Durable and High-Performance SOECs Based on Proton Conductors for Hydrogen Production

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- **Accomplishments to Date**
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  - **Oxygen Electrodes Development**
  - **Development of catalysts to enhance catalytic activity and durability**
    - **Understanding the mechanism of electrode processes**
    - **Rational selection of dopants for better electrolyte, electrode, and catalysts**
  - **Demonstration of high-performance and durable single cells**
- **Summary**
- **Acknowledgment**

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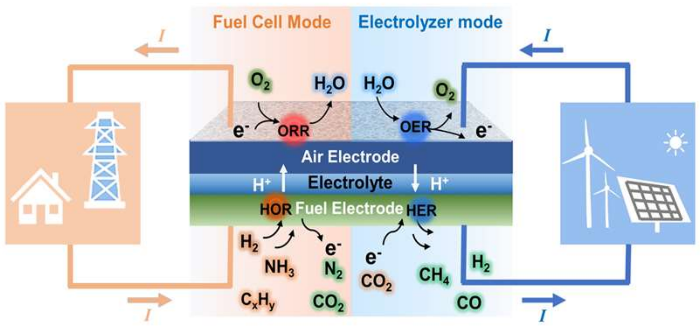
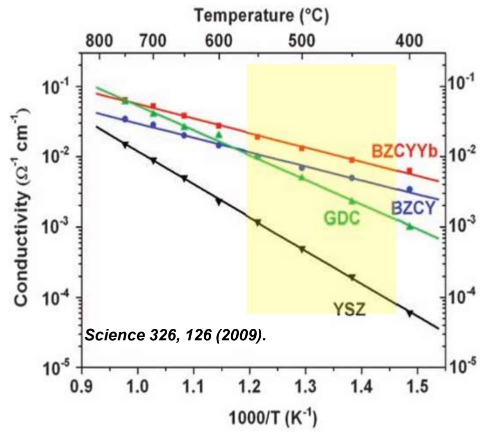
Background





- ◆ **High conductivity**
- ◆ **Low-temperature operation**
  Reduced cost, enhanced durability
- ◆ **Dry H_2 (no need for H_2 separation)**

The most efficient and low-cost option for H_2 production

But, **many challenges still remain** that must be overcome to realize the advantages.

Project Objectives

To establish the scientific knowledge for rational design and demonstration of a robust, highly efficient, and low-cost P-SOEC for H_2 production

- To optimize proton conductivity while enhancing FE and durability of electrolyte under electrolysis conditions
- To develop O-electrode materials with fast ionic/electronic transport, high electro-catalytic activity, and good durability
- To develop ORR and OER catalysts with durability against various contaminations (Cr, CO_2) in high concentration of steam
- To gain insights into degradation mechanisms of cell materials and interfaces under typical operating conditions

Target Performance

End of Project Goal:

1) *Current density* ***>1.8 A cm^{-2} at 1.3 V*** *in electrolysis mode at* ***600 °C***
2) ***≥75%*** *roundtrip efficiency at* ***0.5 A cm^{-2}*** *in both FC/EC modes at* ***≤ 650 °C***
3) ***>500 h*** *operation with a degradation rate of* ***< 0.5% per 1,000 h***

Proton-conducting Electrolyte Development

1) *Conductivity of > 0.01 S/cm*
2) *Ionic transference number >0.95 at 600 °C*
3) *Degradation rate of <0.5% per 1,000 h*

O-Electrode Development

R_p of < 0.2 Ω-cm^2 at 600 °C in wet air

Catalyst Development

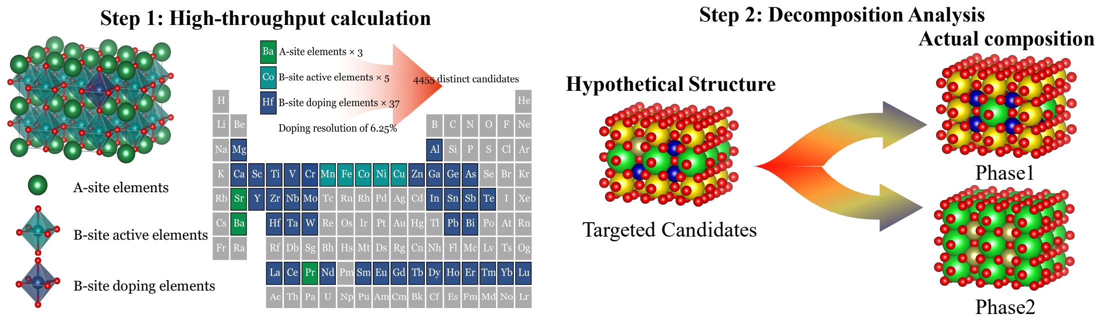
1) *R_p of < 0.15 Ω-cm^2 at 600 °C in wet air*
2) *Degradation rate <0.5% per 1,000h against contaminants*

Technical Approach

Accelerating discovery of materials for P-SOECs via high-throughput computing

- Rationally select dopants for better electrode & catalyst materials
- Predict structural/phase stability under various conditions
- Unravel the mechanisms of electrode and electro-catalytic processes

Illustration of the high-throughput computing framework



Step 1: Calculating computational descriptors of 4,455 perovskite candidates.

Step 2: Phase stability analysis to eliminate unstable structures, thereby obtaining accurate data for all viable candidates

Current status: Identified the structural phases and collected 6 essential computational descriptors for all **4455** candidate materials

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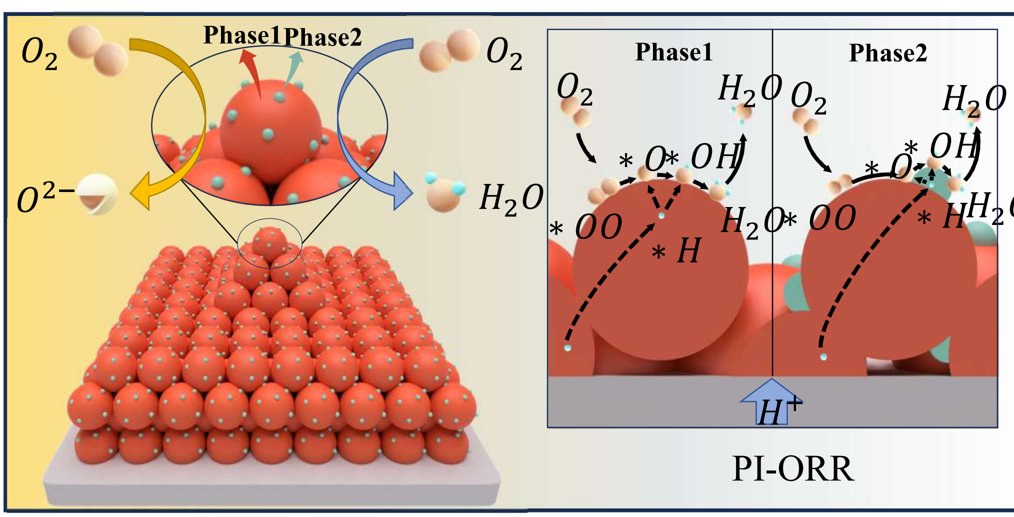
Proposed Proton-Involved ORR Mechanism



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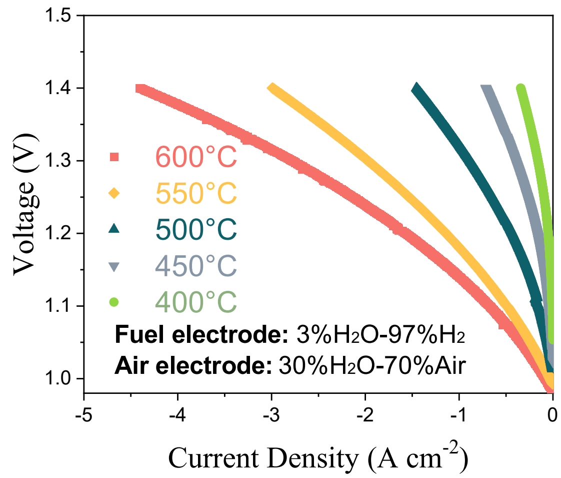
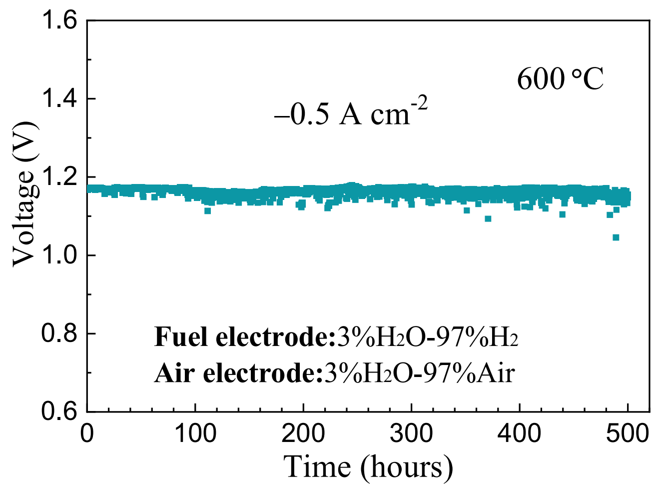
Excellent water electrolysis performance is achieved





A Poster on Computational Studies

- Successfully calculated E_{hull}, *p*-band center, *d*-band center, *E*v, E_H, and *d*-*p* band hybridization using the DFT-based high-throughput calculation.
- A novel data-driven material analysis approach, Decomposition Analysis, is proposed to obtain the actual structural phases for targeted candidates.
- The predicted promising materials, e.g., X-doped $BaCoO_{3-\delta}$, displayed outstanding performance as an oxygen cathode for P-SOCs.

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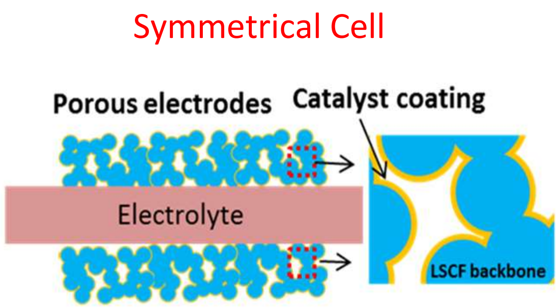
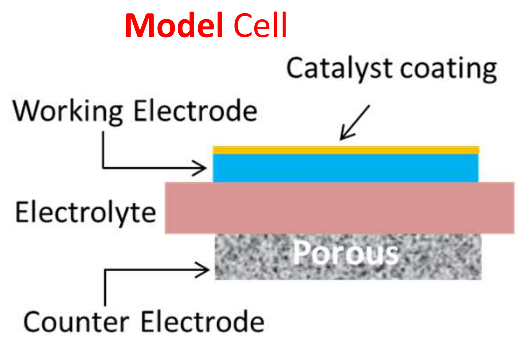
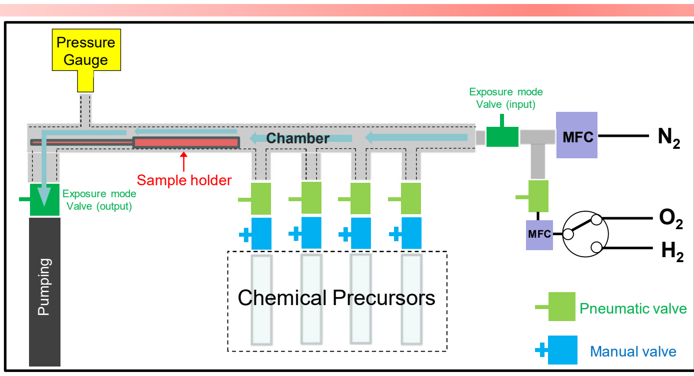
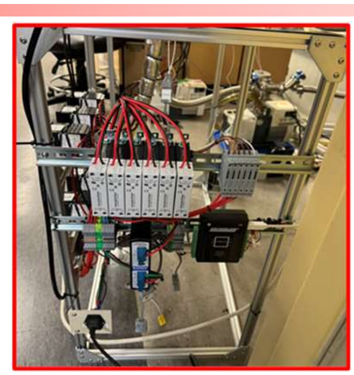
Validation By Experiments





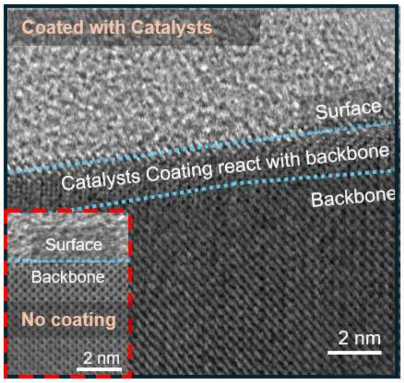
Surface Modification by ALD

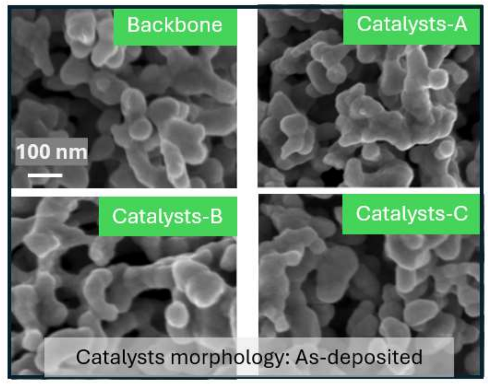




- Built two ALD systems, both with an exposure mode designed to ensure uniform deposition of catalysts across the entire surface of electrodes with high geometric complexity
- The ALD chamber features a one-body tubular design with four chemical precursor inputs, reducing system complexity and potential risk while enabling deposition of multiple catalysts.
- Enable deposition of oxides (Pr_2O_3, Ce_2O_3, CoO, ZrO_2, Nb_2O_5, TiO_2) and metals (Pt and Ru) as well as mixtures of different materials.

Typical Catalyst-Coated Electrode Morphologies





- The catalyst coating applied via ALD provides uniform coverage, preserving the surface texture of the underlying materials.
- The consistent morphology of as-deposited electrodes highlights the precise layer-by-layer feature of the ALD process.
- The ALD coating may interact with the substrate materials, potentially creating a mixed phase on the electrode's surface at operating temperatures.

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Accomplishments: Electrolyte Development

Developed a set of new proton-conducting electrolytes with excellent stability against high concentration of steam and CO_2 while maintaining high conductivity

- Engineered co-doping and defect chemistry for improving both conductivity and durability against high concentration of steam
- Identified co-doped proton conductors with enhanced stability and minimal reaction towards NiO; compatibility with Ni-based electrode is critical to performance

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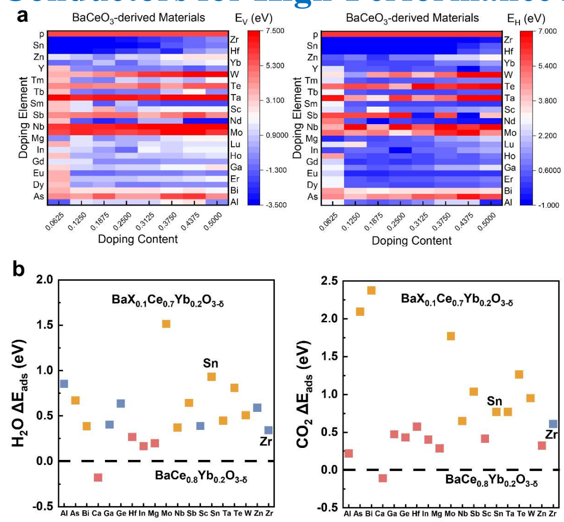
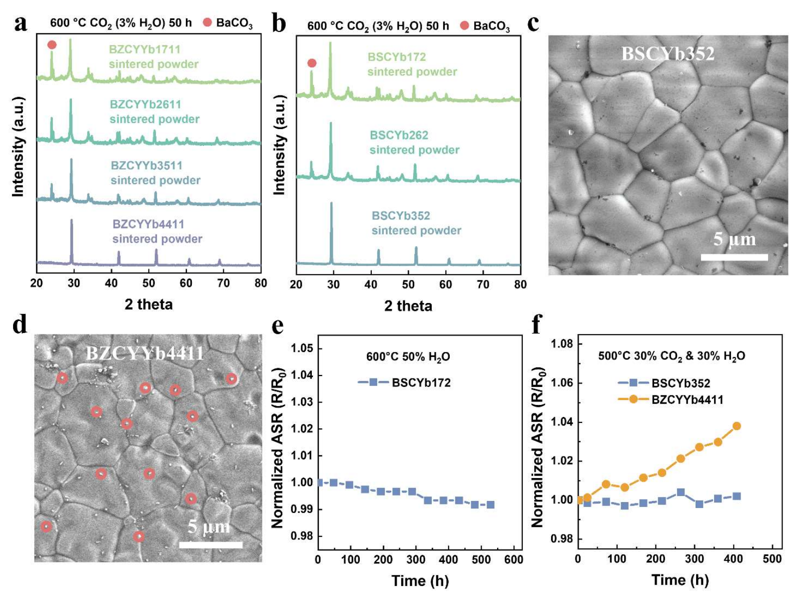
Harnessing High-throughput Computational Methods to Accelerate the Discovery of Proton Conductors for High-Performance P-SOCs

Poster 2:
Electrolyte Development



- **Sn-doped barium cerate** is predicted to exhibit favored oxygen vacancy and proton formation energy (E_V and E_H) and improved chemical stability against H_2O and CO_2

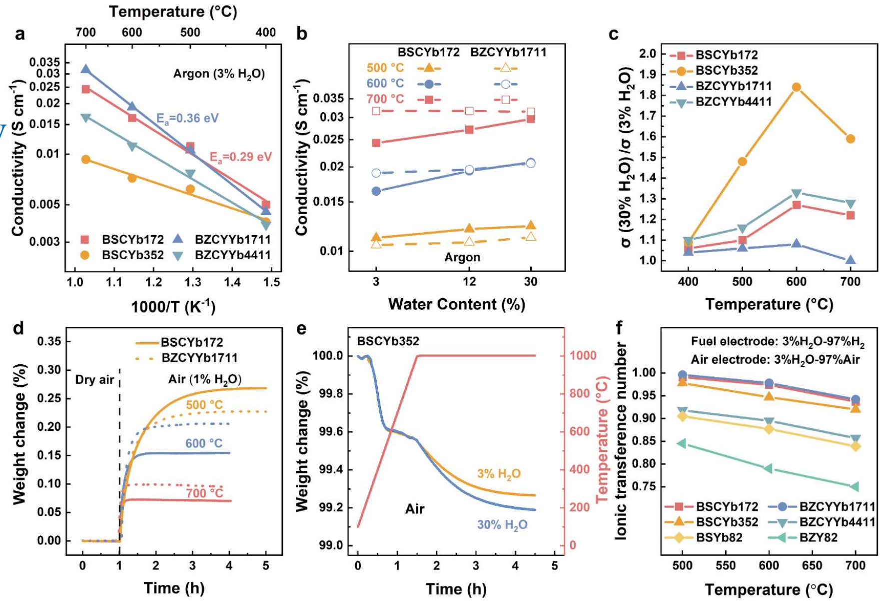
Chemical Stability: Sn-doped ones are more stable than Zr-doped ones
at the same doping concentration



Conductivity

Hydration

t_{ion}



- B**S**CYb exhibits lower activation energy, higher conductivity, improved hydration capability, and enhanced ionic transference number than B**Z**CYYb, especially at low temperatures (≤ 500 °C)

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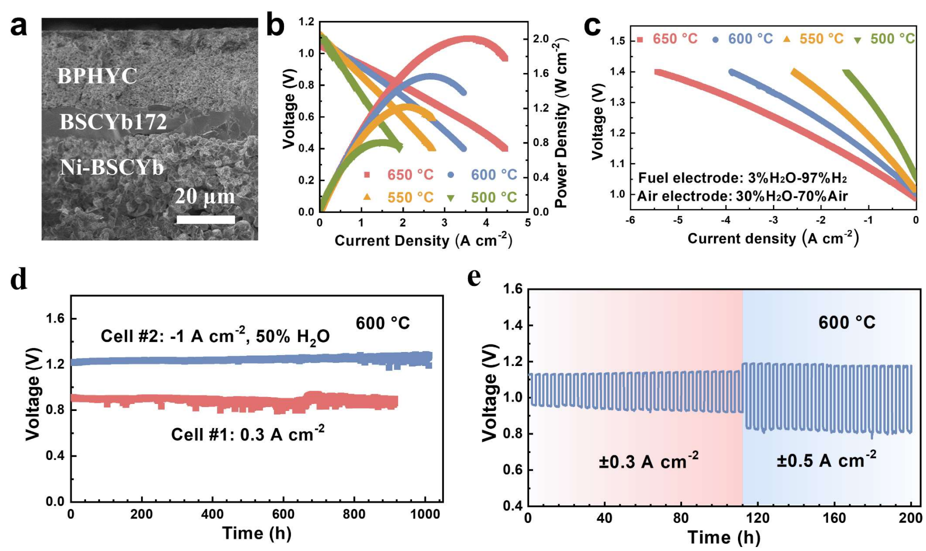
Cell Performance



- Demonstrated durability for over 1,000 h when exposed to 50% H_2O during electrolysis mode
- FC: peak power: 1.57 W cm^{-2} ;   EC: 2.62 A cm^{-2} at 1.3 V at 600 °C

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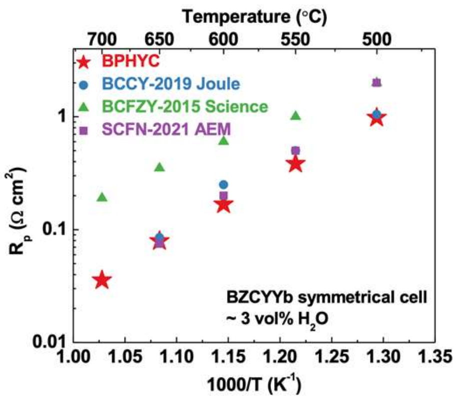
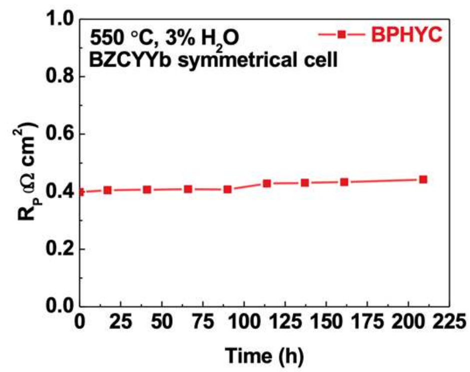
Accomplishments: Electrode Materials

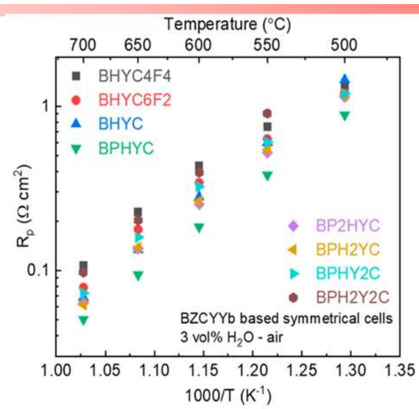
Developed a composite electrode material (BPHYC) with high activity & durability

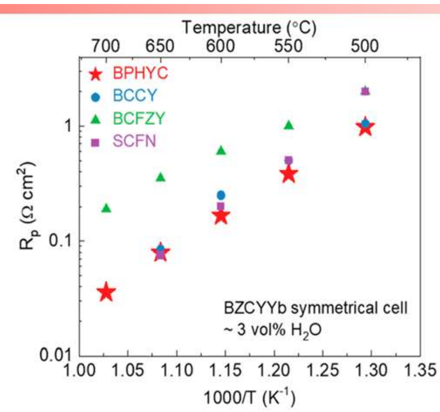




- **Electrode polarization resistance: < 0.2 Ω cm² at 600 ºC**
- **Good stability in humified air**

O-Electrode $Ba_{0.9}Pr_{0.1}Hf_{0.1}Y_{0.1}Co_{0.8}O_{3-\delta}$ (BPHYC)



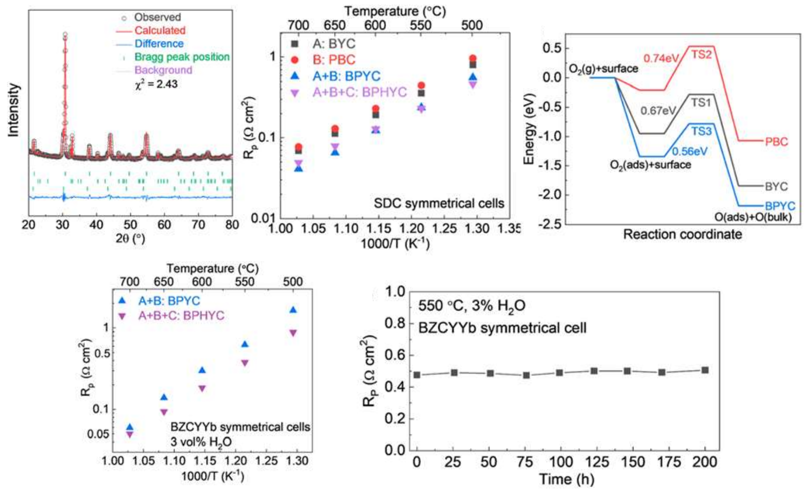


- **A series of** triple-conducting air electrode materials were designed, synthesized, and optimized by rationally doping transition- and rare-earth metal ions (such as Co, Fe, and Pr, *etc.*) into $BaHf_{0.8}Y_{0.2}O_{3-\delta}$.
- Among all of the material candidates, **BPHYC** shows the lowest R_p, surpassing other triple-conducting air electrode materials reported to date, especially at temperatures below 600 °C (**~0.17 Ω-cm² at 600 °C**).

ACS Energy Lett. 2023, 8, 3999.

A synergistic 3-phase, Triple-conducting Electrode

BPHYC has 3 phases: Y-doped $BaCoO_{3-\delta}$ (BYC), $PrBaCo_2O_{5+\delta}$ (PBC), and Y-doped $BaHfO_{3-\delta}$ (BHY)



- BYC and PBC have a synergistic effect on the kinetics of the ORR.
- A mixture of BYC and PBC shows superior oxygen adsorption and dissociation processes.
- The reduction of R_p by adding BHY to BPYC on BZCYYb electrolytes was most likely due to the improvement of proton-related ORR activity.
- BPHYC demonstrated good stability in wet air on BZCYYb electrolytes at 550 °C.

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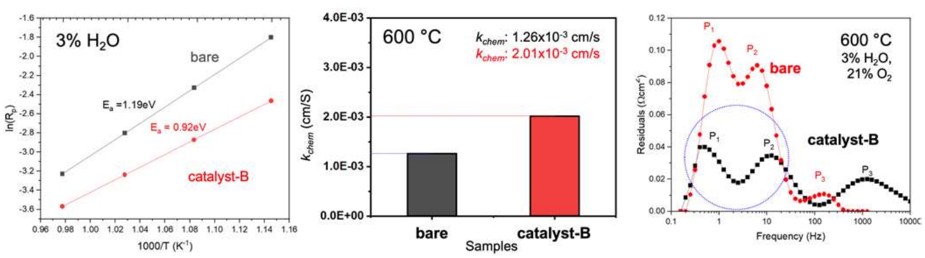
Accomplishments: Catalysts Development

O-Electrodes: $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC), Catalysts: Ruddlesden-popper phased oxide



catalyst-B ORR reactions

$O_{2,bulk} \rightarrow O_{2,ads}$ (adsorption)

$\frac{1}{2} O_{2,ads} \rightarrow O_{ads}$ (dissociation)

$O_{ads} \rightarrow O^-_{ads} + h^\cdot$ (peroxide formation)

$O^- \rightarrow O^{2-} + h^\cdot$ (oxide formation)

$O^{2-} + V_{\ddot{O}} \rightarrow O_O^x$ (ion incorporation)

- Among several MIEC oxides, the Ruddlesden−Popper (RP)-phase type nickelates $Ln_2NiO_{4+\delta}$(Ln = lanthanide) are promising catalyst for O-electrode.
- RP-phase oxides display good tolerance against contaminants, enhancing electrode durability.
- Catalyst-coated PBCC showed lower Rp (e.g, ~**0.10 *vs.* 0.16 Ω-cm²** at 600 C).
- RP-phase catalysts dramatically enhance the oxygen surface kinetics, including adsorption and dissociation reactions for ORRs.

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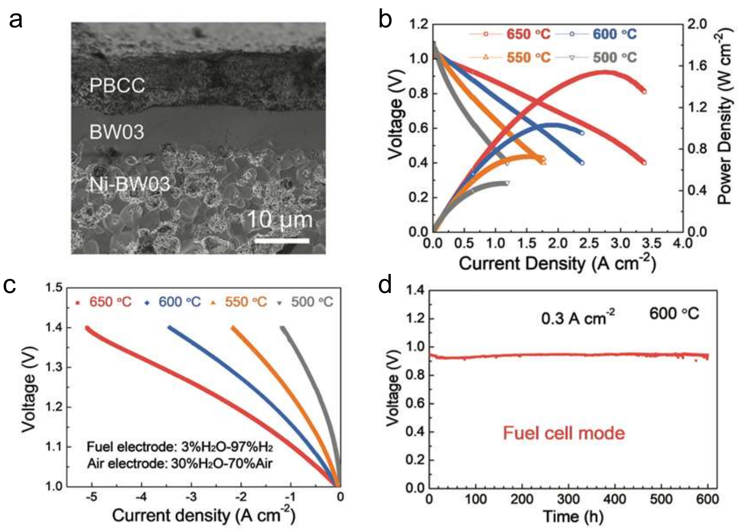
ACS Energy Lett. 2023, 8, 3999−4007

Single Cell Performance

O-Electrodes: $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC), Electrolytes: $BaW_{0.03}Ce_{0.71}Yb_{0.26}O_{3-\delta}$ (BW03)



a) Ni-BW03/BW03/PBCC single cell

b) Typical I–V–P curves measured in the fuel cell mode at 500–650 °C with H_2 (3% H_2O) in the fuel electrode and air in the air electrode.

c) Typical I–V curves measured in the electrolysis mode at 500-650 °C with H_2 (3% H_2O) in the fuel electrode and air (30% H_2O) in the air electrode.

d) fuel cell mode with H_2 (3% H_2O) in the fuel electrode and ambient air in the air electrode at 0.3 A/cm² and 600 °C.

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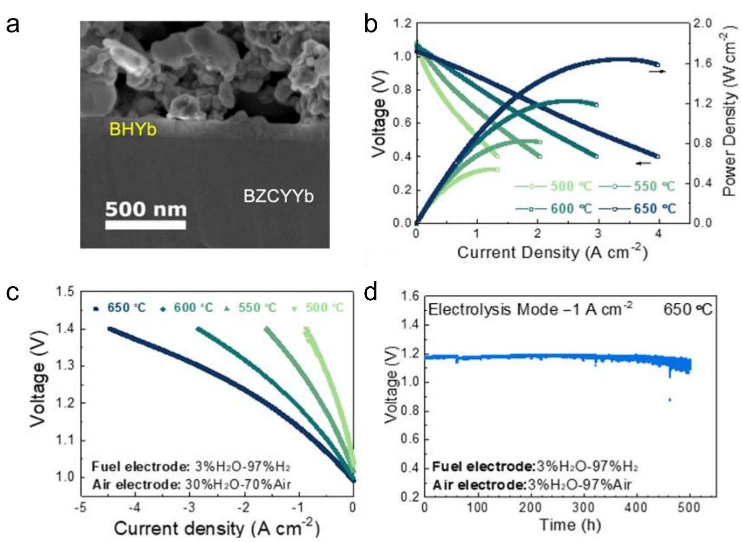
Single Cell Performance

O-Electrodes: $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC), Electrolytes: **BZCYYb1711/$BaHf_{0.8}Yb_{0.2}O_{3-\delta}$** (BHYb82)



a) SEM images of the BHYb bilayer-based single cells after electrode firing at 950 °C for 2 h.
b) b) Typical I−V−P curves in the fuel cell mode with H_2 (3% H_2O) in the fuel electrode and ambient air as the oxidant from 500 to 650 °C.
c) c) Typical I−V curves in the electrolysis mode with H_2 (3% H_2O) in the fuel electrode and 30% H_2O balanced air in the air electrode.
d) d) Long-term stability in the electrolysis mode with c) 3% H_2O balance air in the air electrode.

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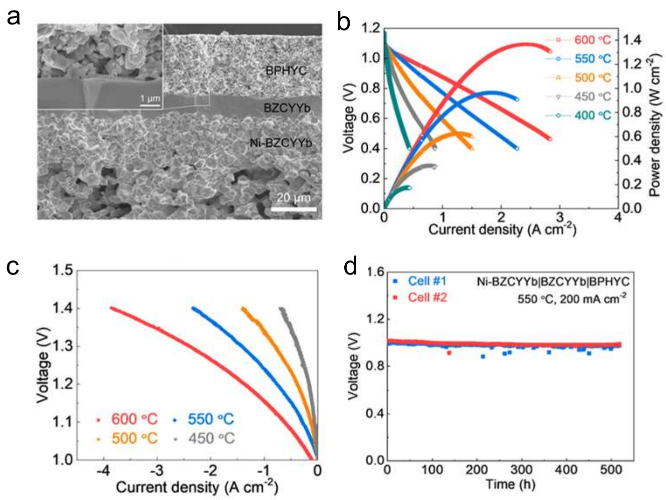
Single Cell Performance

0-Electrodes: $Ba_{0.9}Pr_{0.1}Hf_{0.1}Y_{0.1}Co_{0.8}O_{3-\delta}$ (**BPHYC**), Electrolytes: BZCYYb1711



a) Cross-sectional SEM image of the Ni-BZCYYb|BZCYYb|BPHYC single cell as prepared. Inset: high-magnification SEM image of the air electrode and electrolyte interface.

b) b) I−V−P curves in the fuel cell mode using hydrogen as the fuel and air as the oxidant at different temperatures. Fuel electrode atmosphere: 20 sccm 3% H_2O-H_2. Air electrode atmosphere: 100 sccm air.

c) c) I-V curves of the electrolysis cell with BPHYC as the air electrode at different temperatures. Fuel electrode atmosphere: 20 sccm 3% H_2O-H_2. Air electrode atmosphere: 100 sccm 30% H_2O−air.

d) d) Stability of two single cells operated in the fuel cell mode at 550 °C for over 500 h. Fuel electrode atmosphere: 20 sccm 3% H_2O-H_2. Air electrode atmosphere: ambient air.

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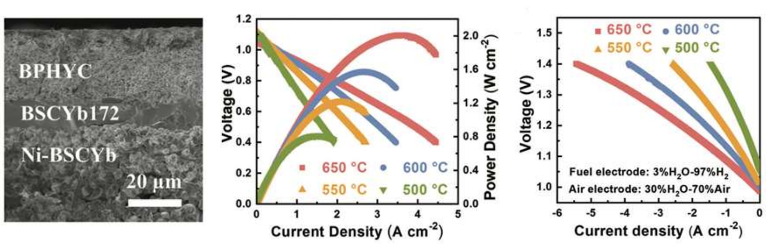
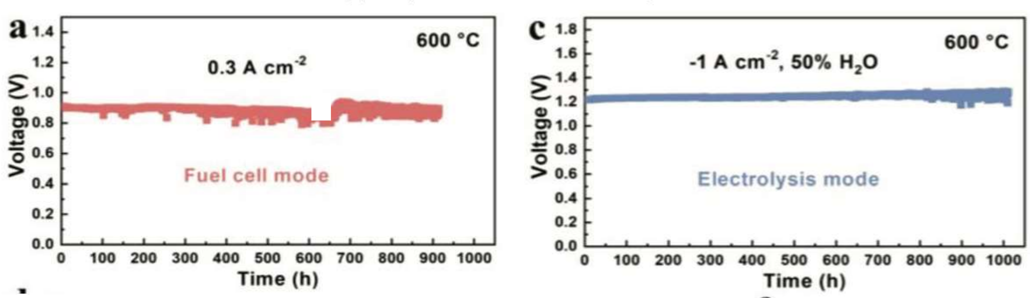
Single Cell Performance

- Air Electrodes: $Ba_{0.9}Pr_{0.1}Hf_{0.1}Y_{0.1}Co_{0.8}O_{3-\delta}$ (BPHYC), Electrolytes: $BaSn_{0.1}Ce_{0.7}Yb_{0.2}O_{3-\delta}$ (BSCYb172)



T (°C)	V_{FC}@0.5A/cm² (V)	V_{EL}@1 A/cm² (V)	Roundtrip Efficiency
600	1.011	1.137	88.9%
550	0.997	1.189	83.8%

~2.8 A/cm² at 1.3 V at 600 °C



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Summary of Cell Performance

A. Cells based on Mo/W-doped Electrolytes

- Current density of **~2.3 A/cm²** at 1.3 V in SOEC mode at 600 °C
- The roundtrip efficiency of **~85%** in both SOFC and SOEC modes at 650 °C
- Degradation rate of **~0.33%kh** in SOFC mode at 600 °C **(~500h operation)**

B. Cells based on Bi-layer BHYb/BZCYYb Electrolytes

- Current density of **~2.0 A/cm²** at 1.3 V in SOEC mode at 600 °C
- The roundtrip efficiency of **~84.7%** in both SOFC and SOEC modes at 650 °C
- Degradation rate of **~0.41%kh** in SOFC mode at 600 °C **(~500h operation)**

C. Cells based on BPHYC triple-conducting air electrodes

- Current density of **~2.5 A/cm²** at 1.3 V in electrolysis mode at 600 °C
- The roundtrip efficiency of **~84.9%** in both SOFC and SOEC modes at **600 °C**
- Degradation rate of **~0.4%kh** in SOFC mode at 600 °C **(~500h operation)**

D. Cells based on Sn-doped Electrolytes

- Current density of **~2.8 A/cm²** at 1.3 V in electrolysis mode at 600 °C
- The roundtrip efficiency of **~88.9%** in both SOFC and SOEC modes at **600 °C**

Task	Milestone Title & Description	Demonstrated
2.1	Electrolyte with conductivity >0.01 S/cm in Ar (3%H_2O) and t_i > 0.95 at 600 °C	**0.02 S/cm; 0.98**
2.2	Bi-layer electrolyte durability: Degradation rate of <0.5% per 1000 h	**0.4%**
3.1	O-electrode with a polarization resistance of < 0.3 Ω-cm² at 600 °C in Air (3%H_2O)	**0.17 Ω · cm²**
3.2	O-electrode optimization with a Rp < 0.2 Ω-cm² at 600 °C in Air (3%H_2O)	**0.15 Ω · cm²**
4.1	Complete the catalyst modification of O-electrode with Rp < 0.15 Ω-cm² at 600 °C in Air (3%H_2O), and the durability evaluation for at least 500 h with a degradation rate of < 0.5% per 1,000 h under the presence of contaminations (*e.g.*, H_2O and Cr).	**0.10 Ω · cm²** **0.49%**
4.2	Complete in situ and ex situ characterization of surface morphology and surface species using experimental and modeling work to determine the activity and stability of the cells in the presence of contaminants under typical operating conditions.	**Completed**
5.1	Demonstrate current density of >1.8 A/cm² at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency at 0.5 A cm² in both SOFC and SOEC modes at ≤ 650 °C.	**2.6 A/cm²** **80%**
5.2	Complete durability evaluation of cells for at least 500 h with a degradation rate of <0.5% per 1,000 h.	**0.49% (1000h)**

Achieved End of Project Goal:

*1) Current density of > **1.8 A cm⁻² at 1.3 V** in electrolysis mode at **600 °C***
*2) **≥ 75%** roundtrip efficiency at **≤ 650 °C***
3) > 500 h** operation with a degradation rate **< 0.5% per 1,000 h

Products: Publications

- **Z. Luo**, X. Hu, Y. Zhou, Y. Ding, W. Zhang, T. Li, M. Liu*, Harnessing High-Throughput Computational Methods to Accelerate the Discovery of Optimal Proton Conductors for High-Performance and Durable Protonic Ceramic Electrochemical Cells, ***Adv. Mater.***,2311159, 2024.
- **Z. Luo**, Y. Zhou, **X. Hu**, **W. Wang**, Y. Ding, **W. Zhang**, **T. Li**, **N. Kane**, Z. Liu and M. Liu, A New Class of Proton Conductors with Dramatically Enhanced Stability and High Conductivity for Reversible Solid Oxide Cells, *Small,* 2208064, 2023
- **N. Kane, Z. Luo**, Y. Zhou, Y. Ding, A. Weidenbach, **W. Zhang**, M. Liu, Durable and High-Performance Thin-Film BHYb-Coated BZCYYb Bilayer Electrolytes for Proton-Conducting Reversible Solid Oxide Cells, *ACS Applied Materials & Interfaces*, 15, 27, 2023.
- **W. Zhang**, Y. Zhou, **X. Hu**, Y. Ding, J. Gao, **Z. Luo**, T. Li, **N. Kane**, XY. Yu, T. Terlier, M. Liu, A Synergistic Three-Phase, Triple-Conducting Air Electrode for Reversible Proton-Conducting Solid Oxide Cells, *ACS Energy Letters*, 8, 10, 3999-4007, 2023.

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Acknowledgement

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