Developing Stable Critical Materials and Microstructure for High-Flux and Efficient H_2 Production through Reversible Solid Oxide Cells

DE-FE-0032111

University of South Carolina
Pacific Northwest National Lab

22nd Annual SOFC Project Review Meeting
November 16-18, 2021

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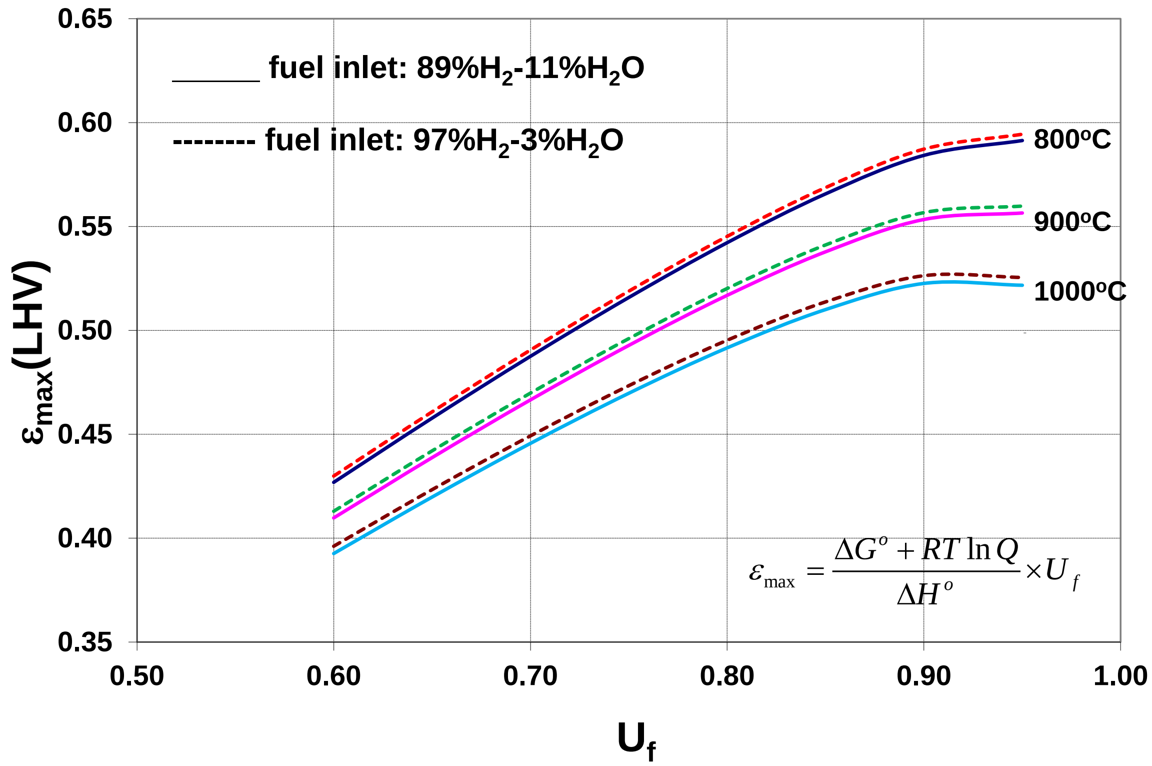
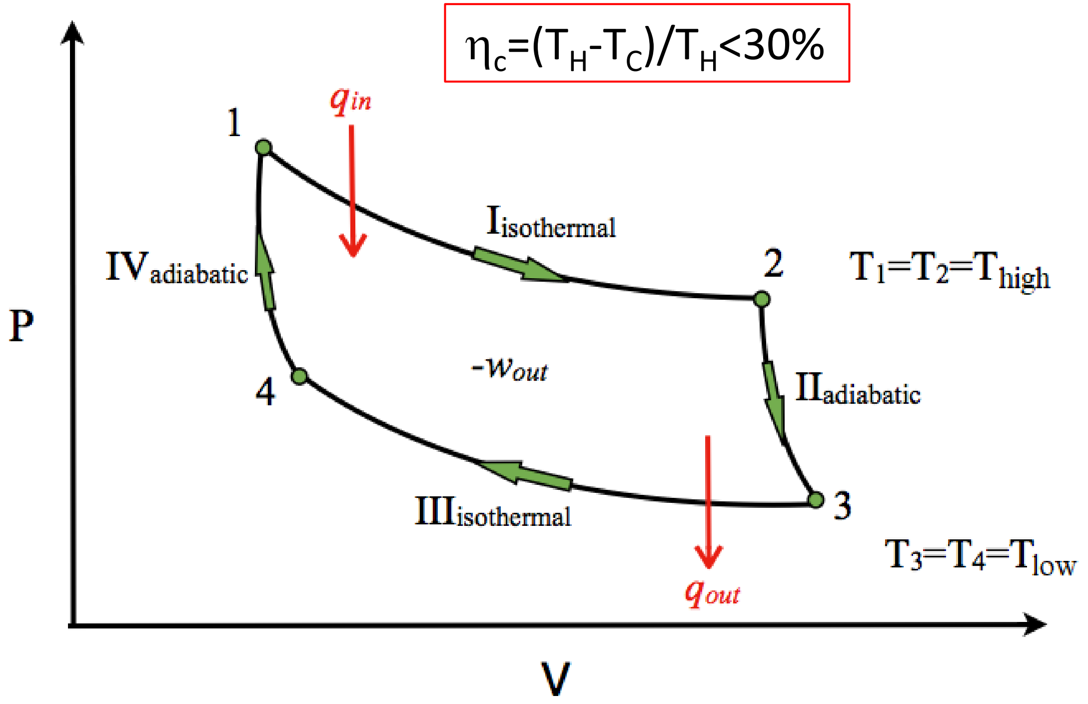
Outline

- Background
- Project Objectives
- Technical Approaches
- Project Schedule
- Milestones
- Success Criteria
- Risk Management

SOFC vs. ICE





SOFCs have lower emissions (CO_2, SO_x and NO_x), noise and maintenance than ICEs

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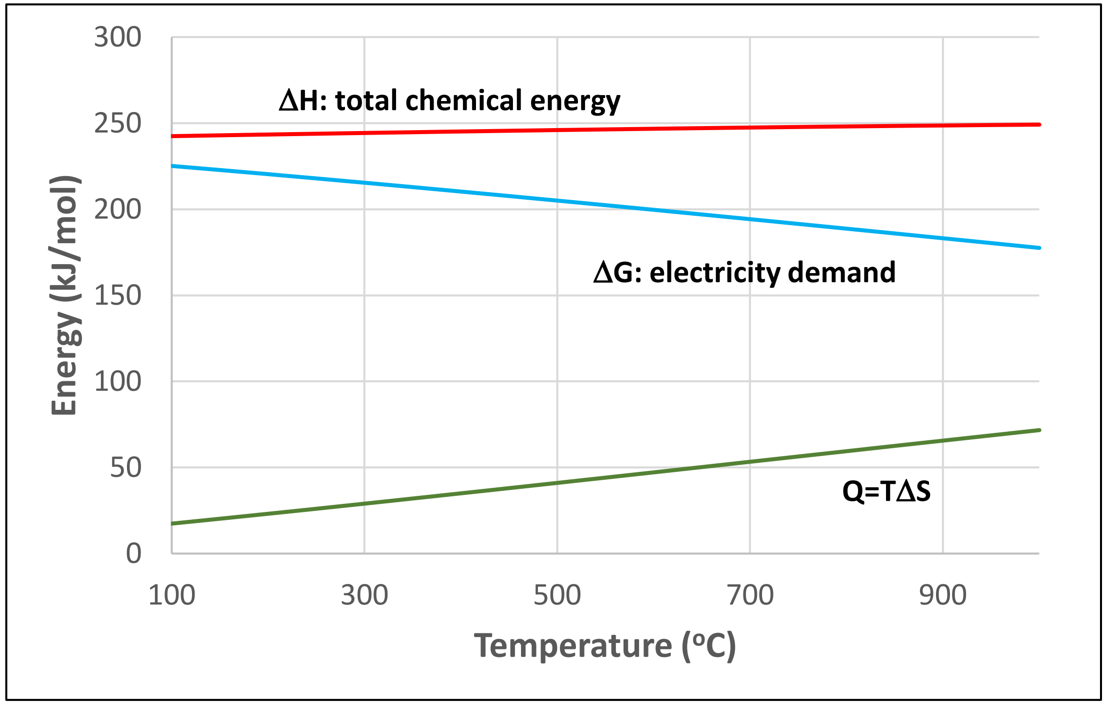
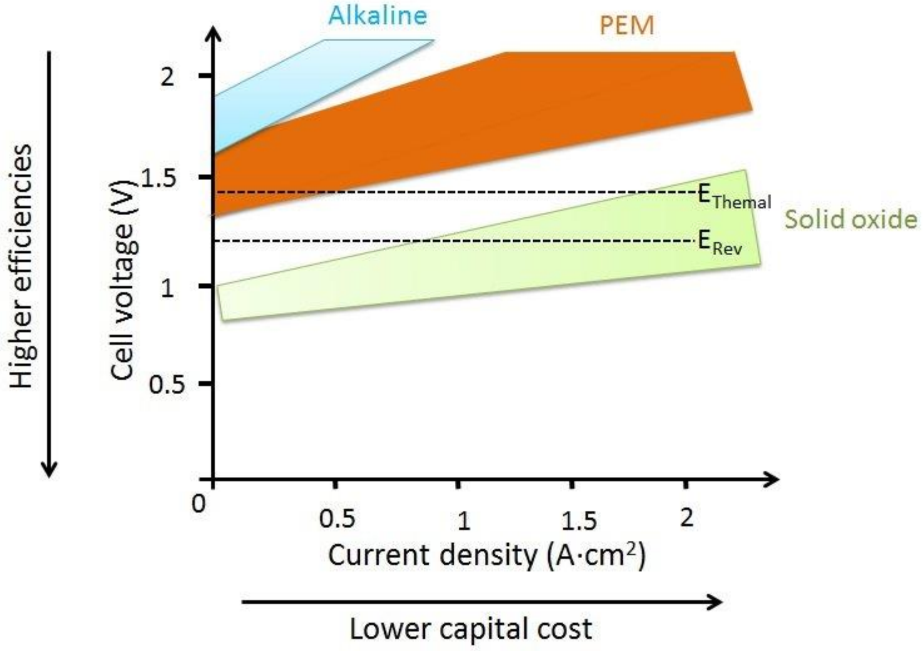
Thermodynamic Advantage of SOECs for H_2O Splitting

$$H_2 + \frac{1}{2}O_2 \underset{SOEC}{\overset{SOFC}{\rightleftarrows}} H_2O$$





Renewable Sustainable Energy Rev., 2011, 15,1–23

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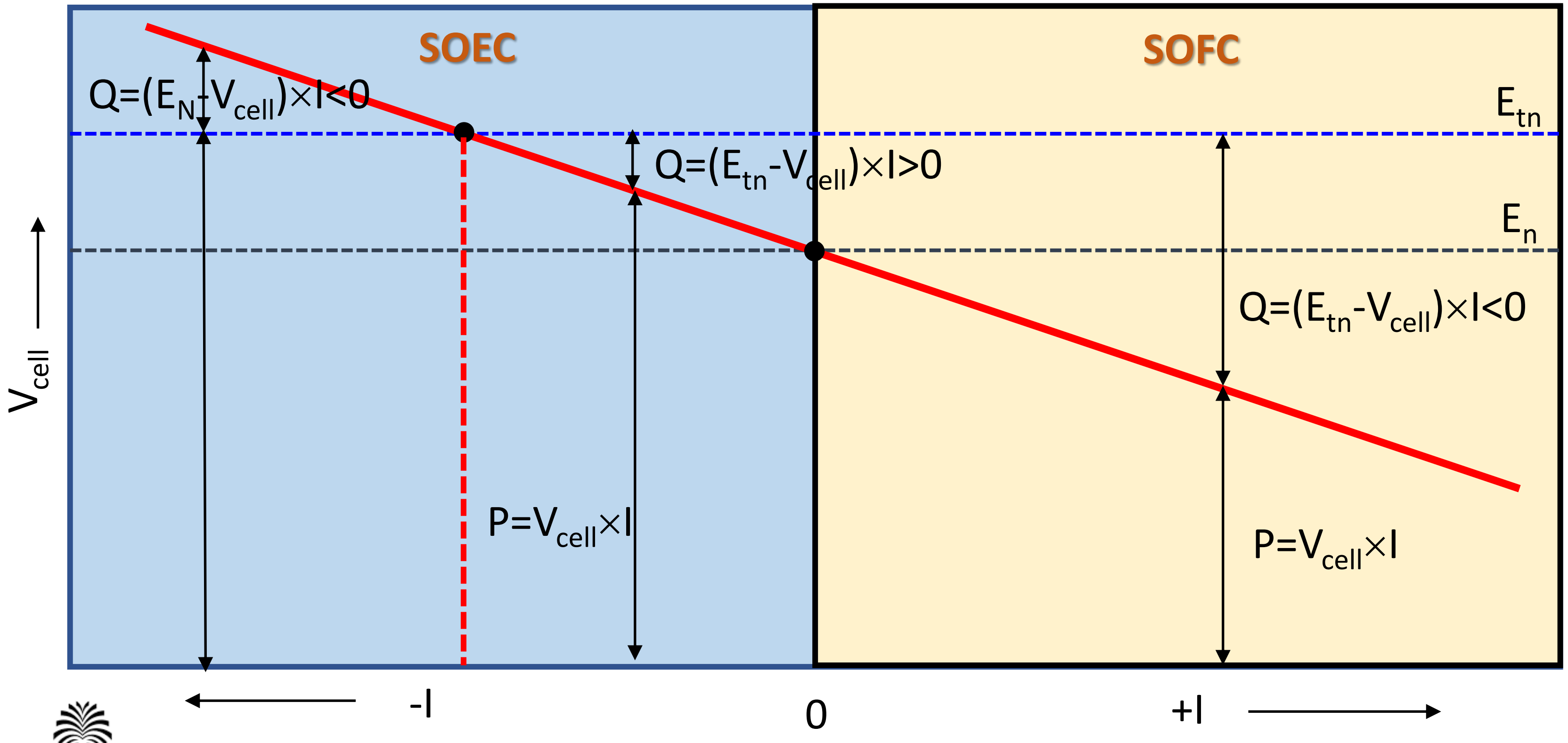

$$E_{tn} = -\frac{\Delta H_f(H_2O)}{2F} = 1.286V\ @\ 800^oC$$

$$E_n = -\frac{\Delta G_f(H_2O)}{2F} = 0.977V\ @\ 800^oC$$

$$\eta_{SOFC}(\max) = \frac{\Delta G_f(H_2O)}{\Delta H_f(H_2O)} = \frac{E_n}{E_{tn}} = 75.9\% \quad @V_{cell} = E_n$$

$$\eta_{SOEC}(\max) = \frac{\Delta H_f(H_2O)}{\Delta H_f(H_2O)} = 100\% \quad @V_{cell} = E_{tn}$$

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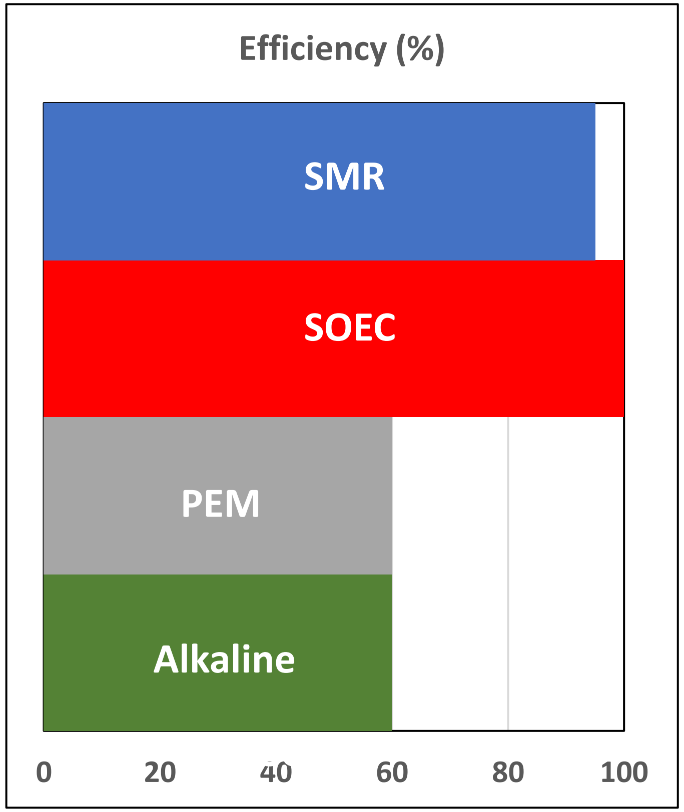
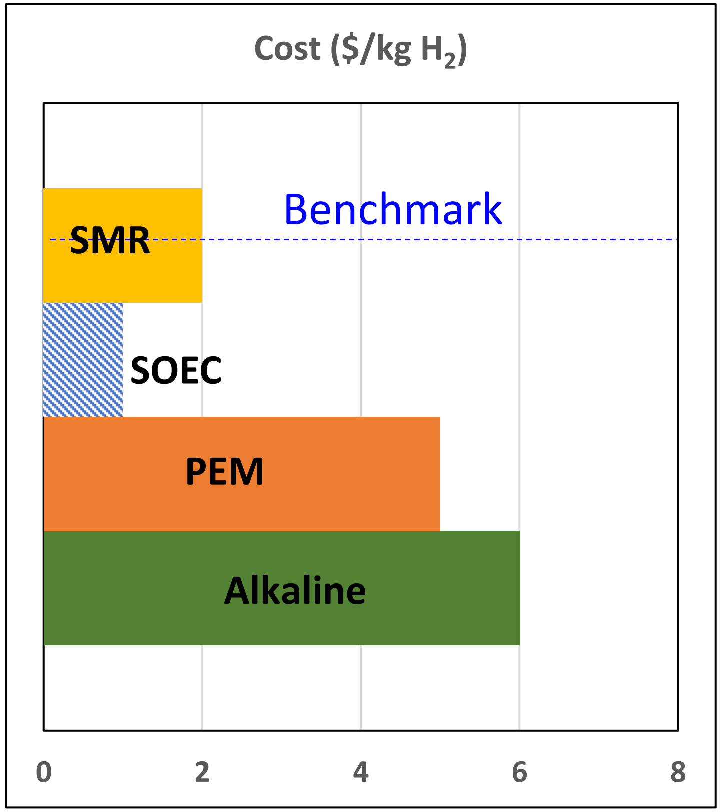
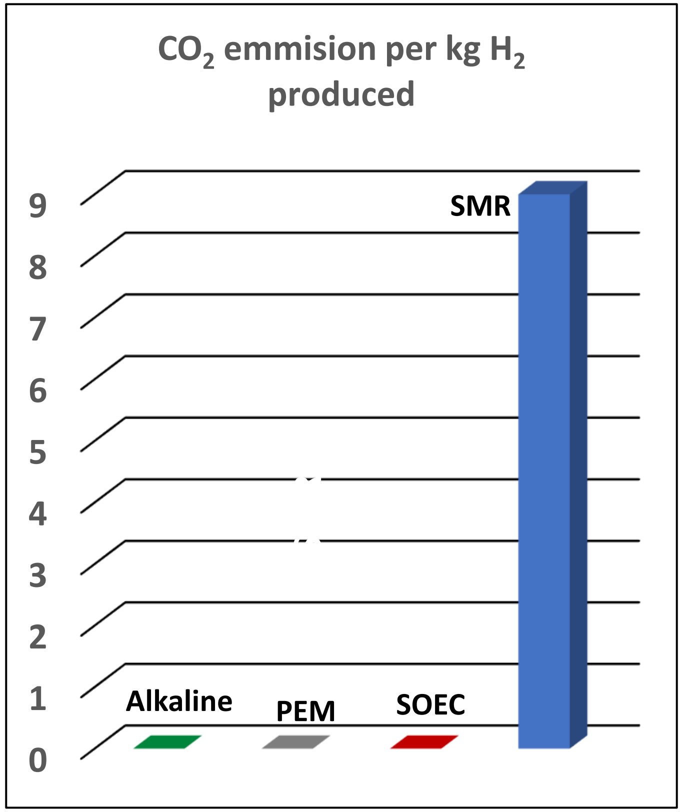
HT-SOECs vs. Alkaline vs. PEM Electrolyzers







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Barriers to SOCs Commercialization

- Cost: high costs in materials and manufacturing of cells, modules and systems
- Reliability: performance degradation in electrodes, electrolyte, interconnects and current collectors

High Priority Research in SOCs

- Reducing the operating temperature of SOCs from current 700-800^oC to 600-700^oC
  - Discovery of new high conductivity electrolytes (The Holy Grill)
  - Discovery of new highly active electrode materials
  - Nanostructuring existing electrodes
  - Shutting down impurity-related degradation mechanisms

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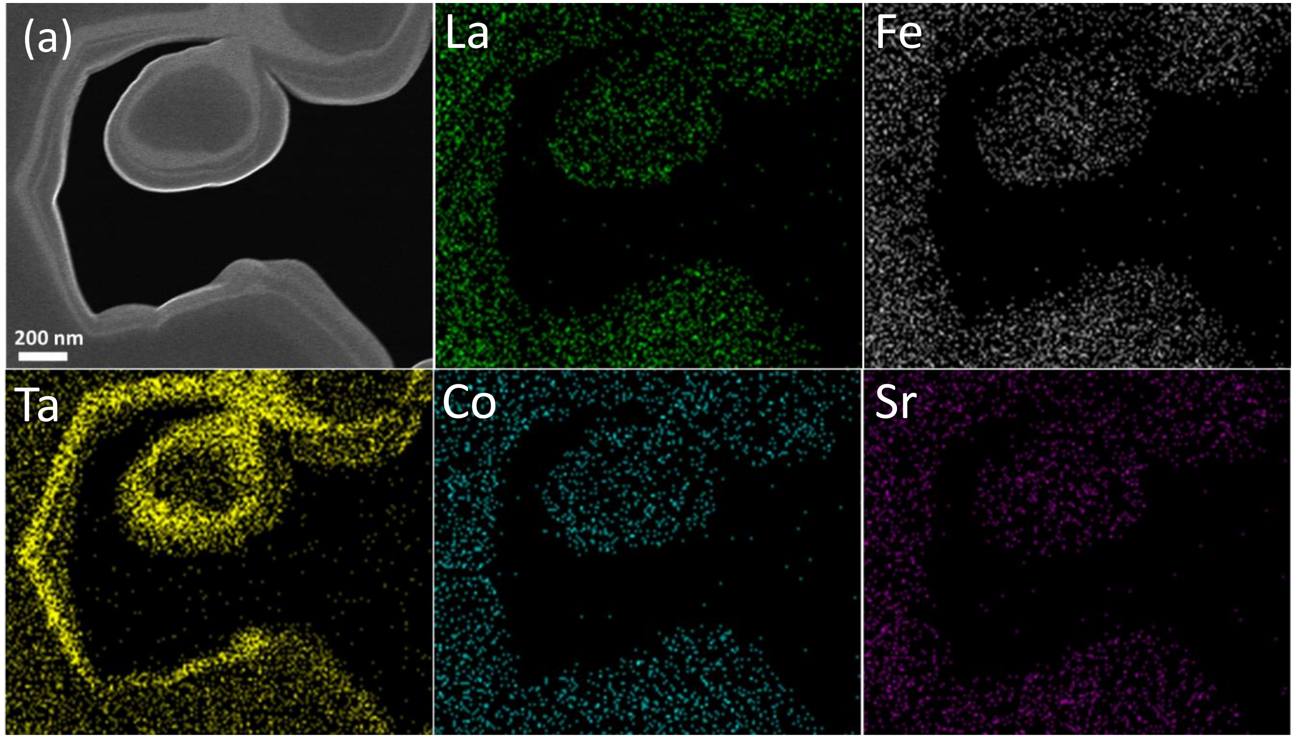
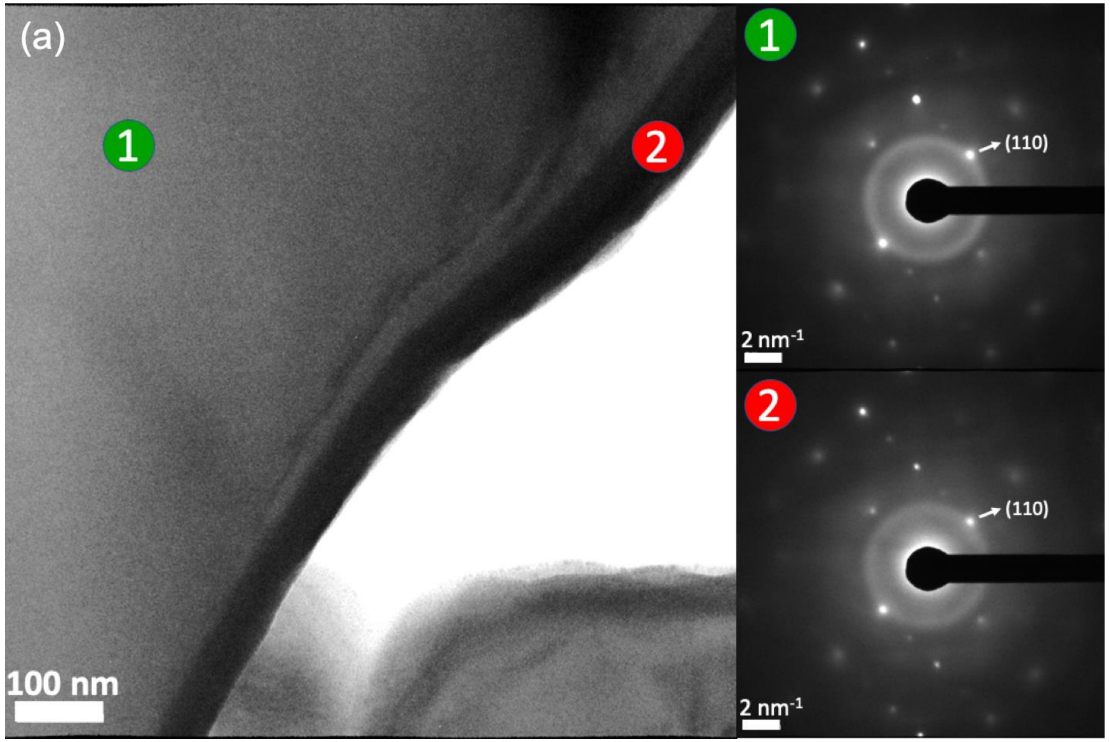
Early Work on Bilayer Oxygen Electrode (BLOE)

$SrCo_{0.9}Ta_{0.1}O_{3-\delta}$(SCT)@LSCF-GDC





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*Yang, and Huang, **J. Mater. Chem. A**, 2020, **8**, 82-86.*

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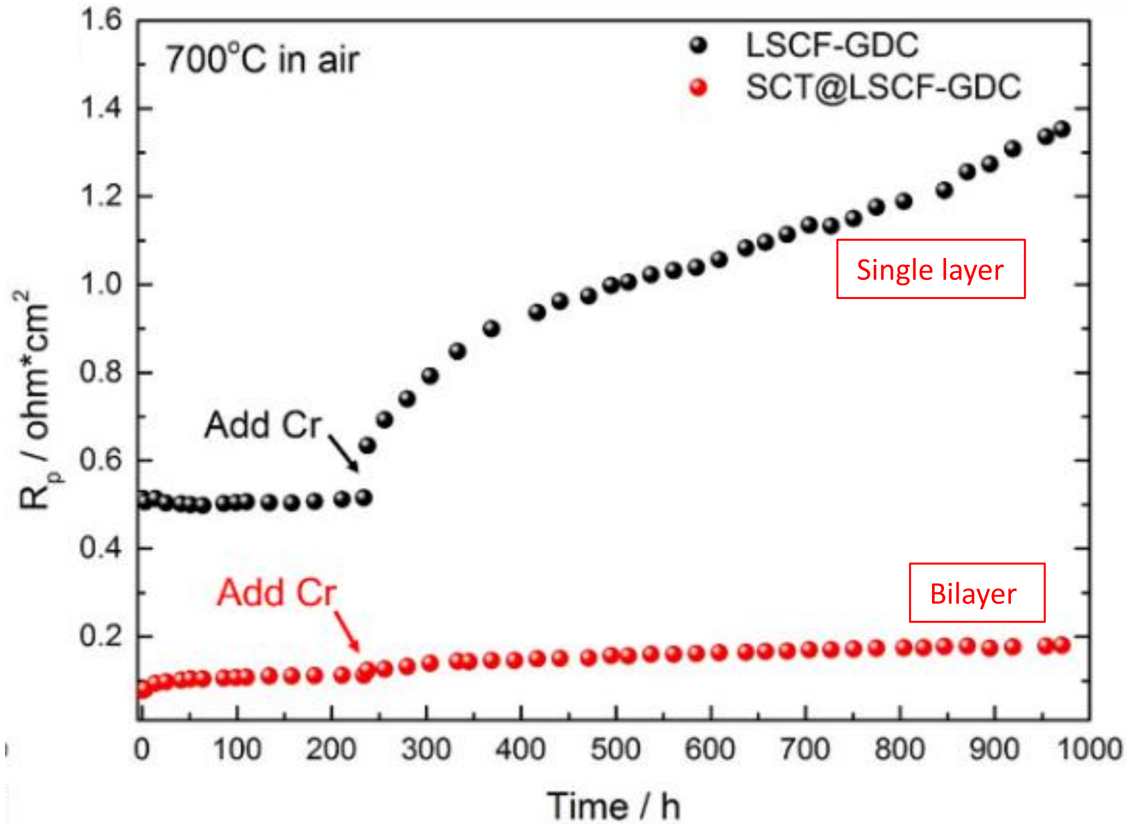
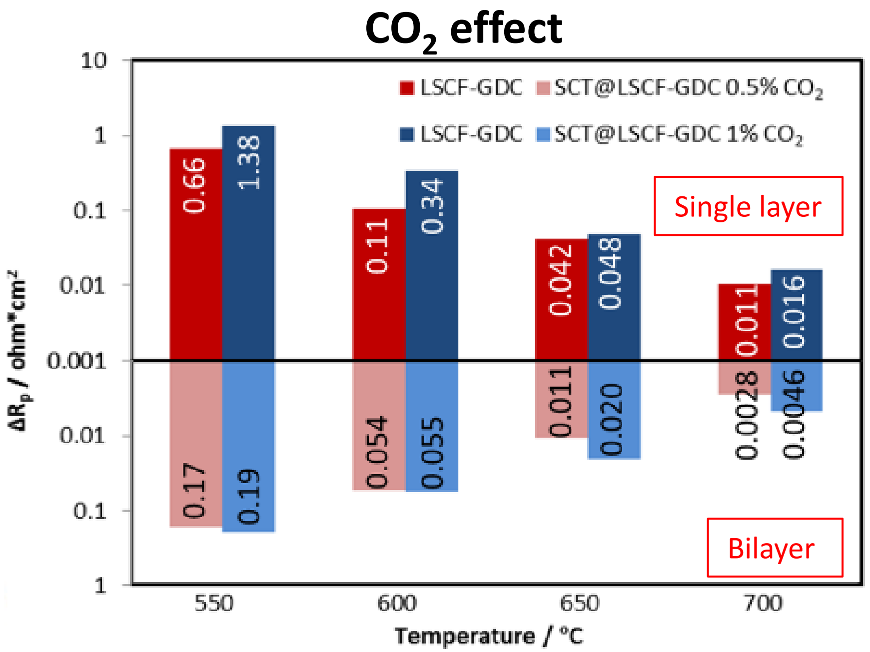
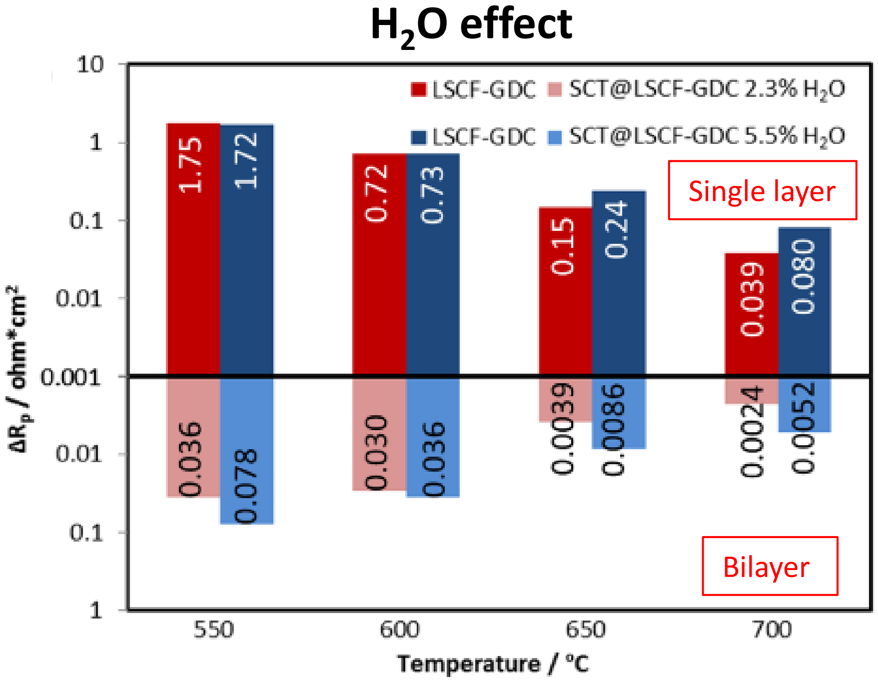
BLOE's Cr-, H_2O- and CO_2-Tolerance







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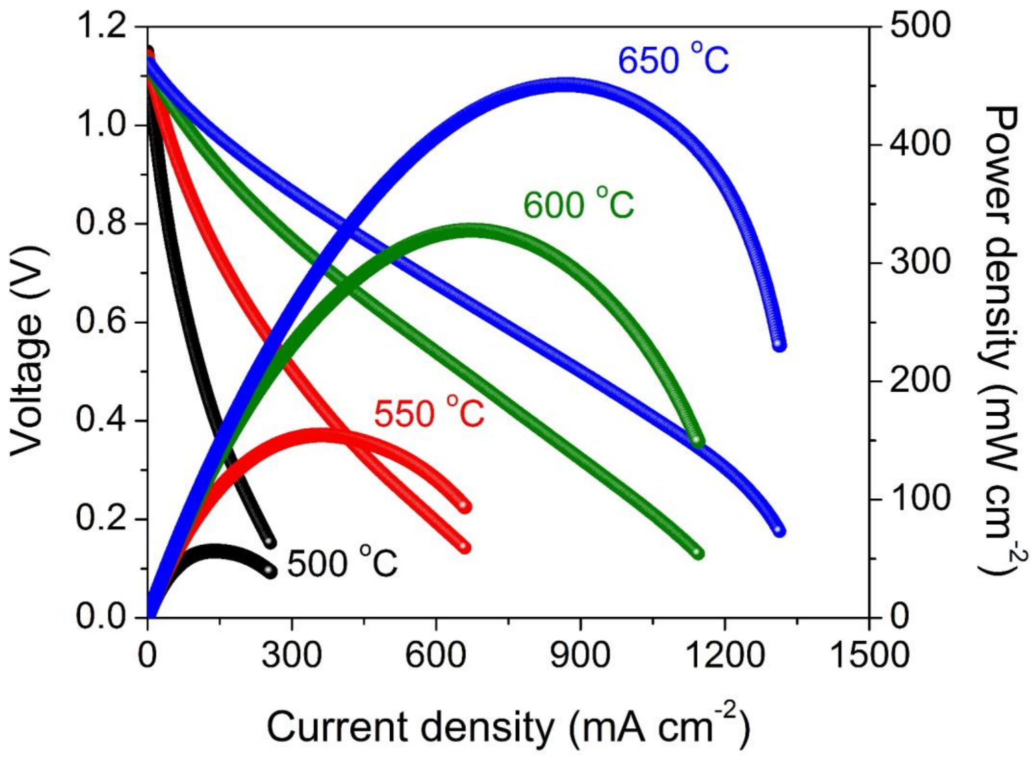
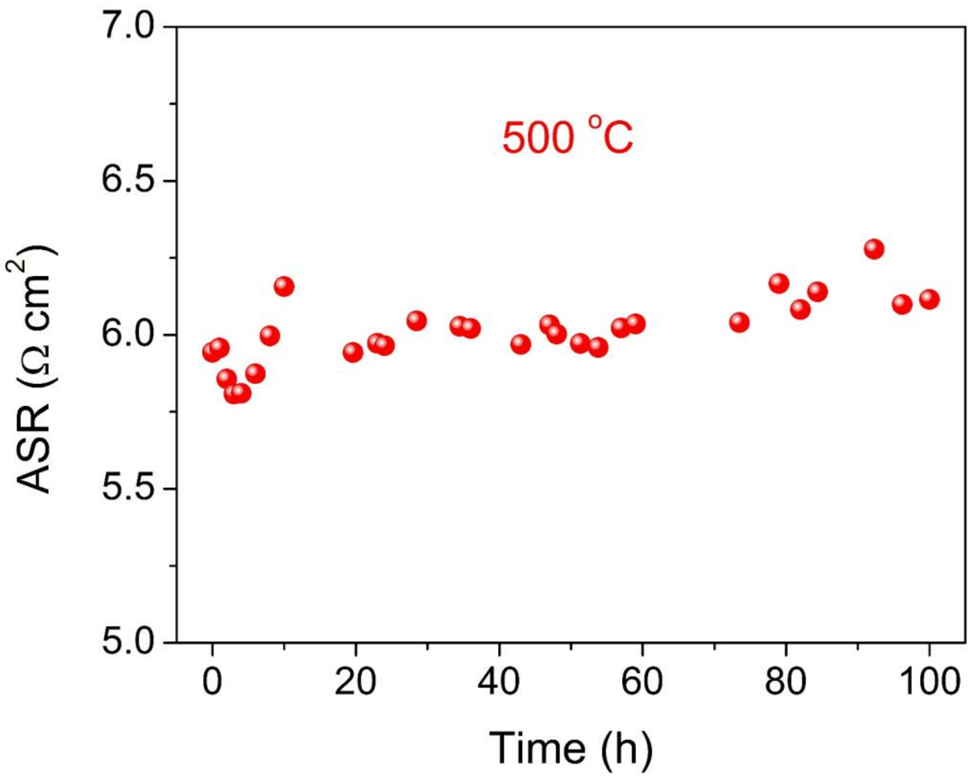
Yang, and Huang, ***J. Mater. Chem. A***, *2020*, ***8***, *82-86.*

Early Work on Barrier Layer Free (BLF) OEs

LSM/BYC Oxygen Electrode





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Zhang and Huang, "A new composite cathode for intermediate temperature solid oxide fuel cells with zirconia-based electrolytes", **Journal of Power Sources**, 342, (2017), 419-426.

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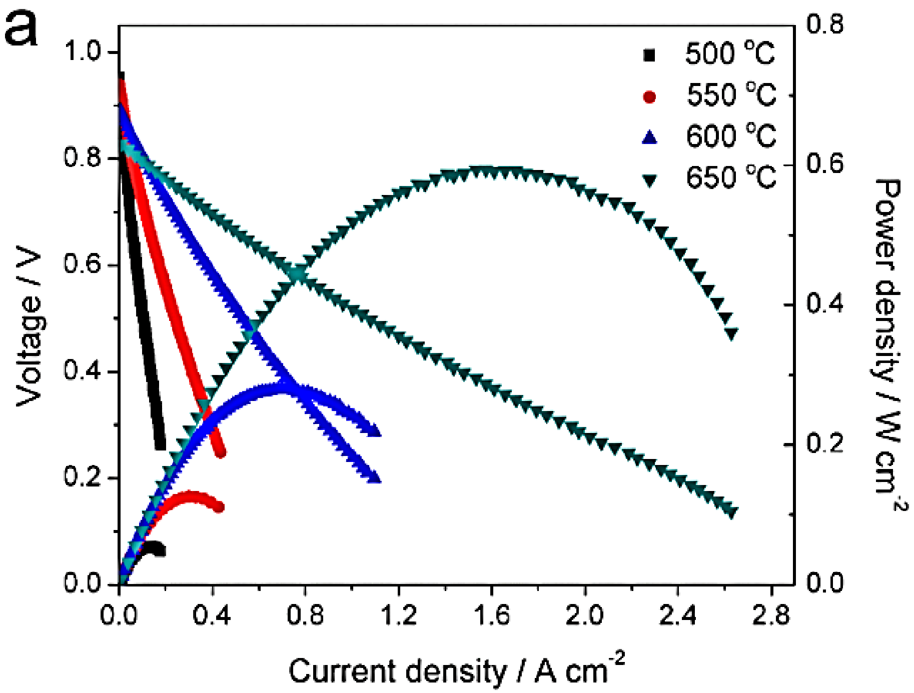
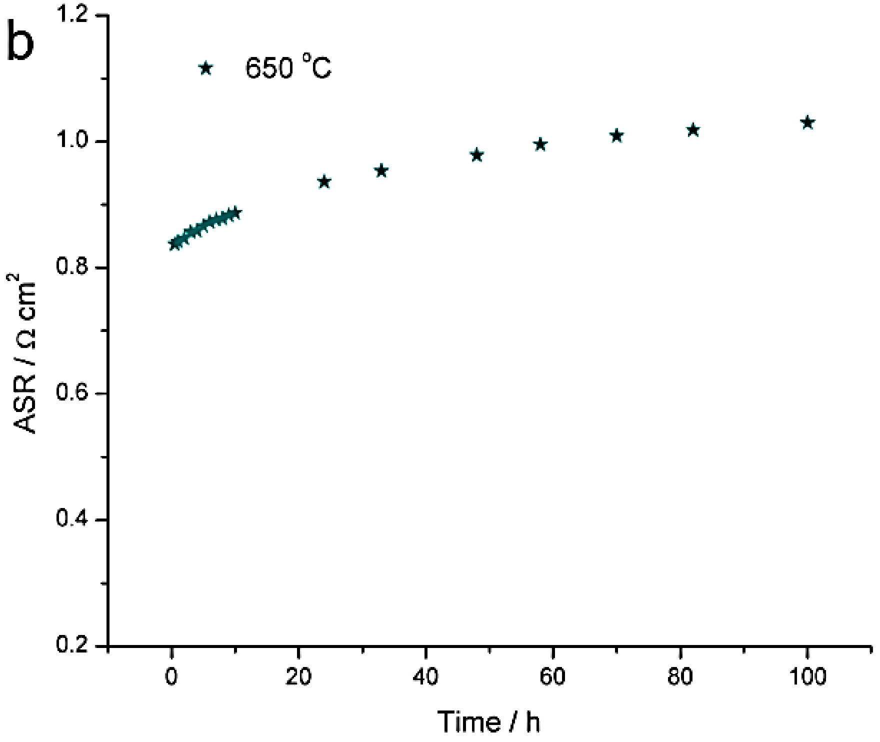
LSM/BYC Oxygen Electrode





Fang and Huang, "In situ synthesis of a high-performance bismuth oxide based composite cathode for low temperature solid oxide fuel cells", **Chem. Commun.**, 2019, 55, 2801.

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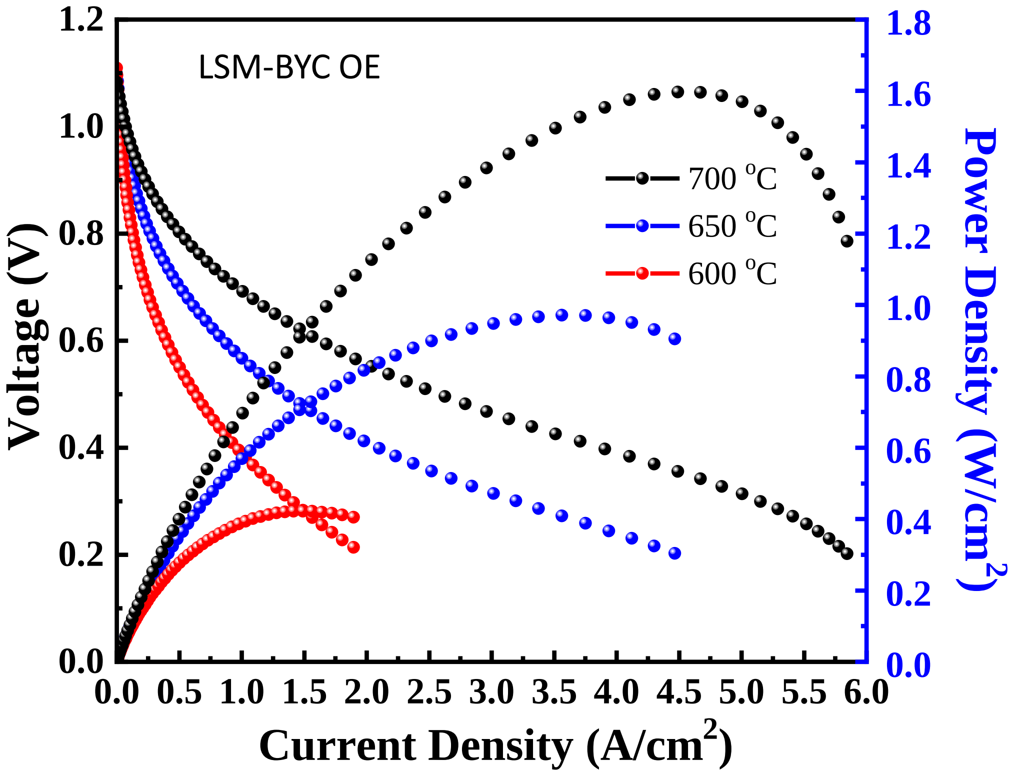
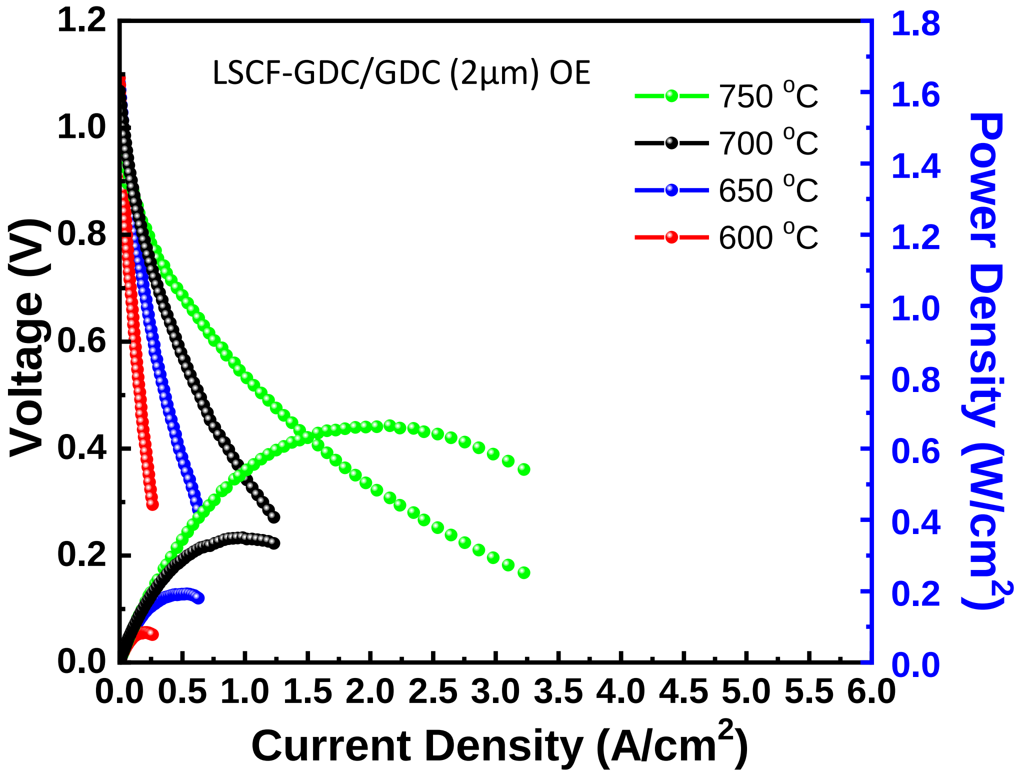
Recent Work on BLF Cell vs. Standard Cell





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

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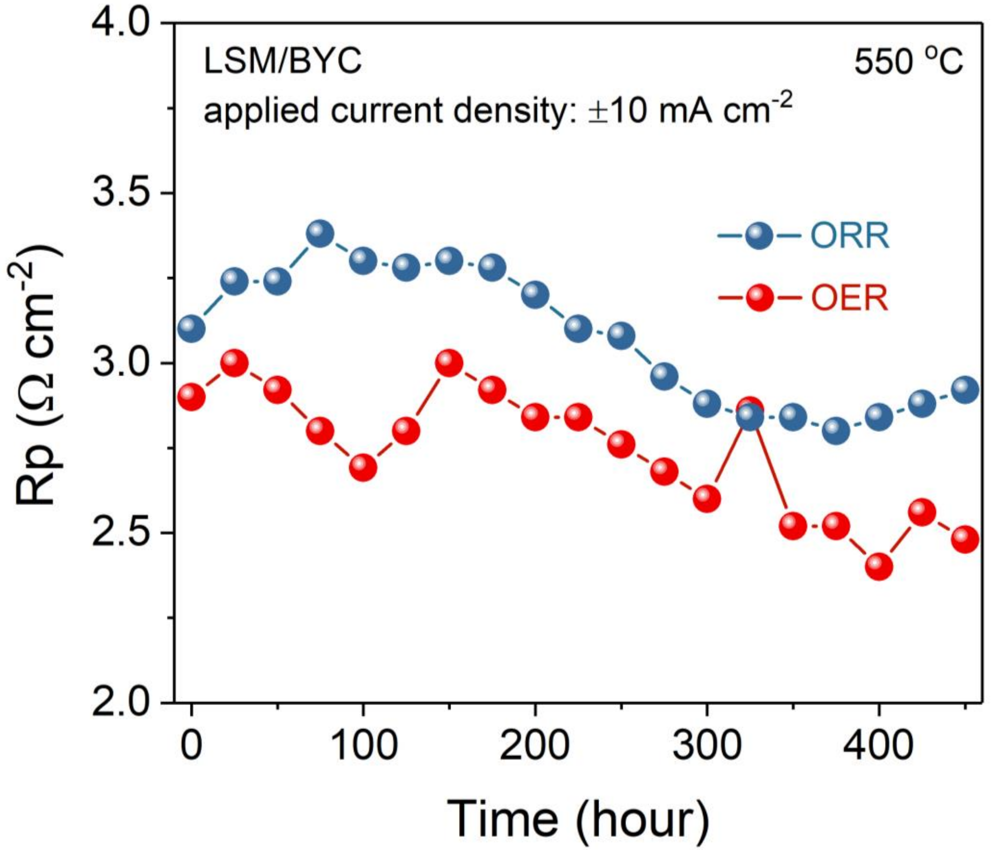
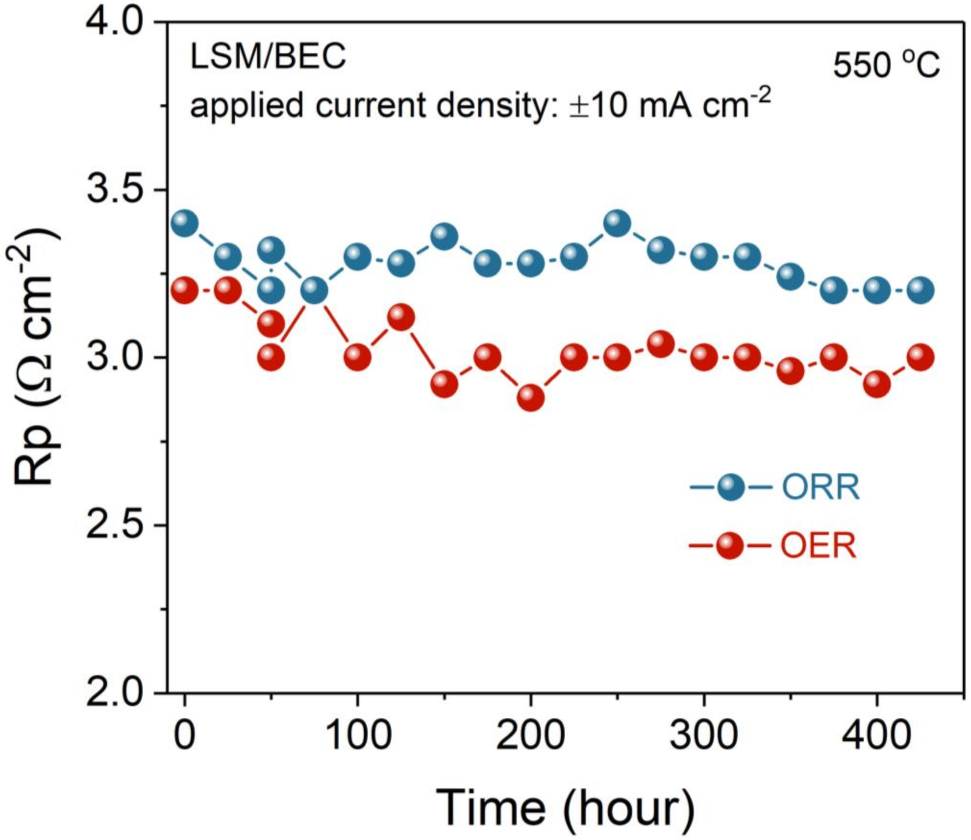
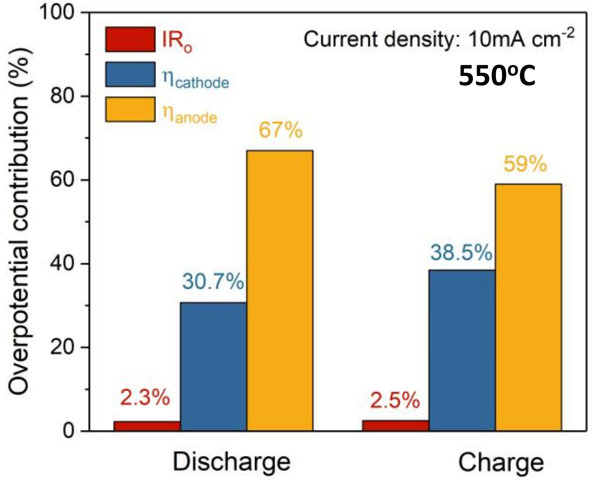
Long-Term Stability of BLF-OE at 550^{o}C and Low Current Density



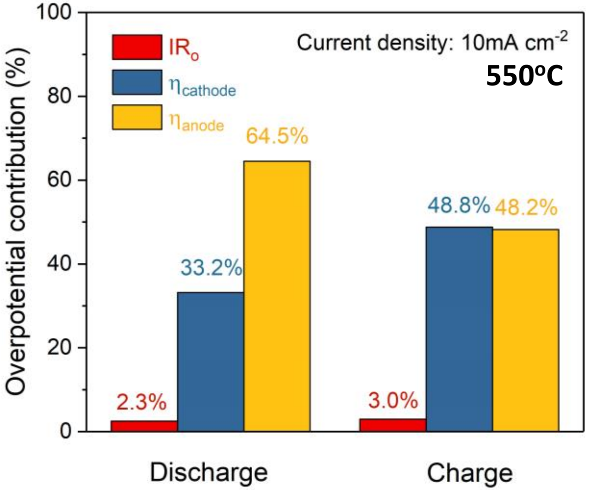


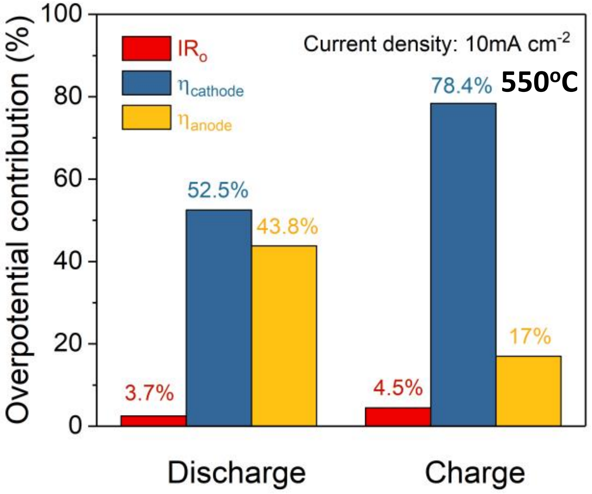
Distribution of Overpotentials: BLF Cells

Pristine

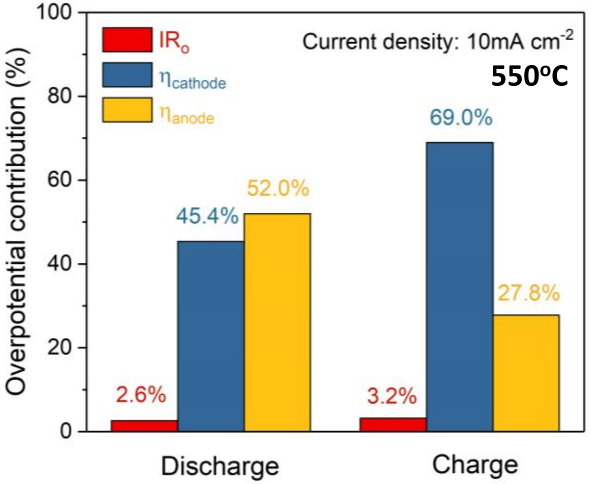


1% GDC

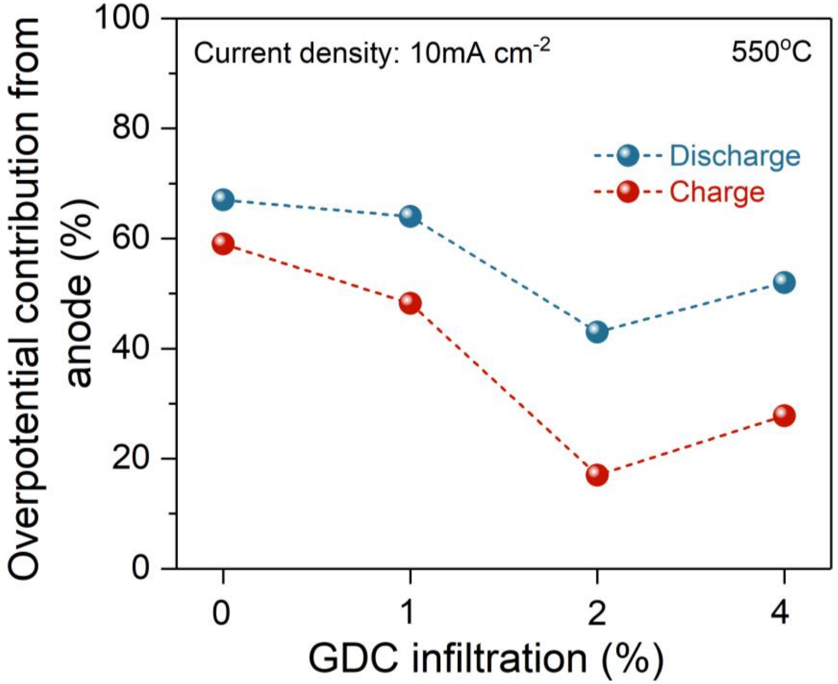




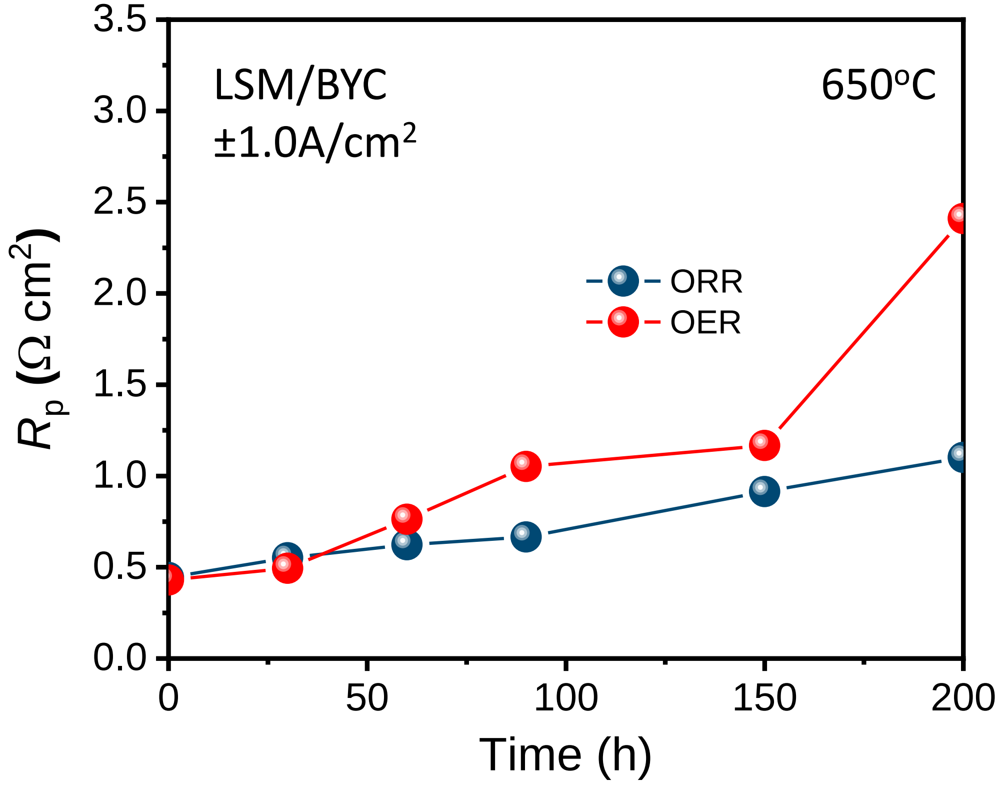
2% GDC

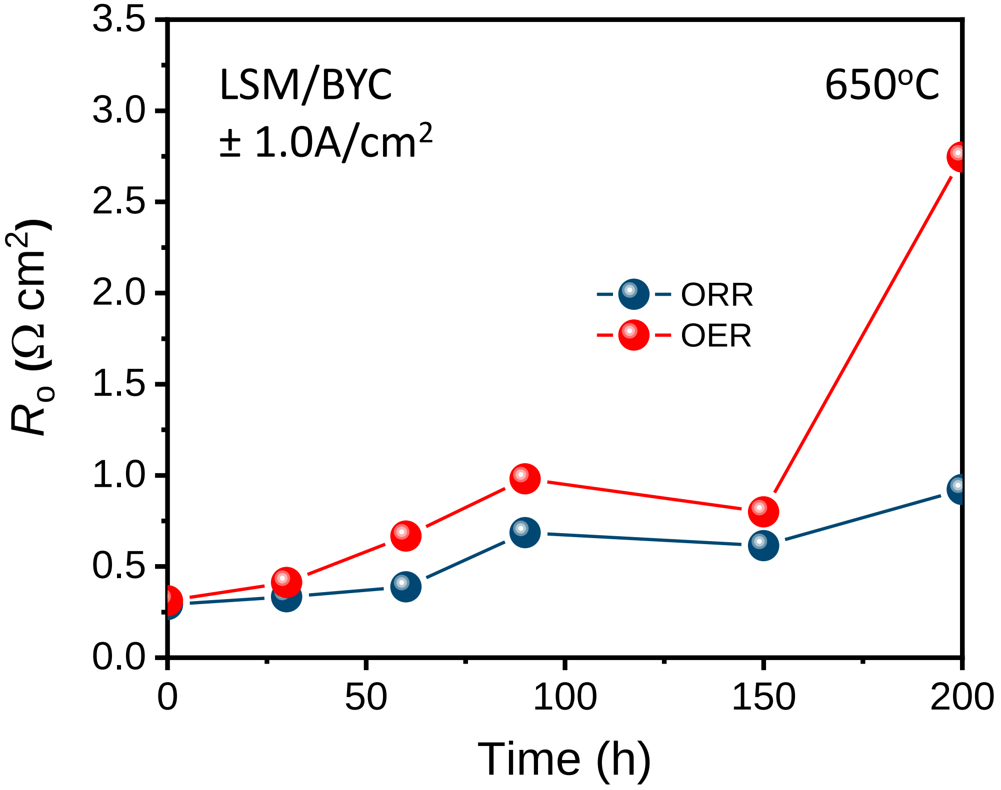


4% GDC



Long-Term Stability of BLF-OE at 650^oC and High Current Density





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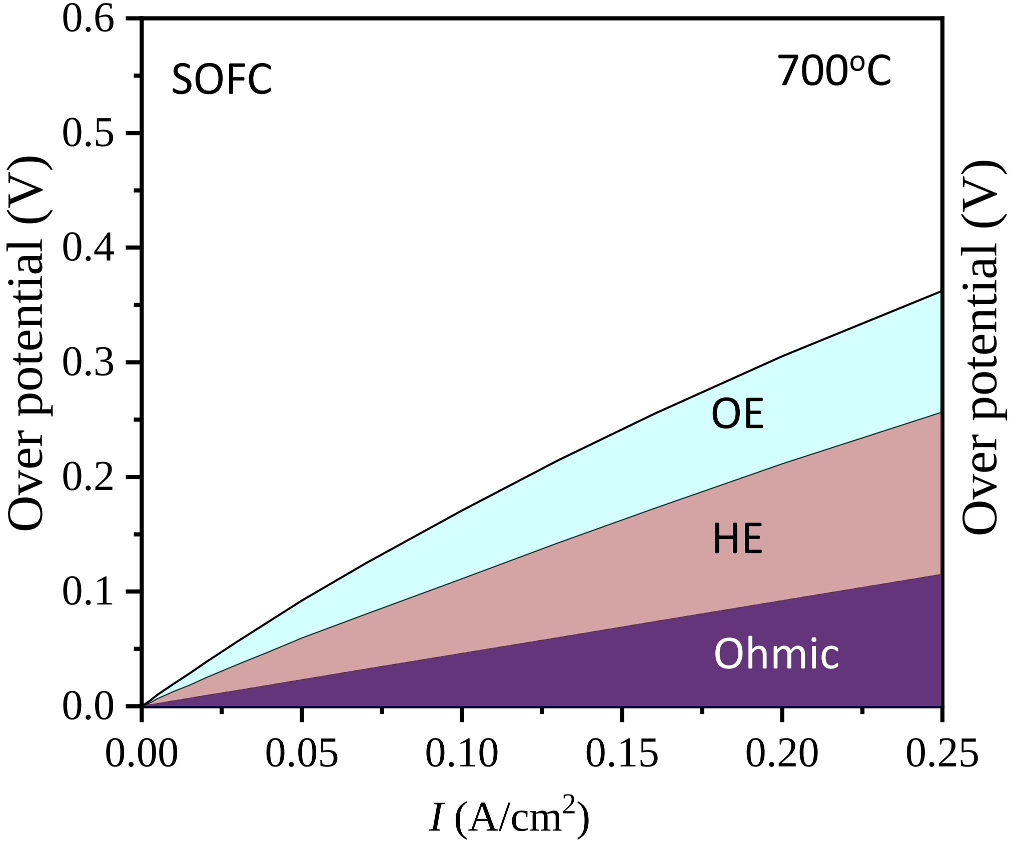
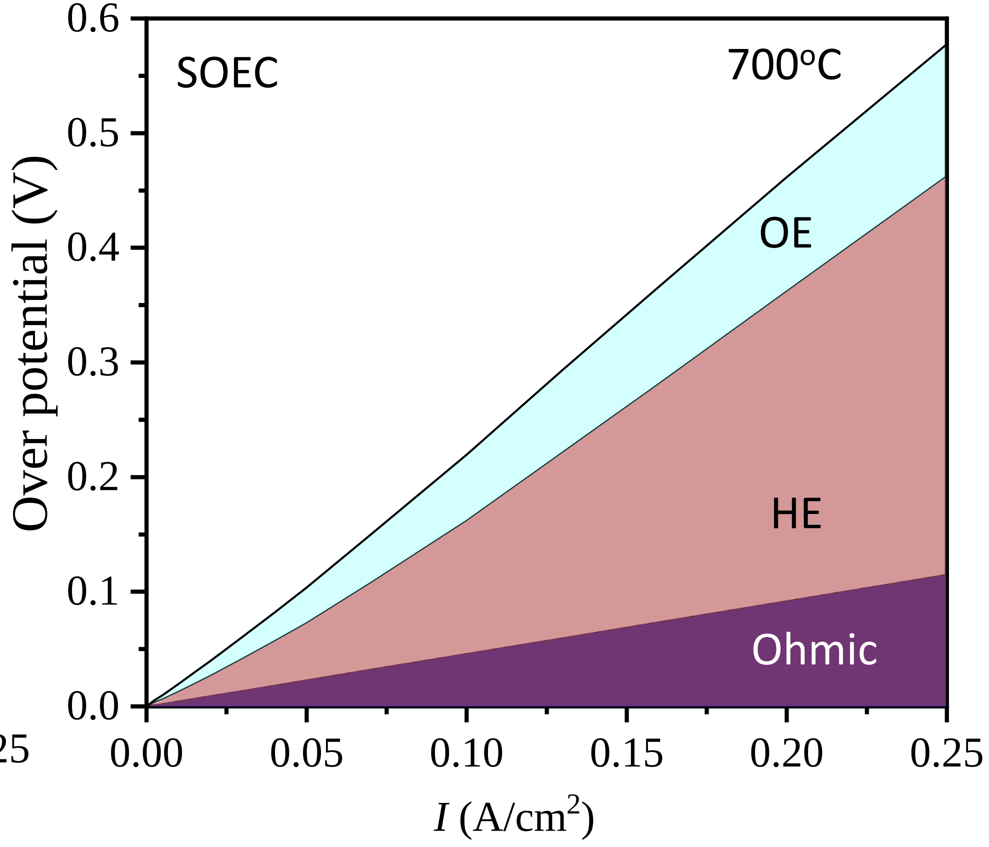
Distribution of Overpotentials: Baseline Cell

LSCF+GDC/GDC/ScSZ/ScSZ+Ni

Half-cell performance tested in air with three-electrode method
Full cell performance tested in 50%H_2O-H_2





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Project Objectives

- The **overarching goal** is to advance reduced temperature ZrO_2-based SOCs technology for high-efficiency and low-cost power and H_2 production
  - Developing BLF OEs to address performance issue at reduced temperatures
  - Developing BLOEs to address delamination and Cr-poisoning issues
  - Developing porosity-graded HE microstructure to minimize concentration polarization
  - Validating the developed new materials/microstructure in small- and large-area cells
  - Developing physics-based electro-chemo-mechano model to comprehend fundamental understanding on OE delamination

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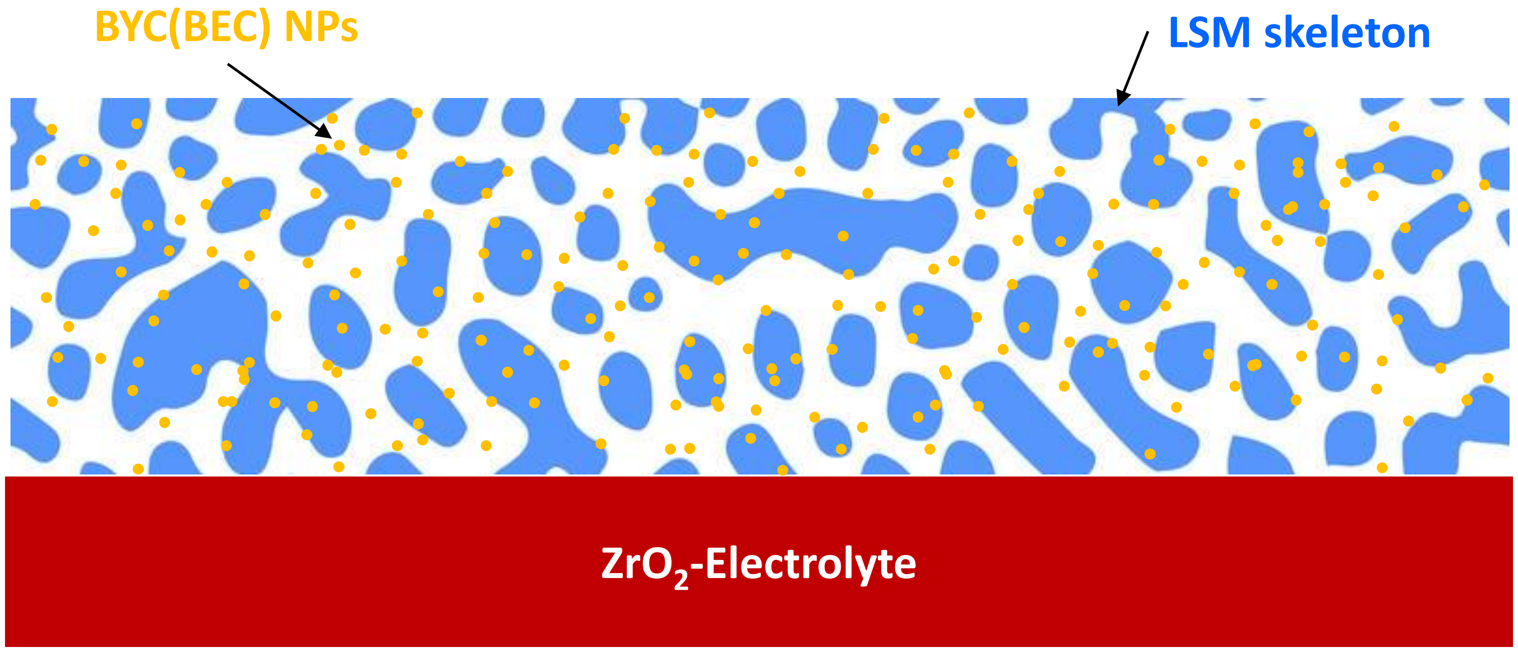
Technical Approach I: (1) Developing Stable BLF OE at 600-650^{o}C and High Current Density



- Understand degradation mechanisms
- Use LSM skeleton to host BYC NPs

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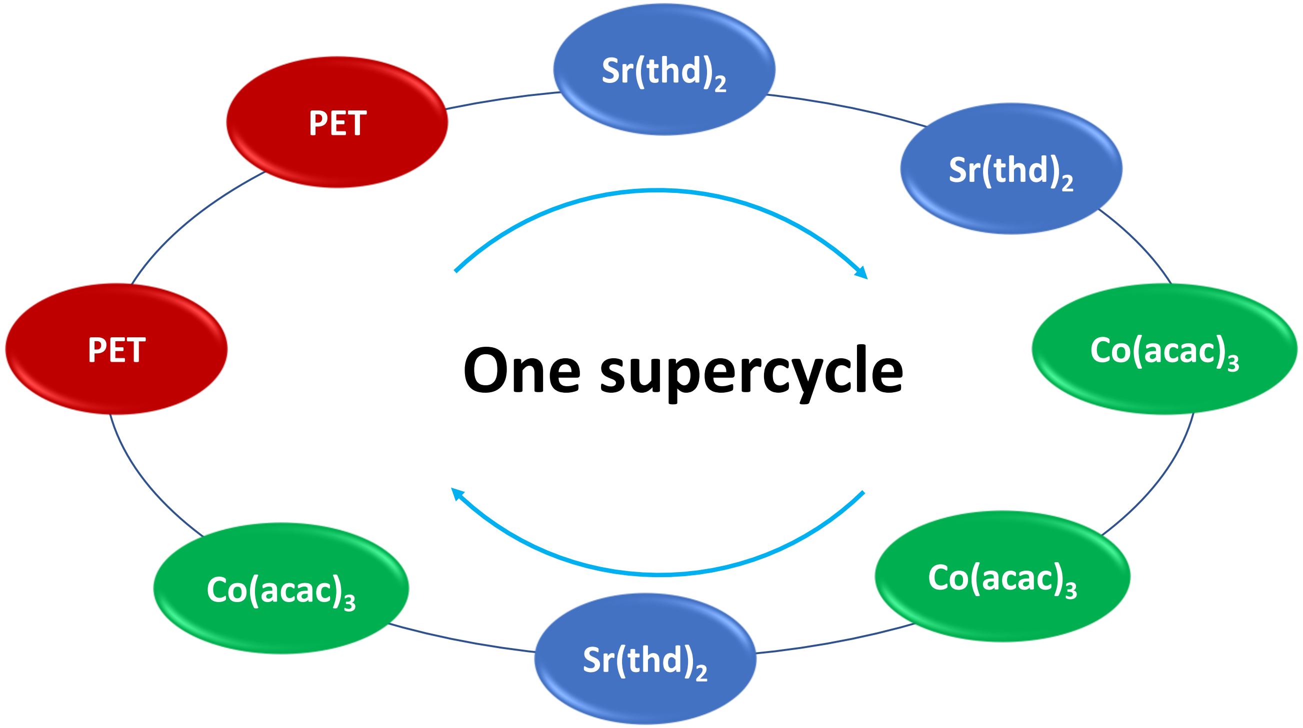
Technical Approach I: (2) ALD Supercycle to Fabricate SCT Overcoat for BLOE



	Precursor	Precursor column T	ALD reactor T
Sr	1) Sr(thd)$_2$, (thd=2,2,6,6-tetramethyl-3,5-heptanedione) 2) Sr(^{i}Pr$_3$Cp)$_2$	110-200°C 90-120°C	190-270°C 150-270°C
Co	1) Bis(cyclopentadienyl)cobalt 2) Cobalt(III) acetylacetonate (Co(acac)$_3$)	110°C 140°C	200°C 270°C
Ta	Pentaethoxytantalum (PET, Ta(OC$_2$H$_5$)$_5$)	160°C	200-270°C

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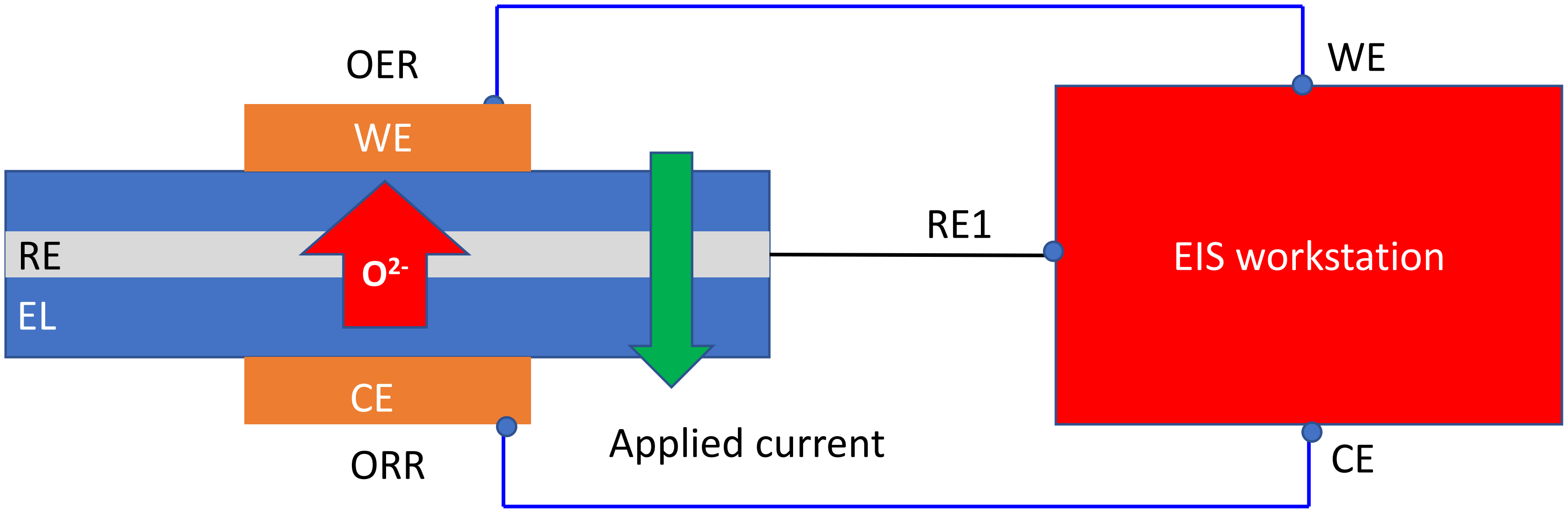
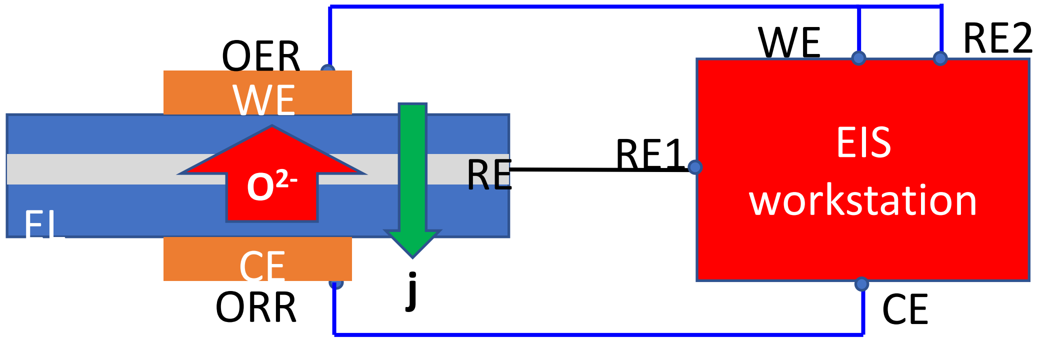
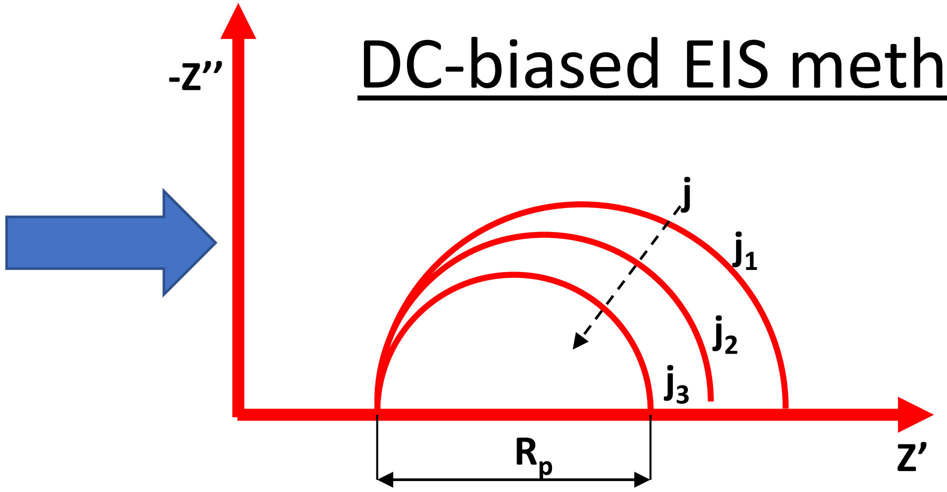
Technical Approach II: Symmetrical Three Electrode Half Cell (STEHC)

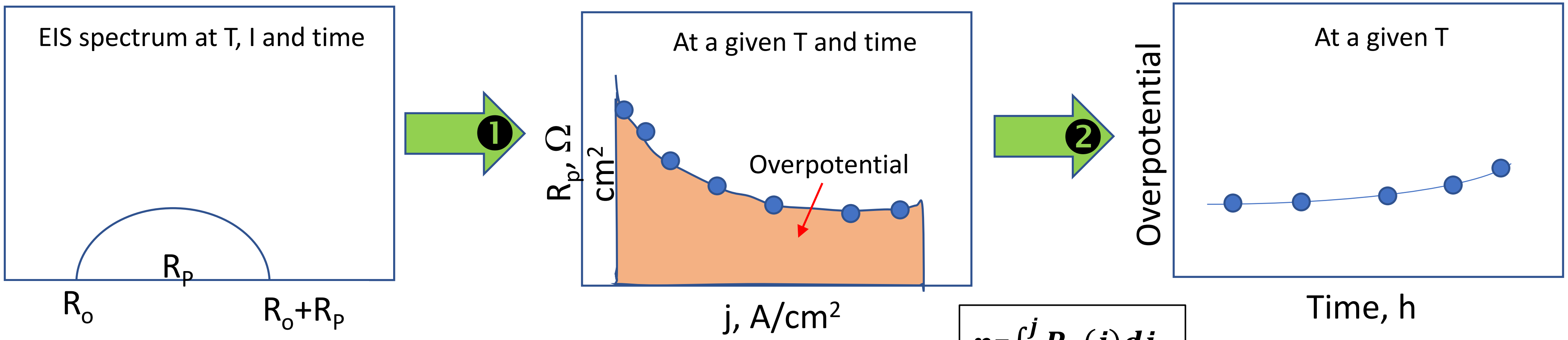


Xinfang Jin and Kevin Huang, *J. Electrochem. Soc.* 2020, **167** 124501

The STEHC Procedure to Extract Overpotential

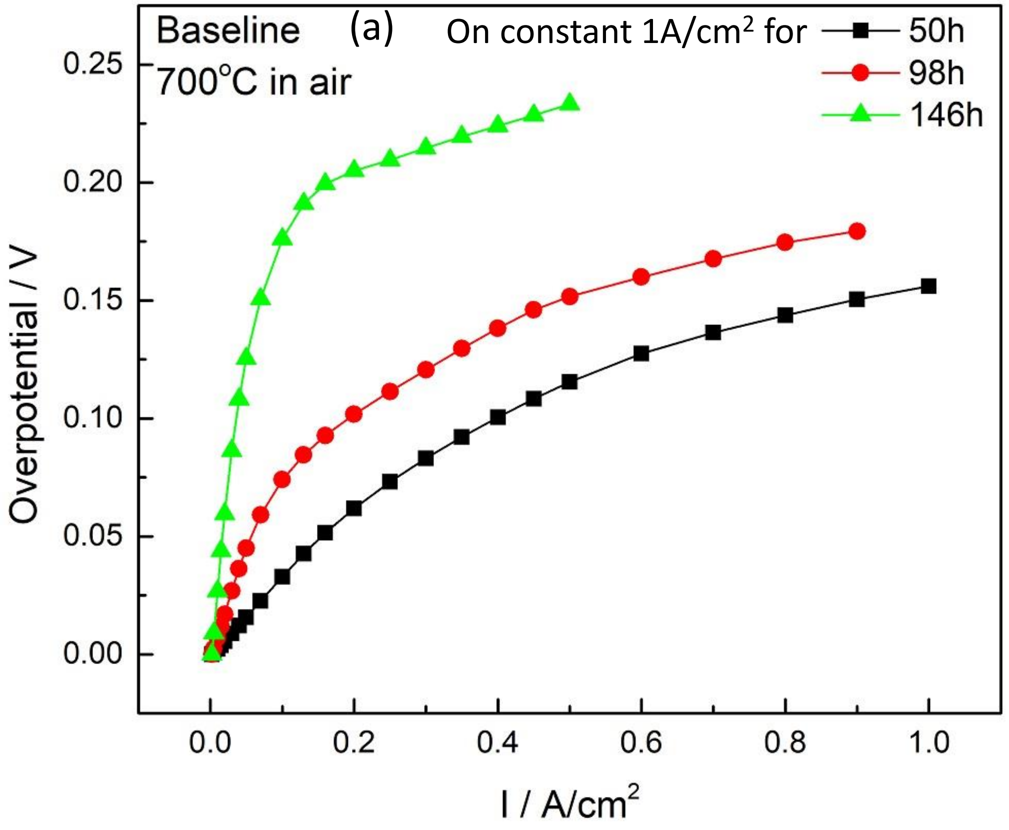


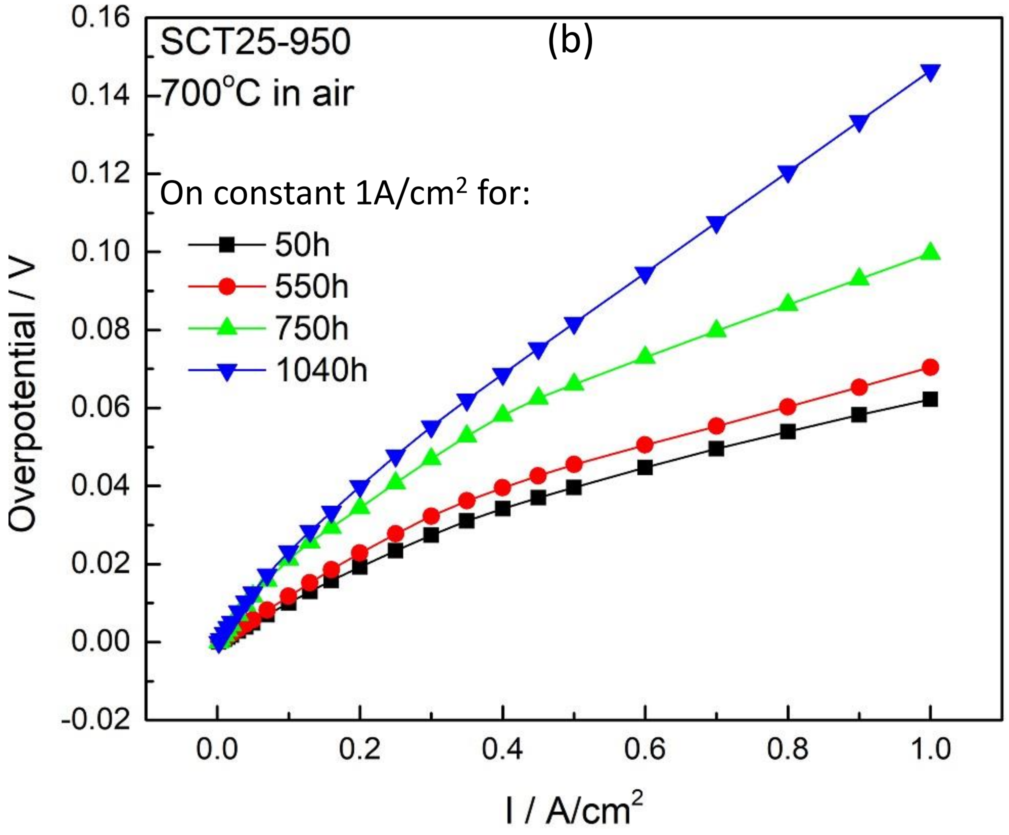




$\eta = \int_{o}^{j} R_p(j)\,dj$

OER Overpotential vs. Current Density





This set of data is used for validating our electrochemical model

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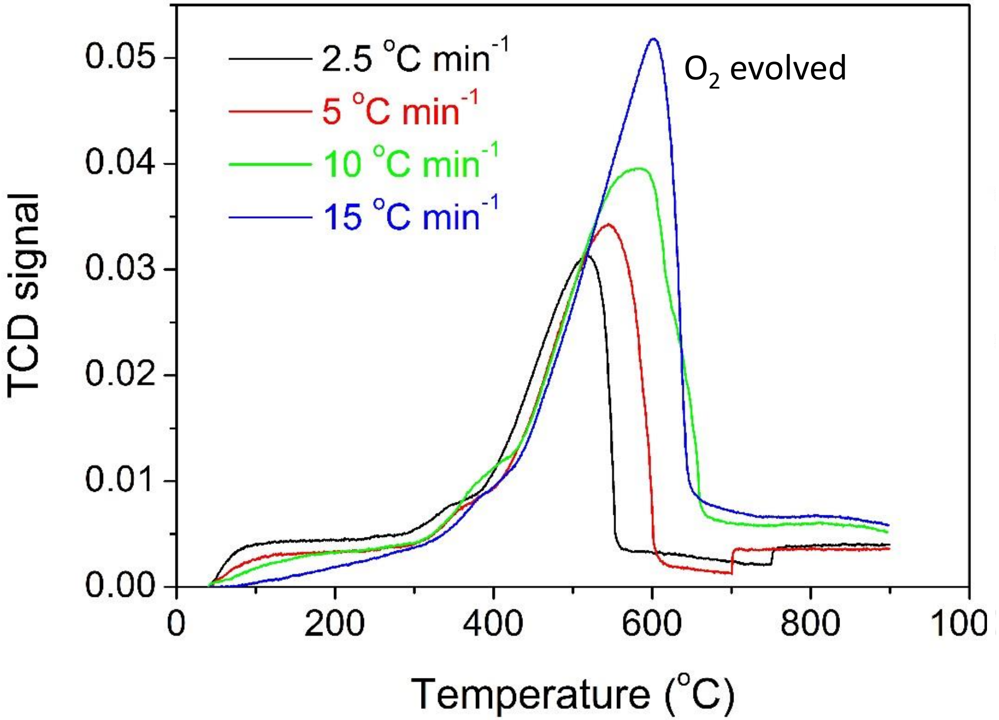
Technical Approach III: TPD Method for Determining the Rate of Oxygen Evolution in OE



$$\ln\left(\frac{\varphi}{T_m^2}\right) = -\frac{E}{RT_m} - \ln\left(\frac{E}{AR}\right) + C$$

$$k(T) = Ae^{-E/RT}$$

$$A = -\frac{E}{RT_m^2} \times \frac{\varphi e^{E/RT_m}}{d\left(\frac{df(\alpha)}{d\alpha}\right)_{T=T_m}}$$

$$f(\alpha) = k(T)t = (1-\alpha)^n$$

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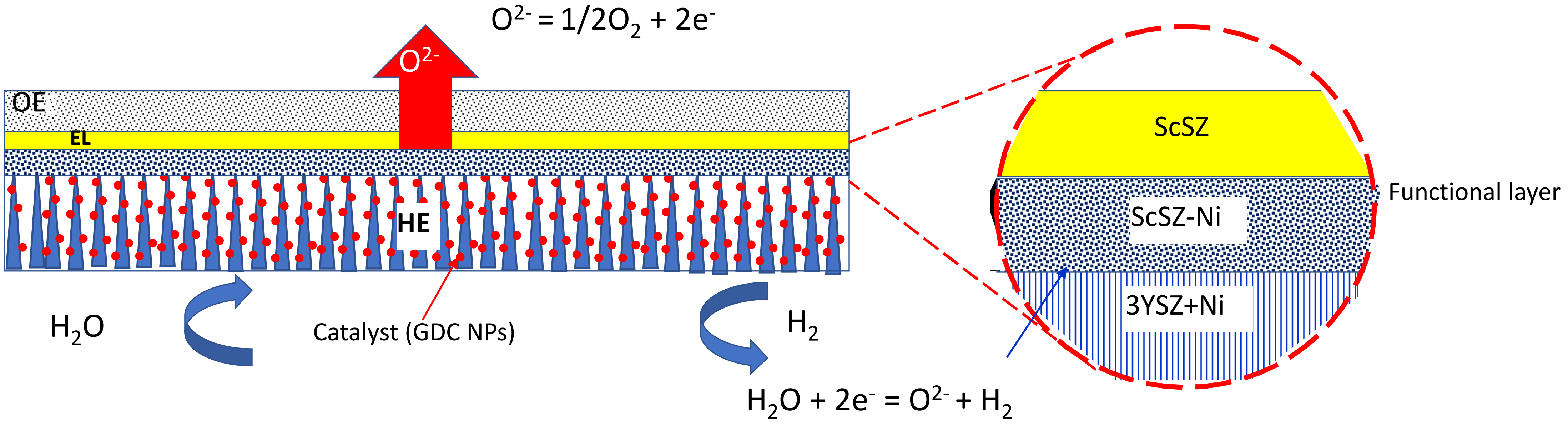
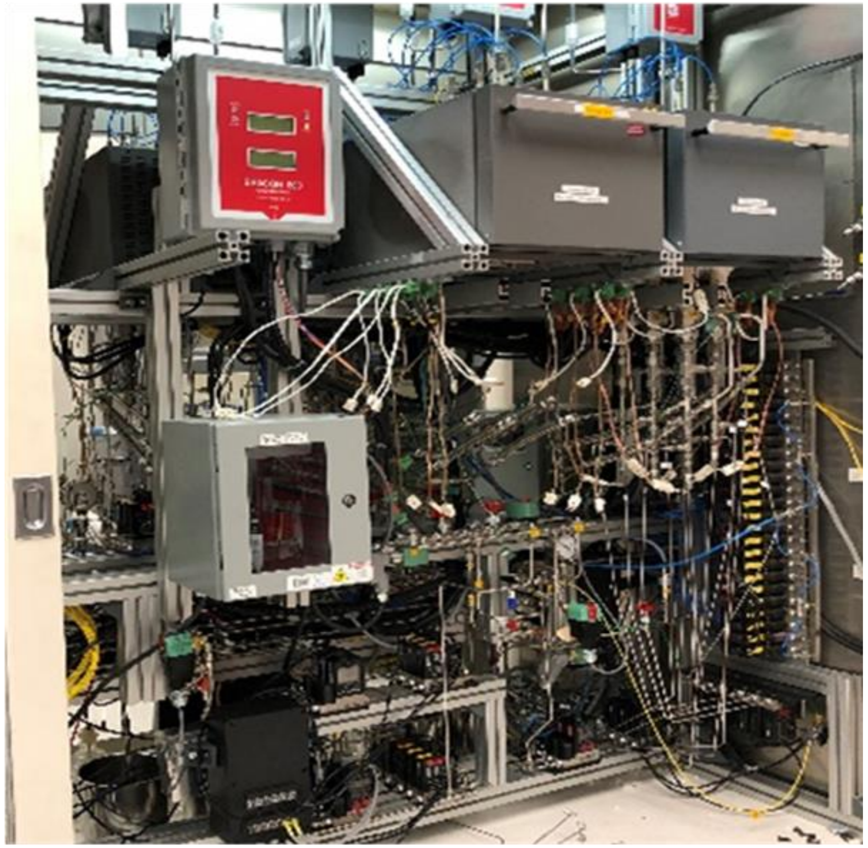
Technical Approach IV: Phase Inversion Method to Fabricate Open Structured HE Substrate

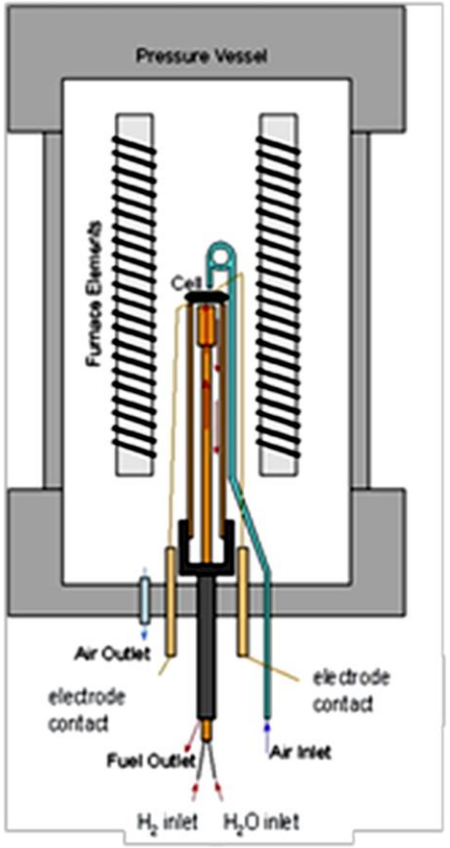


Technical Approach V: Button and Large-Area Cells Testing at PNNL

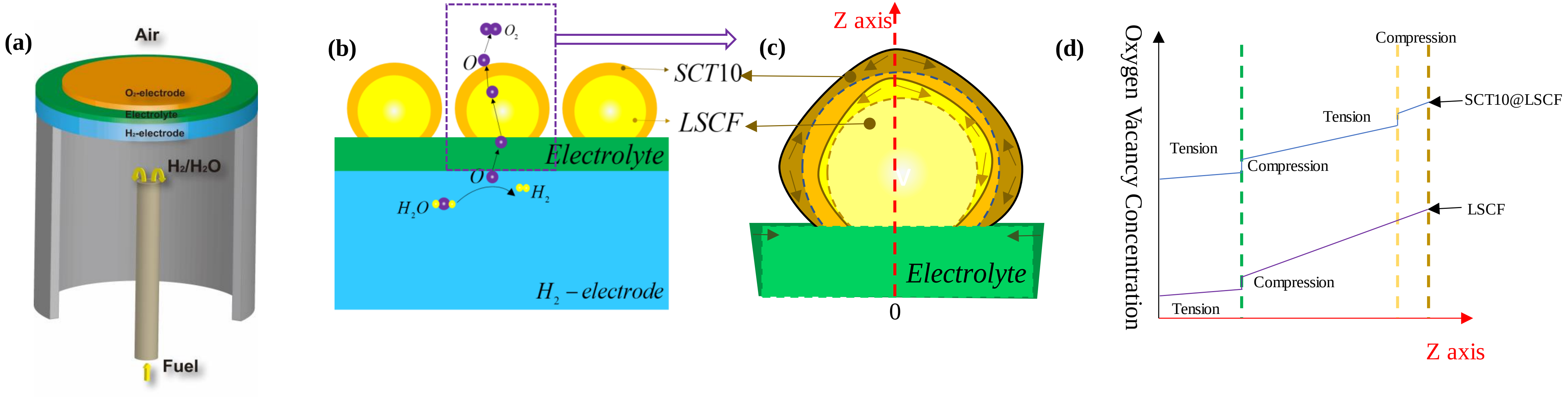
High throughput test stand



Pressurized test stand



Technical Approach VI: Developing Electro-Chemo-Mechano- Model at OE/Electrolyte Interface



- Model construction
- Failure mode and mechanisms identification
- Mitigation strategy development

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