Durable and High-Performance SOECs Based on Proton Conductors for H_2 Production

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Project Manager: **Evelyn Lopez**

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Outline

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- **Project Objectives**
- **Technical Approaches**
- **Accomplishments to Date**
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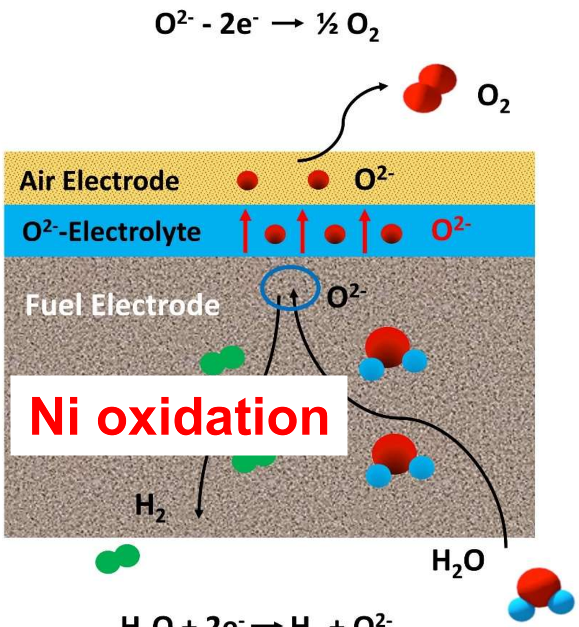
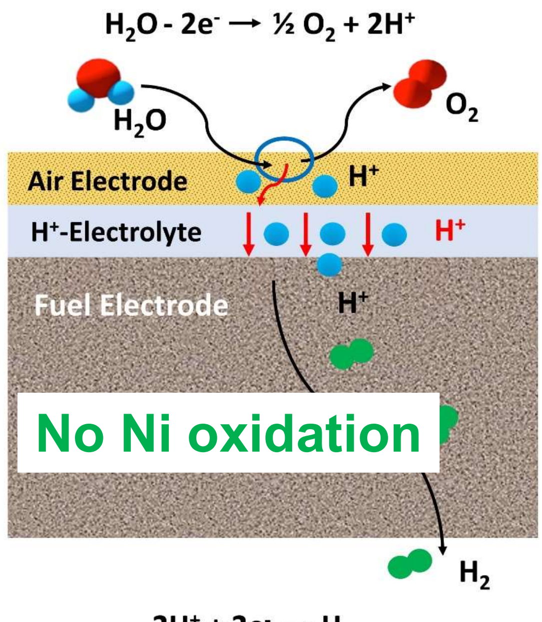
  - Single-phase Proton Conductors
  - Air Electrode Materials
- **Summary and Future Work**
- **Acknowledgement**

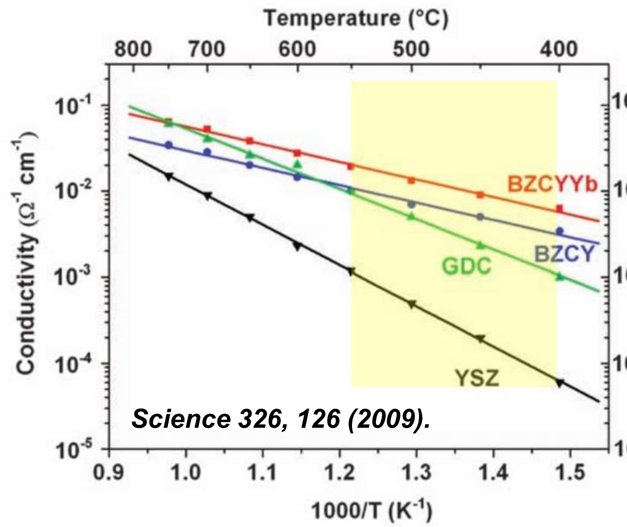
Background



O-SOEC



H-SOEC



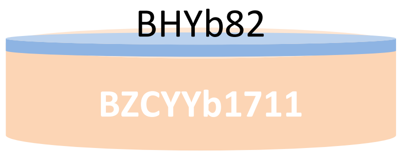
- **High conductivity**
- **Low-temperature operation**
  Reduced cost, enhanced durability
- **Dry H_2 (no need for H_2 separation)**

The most efficient and low-cost option for H_2 production

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

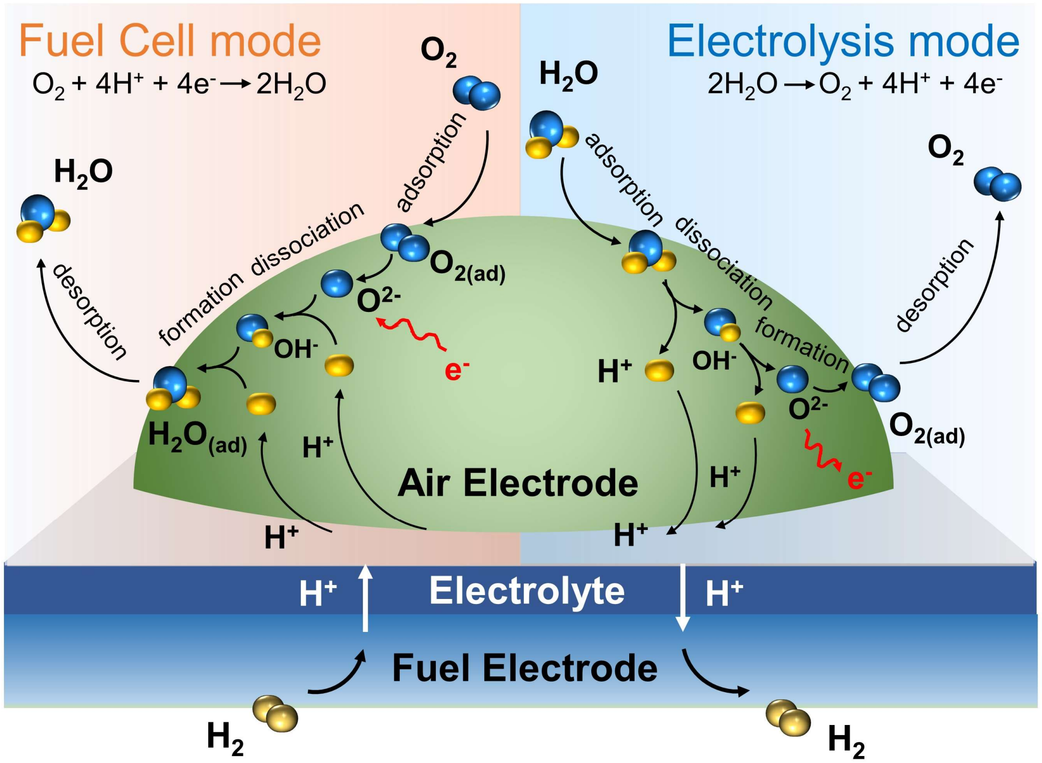
Challenges for Proton Conductors

- $BaZr_xCe_{0.8-x}Y_{0.2-y}Yb_yO_{3-\delta}$ (BZCYYb)
  Performance is limited by a tradeoff between stability & conductivity
- $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb1711)
  - Achieves **high** conductivity and t_H
  - But questionable long-term stability during electrolysis
  - BZCYYb4411 is more stable but less conductive



- $BaHf_{0.8}Yb_{0.2}O_{3-\delta}$ (**BHY82**)
  - Excellent **stability** against high concentration of H_2O/CO_2
  - But relatively low conductivity
- The optimal composition for **bulk** and **surface** should be different.
  The bulk is optimized for conductivity while the surface is for stability.

Challenges for Air Electrode of rSOCs-H^+



Burden is shifted to air electrode.

Electrode reactions are **different.**

H^+ transport would be helpful.

H^+, $V_O^{\cdot\cdot}$, e' $\rightarrow$ $\boldsymbol{MIEC\ surface}$

LSCF/LSM are not suitable.

- **Unstable in high conc. of steam**
- **Higher Rp**

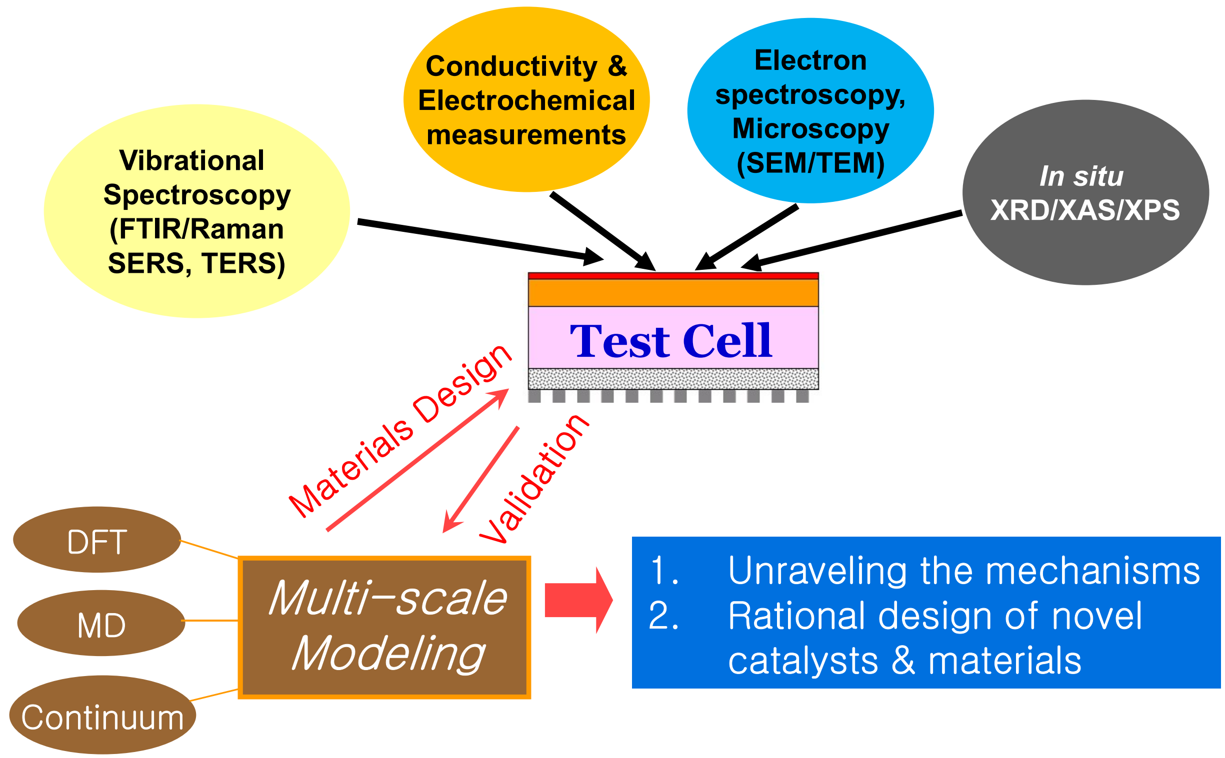
- **How to maintain long-term stability against H_2O and Cr?**
- **How to develop highly active air electrodes for low-temperature operation?**

Objectives

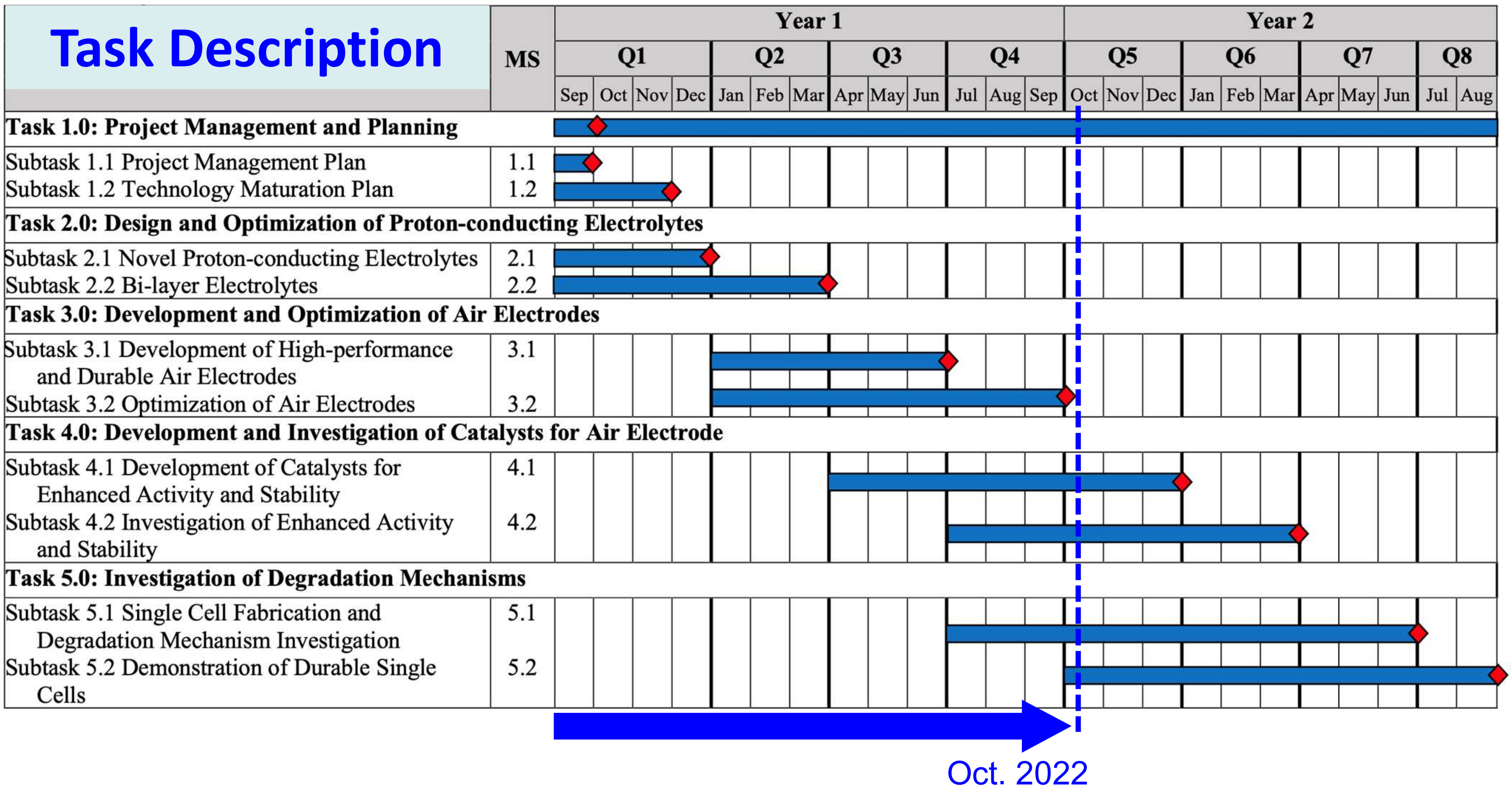
- To develop and optimize a surface modification process (sputtering, SSG, ALD) for deposition of conformal coatings on electrolyte/electrode surface with controlled composition and morphology
- To characterize the electrochemical properties of surface-modified electrolyte/electrodes under typical operating conditions and correlate the properties with the microscopic features of the coating
- To develop and optimize surface modification layers that greatly enhance stability while maintaining high electrochemical performance
- To synthesize the information in order to establish the scientific basis for rational design of ***durable*** electrolytes, electrodes, and catalysts for rSOCs

Technical Approach

- ✓ Developing new composition and structure of proton conducting electrolytes;
- ✓ Tailoring the compositions, structure, and architecture of air electrodes;
- ✓ Optimizing compositions, thickness, morphology, and fabrication processes of surface coatings;
- ✓ Understanding the degradation mechanisms using various *in situ*, *ex situ*, and *operando* measurements guided by theoretical analysis.



Tasks and Project Schedule



Status of Milestones

Date	Milestone	% Complete
12/21	Complete electrolyte development with conductivity >0.01 S cm^{-1} in Ar (3%H_2O) and ionic transference numbers >0.95 at 600 ºC.	100
03/22	Complete bi-layer electrolyte development with the durability of at least 500 h with a degradation rate of <0.5% per 1,000 h.	100
06/22	Complete air electrode development with a R_p of <0.3 Ω cm^2 at 600 ºC in Air (3%H_2O).	100
09/22	Complete air electrode optimization with a R_p of <0.2 Ω cm^2 at 600 ºC in Air (3%H_2O).	100
12/22	Complete the catalyst modification of the air electrode with a R_p of <0.15 Ω cm^2 at 600 ºC 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).	50
03/23	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 as a function of contaminant presence, relevant operating conditions, and catalyst content.	10
06/23	Complete the fabrication of button cells with a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C.	5
09/23	Complete the long-term durability evaluation of button cells for at least 500 h with a degradation rate of <0.5% per 1,000 h.	Not started

Accomplishments to date: Bi-layer electrolyte via co-sputtering

Hypothesis:

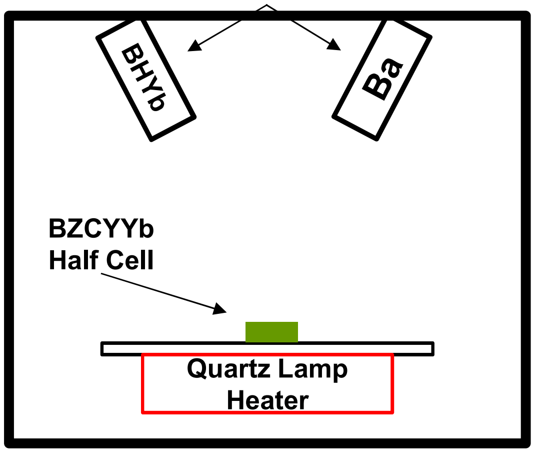
Thin, highly-stable electrolyte layers can protect highly-conductive bulk electrolytes from degradation

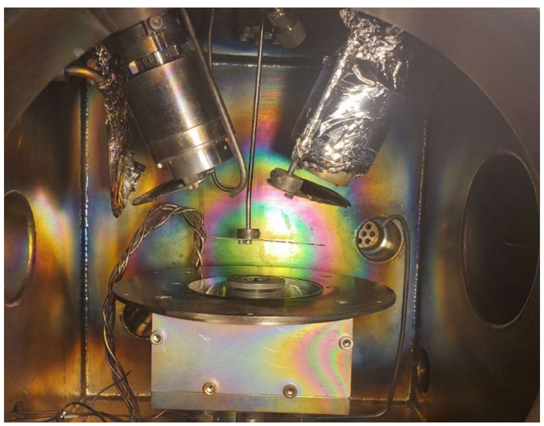
Approaches:

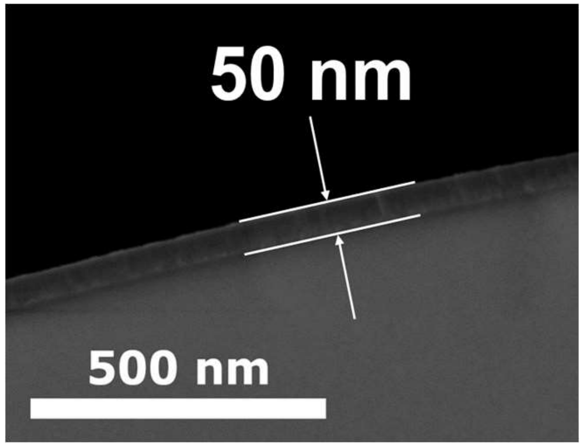
- Fabrication of **dense thin films** on dense electrolytes
- Characterization of the ***structural, morphological***, and ***electrochemical properties***
- Correlation between **electrochemical performance** and **microscopic features** of the films

Optimized co-sputtering conditioins

Sputtering Guns: Co-sputtering



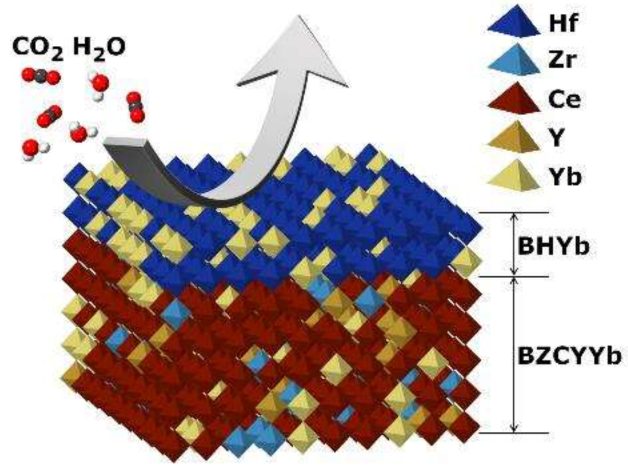




Optimized Parameters

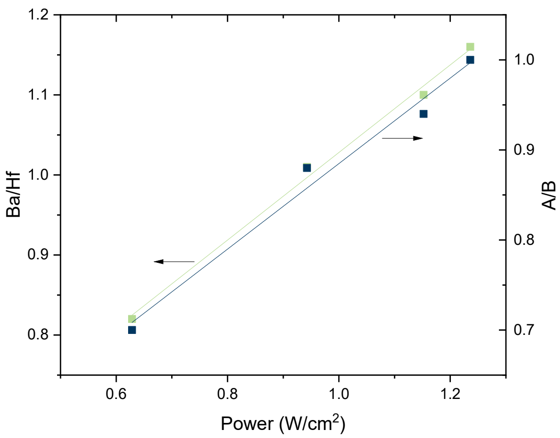
- $BaHf_{0.8}Yb_{0.2}O_3$
- Pure Ar
- 5 mTorr
- BHYb82: 4 W/cm^2
- Ba: 0.8 W/cm^2, Throttled to 40%
- T_{sub} 650 °C
- T_{anneal} 950 °C

BHYb: a thin-film less conductive but highly stable against CO_2/H_2O



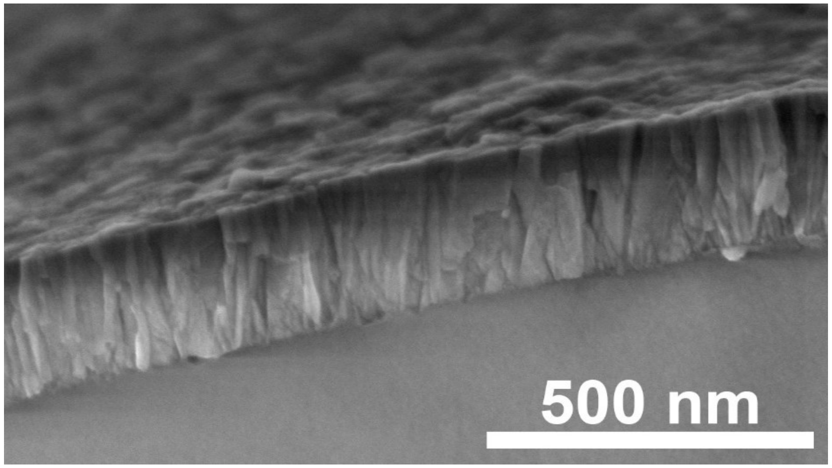
BZCYYb1711: a highly conductive but less stable substrate

Co-sputtering achieves dense films with proper stoichiometry

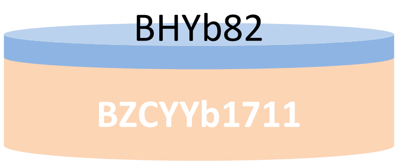


Element	Atomic %
Ba	6.05
Hf	5.01
Yb	1.06
Ag	23.29
O	64.03
Ba:Hf	1.21
A:B	1.00

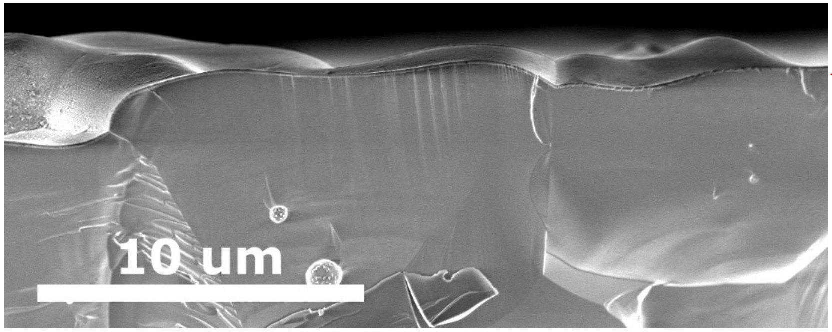
Dense, columnar BHYb film on BZCYYb



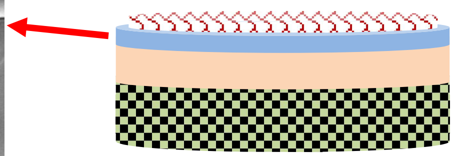
Electrolyte-supported Cell



Well adhered and continuous over the entire electrolyte

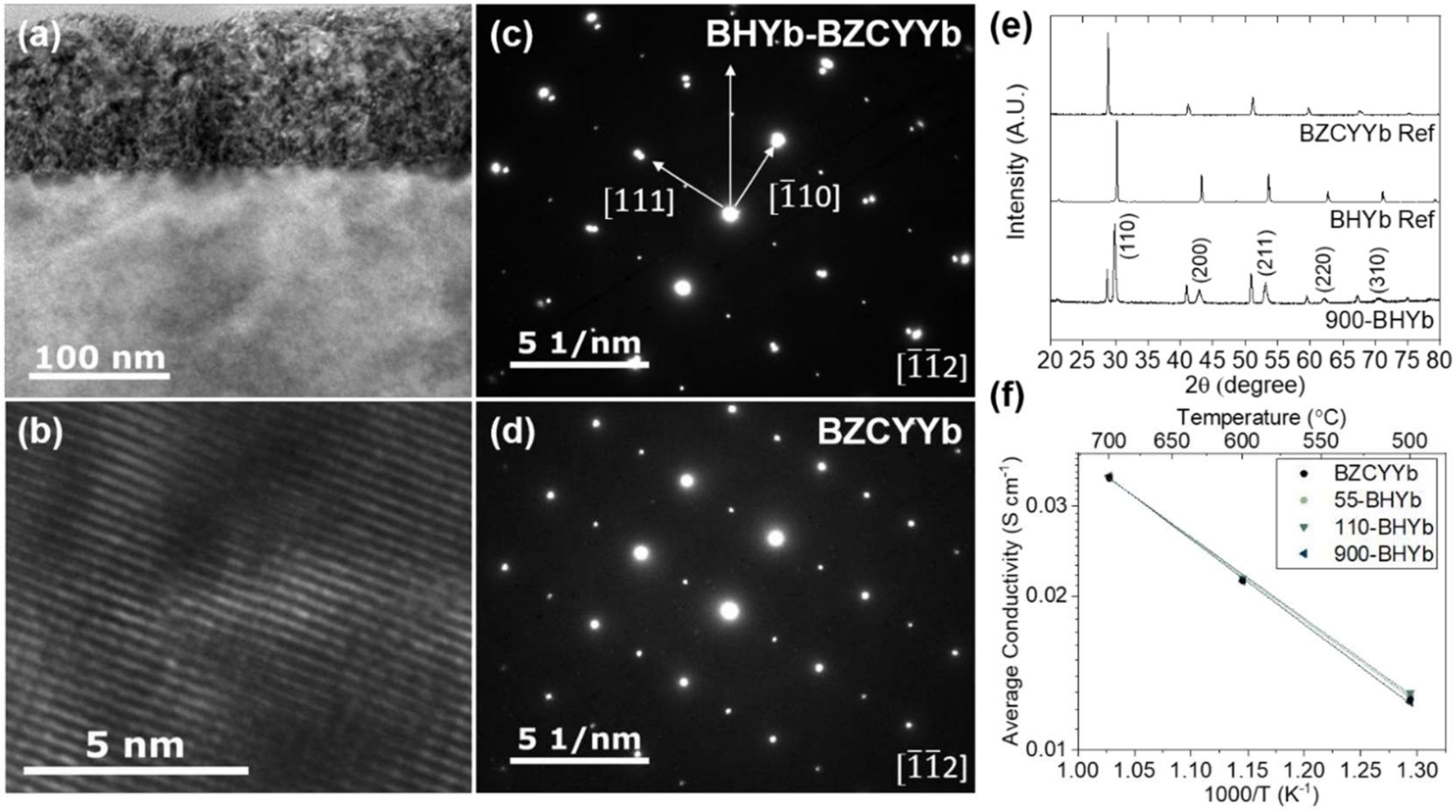


Anode-supported Single Cell



Structural Features and Conductivity

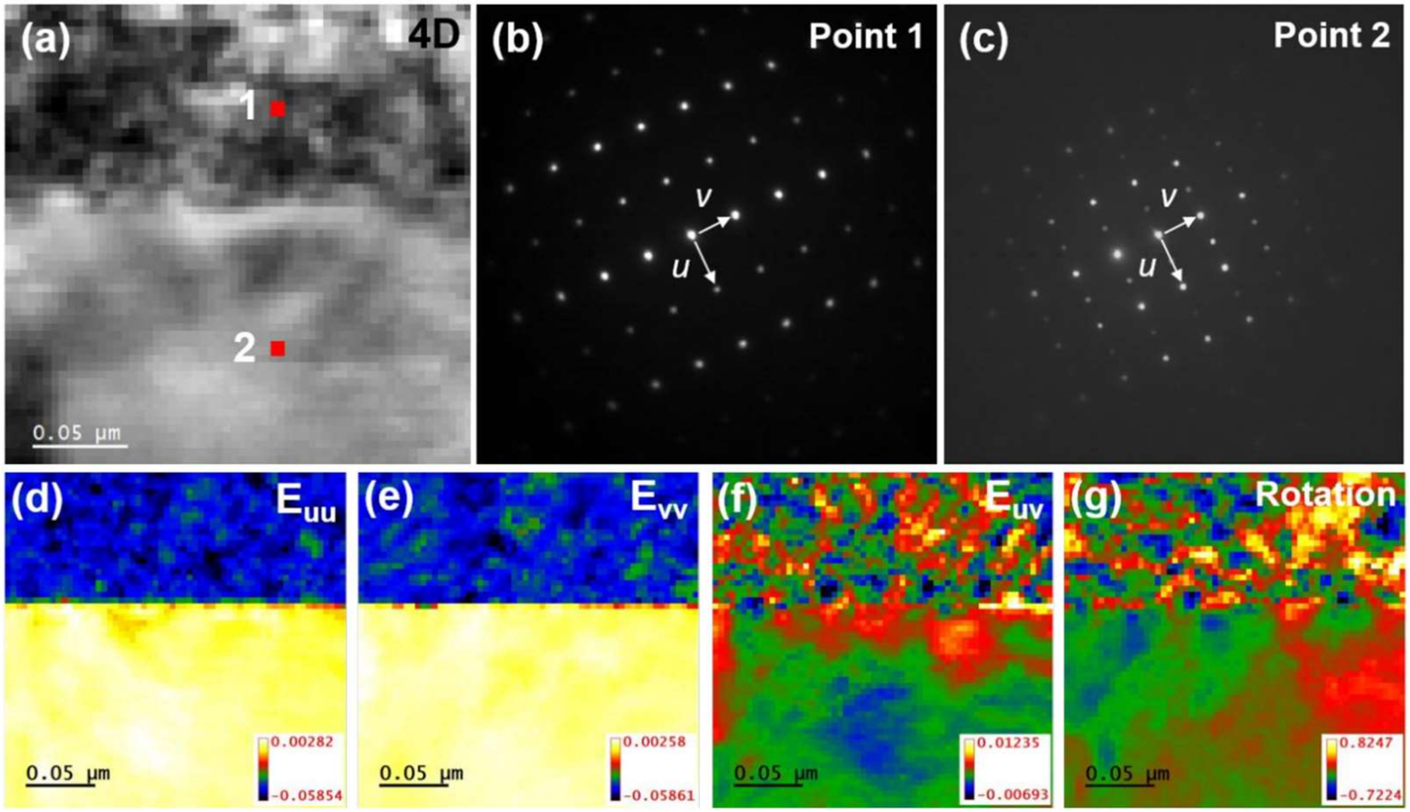
Lattice constant of **BHYb82** film is **~5.8%** smaller than that of the **BZCYYb1711** substrate.



- **Epitaxially** orientated ~110 nm BHYb coating was fabricated on the BZCYYb1711 substrate
- Conductivity of the bi-layer electrolyte is comparable to the unmodified BZCYYb1711

Local Structure and Strain

Each pixel represents the location of an SAED pattern



d) in-plane and
e) out-of-plane strain maps

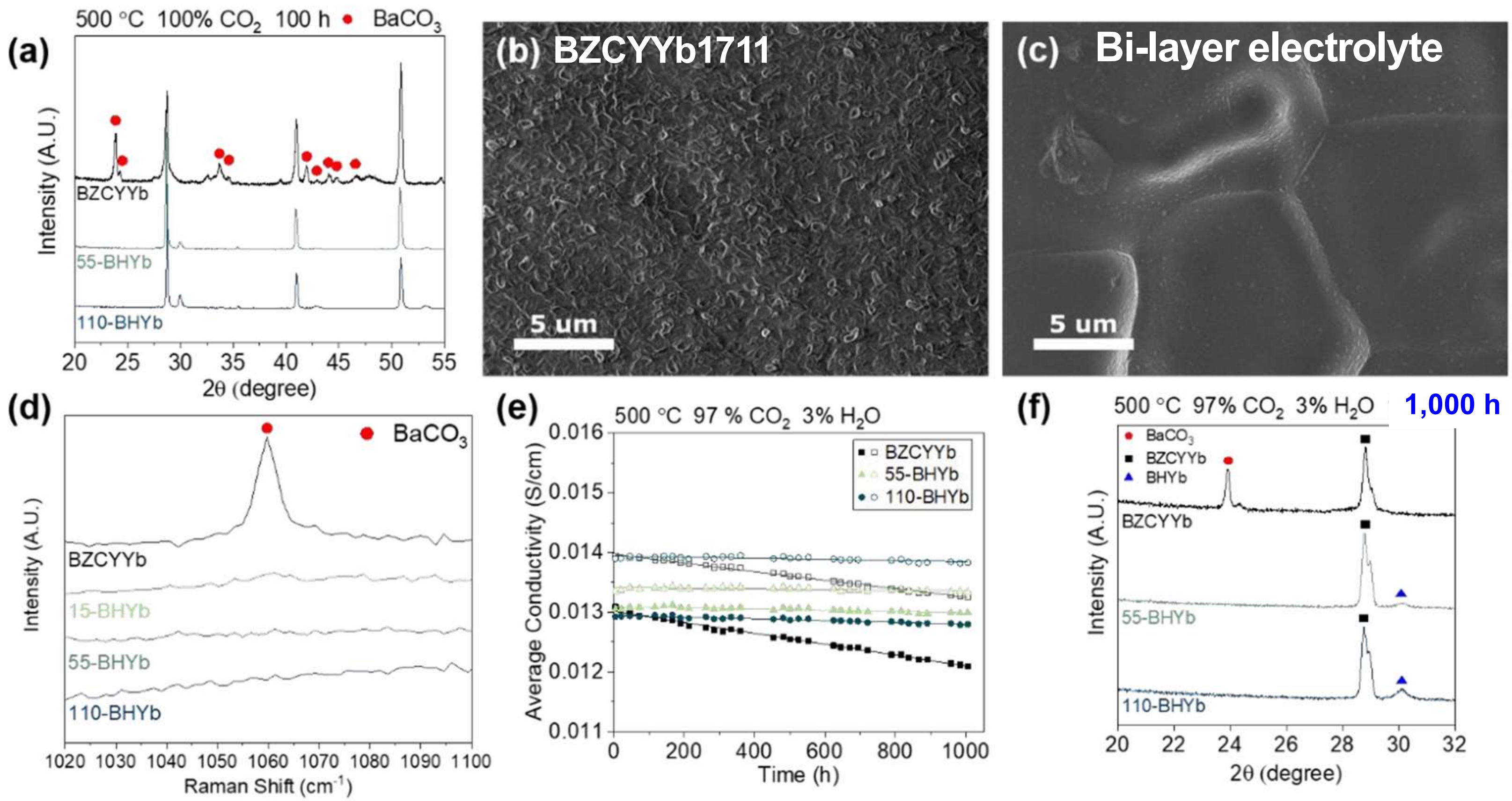
f) shear strains around the interface and extending 200 nm into bulk

- **Local structure of the electrolytes at the interface is confirmed by 4D STEM analysis**
- **Shear strains around the interface are observed due to the difference in lattice parameters**

Stability Against CO_2

100 h

Raman: More sensitive to surface

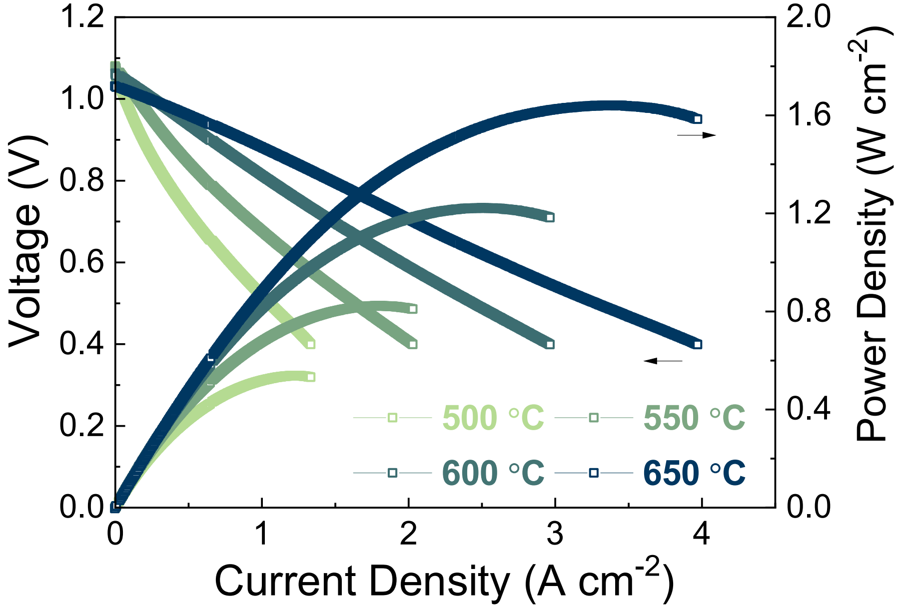


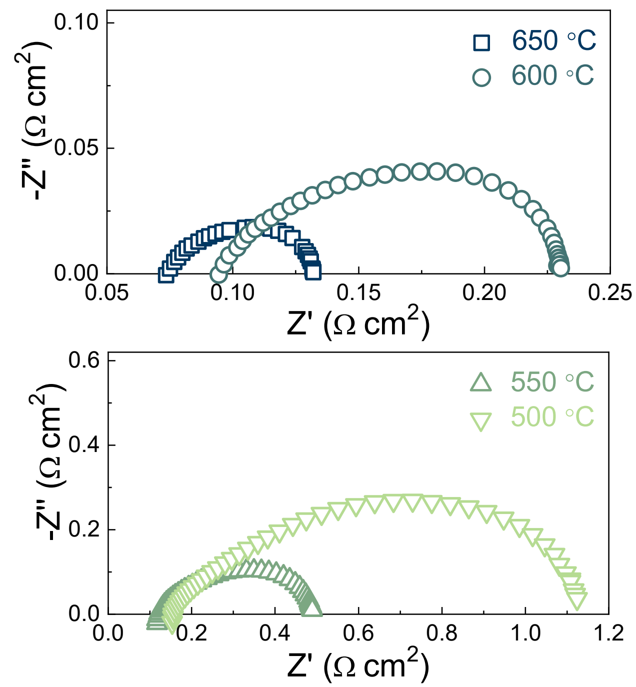
1,000 h

- **Bi-layer electrolyte shows high chemical stability against CO_2**

Performance of the bilayer electrolyte-based cells

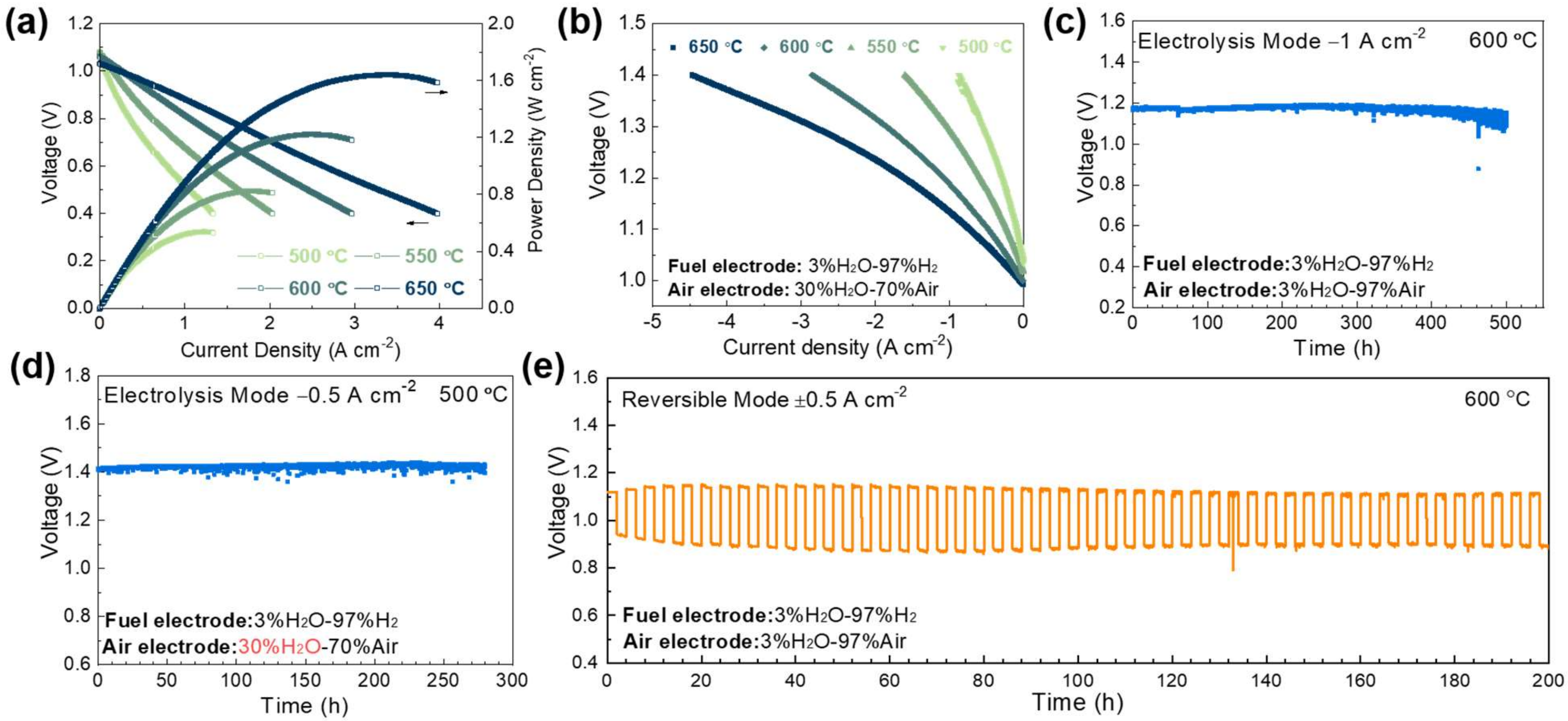
- PPD of unmodified cell: **1.58 W cm^{-2} at 650 °C** (Ref.)
- PPD: **1.64 W cm^{-2} at 650 °C** while maintain excellent stability, effectively circumventing tradeoff between stability and conductivity





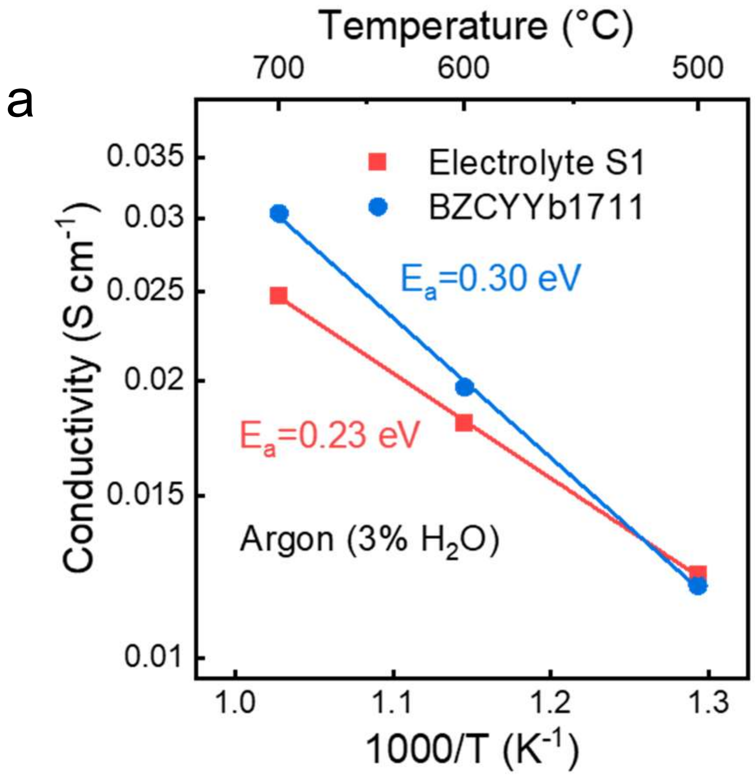
Y. C. Zhou, E. Z. Liu, Y. Chen, Y. C. Liu, L. Zhang, W. L. Zhang, Z. Y. Luo, N. Kane, B. Zhao, L. Soule, Y. H. Niu, Y. Ding, H. P. Ding, D. Ding and M. L. Liu, *ACS Energy Letters, 2021,* ***6, 1511-1520.***

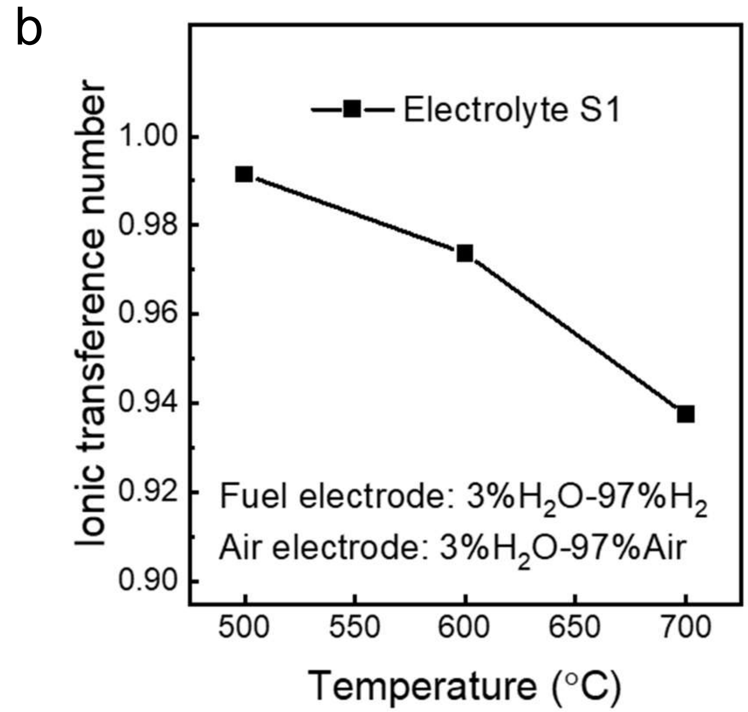
Performance in SOFC & SOEC modes



- Single cells with the bi-layer electrolyte show high performance and stability in both fuel cell and electrolysis modes.

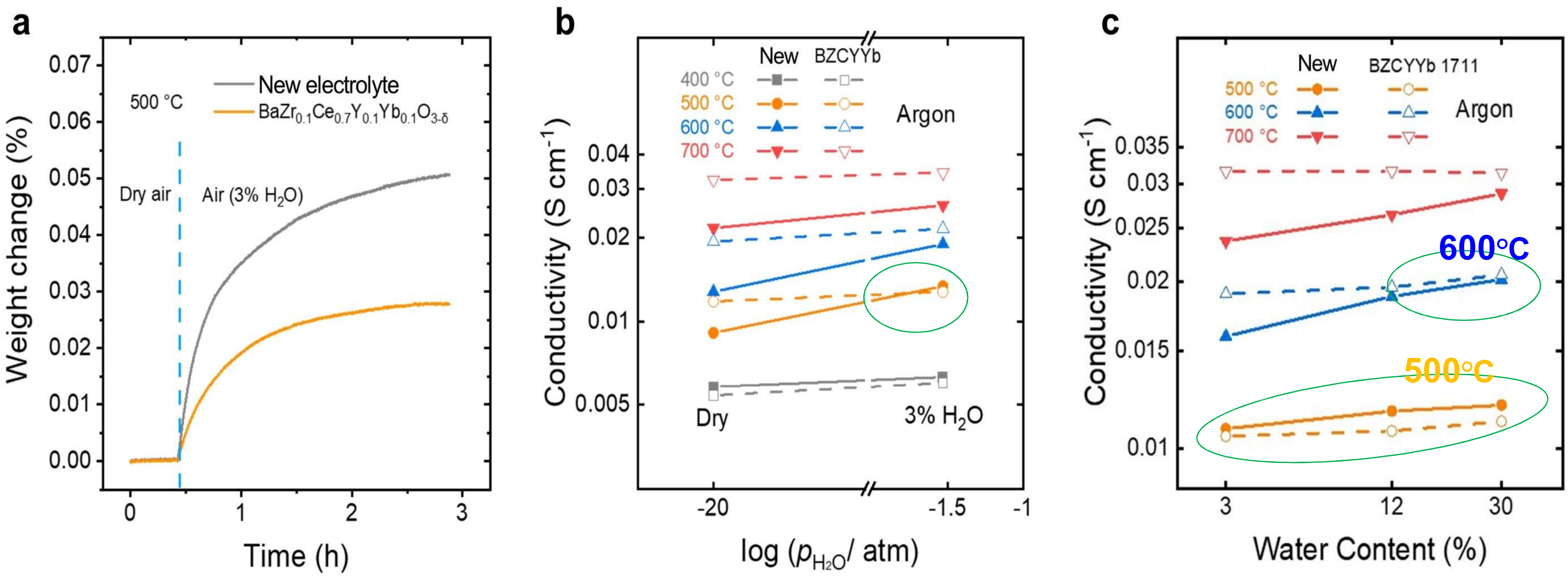
Accomplishments to date: Single-phase Electrolytes





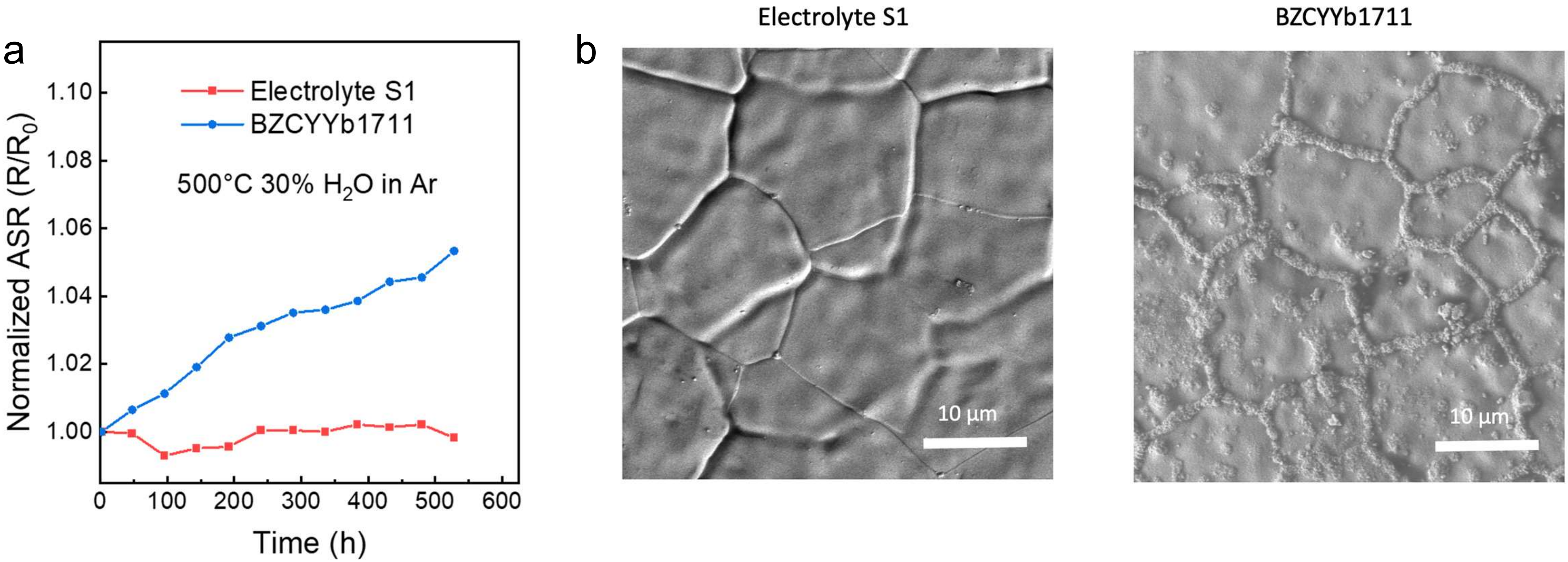
- **Developed a new family of proton-conducting electrolytes (S1) with high stability**
- **High conductivity (0.02 S cm^{-1}) and ionic transference number (0.97) at 600 °C**

p_{H2O} Dependence of Conductivity



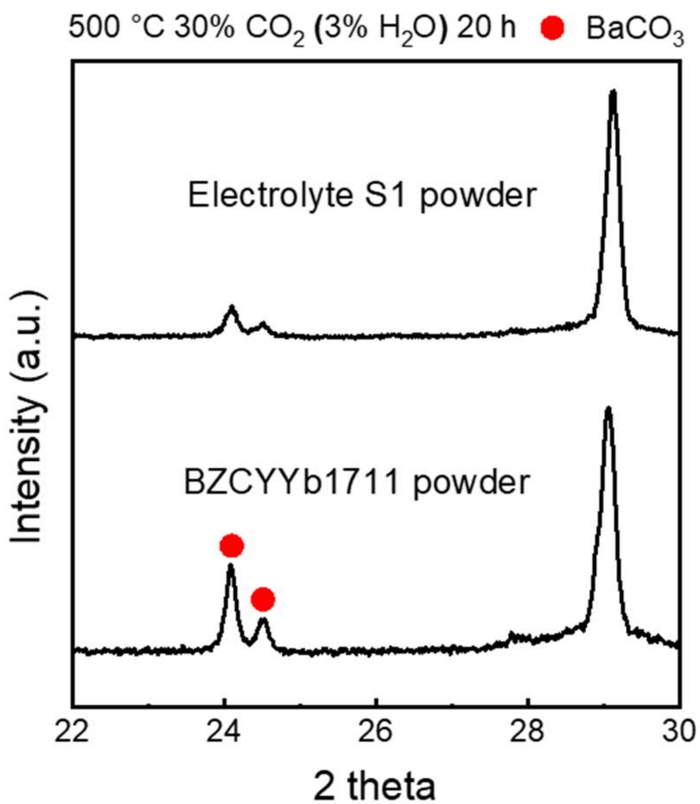
- **The new electrolyte has higher water-uptake capability than BZCYYb.**
- **The conductivity depends strongly on water content, making it a well-suited candidate for water electrolysis**

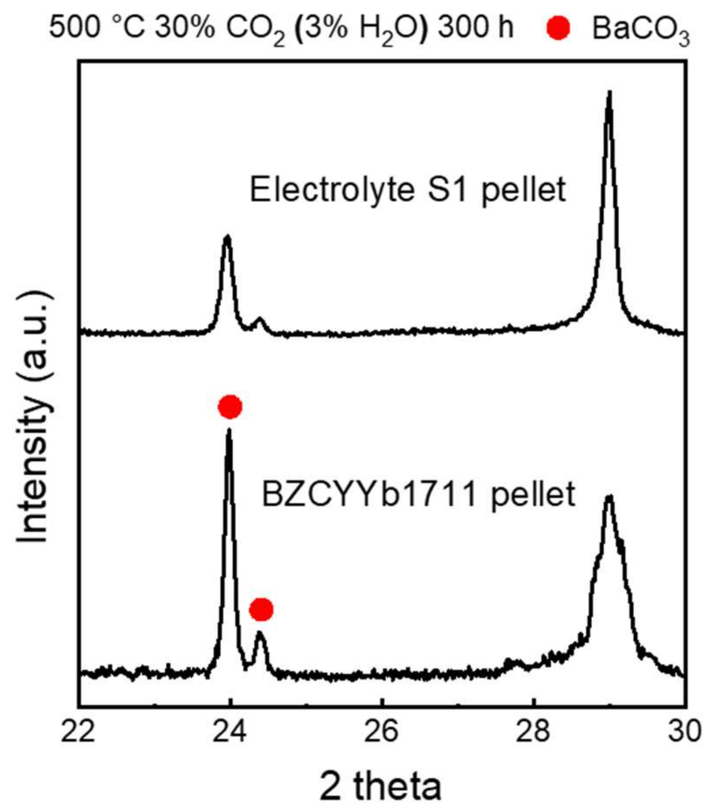
Stability Against H_2O



- New electrolyte S1 exhibits excellent stability against 30% steam
- Secondary particles were observed on BZCYYb1711 electrolyte surface, highly concentrated along the grain boundaries

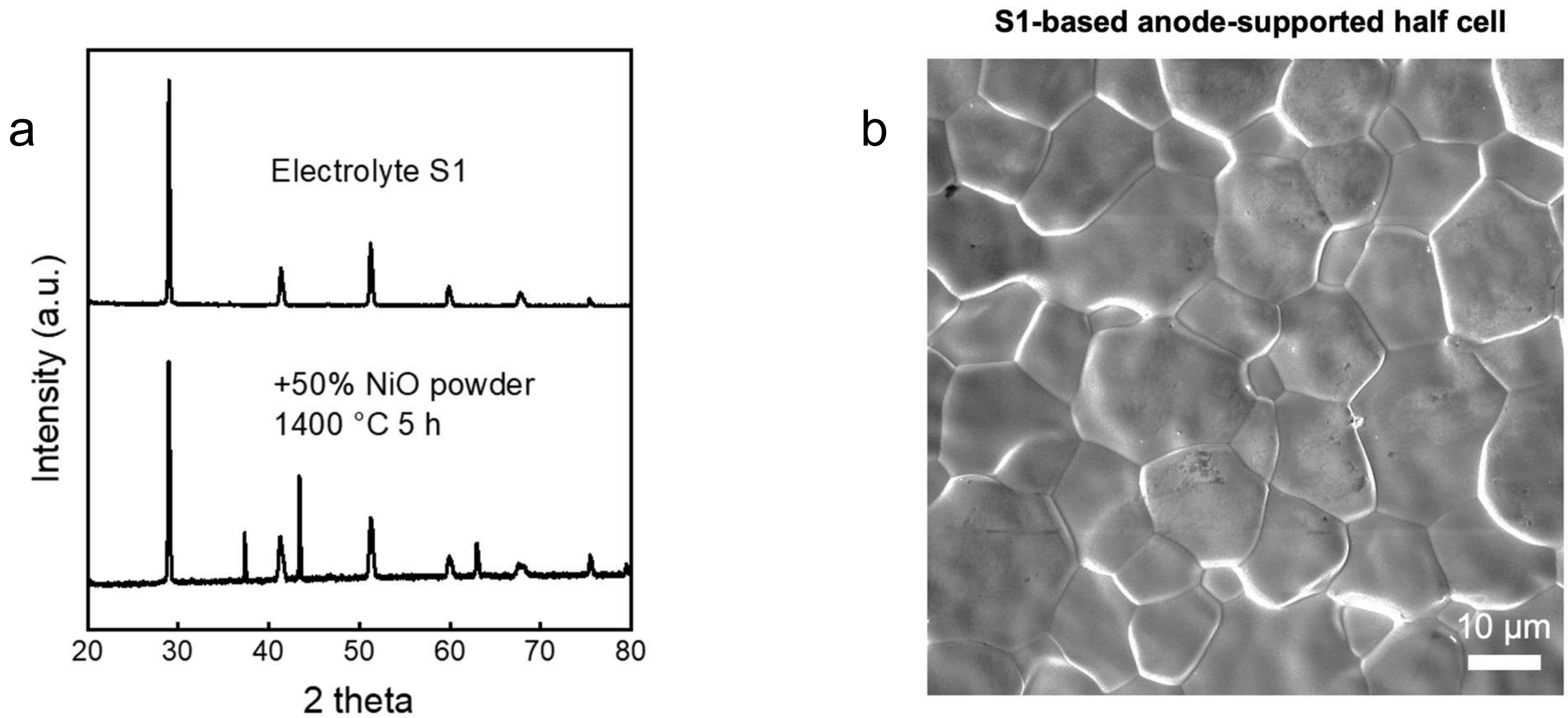
Stability Against CO_2





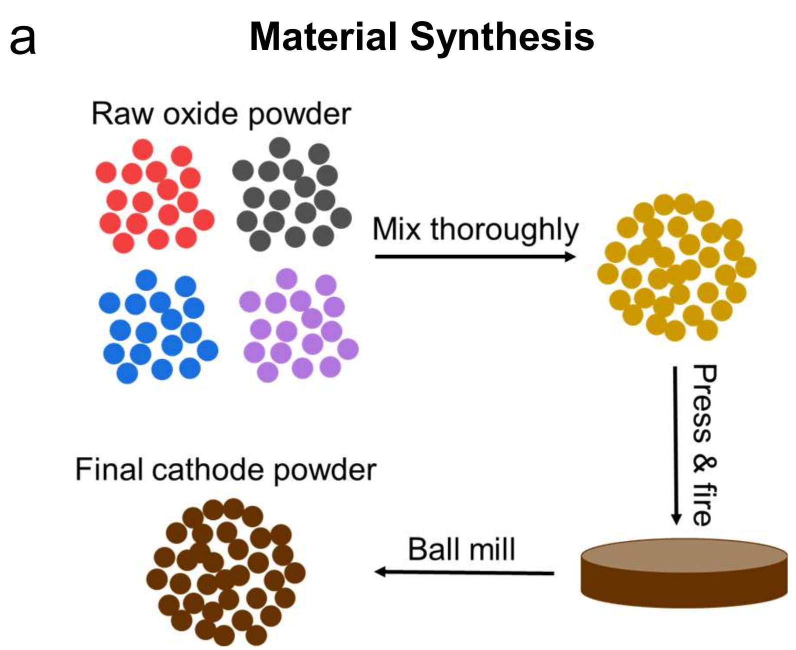
- **New electrolyte S1 shows better stability against CO_2 than BZCYYb1711.**

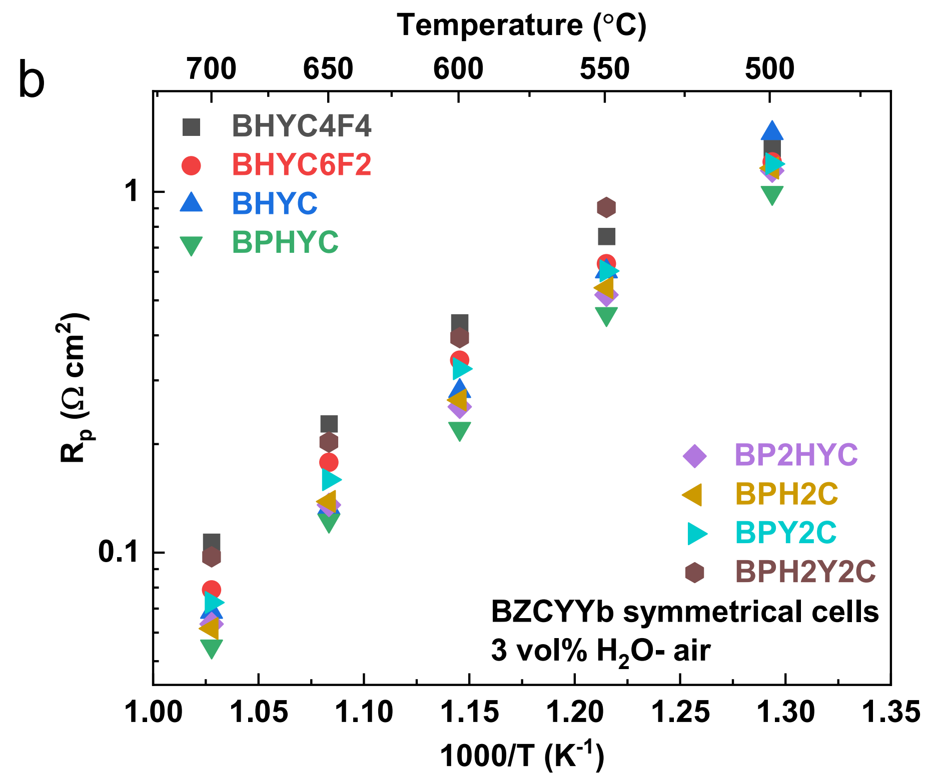
Chemical Compatibility with NiO



- **New electrolyte S1 shows good chemical compatibility with NiO during co-sintering at 1400 °C for 5 h**

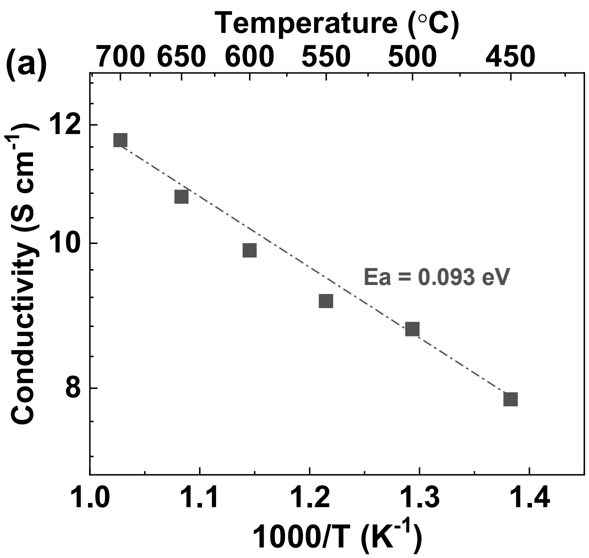
Accomplishments to date: Air Electrode Development



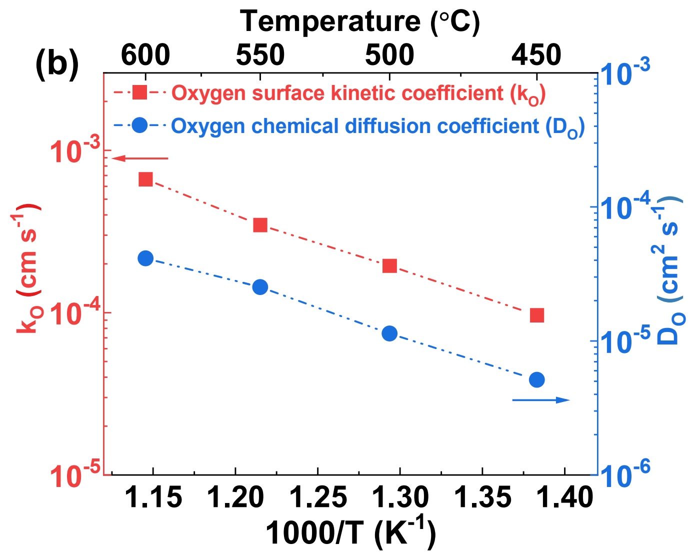


- **Developed a new family of air electrode (BPHYC) with high ORR/OER activity**

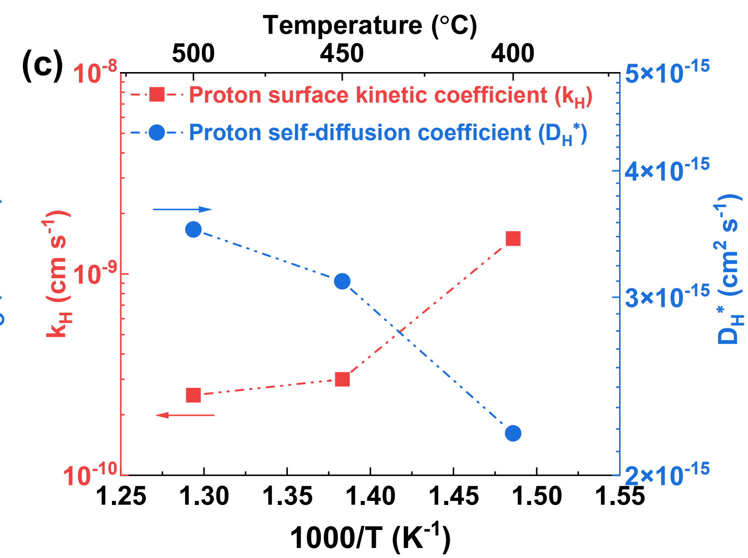
Triple (H^+ ,$V_O^{\bullet\bullet}$, e') Conduction of BPHYC



Total electrical conductivity dominated by electronic conduction



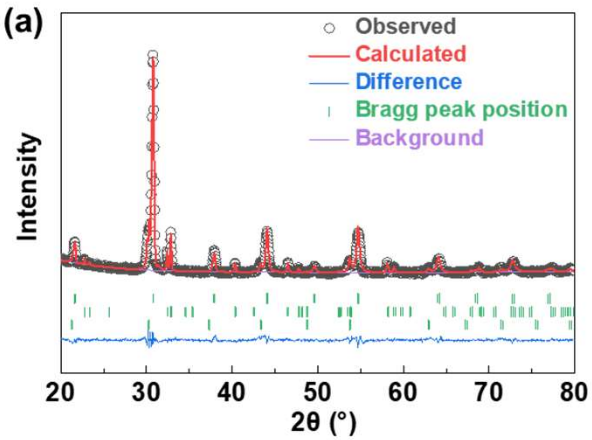
Oxygen surface exchange coefficient and diffusivity, from ECR method



Proton surface kinetic coefficient and diffusivity, from isotope exchange diffusion profile (IEDP)

BPHYC: a multi-phase composite

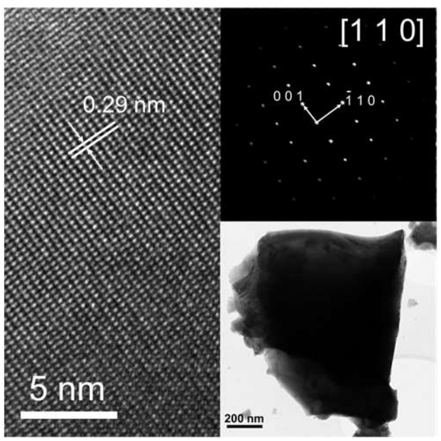
(a)



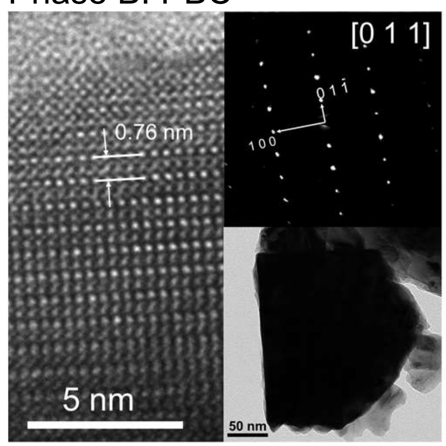
(b)

	a (Å)	b (Å)	c (Å)	Volume (Å^3)
BYC (phase A)	4.111	4.111	4.111	69.465
PBC (phase B)	3.905	3.905	7.618	116.172
BHY (phase C)	4.178	4.178	4.178	72.940

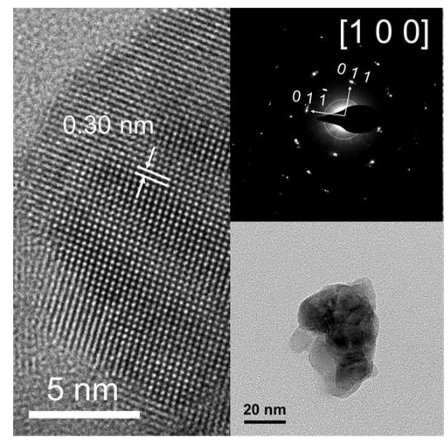
(c) Phase A: BYC



(d) Phase B: PBC

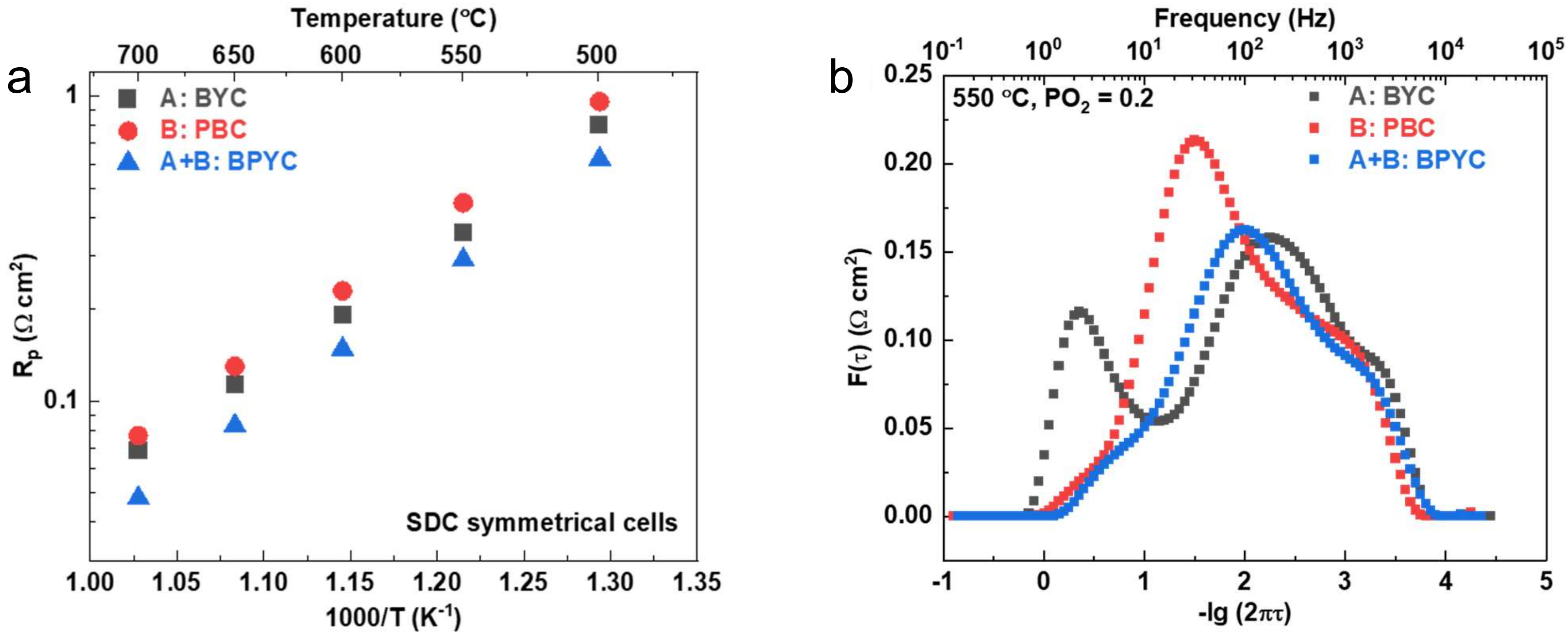


(e) Phase C: BHY



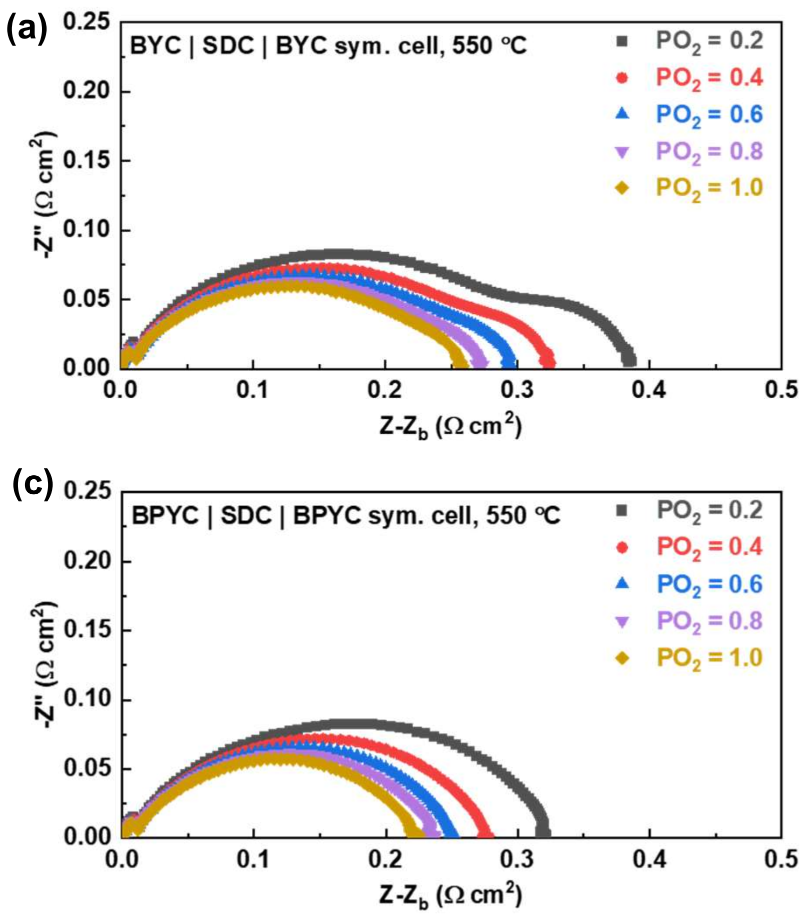
- **Three phases (BYC, PBC, and BHY)** are identified in BPHYC by XRD and HR-TEM

Contribution of Each Phase



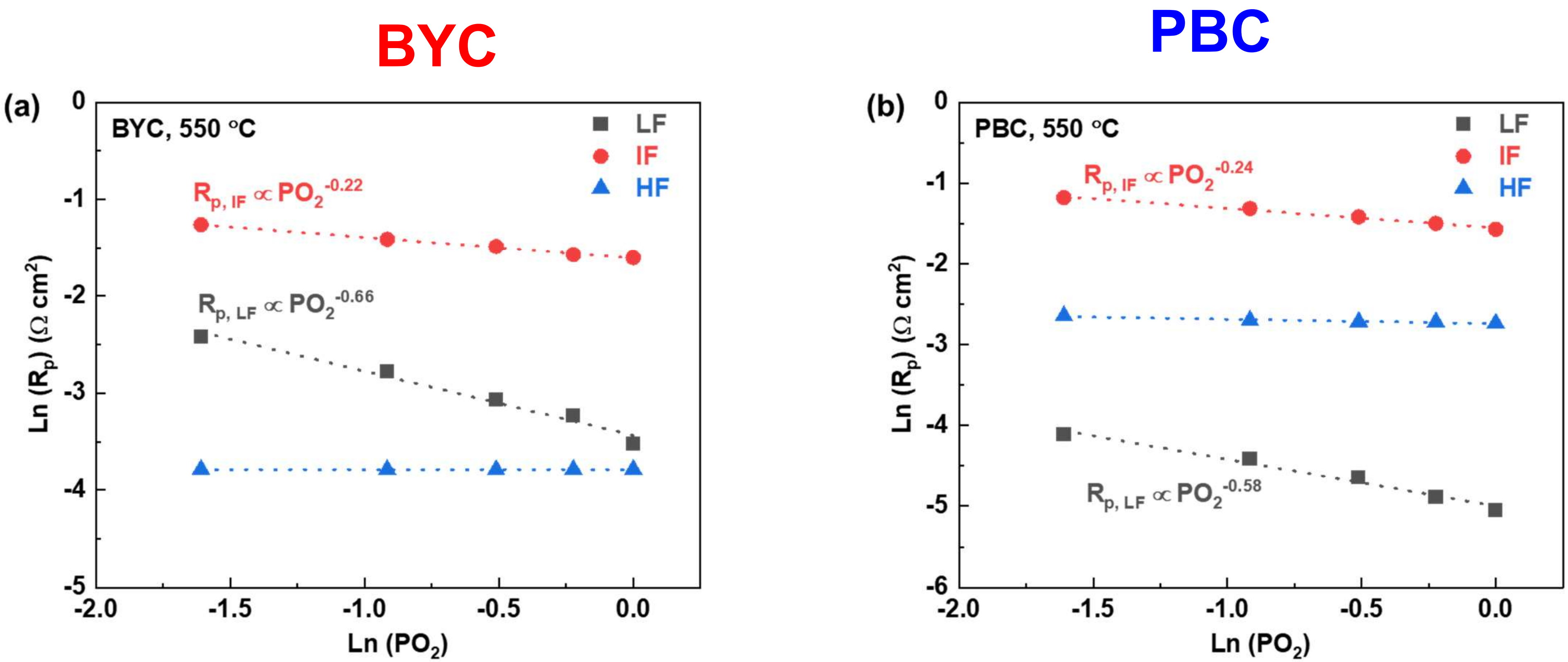
- Mixture of BYC and PBC shows reduced polarization resistance.
- BYC and PBC shows a synergistic effect on the electro-catalytic activity.

Impedance Spectra of Symmetric Cells

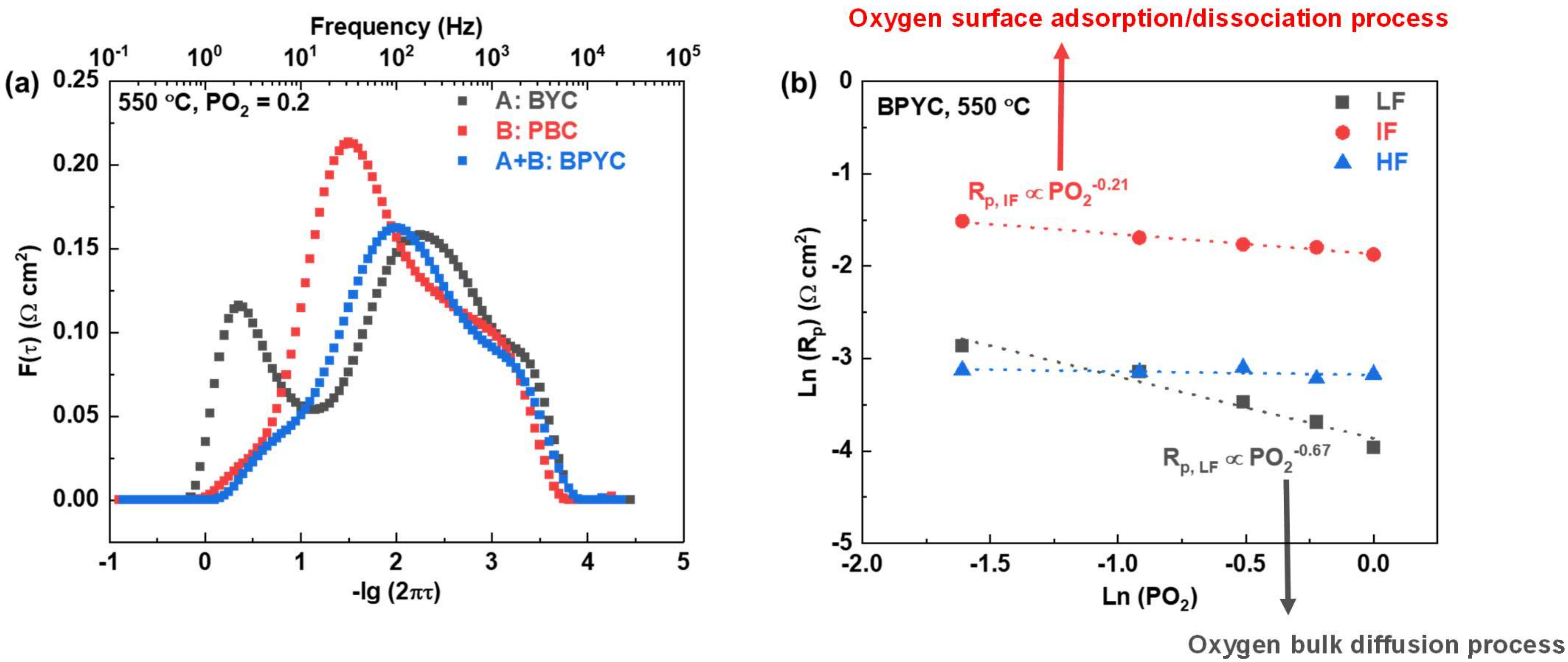


Impedance spectra of symmetrical cells with BYC, PBC, and BPYC electrodes were measured under **different oxygen partial pressures.**

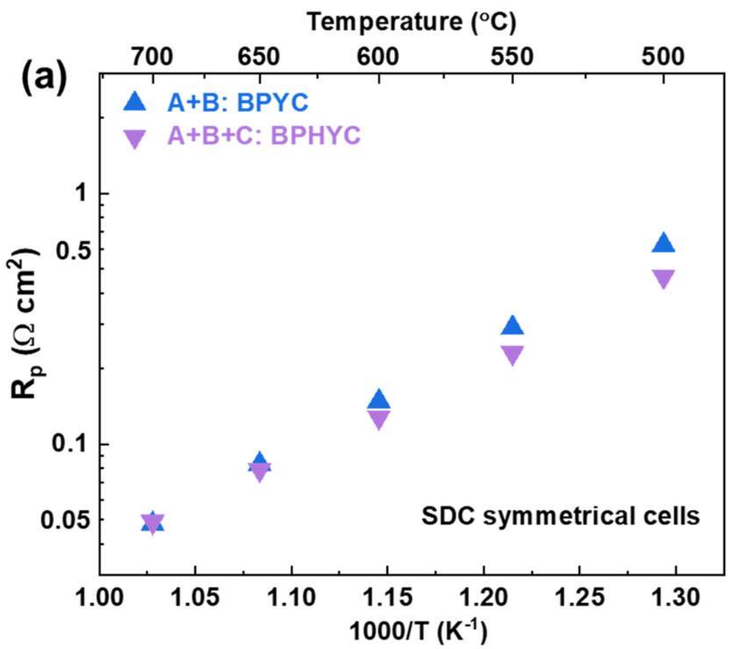
Effect of pO_2 on BYC and PBC: DRT Analysis



Effect of pO_2 on BPYC: DRT Analysis

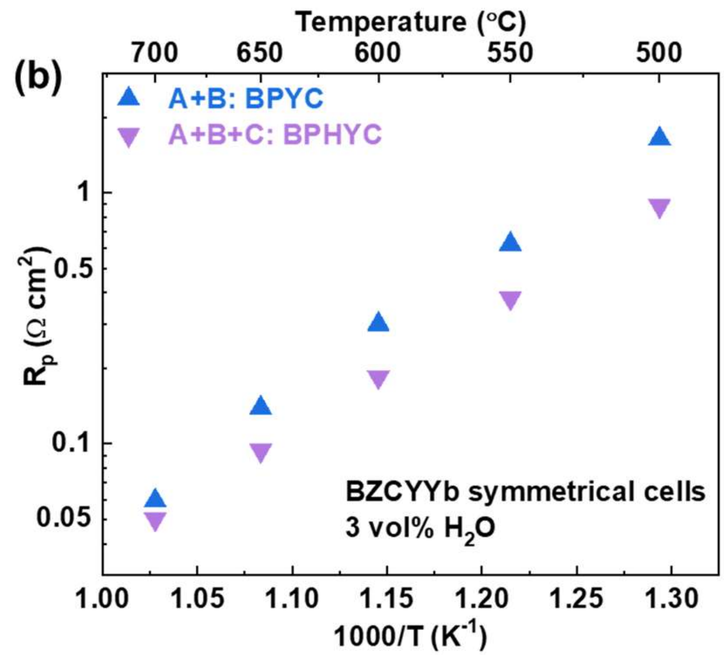


R_P in SDC and BZCYYb-based Cells



Oxygen-ion conducting electrolyte

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

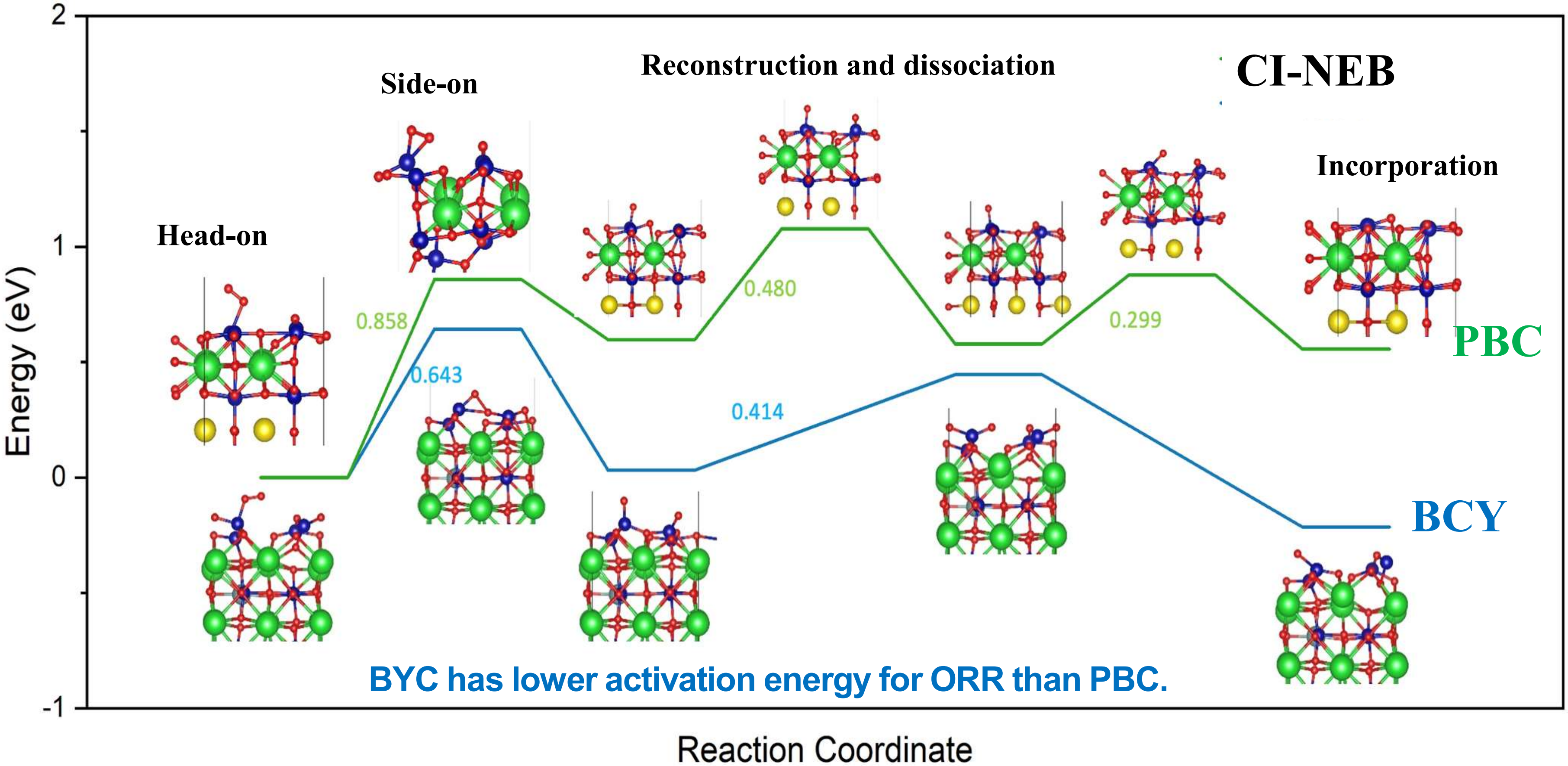


Proton conducting electrolyte

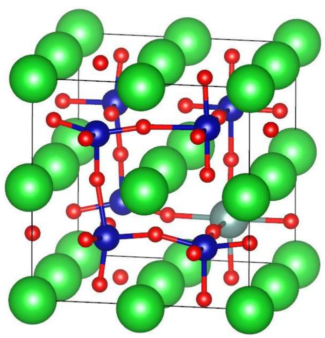
$$O_2 + 4H^+ + 4e^- \rightarrow 2\mathrm{H_2O}$$

- **BPYC phase contributes more to the proton-related ORR kinetics**

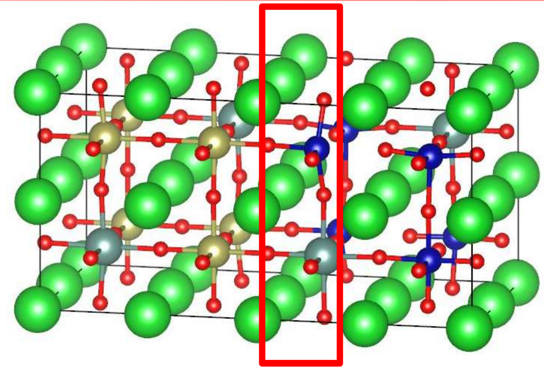
Understanding of the ORR Process



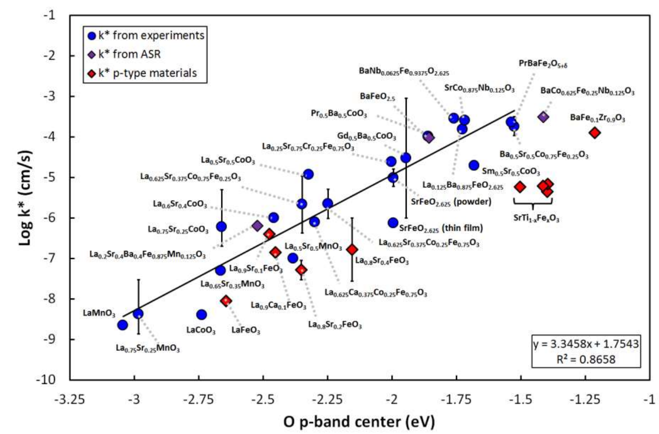
Oxygen p-band center calculation

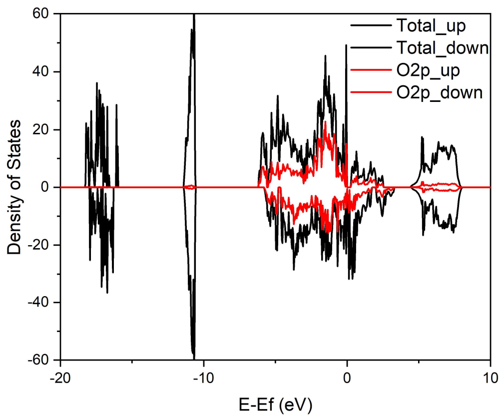


$BaY_{0.125}Co_{0.875}O_3$ (BYC)

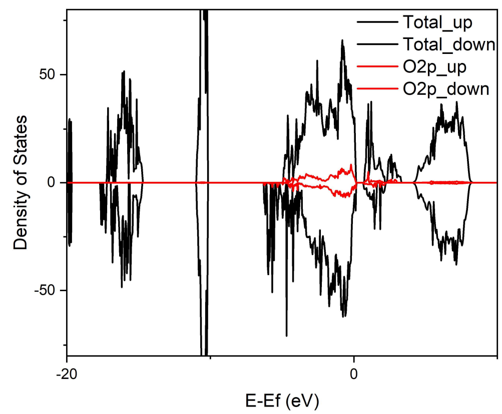


$BaY_{0.125}Co_{0.875}O_3$+$BaHf_{0.75}Y_{0.25}O_3$ (BYC+BHY)

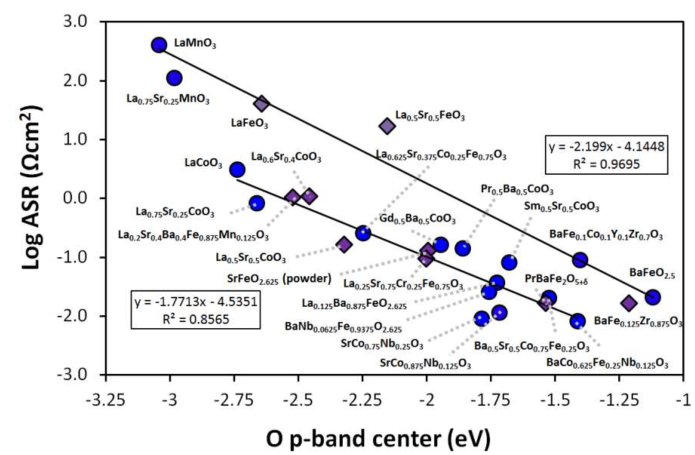




DOS for BCY
p band center = -2.268 eV



DOS for BCY+BHY
p band center = -1.901 eV



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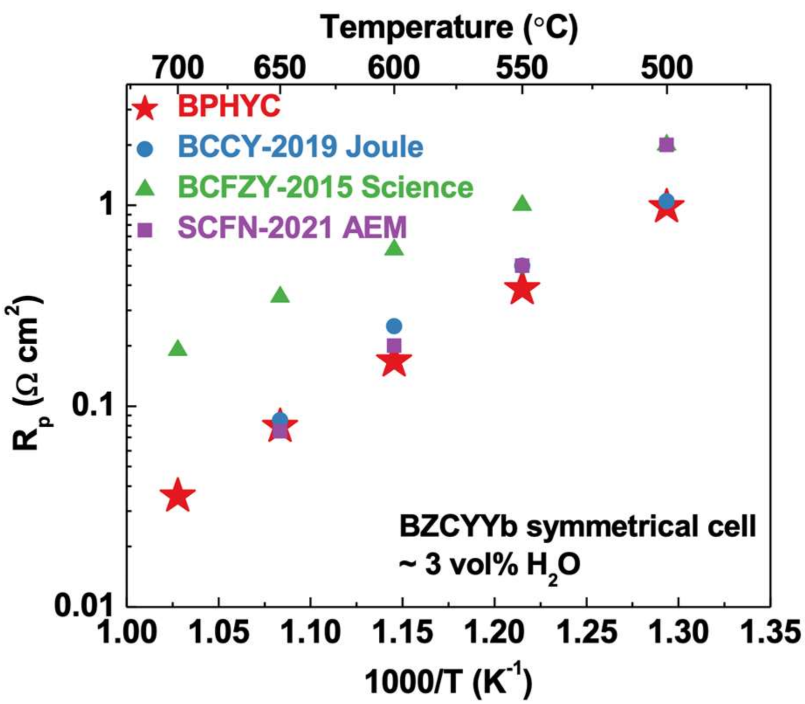
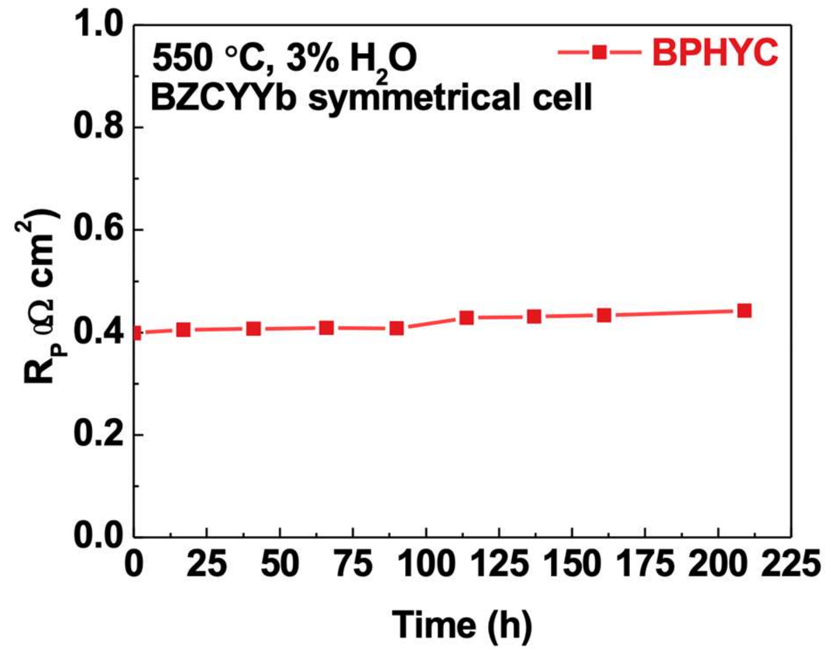
- Introduction of BHY **enhances the oxygen transport kinetics** of BYC

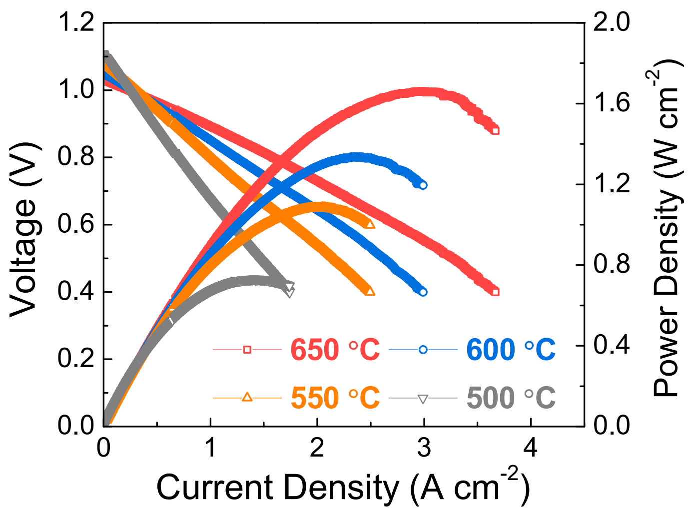
Optimized Activity and Stability

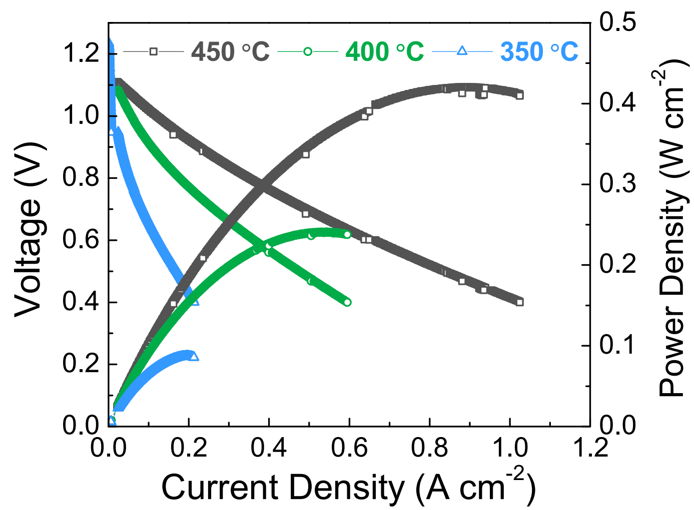


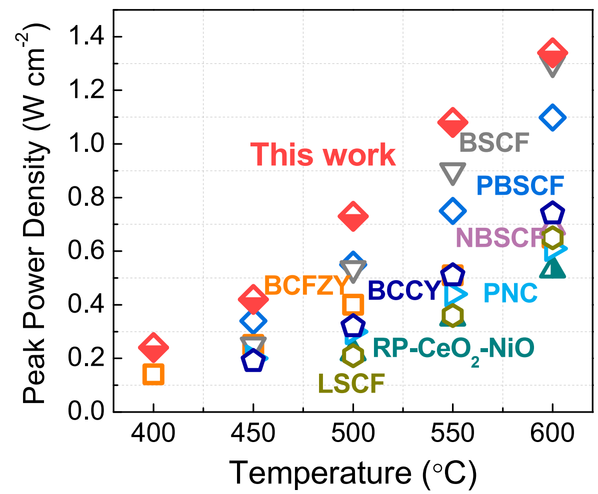


- Electrode polarization resistance: < 0.2 Ω cm^2 at 600 ºC
- Good stability in humified air

Cell Performance in the Fuel Cell Mode

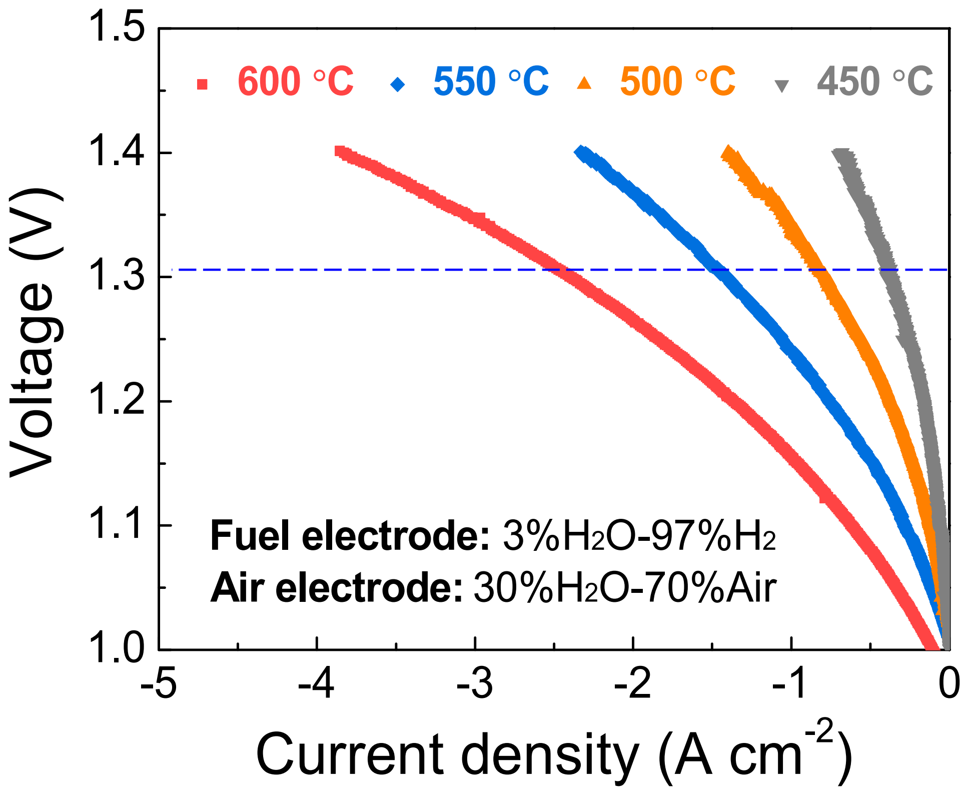


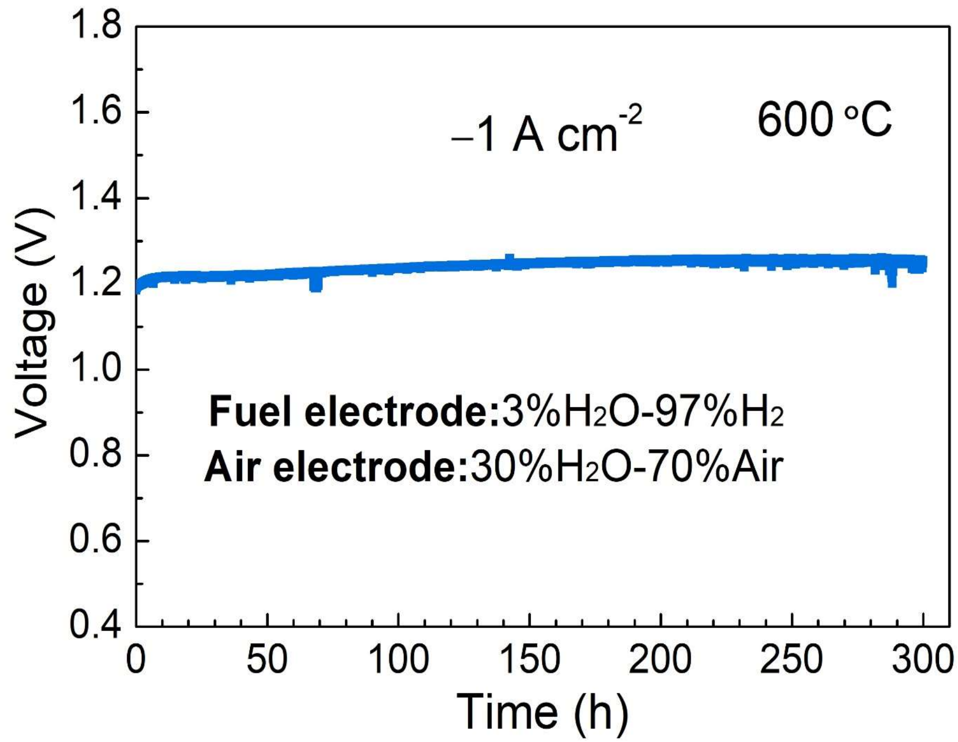




- **Very high performance in the fuel cell mode**

Cell Performance in the Electrolysis Mode





Summary

- ❑ Achieved all milestones as scheduled
- ❑ Demonstrated that a protective coating is effective to enhance stability, resulting in conductive and stable bi-layer electrolyte
- ❑ Developed a new proton-conducting electrolyte with excellent stability against high concentration of steam and CO_2 while maintaining high conductivity
- ❑ Developed a composite air electrode with high ORR/OER activity and durability
- ❑ Demonstrated high performances in both fuel cell and electrolysis mode
  - Peak power density of 1.34 W cm^{-2} and electrolysis current density of 2.4 A cm^{-2} at 1.3 V and 600 °C
  - 500 h operation at 600 °C with no minimum degradation

Future Work

Date	Brief Description	Complete
12/22	Complete the catalyst modification of the air electrode with a R_p of <0.15 Ω cm^2 at 600 ºC 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).	50%
03/23	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 as a function of contaminant presence, relevant operating conditions, and catalyst content.	Not started

End of Project Goal:	Demonstrate a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C. Complete >500-h operation with a degradation rate of <0.5% per 1,000 h.	FY23

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and other DOE management team members

U.S. Department of Energy
Award No. FE0032115

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