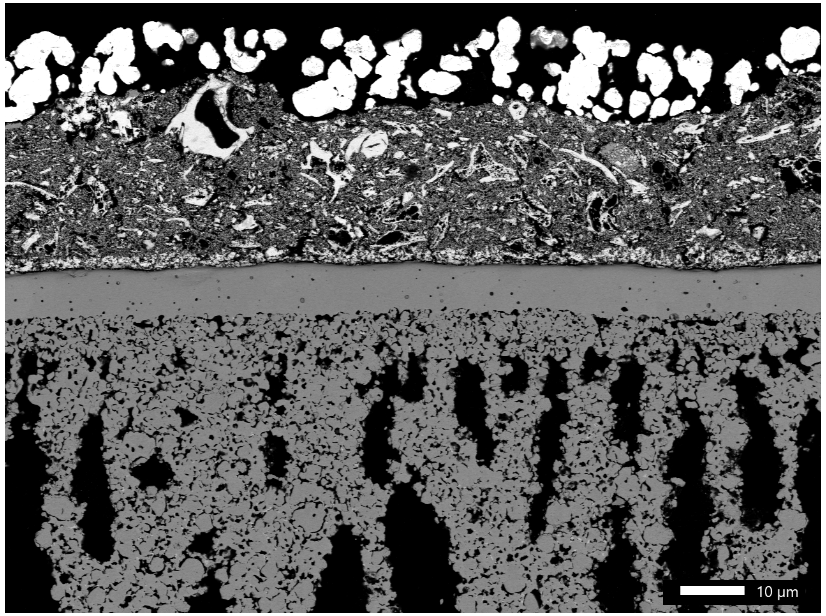

Cell has straight pillar-like columnar structure

221361 EXP
2022_06_22_N2 c9
USC#3 (lowest performance)




- Thicker electrolyte
- More Pores in YSZ
- Thicker AFL
- Poor OE/EL bonding

221361 EXP
2022_06_22_N2 c7
USC#1 (highest performance)




- Bi-rich layer at OE/EL interface
- Thinner electrolyte
- Smaller pores in YSZ
- Thinner AFL
- Weak OE/EL bonding

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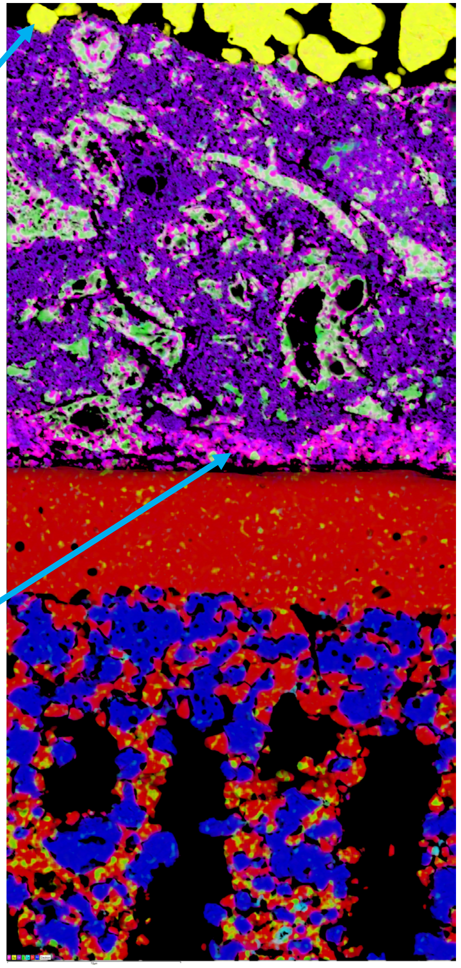
Cell has a continuous layer of gold particles layer

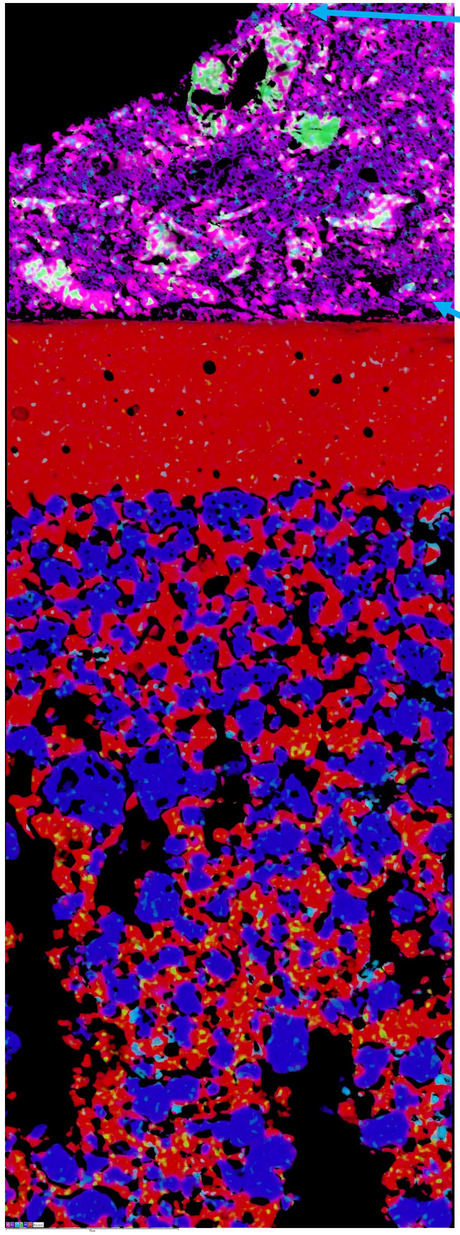
Cell has a continuous light contrast layer on top of the YSZ

| Layer on top of electrolyte | Atomic % |
|---|---|
| O | 62.70 |
| Bi | 15.36 |
| Y | 6.90 |
| La | 6.06 |
| Ce | 4.31 |
| Zr | 3.63 |
| Other | Bal. |



USC#1

USC#3



Cell has little if any gold particles on top

Cell has no light contrast layer on top of the YSZ

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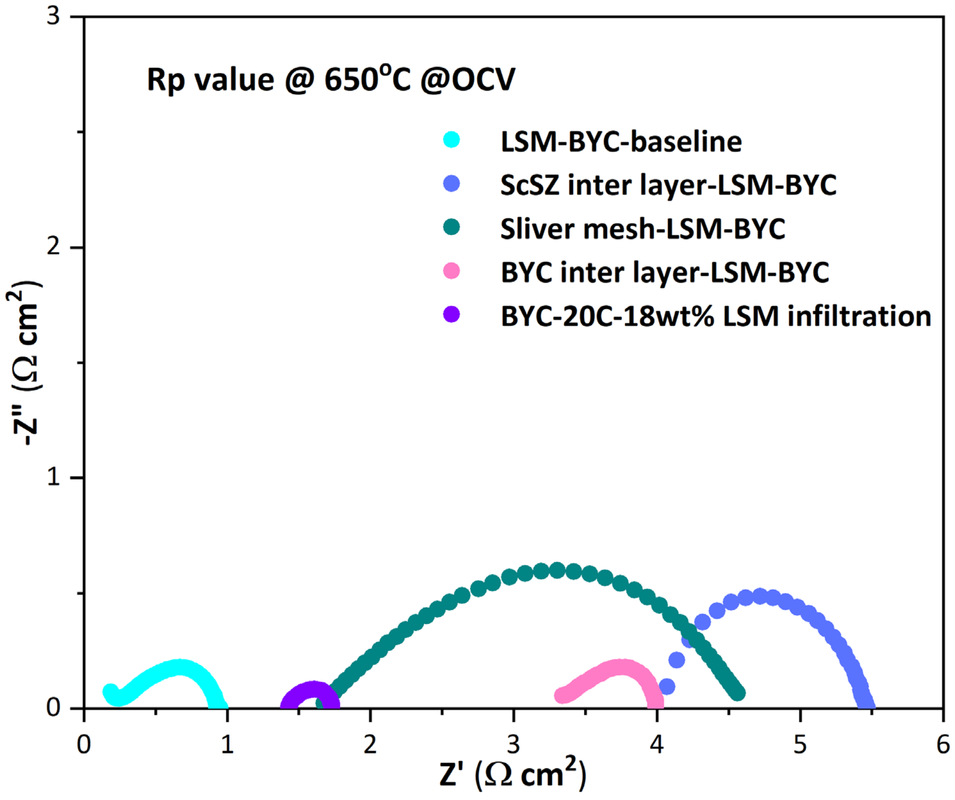
# Exploring Ways to Improve the OE Performance




- The $R_p$ value of LSM-BYC baseline is around 0.64 Ω cm$^2$
- The $R_p$ increase to around 3.0 Ω cm$^2$ when adding ScSZ roughing layer between electrolyte and OE
- The $R_p$ increase to 1.4 Ω cm$^2$ if embedding sliver mesh inside LSM-BYC
- The $R_p$ slightly decreased (0.60 Ω cm$^2$) when adding BYC layer between screen printed LSM-BYC and EL
- The $R_p$ decreases to 0.30 Ω cm$^2$ when infiltrating 18wt% LSM into BYC scaffold

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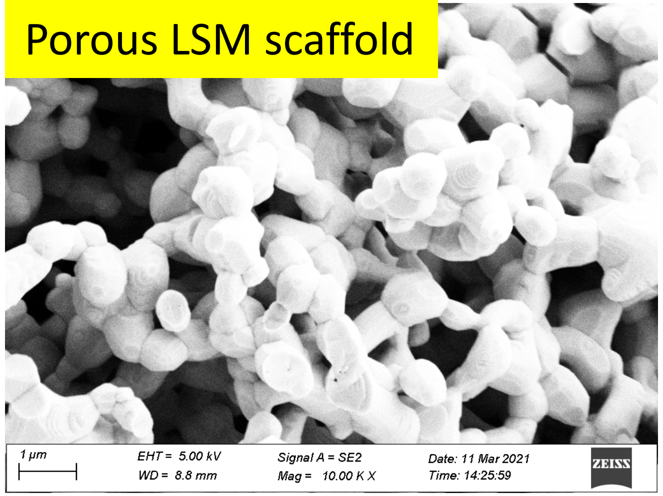
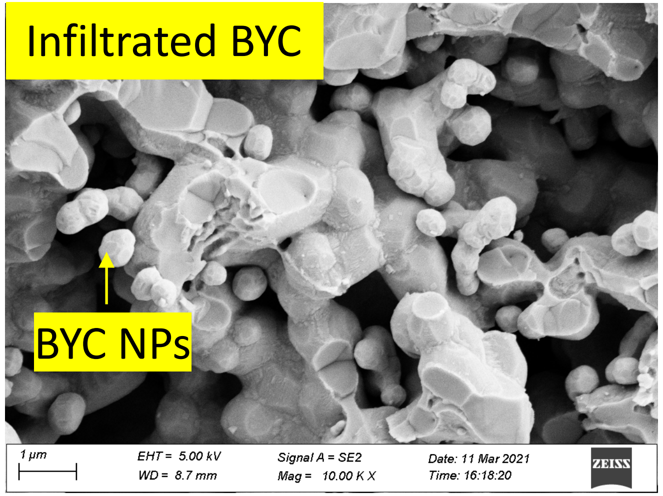
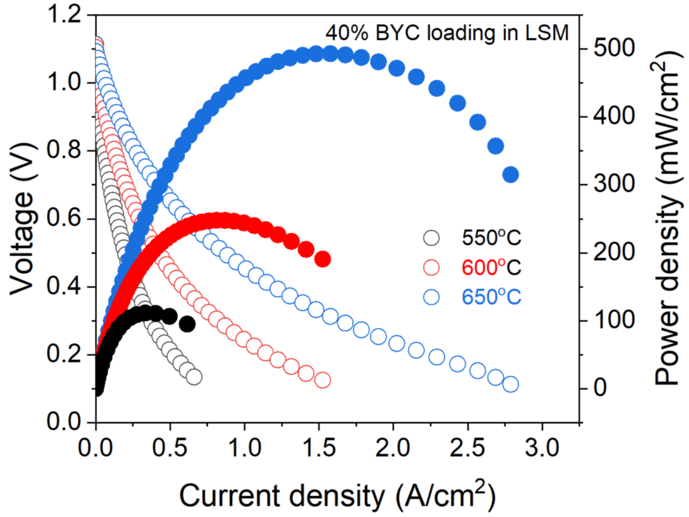
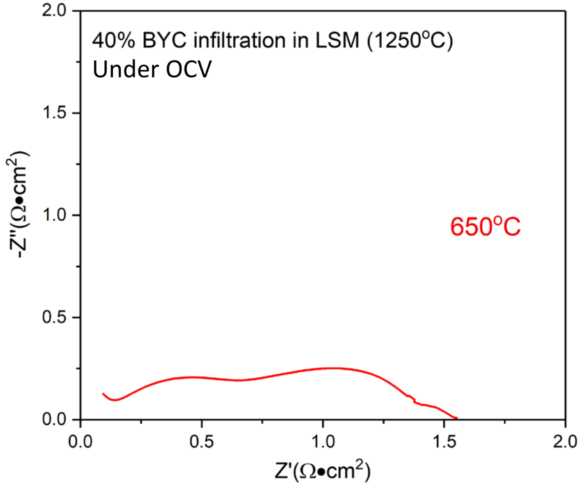
# Infiltrating BYC NPs into LSM Scaffold Sintered at 1200°C/5h



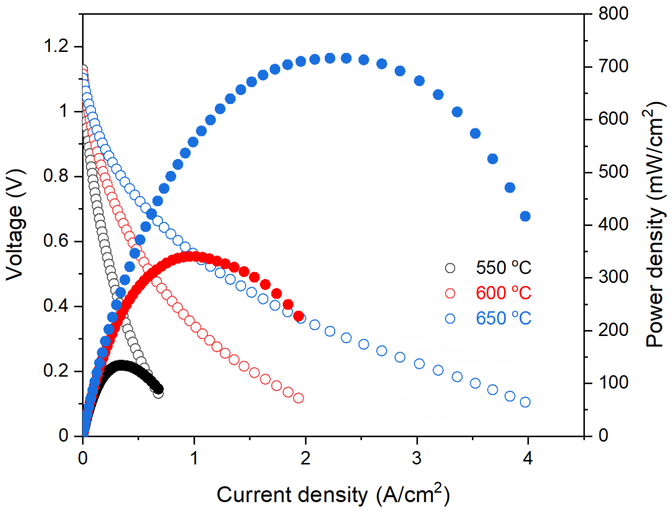



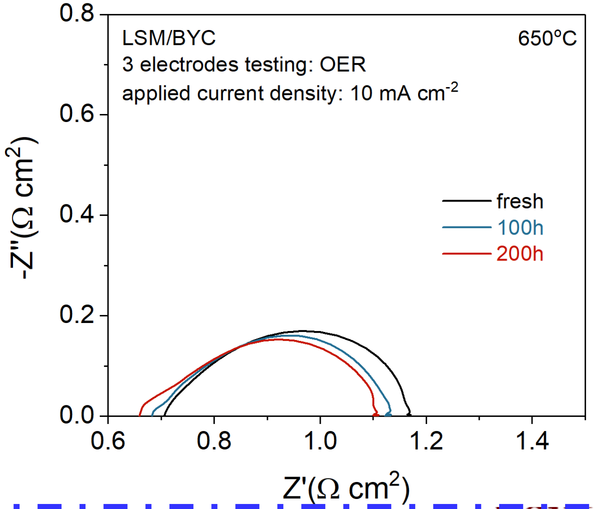

Infiltrated BYC into LSM scaffold, calcined@500°C/2h




Screen printed LSM/BYC=40/60, calcined@800°C/2h

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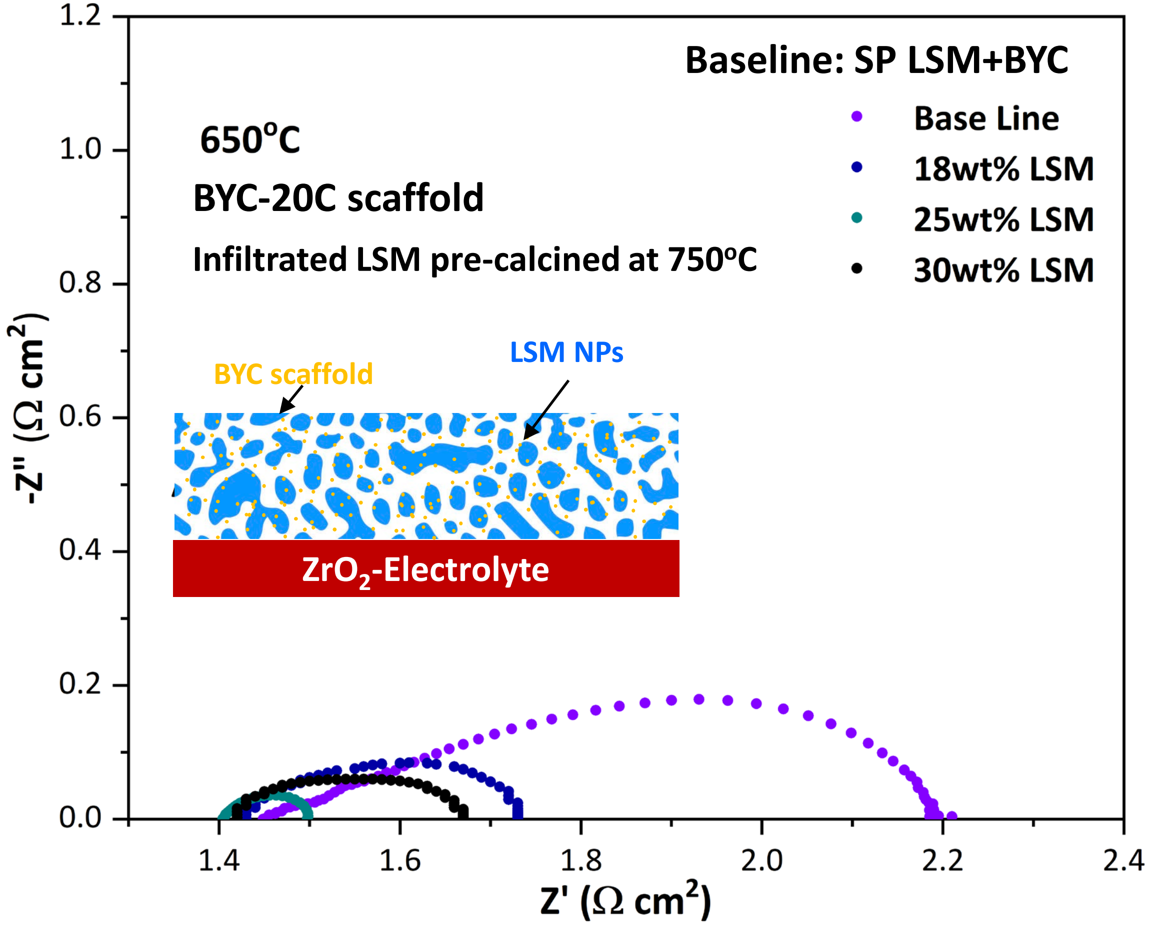
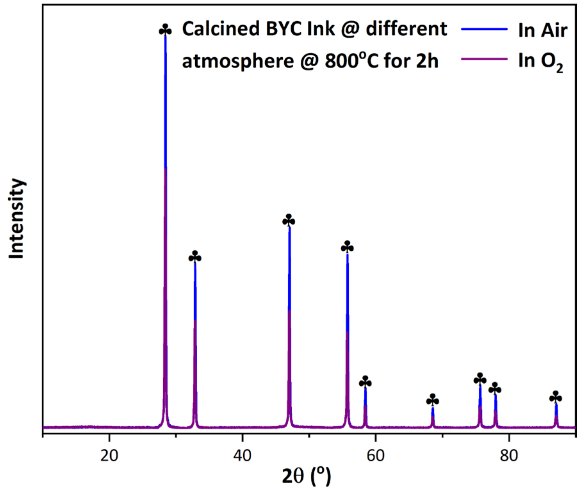
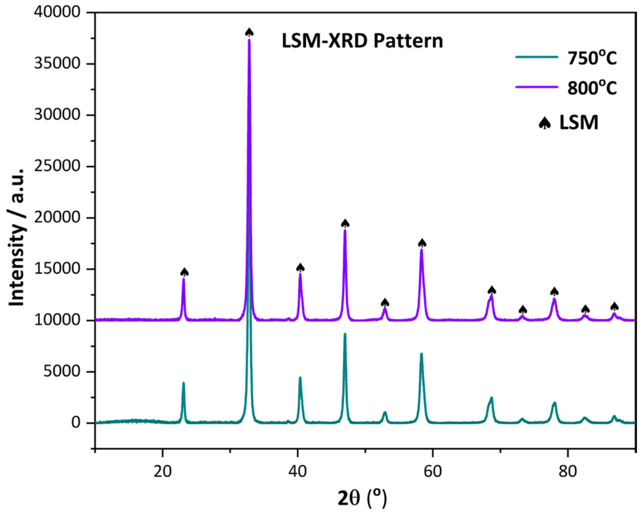
# Infiltrating LSM NPs into BYC Scaffold Sintered at 800°C/5h




| 650°C | BYC-20C-baseline (SP) | BYC-20C-18wt%LSM | BYC-20C-25wt%LSM | BYC-20C-30wt%LSM |
|---|---|---|---|---|
| $R_o$ (Ω $cm^2$) | 1.44 | 1.41 | **1.41** | 1.42 |
| $R_p$ (Ω $cm^2$) (OCV) | 0.64 | 0.30 | **0.10** | 0.15 |

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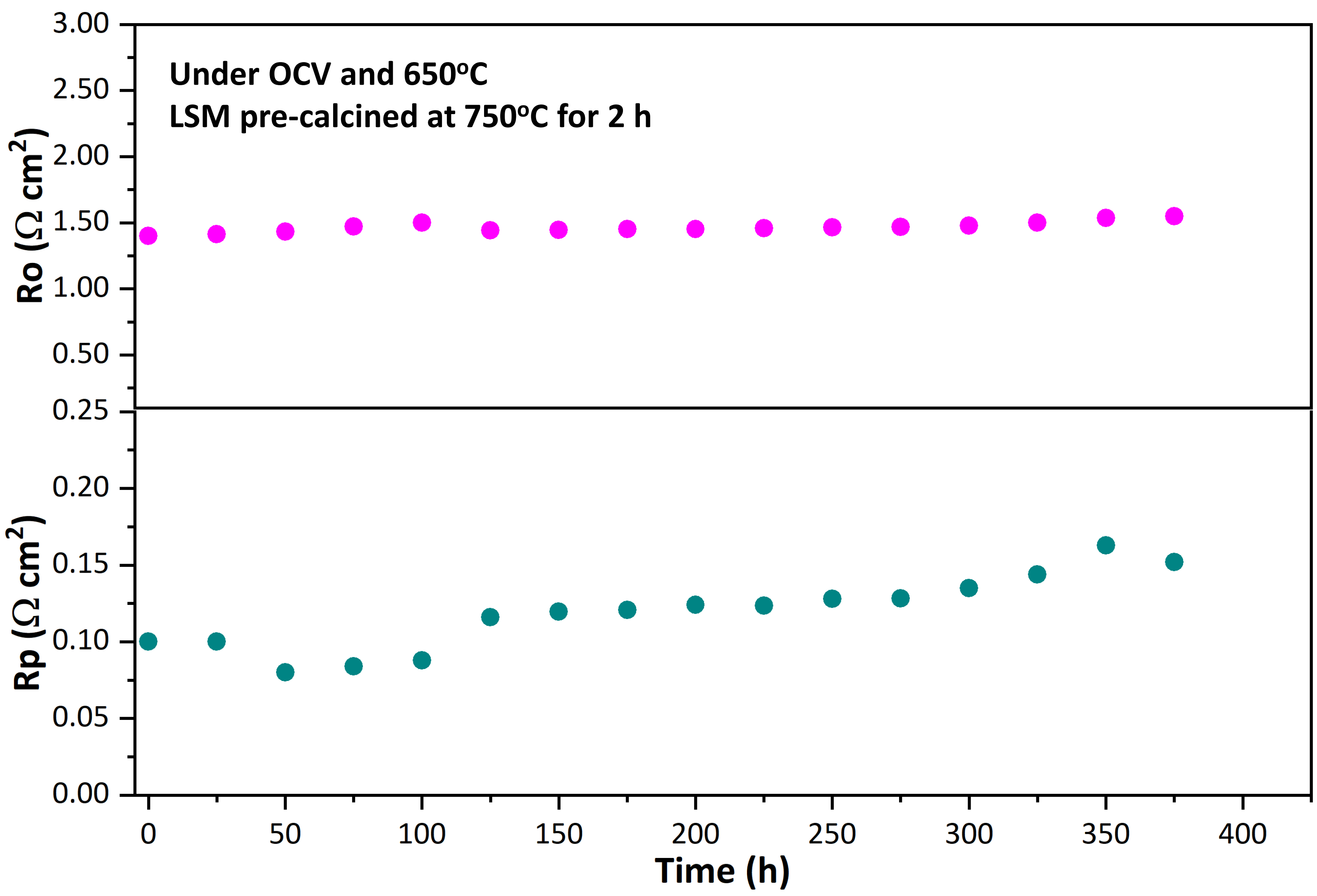
# Stability of BYC–20C-25wt% LSM

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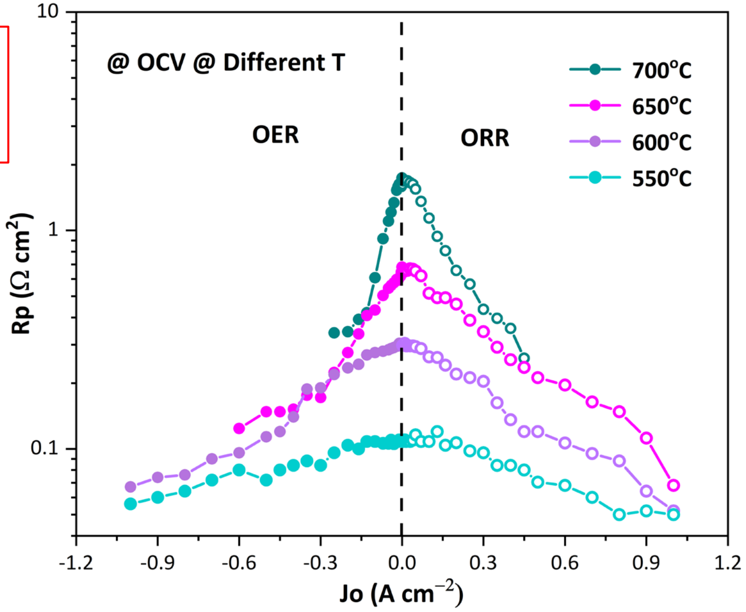
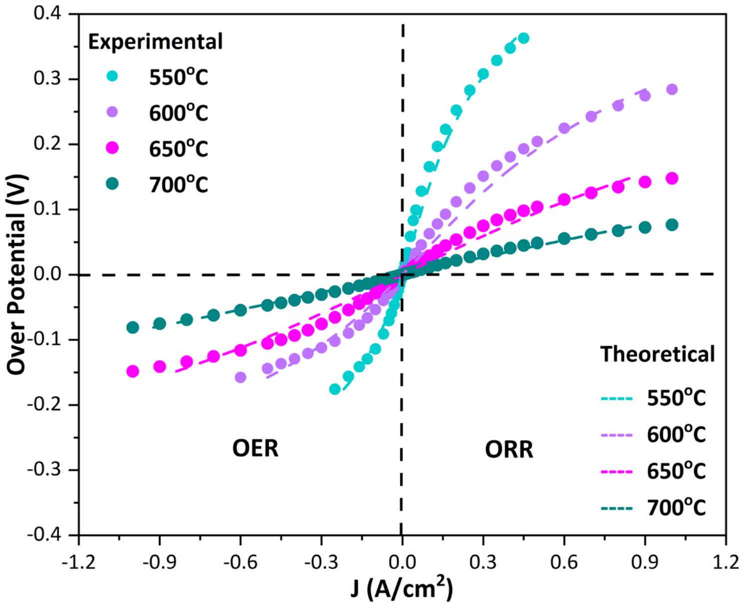
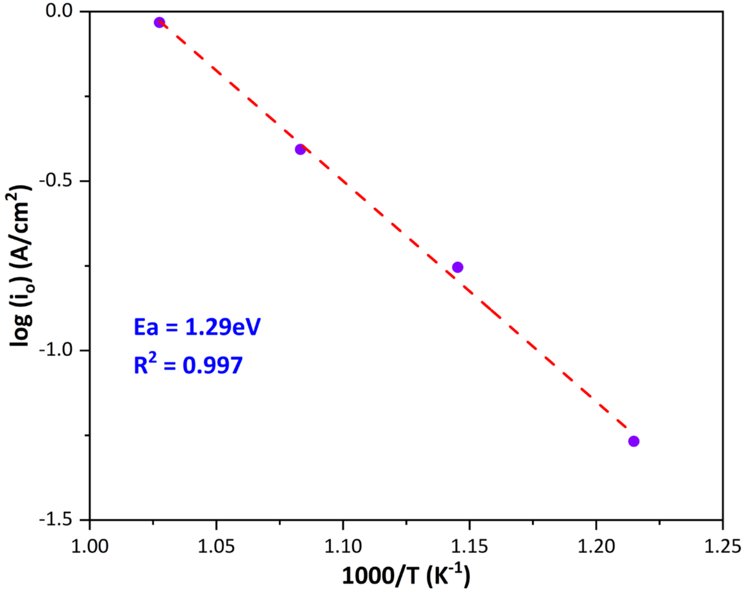
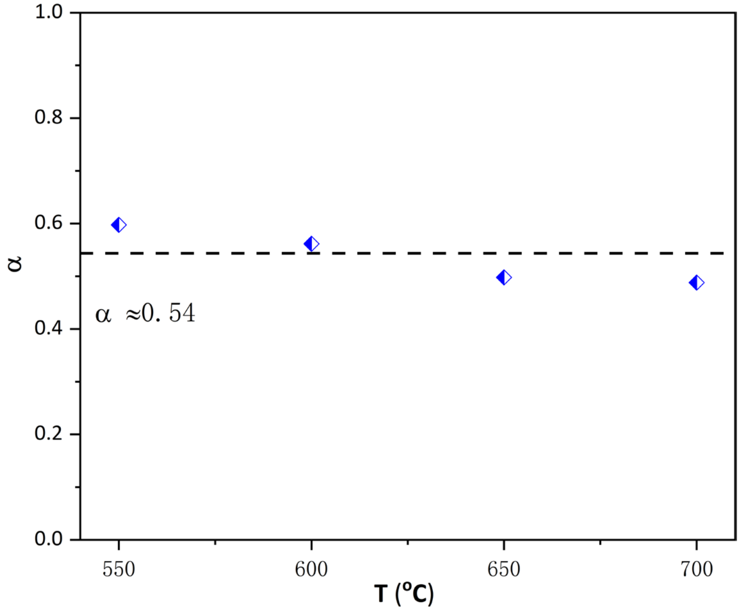
# $R_P$ and η of IL-BLF-OE (BYC-20C-18wt%LSM)

Measured by STEC method

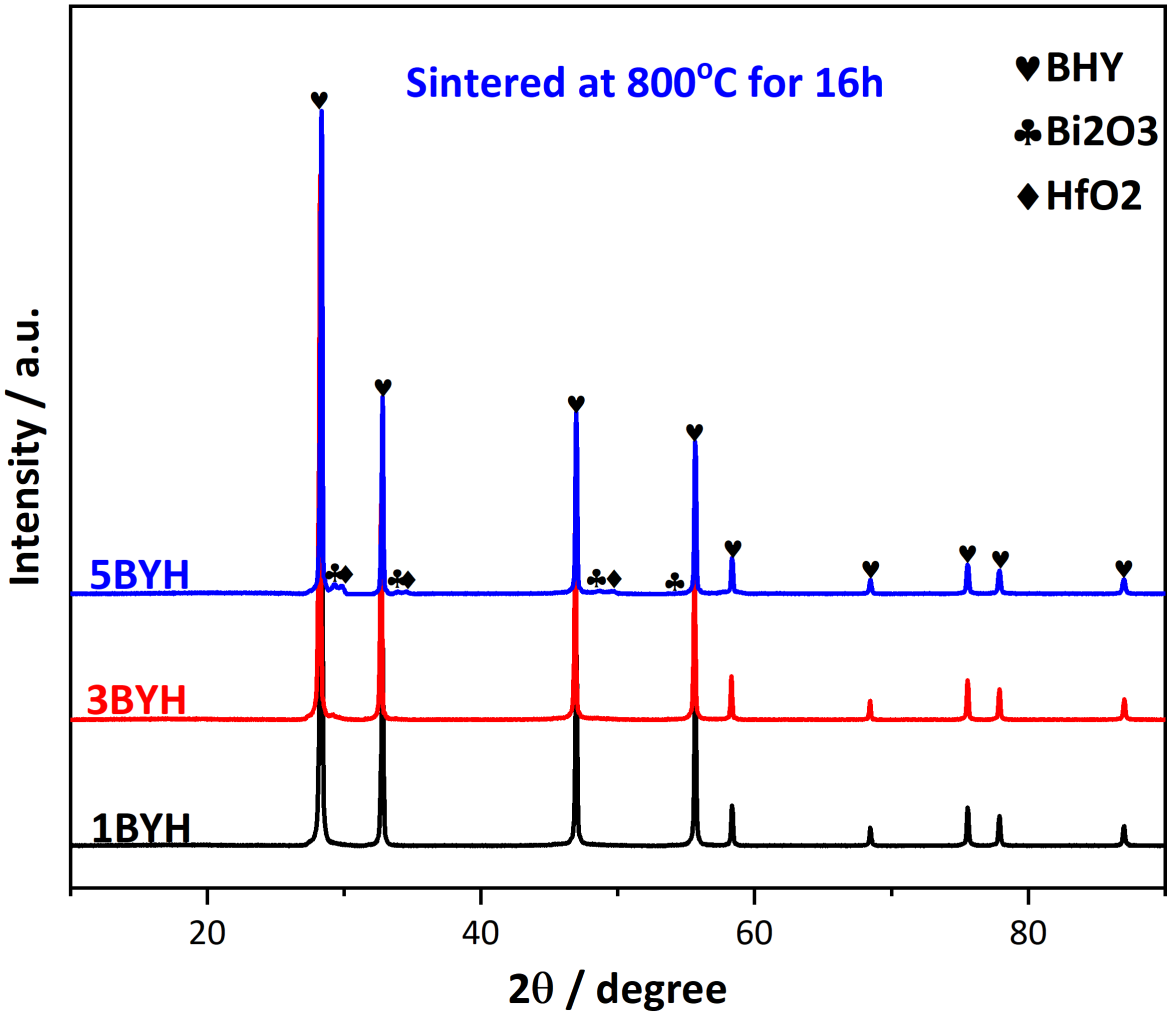


# $(Bi_{0.75}Y_{0.25})_{1-x}Hf_xO_{2-\delta}$ (BYH) Series: XRD Patterns

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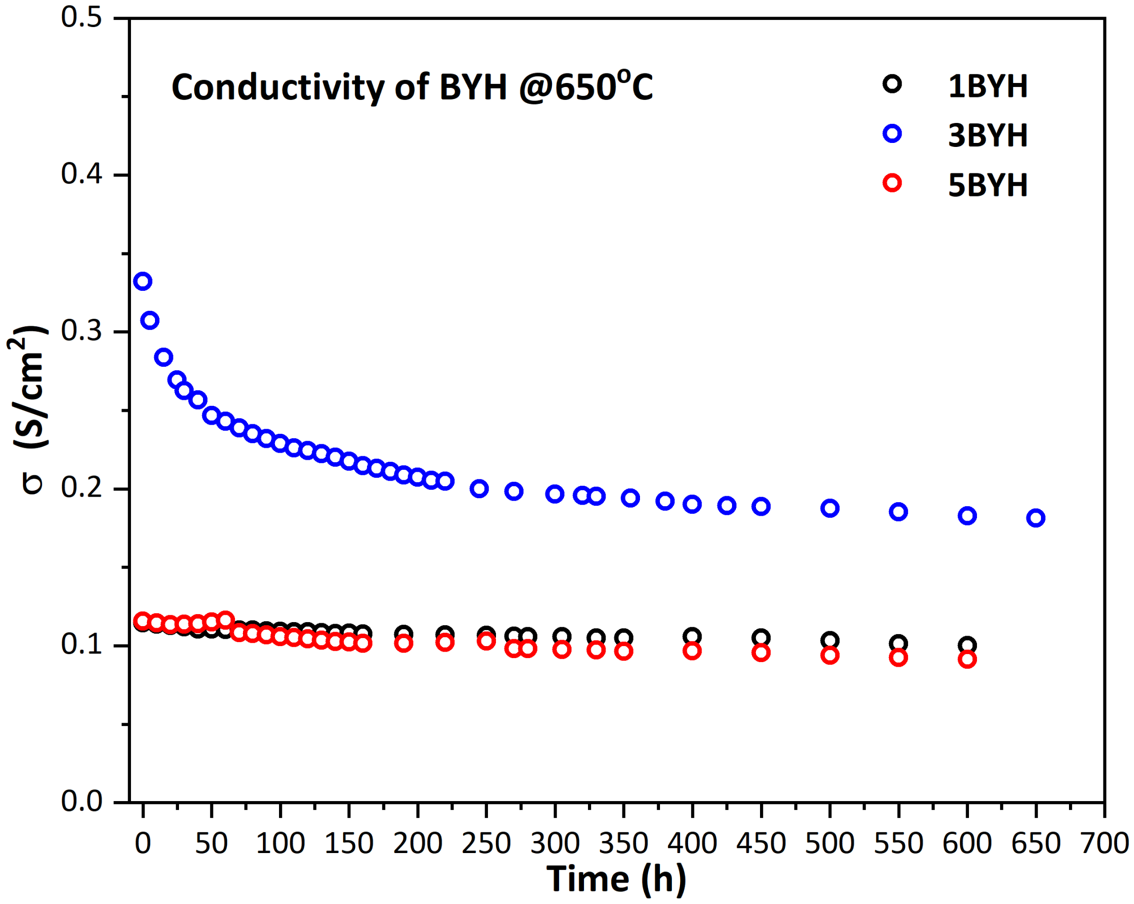
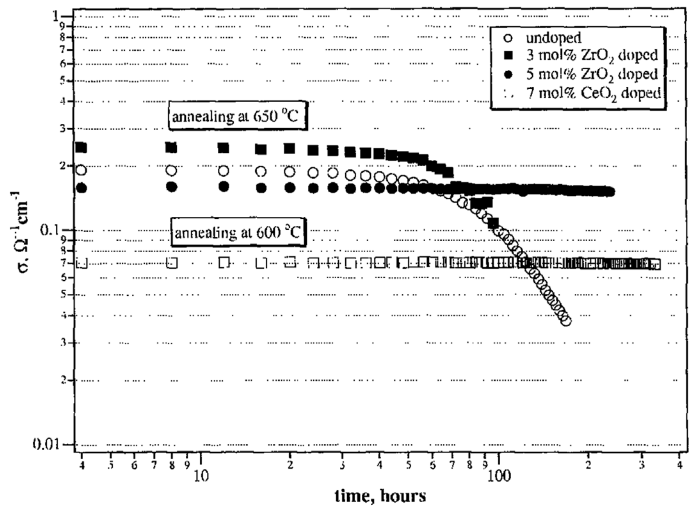
# $(Bi_{0.75}Y_{0.25})_{1-x}Hf_xO_{2-\delta}$ (BYH) Series: Conductivity Stability



# Summary

- We have demonstrated the feasibility of BYC-LSM as a barrier layer free oxygen electrode for $\leq 650^oC$ SOCs
- Phase inversion process has been demonstrated to produce hydrogen substrates with graded porosity and open structure
- Independent testing at PNNL revealed that a good BLF-OE has a Bi-rich layer at the electrolyte interface; it also revealed that the BLF-OE has a weak bonding with the electrolyte
- New BYC scaffolded BLF-OE has shown $R_p = 0.1\ \Omega cm^2$ at $650^oC$ and the potential to address the bonding issue
- BYH series might be a better oxide-ion conducting phase

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# Next Step

- Fabricate 1.5 $cm^2$ BYC-scaffolded BLF-OE cells for independent testing at PNNL
- Continue to optimize BYH oxide-ion conductor for BLF-OE
- Develop ALD supercycles for SCT overcoat on LSCF-GDC
- Complete electro-chemo-mecho model

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# 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: $\leq 0.15V@\pm 1A/cm^2@650^oC$ | 2.2 | 03/31/23 | complete | STEC and Report to DOE |
| 4 | Demonstration of ALD bilayer OE performance: Overpotential: $\leq 0.15V@\pm 1A/cm^2@700^oC$ | 3.2 | 06/30/2023 | 40% | 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 | 50% | Cell testing and Report to DOE |
| 7 | Demonstration of large-area cell (15 $cm^2$) performance specified in the Success criteria | 5.4 | 09/09/2023 | NYS | Cell testing and Report to DOE |
| 8 | A multiphysics model detailing OE failure mechanisms and modes | 6.0 | 09/09/2023 | 70% | Report to DOE |

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# Acknowledgements


- We are grateful to DOE-NETL SOFC program for the financial support.
- We thank the project manager, Dr. Evelyn Lopez, for many useful discussion and suggestions during our monthly meetings.


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