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

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About Project

Project Goal

• To advance reduced temperature (≤700°C) ZrO₂-based SOCs technology for high-efficiency and low-cost power and H₂ production.

• Tasks:
  1. Developing barrier layer free oxygen electrode (BLF-OE) for SOCs operation at ≤ 650°C
  2. Developing ALD-SCT (SrCo₀.₉Ta₀.₁O₃₋δ)@LSCf-GDC bilayer OEs for SOCs operation at ≤ 700°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
**Tasks**

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

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

- BYC (or LSM) NPs
- LSM (or BYC) scaffold
- ZrO$_2$-Electrolyte
Tasks

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

Task-4: Independent Cells Testing at PNNL

H₂O + 2e⁻ = O²⁻ + H₂

O²⁻ = 1/2O₂ + 2e⁻
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
Functional Layers in ZrO$_2$-based SOCs

- ZrO$_2$-based electrolyte (EL)
- Hydrogen electrode (HE)
- Oxygen Electrode (OE)
- Barrier layer (BL) (CeO$_2$-based)

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
First and Latest Reported BLF-OEs

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


CoFe₂O₄·Er₀.4Bi₁.6O₃/YSZ/YSZ-Ni

Kim, et al., J. Mater. Chem. A, 2022, 10, 2045
Our Early Work on BLF-OEs: LSM-BYC

BYC7: (Bi_{0.75}Y_{0.25})_{0.93}Ce_{0.07}O_{2-δ}
LSM: La_{0.8}Sr_{0.2}MnO_{3}


C. Zhang, K. Huang, *J. Power Sources*, **342** (2017) 419-426
LSM-BYC Phase and Cell Microstructure

“One-Pot” wet-chemical method

\[
\frac{(Bi_{0.75}Y_{0.25})_{0.93}Ce_{0.07}O_{1.5\pm\delta}}{La_{0.8}Sr_{0.2}MnO_{3-\delta}}
\]

Bi\(_{0.75}\)Y\(_{0.25}\)O\(_{1.5}\)

PDF#84-1450

La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_{3-\delta}\)

PDF#70-4009

La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_{3-\delta}\) - FYC

La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_{3-\delta}\)

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

$R_p$ and $\eta$ of SP-BLF-OE

Measured by STEC method

Stability under ORR and OER Modes of BLF-OE

ORR: 1.0 A/cm² @650°C

OER: 1.0 A/cm² @650°C

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

Delamination?
Overpotential Distributions in a Single SOC

Air/LSM-BYC/ScSZ/FL/HE/30%H₂O-H₂

650°C, SOFC

650°C, SOEC

Overpotential (V) vs. I (A/cm²)

OE
HE
Electrolyte
Phase Inversion Process: Working Principle

Jaydevsinh M. Gohil, Rikarani R. Choudhury, in Nanoscale Materials in Water Purification, 2019
Phase Inversion Process to Fabricate HE Substrate (Task 3)

- PVP (4 wt.%)
- PESF (16 wt.%)
- NMP (80 wt.%)
- 4YSZ (40 wt.%)
- NiO (60 wt.%)

Ball mill 4 h

- 30 wt.%
- 70 wt.%

Ball mill 24 h

Casting

Water soaking at RT for 12 h

Cut into φ1.25” pallets
Heat-treated at 1000 °C

Functional layer dip-coating
Heat-treated at 1000 °C

Electrolyte dip-coating
Sintered at 1400 °C

Cathode, screen-printing
Heat-treated at 800 °C

Anode catalysis infiltration
Heat-treated at 950 °C
φ1.25” Phase Inversion Cell at Different Stages

For BLF cells
SOEC Performance Testing at PNNL

Ramping up from OCV to 1.3V with step of 50mV every 12h

Fixed voltage at 1.3V

650°C

Current density (A/cm²)

0 50 100 150 200 250 300

Time (hours)

0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8

ASR under bias (Ω cm²)

0 2 4 6 8 10 12 14 16

Time (hours)

USC-1 (c7) USC-2 (c8) USC-3 (c9)

Activation in SOFC mode @ 1V, 15h
SOEC Performance Testing at PNNL

650°C, 50% H₂O - H₂

After 96h

C7 = USC-1
C8 = USC-2
C9 = USC-3

650°C, 50% H₂ / 50% H₂O EIS at OCV

96h, 50% H₂ / 50% H₂O EIS at 1.3V
Separation of Current Collector from OE
Post-test Microstructural and Composition Analysis (USC#1)
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### Position 1

- **Position 1**: Y
- **Position 2**: Ce

### Position 2

- **Position 2**: Y
- **Position 3**: C

---

### Position 3

- **Position 3**: C
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
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.

Cell has little if any gold particles on top

Cell has no light contrast layer on top of the YSZ
Exploring Ways to Improve the OE Performance

- The $R_p$ value of LSM-BYC baseline is around $0.64 \, \Omega \, \text{cm}^2$

- The $R_p$ increase to around $3.0 \, \Omega \, \text{cm}^2$ when adding ScSZ roughing layer between electrolyte and OE

- The $R_p$ increase to $1.4 \, \Omega \, \text{cm}^2$ if embedding sliver mesh inside LSM-BYC

- The $R_p$ slightly decreased ($0.60 \, \Omega \, \text{cm}^2$) when adding BYC layer between screen printed LSM-BYC and EL

- The $R_p$ decreases to $0.30 \, \Omega \, \text{cm}^2$ when infiltrating 18wt% LSM into BYC scaffold
Infiltrating BYC NPs into LSM Scaffold Sintered at 1200°C/5h

Porous LSM scaffold

Infiltrated BYC

BYC NPs

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

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

40% BYC loading in LSM

Voltage (V)

Power density (mW/cm²)

Current density (A/cm²)

40% BYC infiltration in LSM (1250°C) Under OCV

3 electrodes testing: OER
applied current density: 10 mA cm⁻²

650°C

Z''(Ω cm²)

Z'(Ω cm²)
Infiltrating LSM NPs into BYC Scaffold Sintered at 800°C/5h

Baseline: SP LSM+BYC

650°C
BYC-20C scaffold

Infiltrated LSM pre-calcined at 750°C

- Base Line
- 18wt% LSM
- 25wt% LSM
- 30wt% LSM

Ro (Ω cm²) 1.44 1.41 1.41 1.42
Rp (Ω cm²) (OCV) 0.64 0.30 0.10 0.15

ZrO₂-Electrolyte

LSM NPs

BYC scaffold
Stability of BYC–20C-25wt% LSM

Under OCV and 650°C
LSM pre-calcined at 750°C for 2 h

Graph showing the stability of BYC–20C-25wt% LSM under OCV and 650°C, with LSM pre-calcined at 750°C for 2 hours.
$R_p$ and $\eta$ of IL-BLF-OE (BYC-20C-18wt%LSM)

Measured by STEC method
$(\text{Bi}_{0.75}\text{Y}_{0.25})_{1-x}\text{Hf}_x\text{O}_{2-\delta}$ (BYH) Series: XRD Patterns

Sintered at 800°C for 16h

Intensity / a.u.

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

• We have demonstrated the feasibility of BYC-LSM as a barrier layer free oxygen electrode for $\leq 650^\circ C$ 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 $650^\circ C$ and the potential to address the bonding issue
• BYH series might be a better oxide-ion conducting phase
Next Step

• Fabricate 1.5 cm² 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
## Milestone Status

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<th>Milestones</th>
<th>Task</th>
<th>Planned</th>
<th>Actual</th>
<th>Verification method</th>
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<td>PMP submitted to DOE</td>
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<td>Submit initial Technology Maturation Plan</td>
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<td>Demonstration of barrier-layer-free OE performance: Overpotential: ( \leq 0.15V @ \pm 1A/cm^2 @ 650^\circ C )</td>
<td>2.2</td>
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<td>STEC and Report to DOE</td>
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<td>Demonstration of ALD bilayer OE performance: Overpotential: ( \leq 0.15V @ \pm 1A/cm^2 @ 700^\circ C )</td>
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<td>Demonstration of optimized PI process conditions to produce quality porosity-graded open-channel HEs</td>
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<td>Demonstration of button cell (1.5 cm(^2)) performance specified in the Success criteria</td>
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<td>A multiphysics model detailing OE failure mechanisms and modes</td>
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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.