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

Present to 2023 FECM Spring Project Review Meeting, Pittsburgh, April 18-20, 2023

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About Project

Project Goal

- To advance reduced temperature ($\leq$700^{o}C) 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^{o}C
  2. Developing ALD-SCT ($SrCo_{0.9}Ta_{0.1}O_{3-\delta}$)@LSCF-GDC bilayer OEs for SOCs operation at $\leq$ 700^{o}C
  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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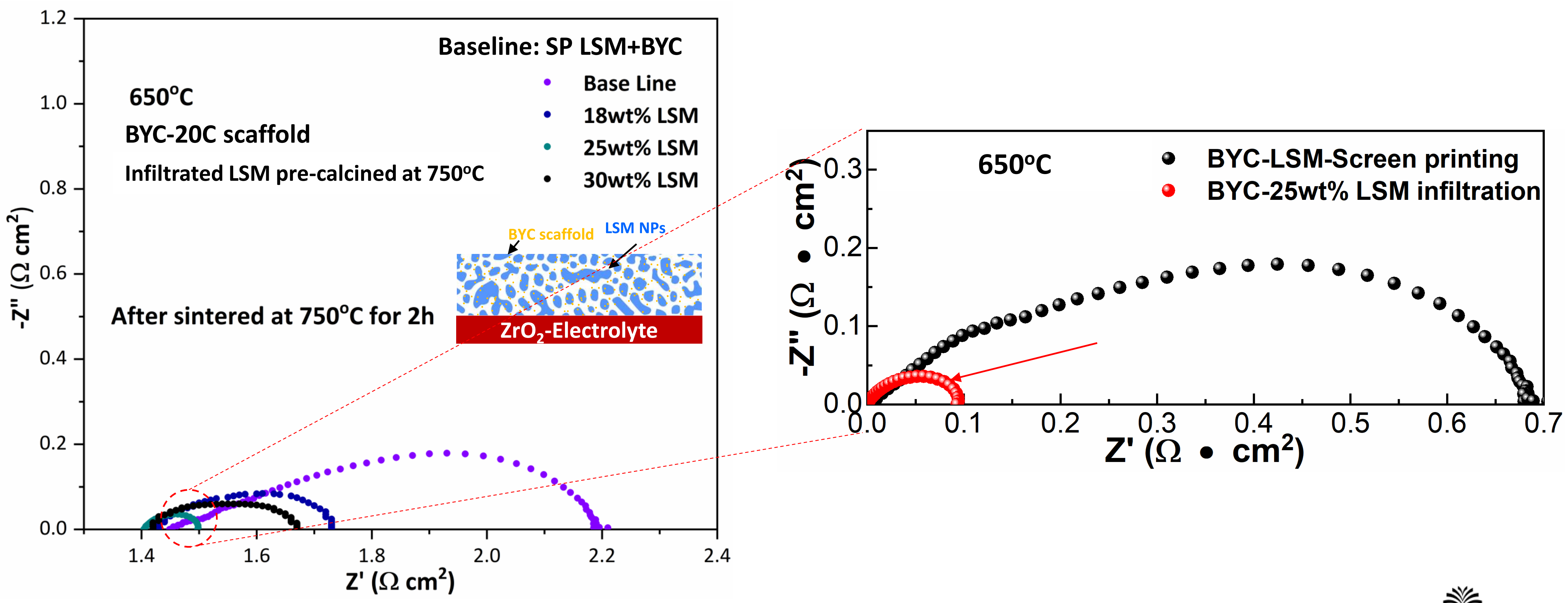
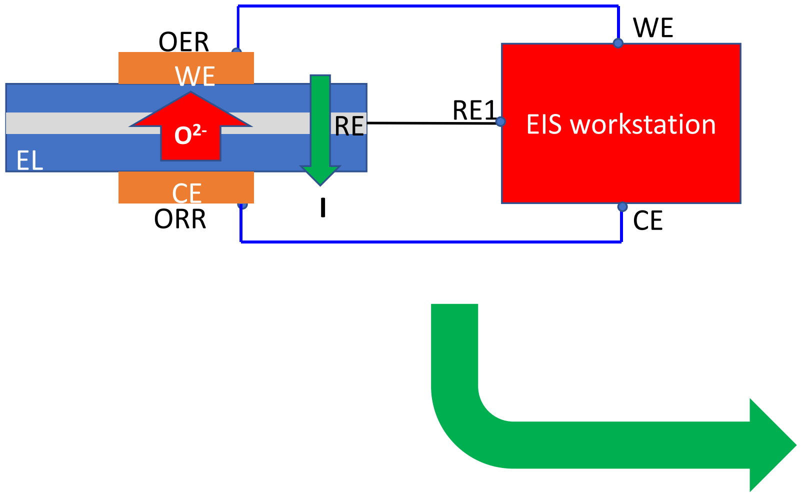
Barrier Layer Free Oxygen Electrode: BYC+LSM

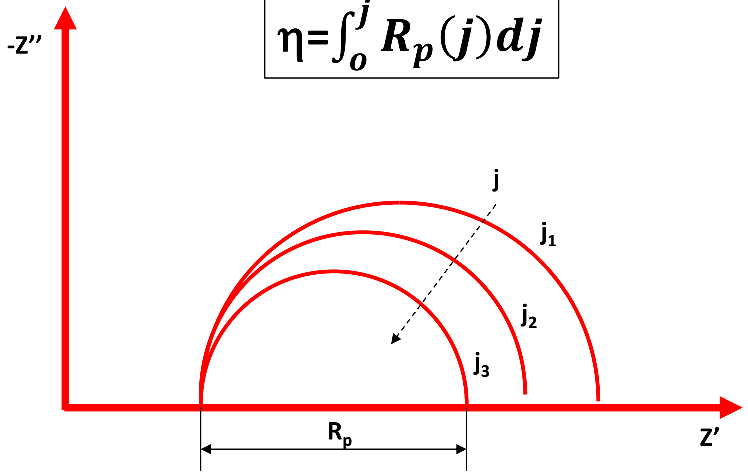


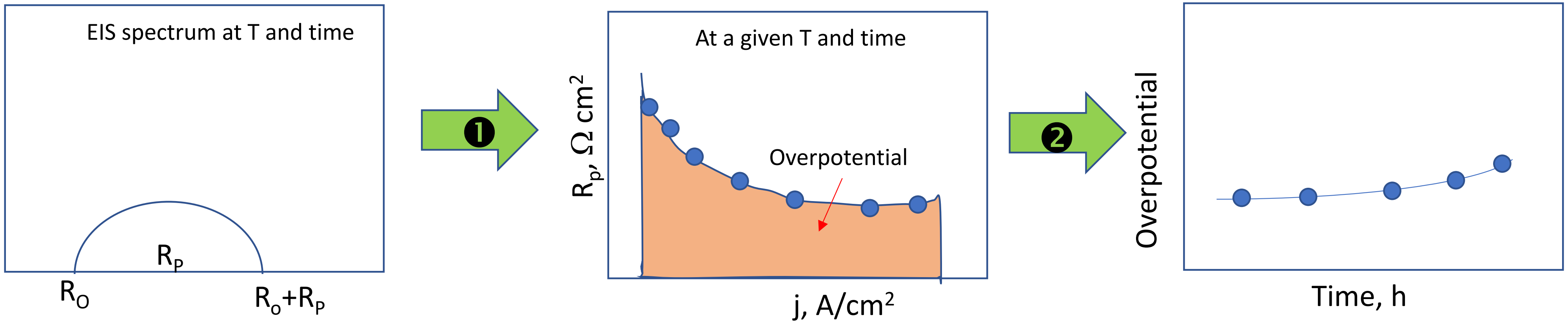
Symmetrical Three Electrode Cell (STEC) Method



DC-biased EIS method

$$\eta=\int_o^j R_p(j)dj$$





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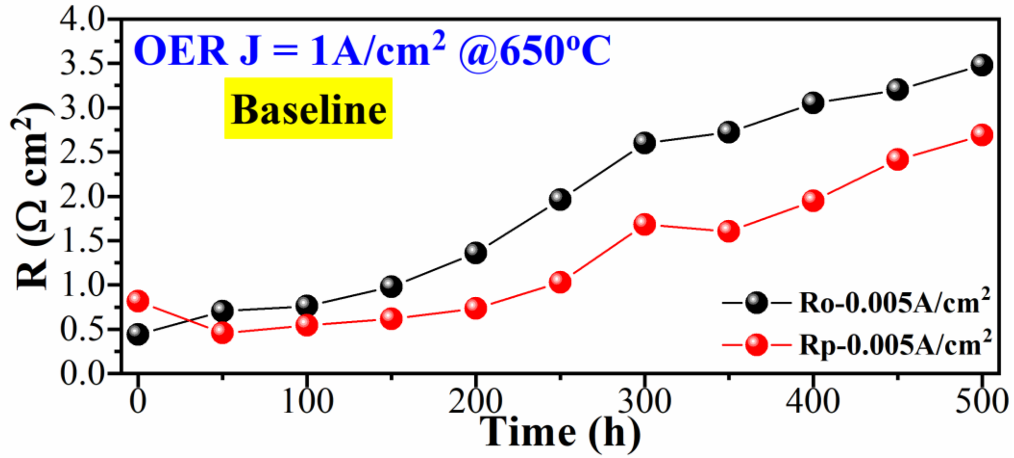
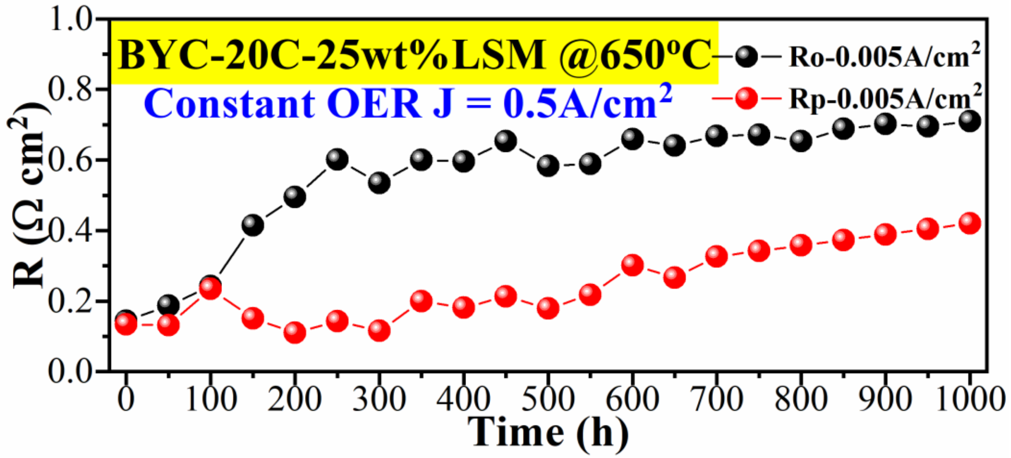
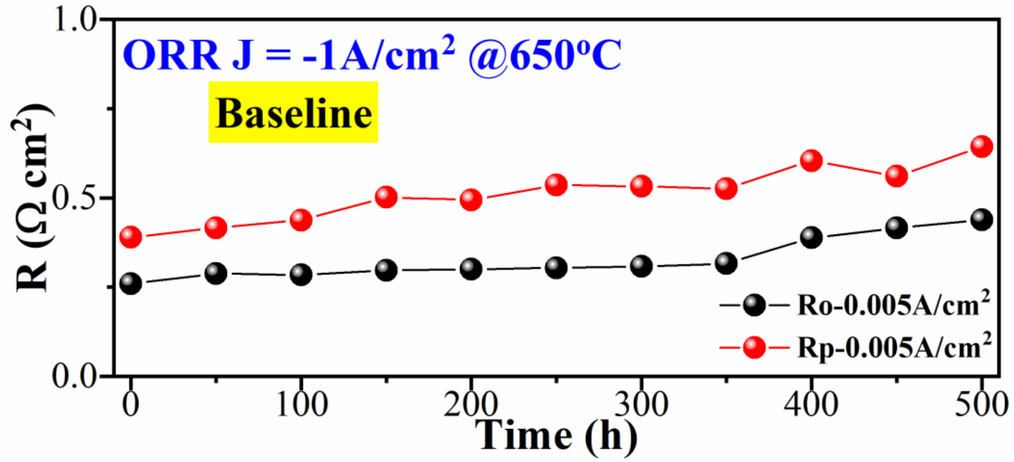
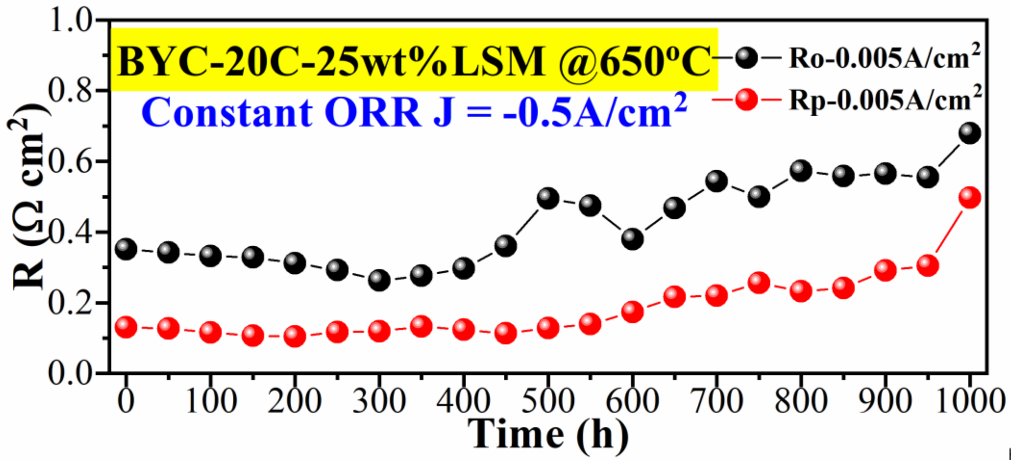
Stability of OEs under Unidirectional Polarization in Half Cells









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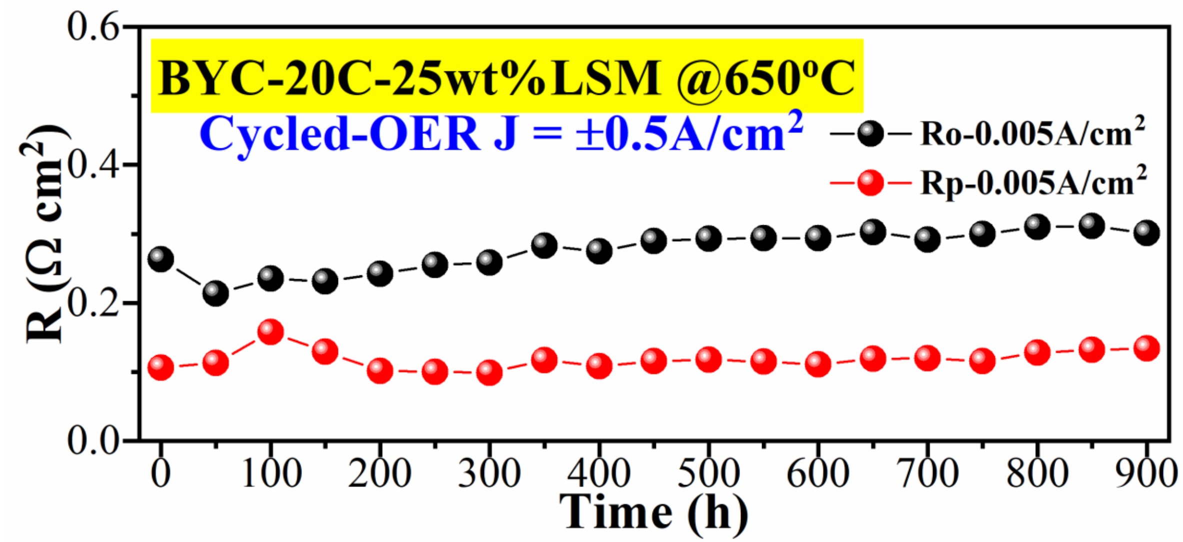
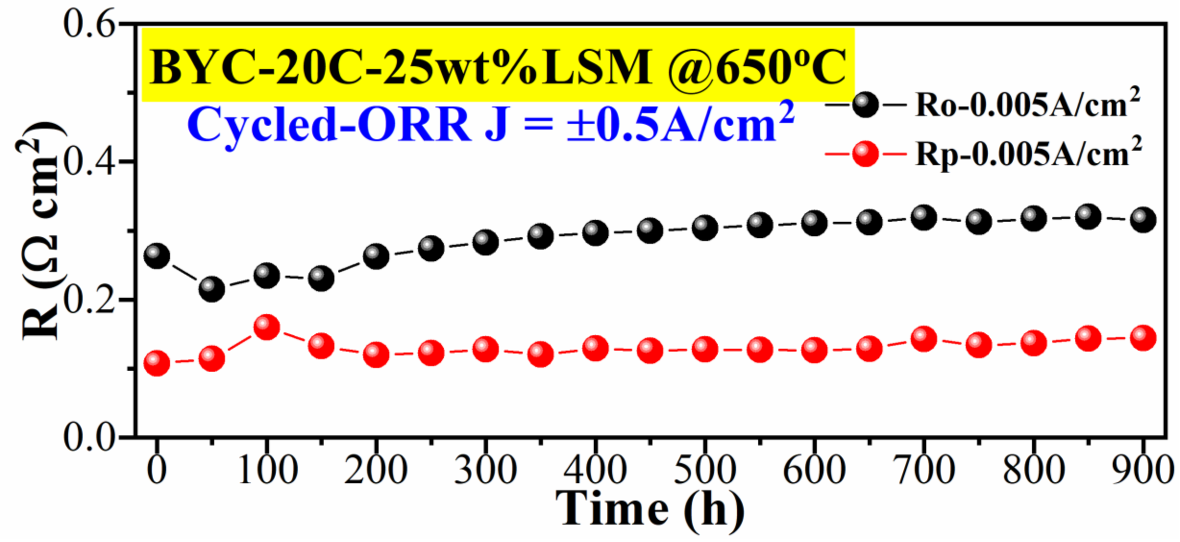
Stability of OEs under Bidirectional Polarization in Half Cells

- J=±0.5A/cm^2, duration =4h for each cycle





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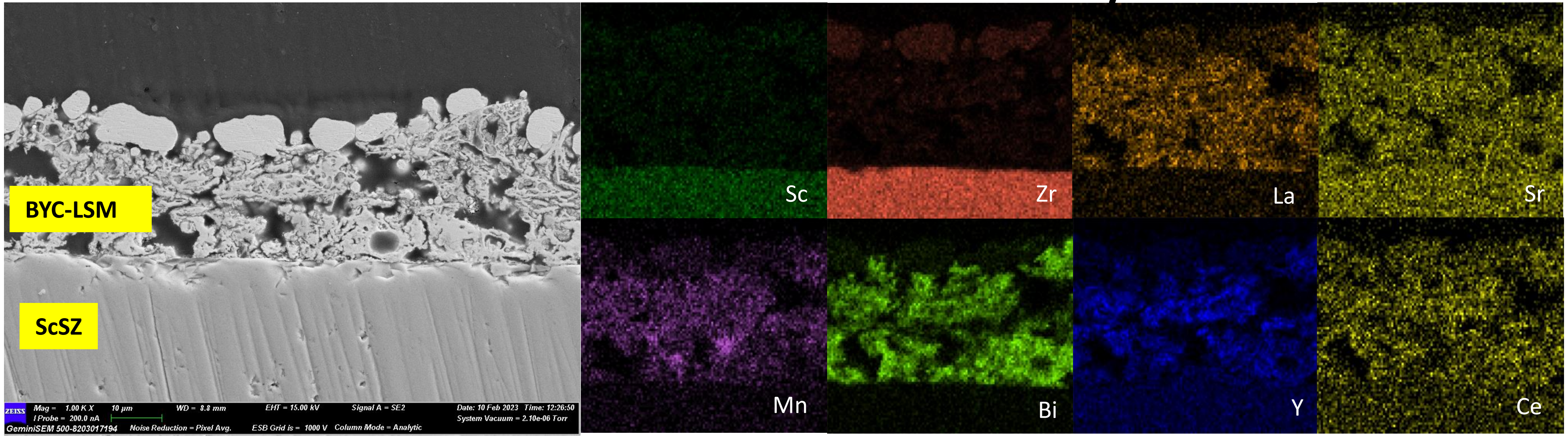
Microstructure and Composition of SP-OE

after 1000h Treatment at ±0.5A/cm^2

OER



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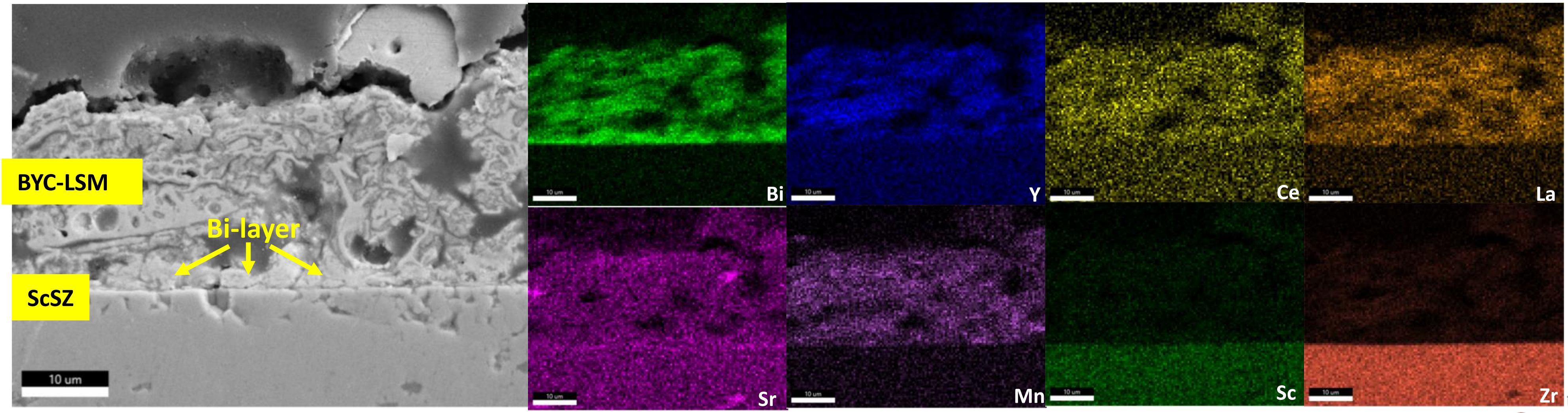
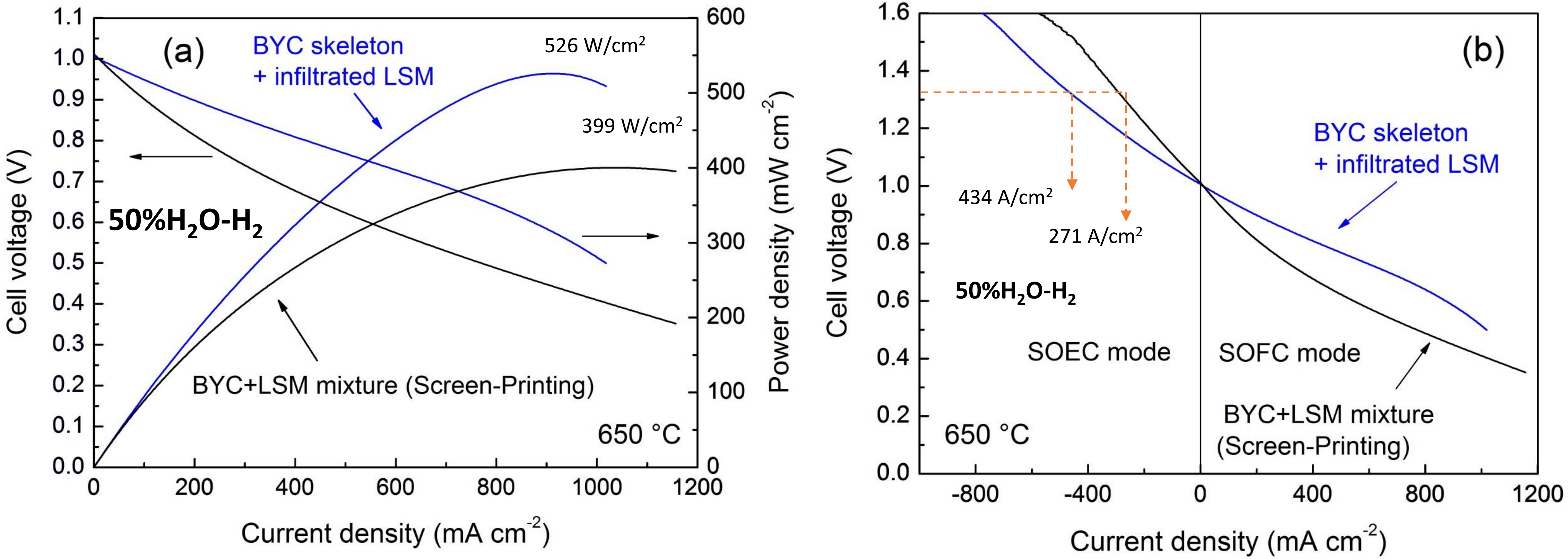


Initial Button Cell Performance Tested at USC

PI-Ni-4YSZ HE/Ni-ScSZ FL/ScSZ electrolyte/BYC+LSM



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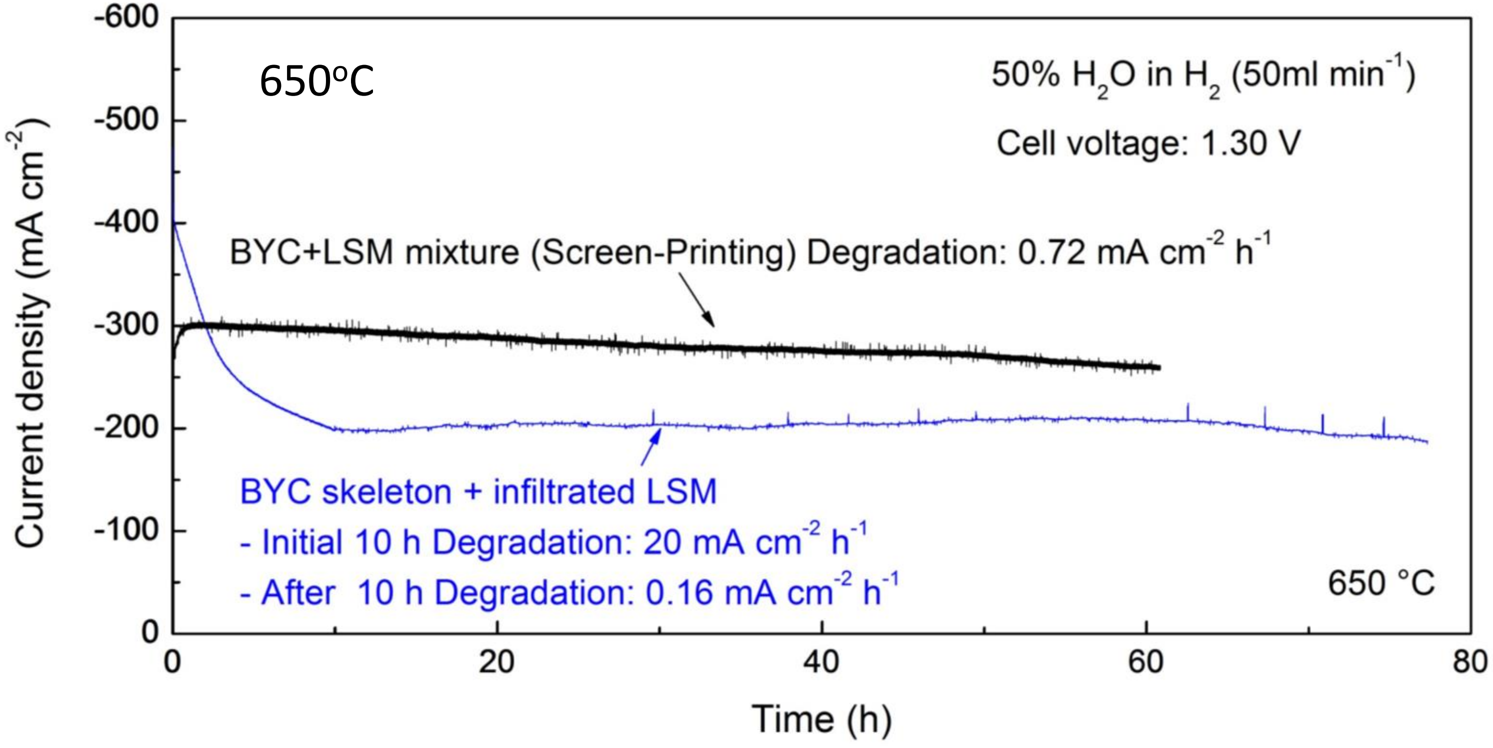
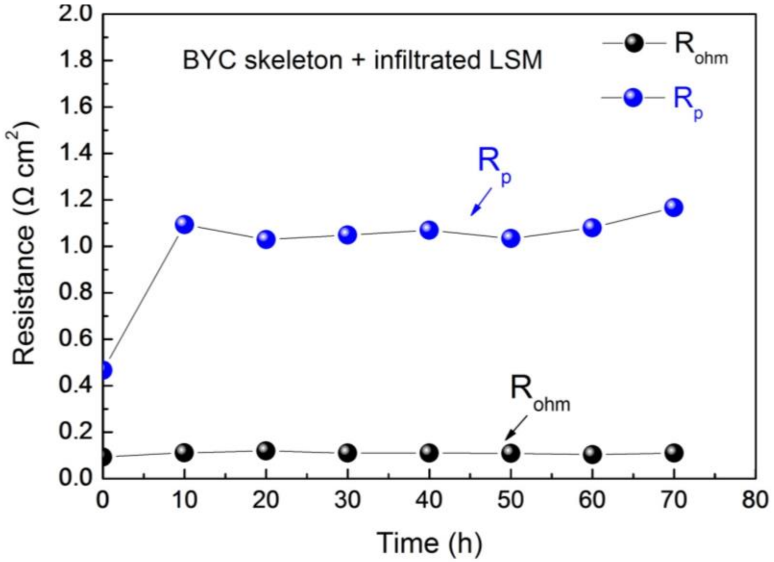
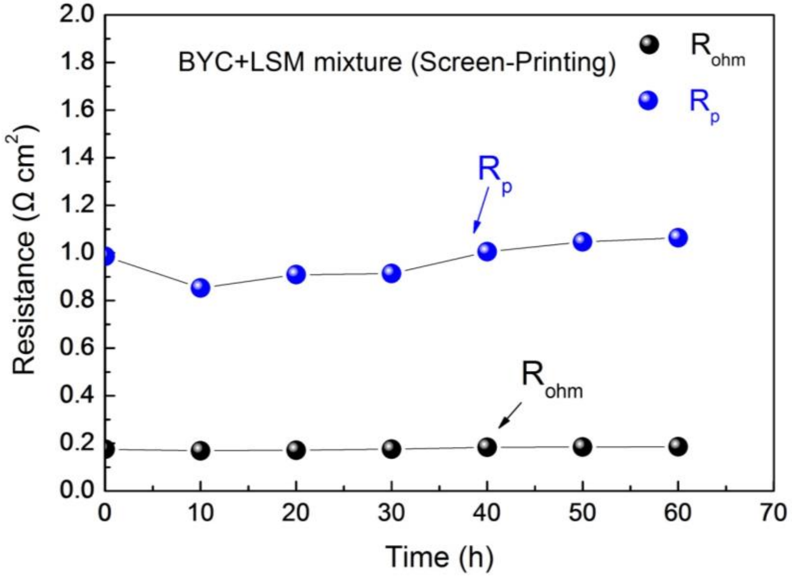
Button Cell Stability Tested at USC

Screen Printed vs. Infiltrated







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SOEC Testing Capability at PNNL: Button Cells

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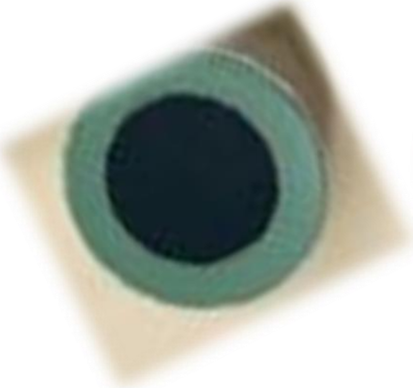
1-16 cm^2 active area



Pressurized (1- 8 bar) SOEC testing rig

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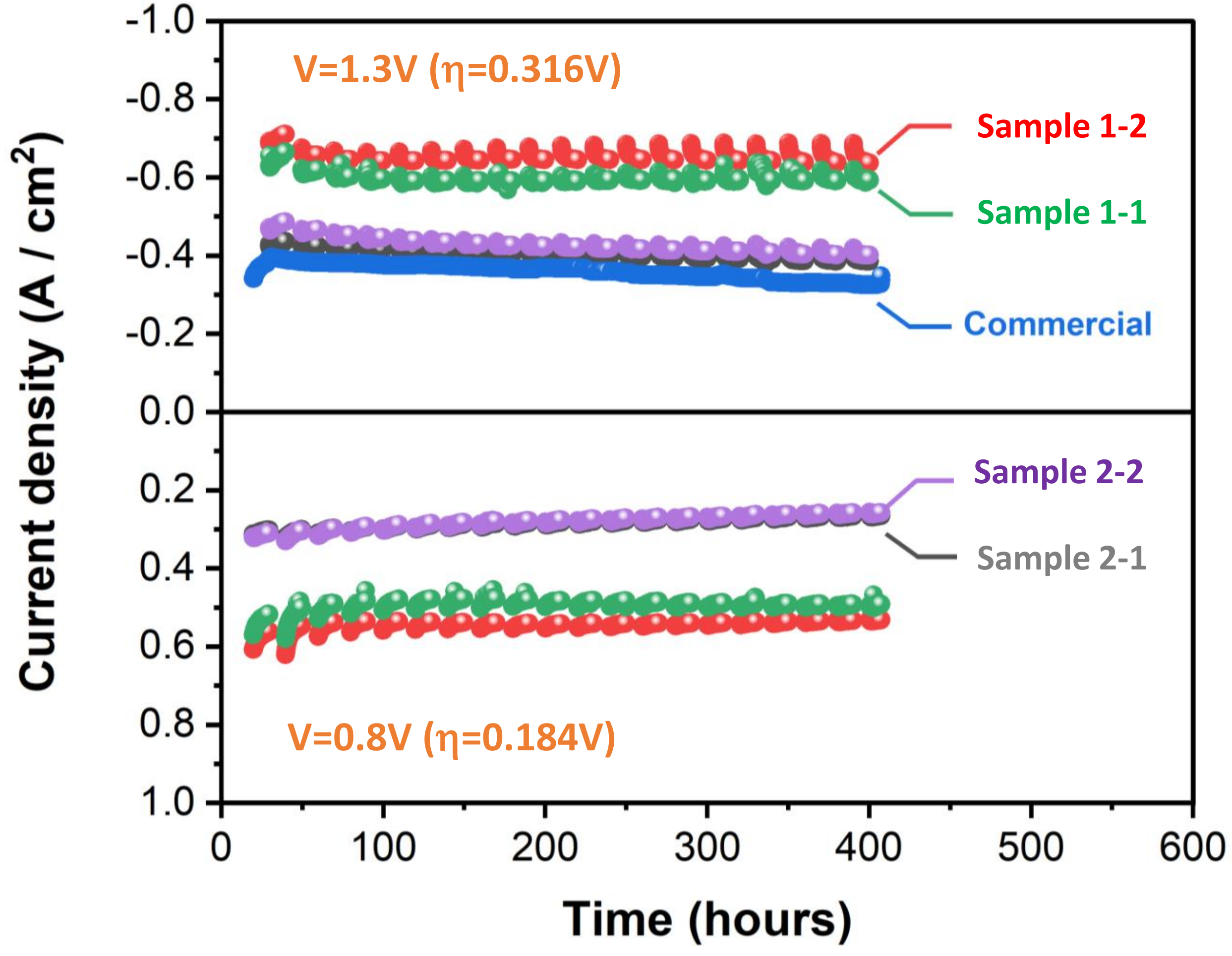
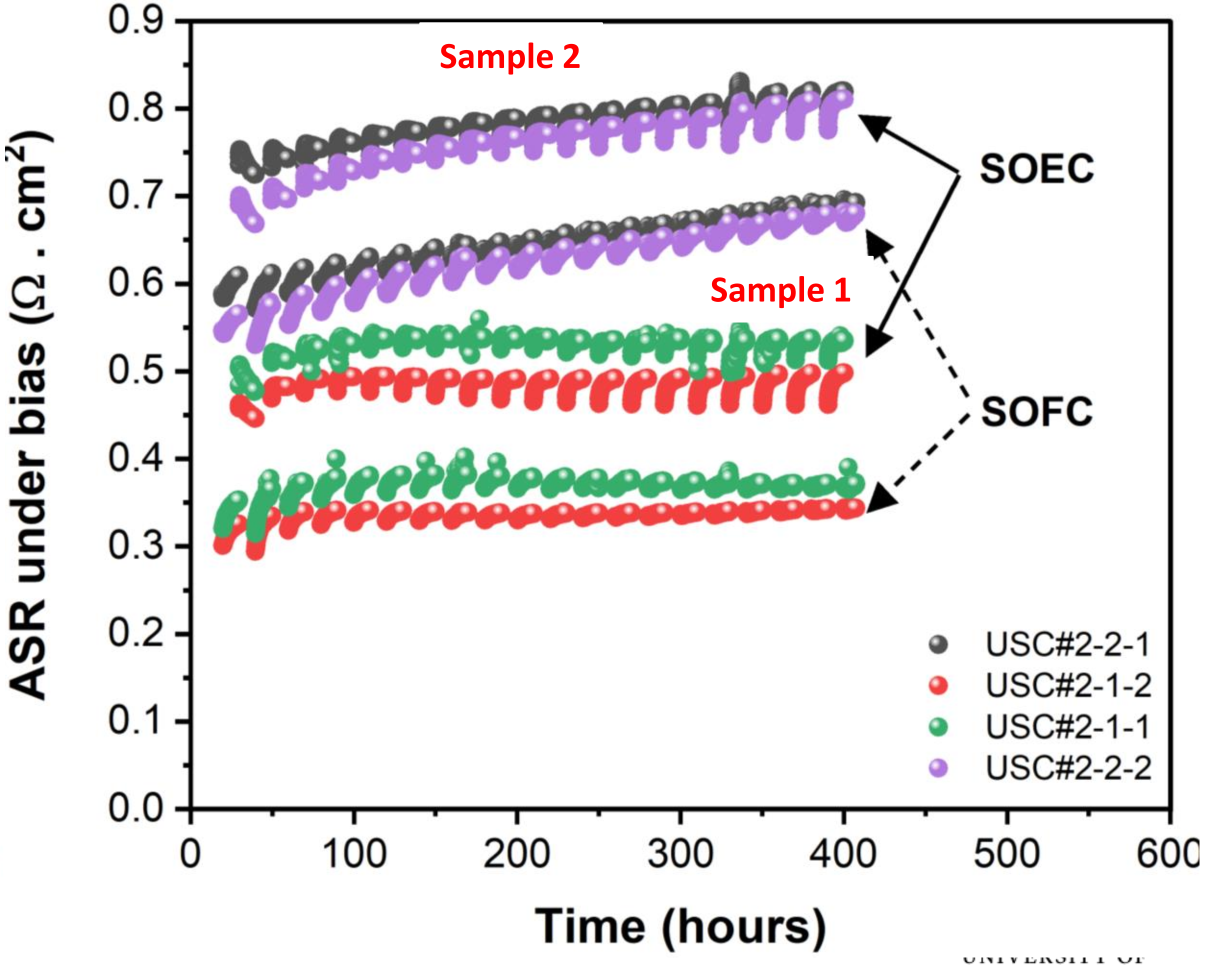
SOEC Performance Tested at PNNL

Samples: Smaple-1: IL BYC-25wt%LSM; Sample-2: SP BYC-LSM (50:50 wt%)
Testing conditions: SOFC, 10 hours at 0.8V, SOEC, 10 hours at 1.3V, 650^{o}C





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SOEC Performance Tested at PNNL

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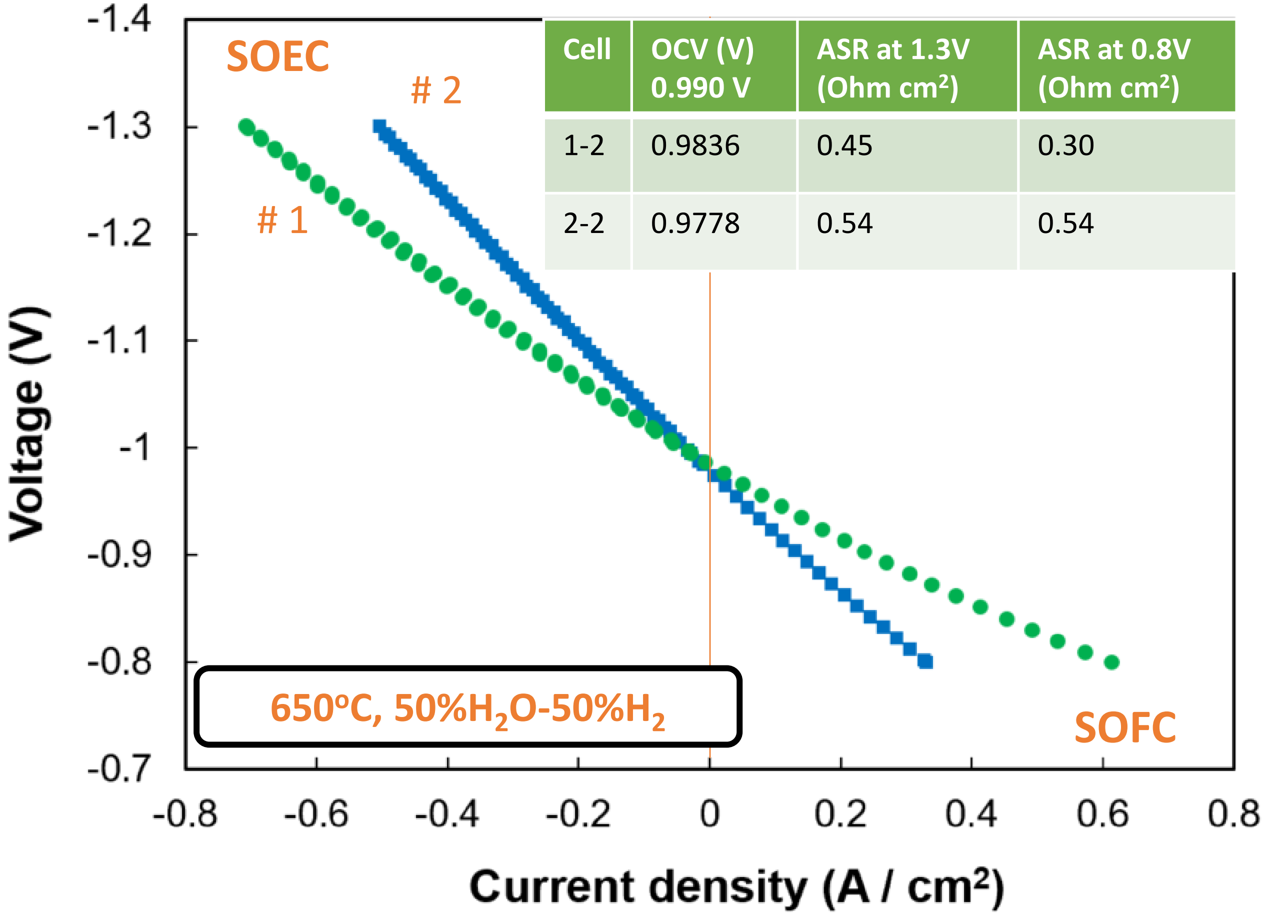
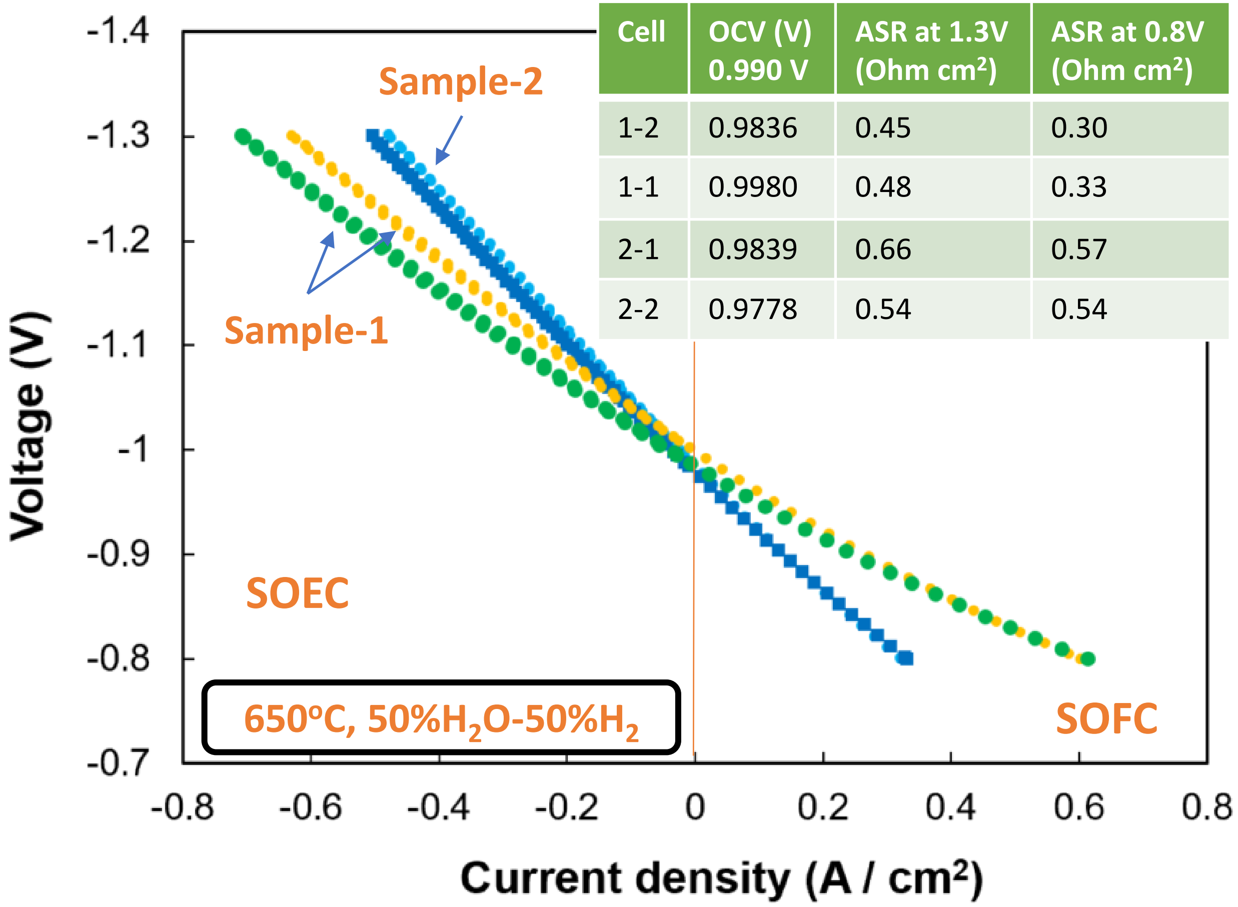


Cell	OCV (V) 0.990 V	ASR at 1.3V (Ohm cm²)	ASR at 0.8V (Ohm cm²)
1-2	0.9836	0.45	0.30
2-2	0.9778	0.54	0.54



Cell	OCV (V) 0.990 V	ASR at 1.3V (Ohm cm²)	ASR at 0.8V (Ohm cm²)
1-2	0.9836	0.45	0.30
1-1	0.9980	0.48	0.33
2-1	0.9839	0.66	0.57
2-2	0.9778	0.54	0.54

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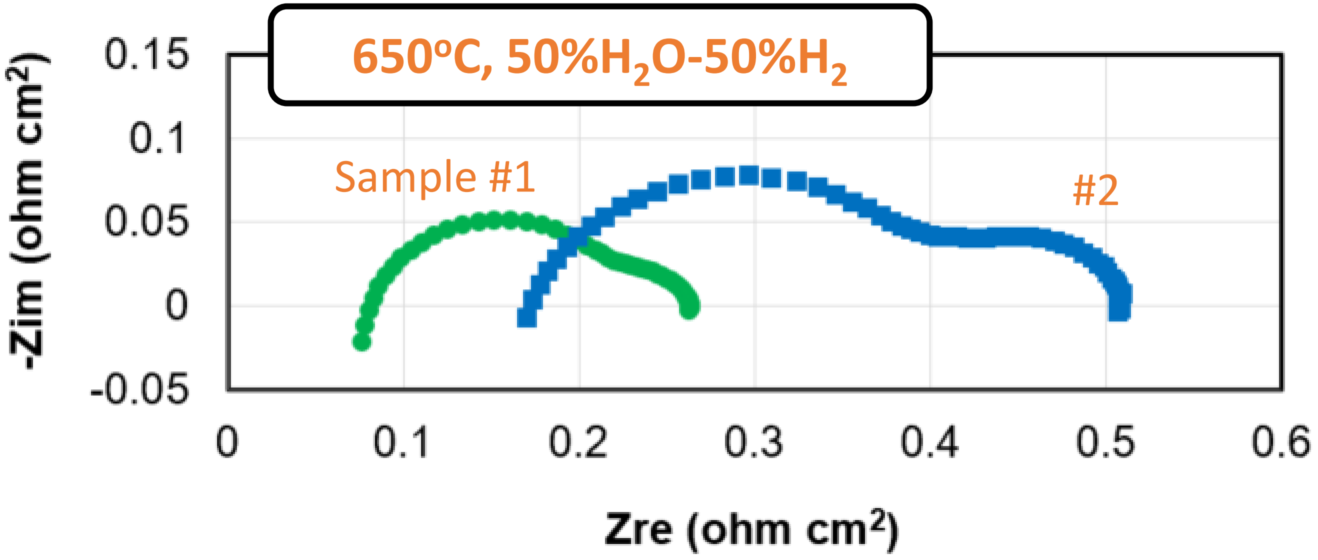
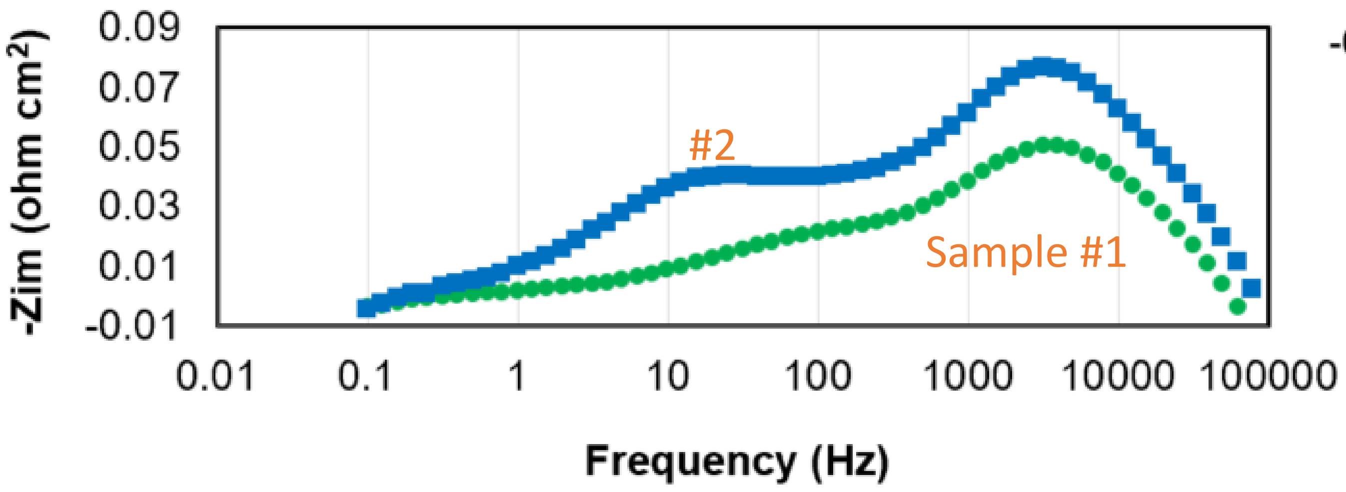
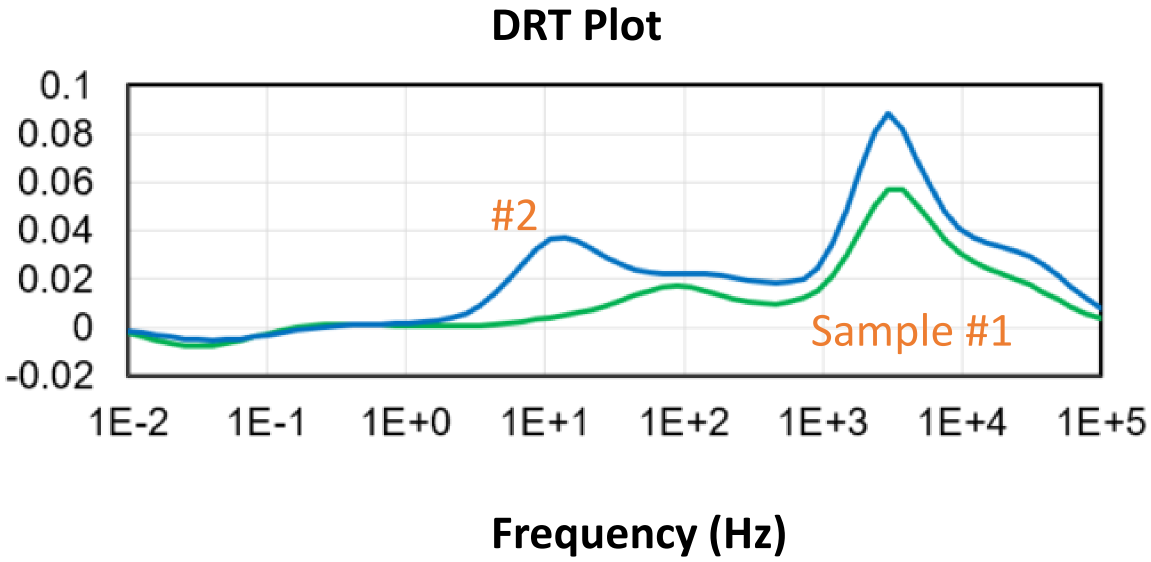
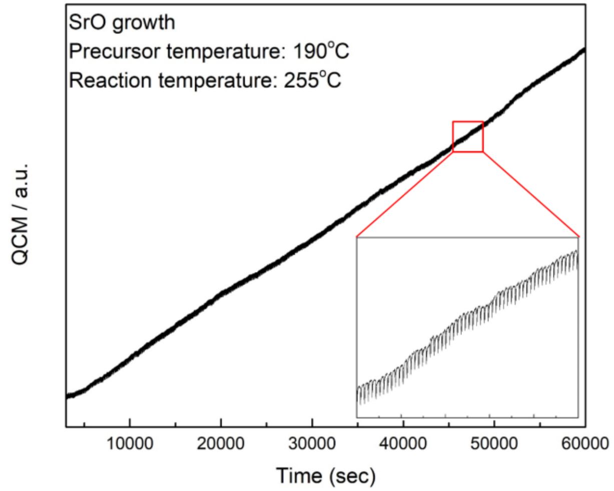
SOEC Performance Testing at PNNL: EIS



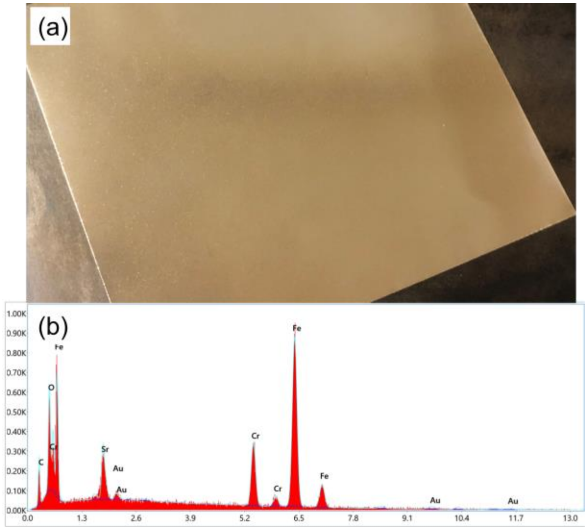




Development of ALD-SCT ($SrCo_{0.9}Ta_{0.1}O_{3-\delta}$)



QCM plot of 1000 cycles of SrO deposition



Growth rates and required cycles

Target Species Molar Ratio	Growth rate (nm/cycle)	Cycles needed in a super cycle	Growth in a super cycle (nm)
Sr(1)	0.014	15	0.21
Co(0.9)	0.020	10	0.2
Ta (0.1)	0.030	1	0.03

We have a poster on ALD-SCT on Wednesday night. Please stop by for details.

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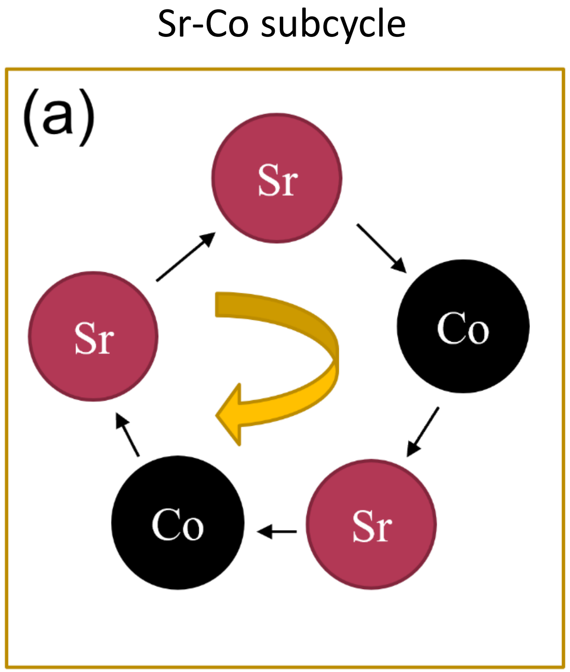
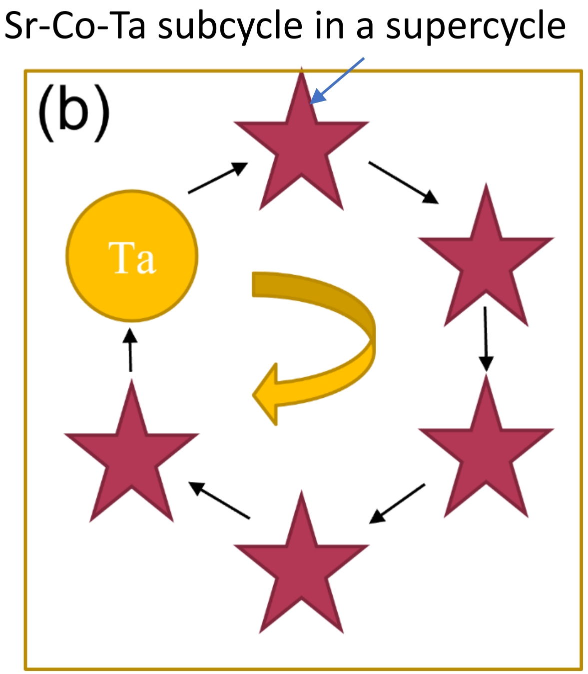
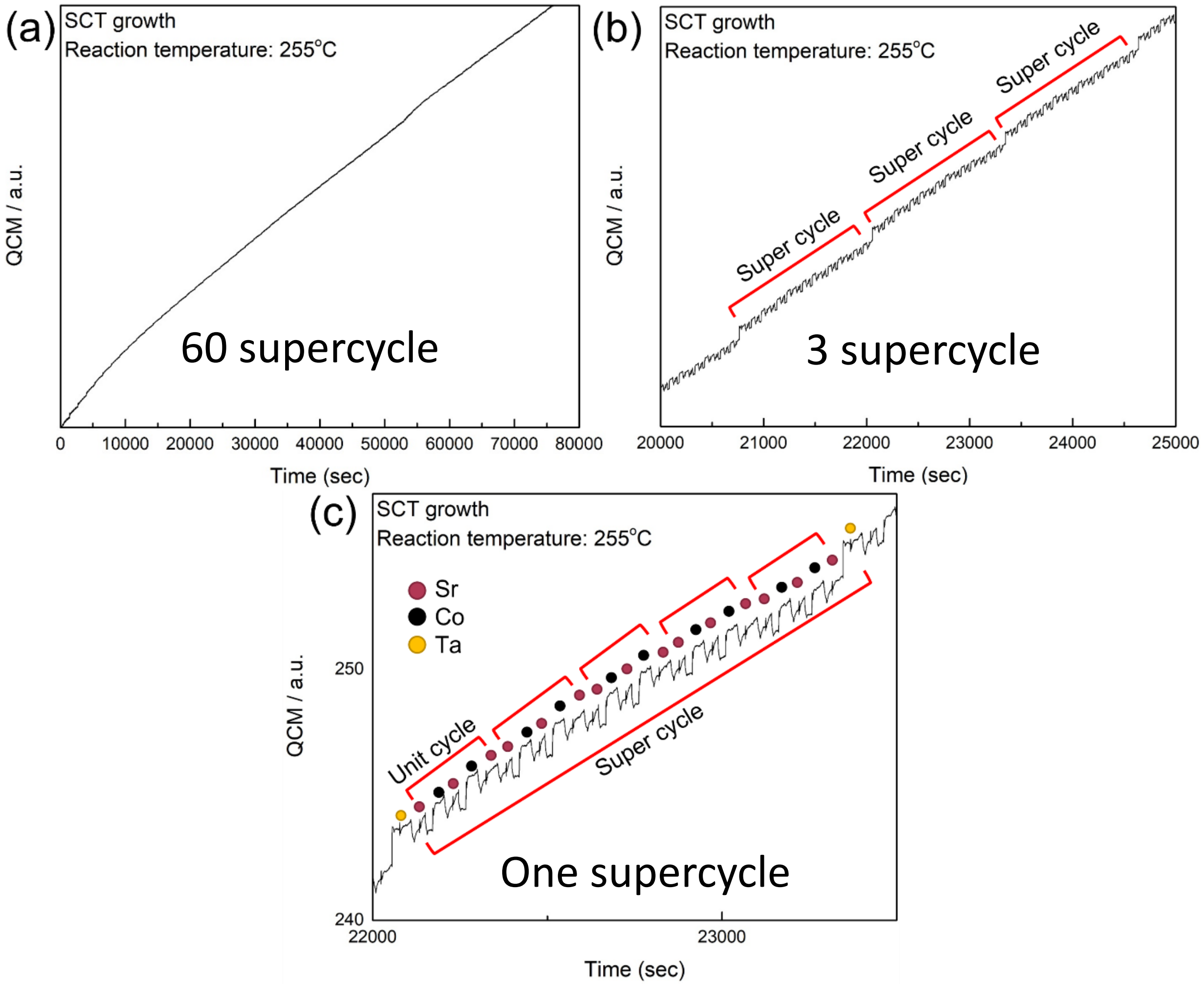
SCT Supercycles







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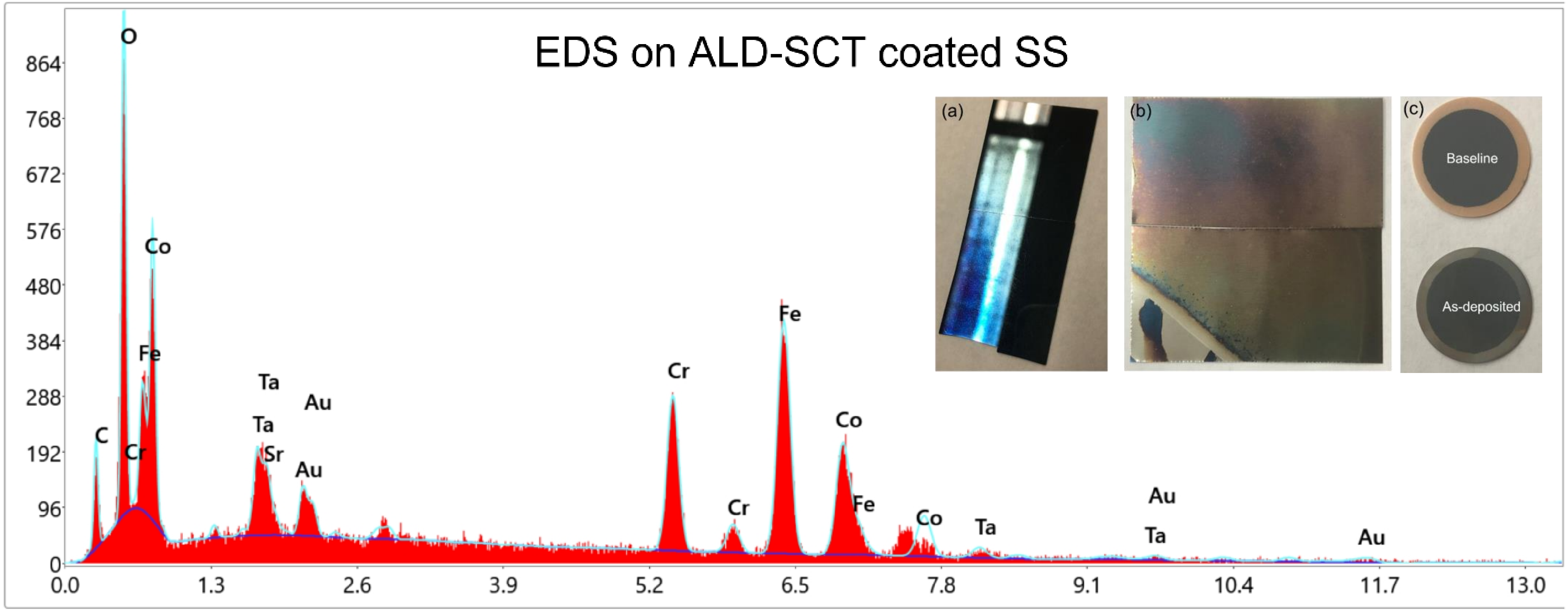
Run#1: 60 Supercycles (15 Sr, 10 Co and 1 Ta Single Cycle)



Det: Octane Elect Super

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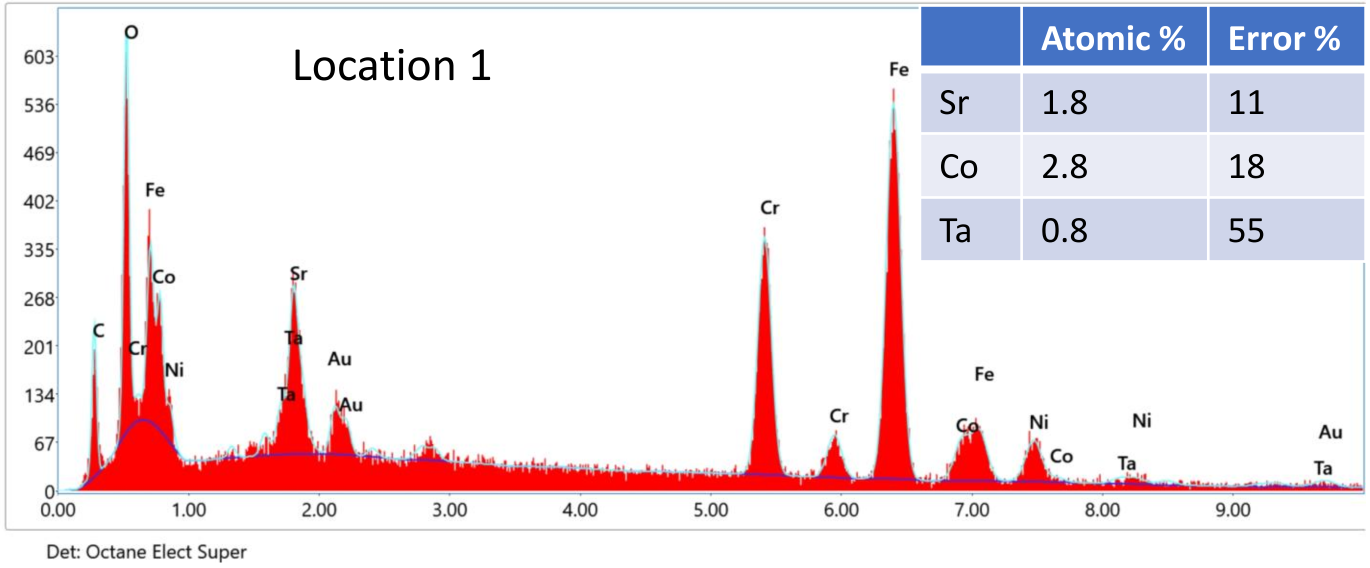
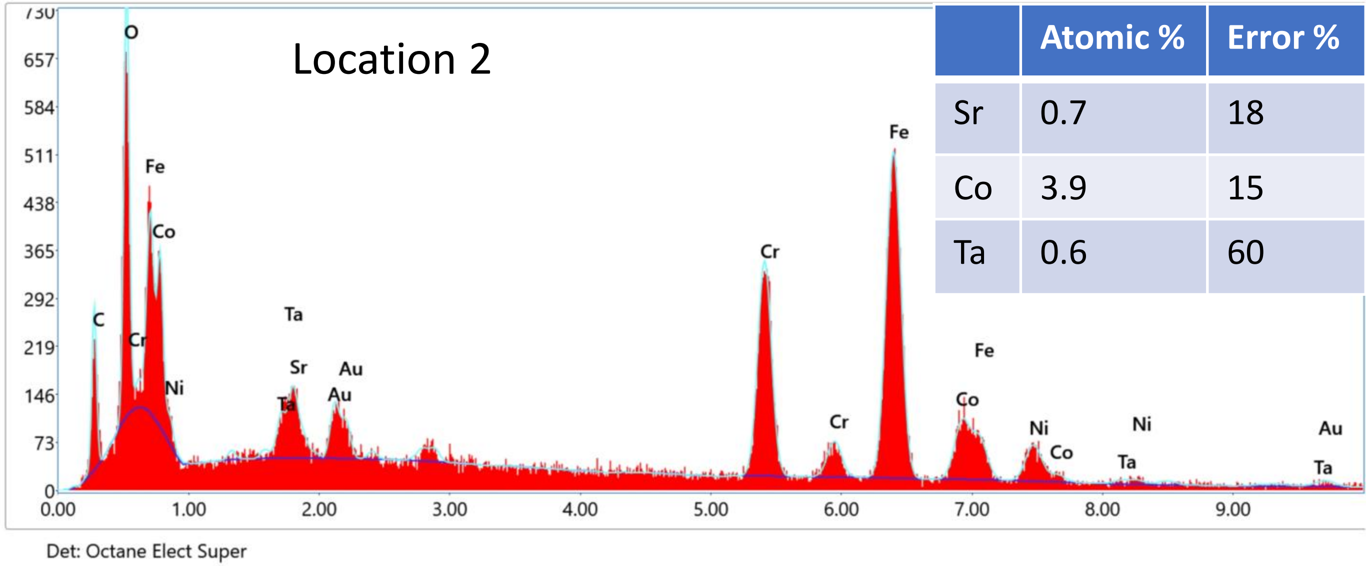
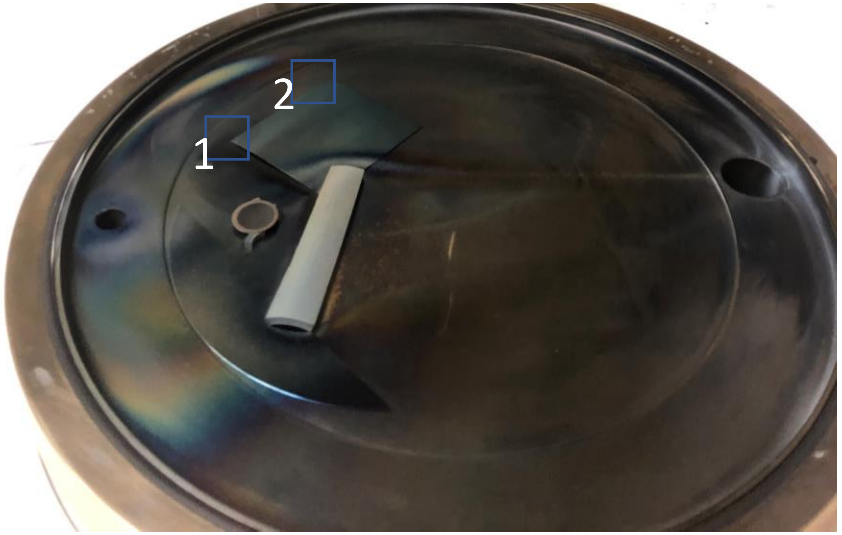
Run#2: 30 Sr, 10 Co, 1 Ta (40 Super Cycle)



	Atomic %	Error %
Sr	1.8	11
Co	2.8	18
Ta	0.8	55



	Atomic %	Error %
Sr	0.7	18
Co	3.9	15
Ta	0.6	60



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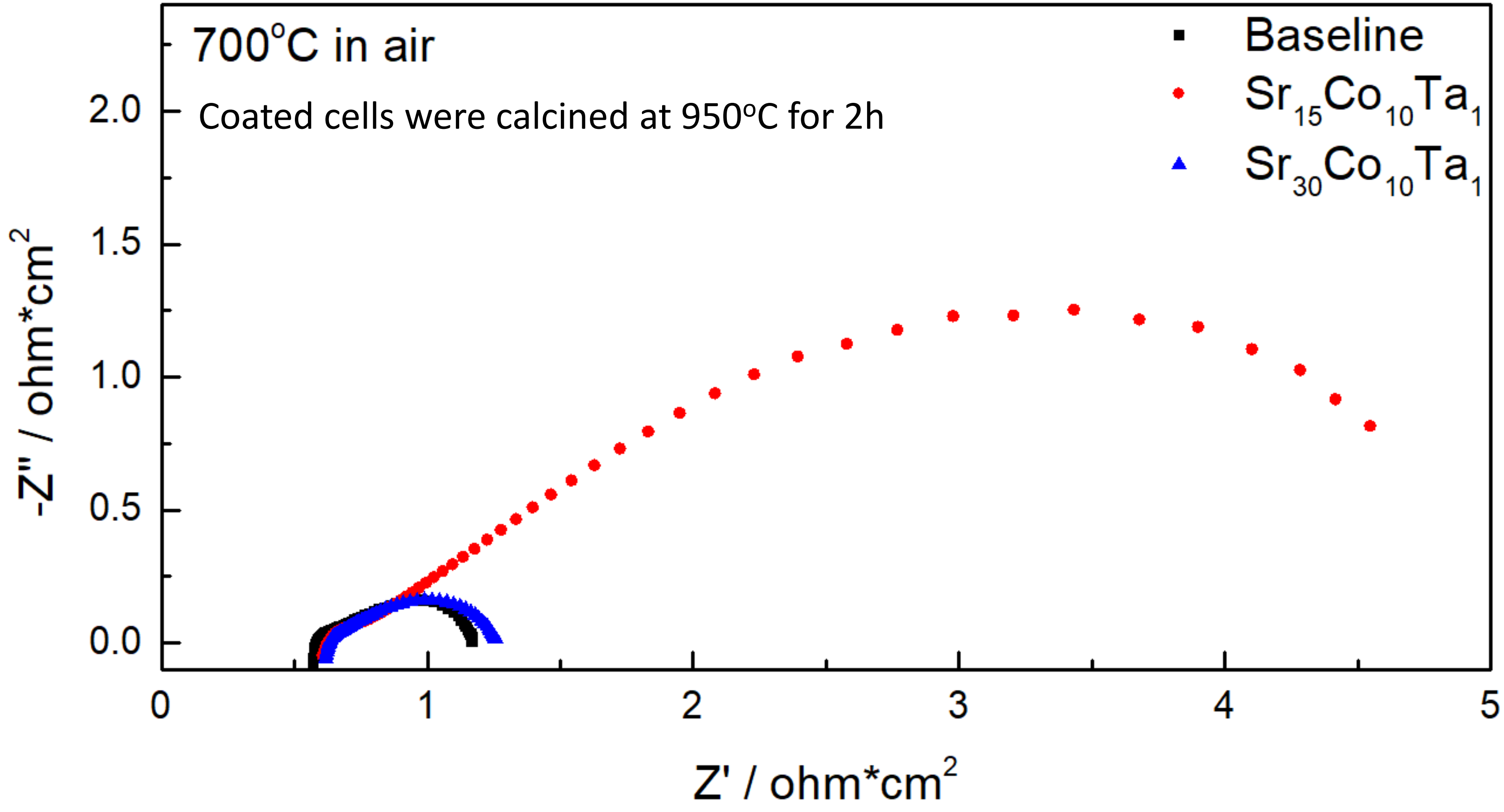
Comparison of EIS Spectra



60 super cycle

40 super cycle

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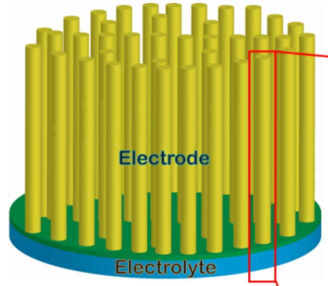
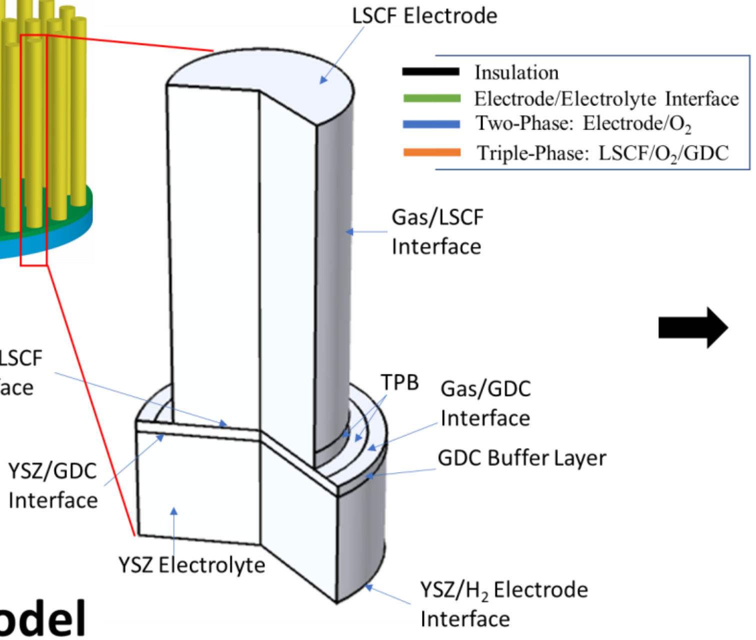
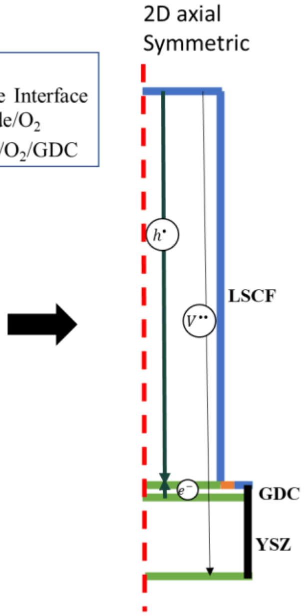
Electrochemical-Chemical Modeling





New Updates
- Validation
- Parametric study
  - Single Layer
  - Bilayer

Microscale Model



OE - LSCF

$$-\nabla\left(D_{V,LSCF}\nabla c_{V,LSCF}\right)=0$$

Buffer layer GDC

$$\nabla\left(-D_{V,GDC}\left(\nabla c_{V,GDC}+\frac{Z_vF}{RT}c_{V,GDC}\nabla\phi\right)\right)=0$$

$$\nabla\left(-D_{e,GDC}\left(\nabla c_{e,GDC}+\frac{Z_eF}{RT}c_{e,GDC}\nabla\phi\right)\right)=0$$

$$Z_vc_v+Z_ec_e+Z_bc_b=0$$

EL - YSZ

$$-\nabla\left(\sigma_{ysz}\nabla\phi_i\right)=0$$

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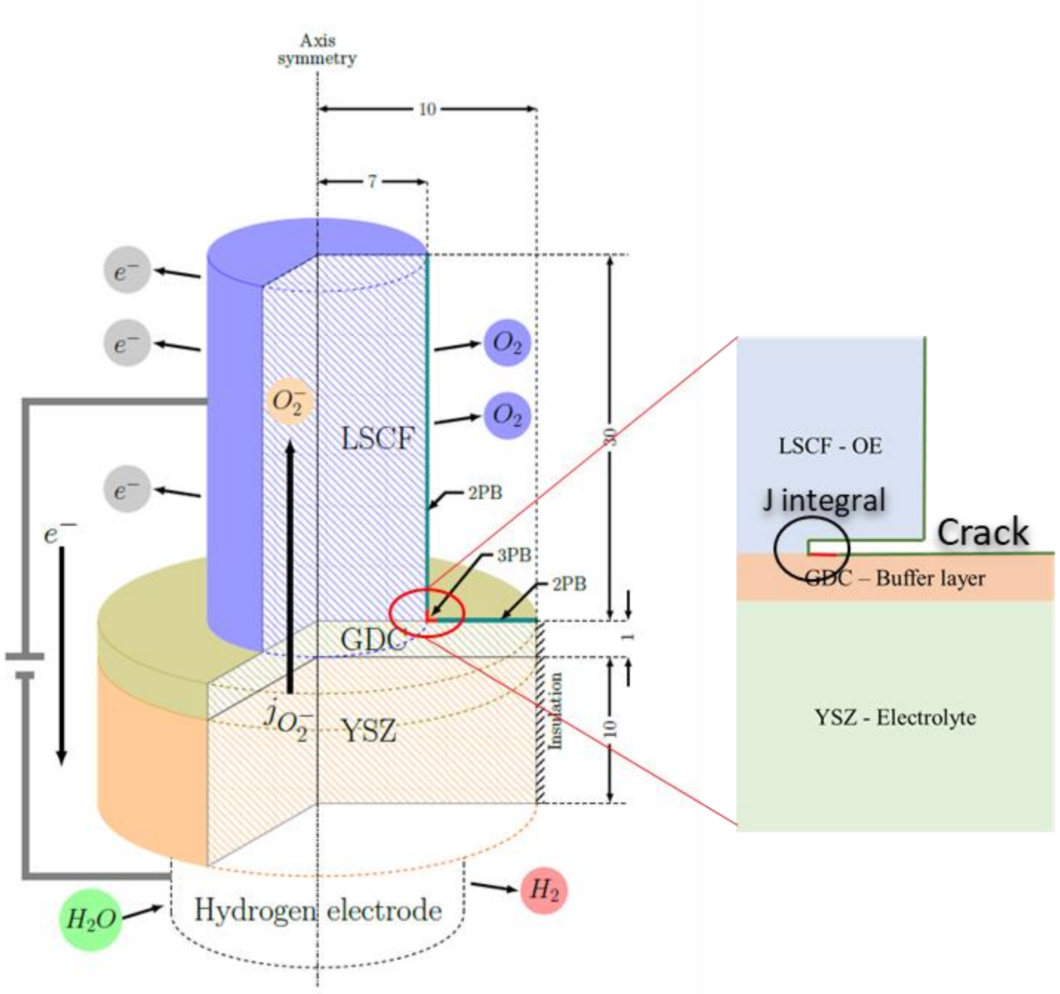
Fracture Mechanics Model



J-integral

$$J = \int_{\Gamma} W dz - \mathbf{T}\frac{\partial \mathbf{u}}{\partial r} ds + \iint_{A} \boldsymbol{\sigma}\frac{\partial \boldsymbol{\varepsilon}^{\mathbf{T}}}{\partial r} dA$$

$$= \left(\int_{\Gamma} W n_r - \sum T_i \frac{\partial u_i}{\partial r} \right) ds + \iint_{A} \sum \sigma_{ij} \frac{\partial \varepsilon_{ij}^{C}}{\partial r} dA$$

$$W = \frac{1}{2}\left(\sigma_r \cdot \varepsilon_r + \sigma_z \cdot \varepsilon_z + \sigma_\phi \cdot \varepsilon_\phi + \sigma_{rz} \cdot 2\varepsilon_{rz}\right)$$

$$T_i \frac{\partial u_i}{\partial r} = \begin{bmatrix} \sigma_r \cdot n_r + \sigma_{rz} \cdot n_z \\ \sigma_{rz} \cdot n_r + \sigma_z \cdot n_z \end{bmatrix} \begin{bmatrix} \frac{\partial u_r}{\partial r} & \frac{\partial u_z}{\partial r} \end{bmatrix}$$

$$\sigma_{ij}\frac{\partial \varepsilon_{ij}^{C}}{\partial r} = \sigma_r \frac{\partial \varepsilon_r^{C}}{\partial r} + \sigma_z \frac{\partial \varepsilon_z^{C}}{\partial r} + \sigma_\phi \frac{\partial \varepsilon_\phi^{C}}{\partial r}$$

Stress intensity factor K_I

$$J = \frac{K_I^2}{E/\left(1-\nu^2\right)}$$

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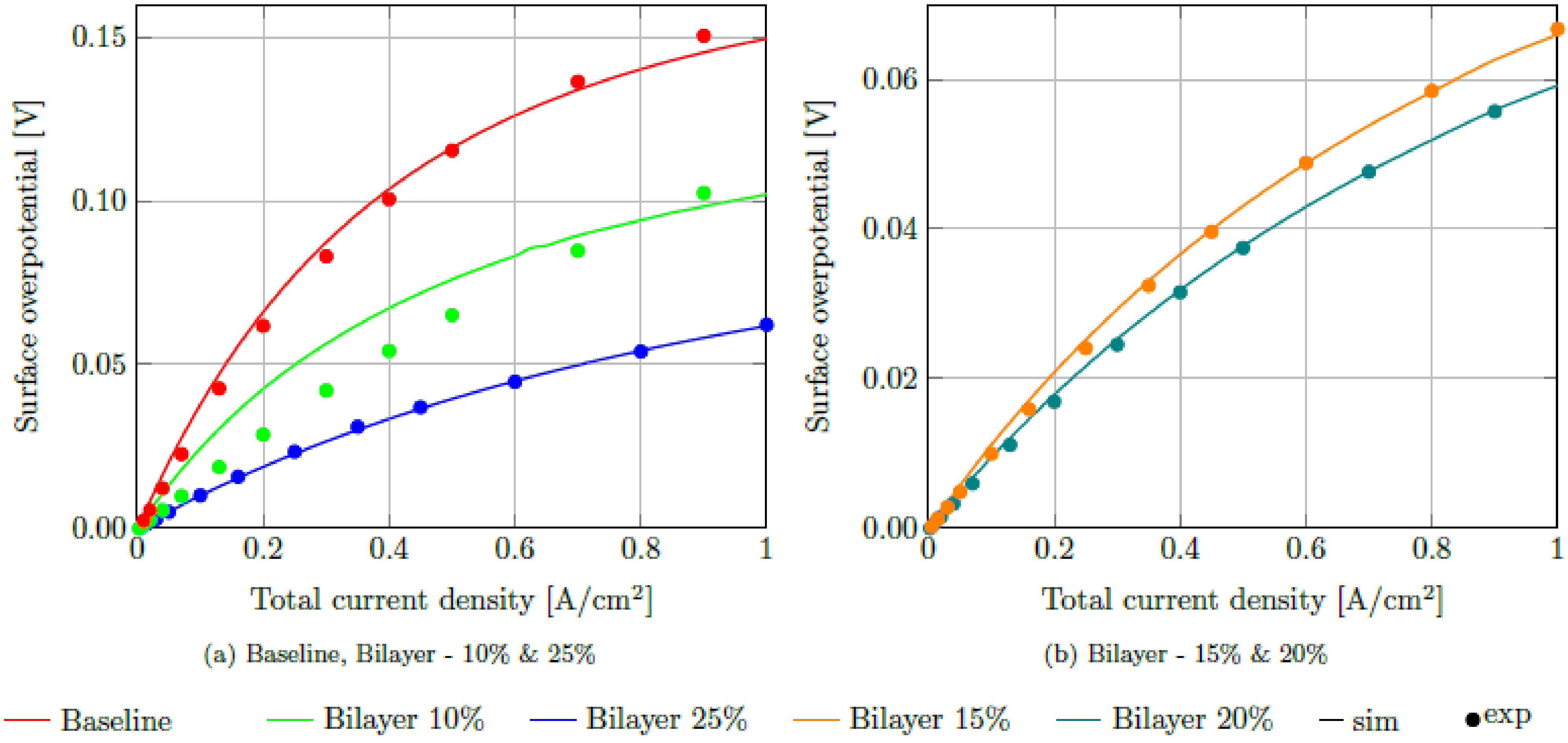
η vs. J: Experimental vs. Modeling



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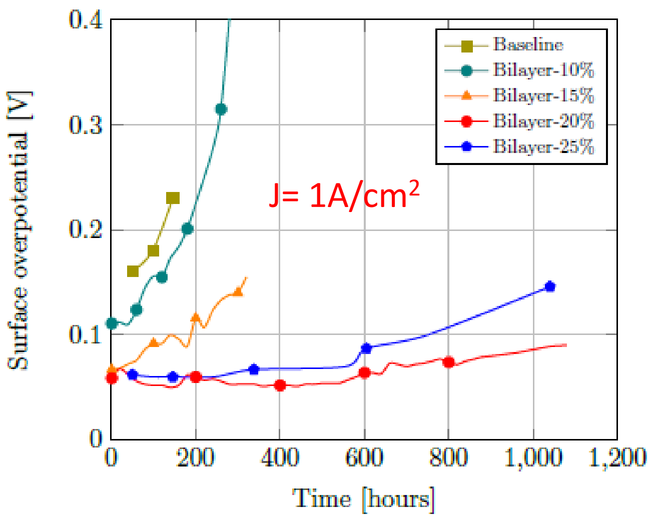
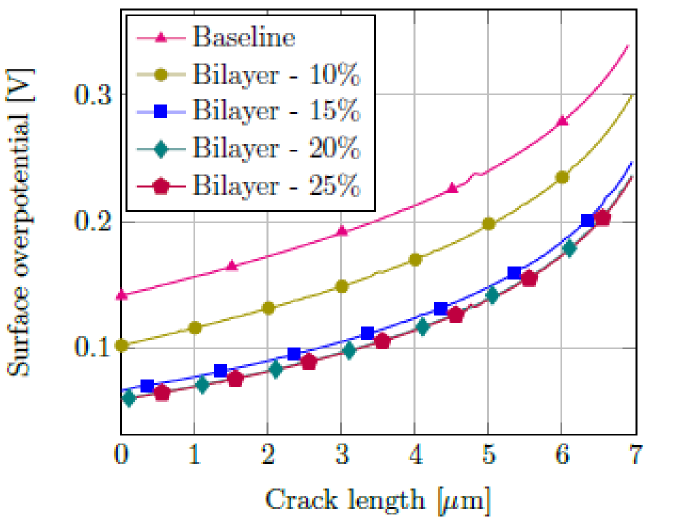
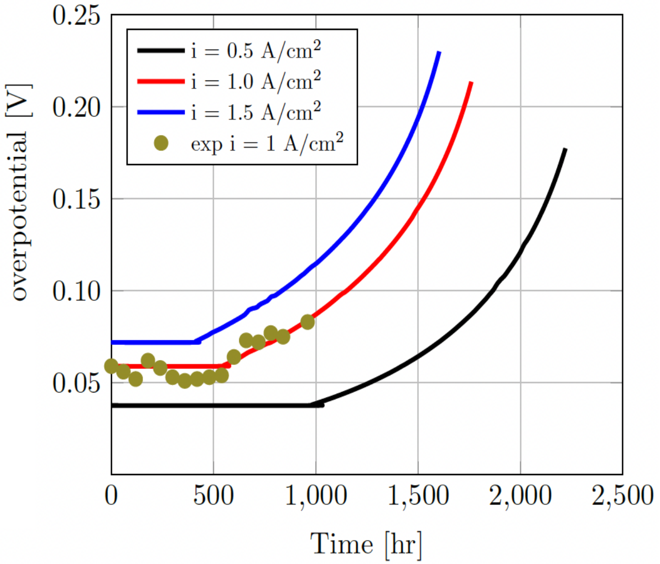
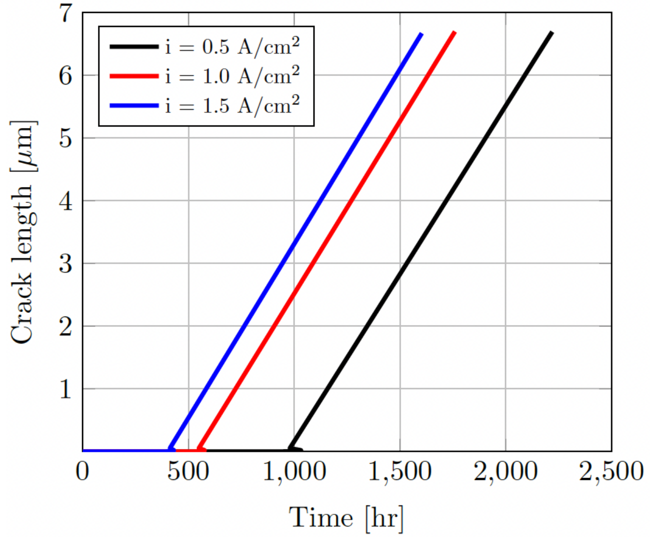
η vs. Time and Crack Length





Model Projection





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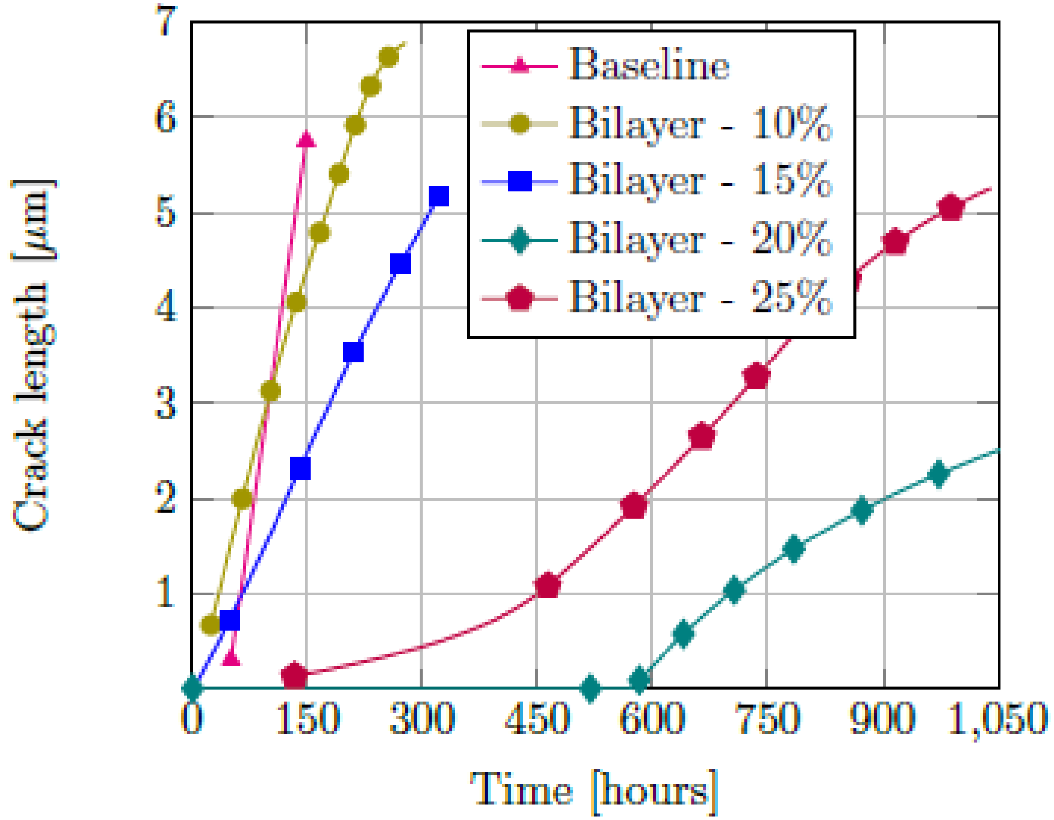
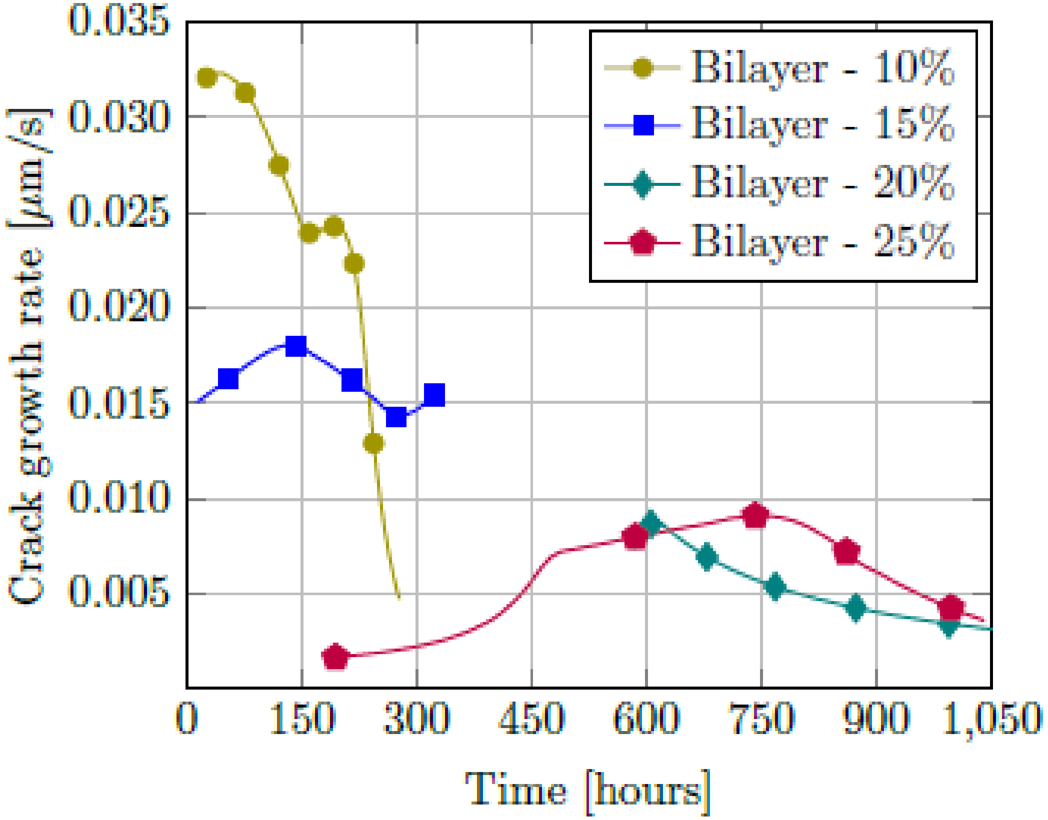
Crack Length and Crack Rate Under J=1 A/cm^2



(c) ıck length vs time



Crack growth rate

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Summary

- Achieved R_p= 0.1 $\Omega \cdot cm^2$ at 650^{o}C for BYC-LSM barrier layer free OE
- Demonstrated the improved stability under bidirectional operation for BYC-LSM OE in half cells.
- Independently confirmed good full cell performance under bidirectional operation for BYC-LSM-based SOCs at PNNL
- Developed one ALD recipe for SCT supercycle.
- Developed an OE delamination model encompassing coupled electrochemical, chemical and mechanical submodels.

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Currently

- Continue independent button cell testing (both ambient and pressurized) at PNNL.
- Continue optimizing ALD supercycle recipe.
- Continue developing OE delamination model with more experimental calibrations.
- Making 15 cm^2 planar cells with BLF OE for testing at PNNL.

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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	50%	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	70%	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-FECM 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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