A Highly Efficient and Affordable Hybrid System for Hydrogen and Electricity Production

Junsung Hong: Phillips 66
Meilin Liu: Georgia Tech

DE-FE0031975

23rd Annual SOFC Project Review Meeting
October 26, 2022

BARTLESVILLE BUSINESS OPERATIONS & INNOVATION CENTER

Acknowledgments

This material is based upon work supported by the Department of Energy [National Nuclear Security Administration] under Award Number DE-FE0031975.

Disclaimer

Outline

- Project Overview
- Project Objective
- Technical Approach
- Project Progress
    - Electrolyte Development
    - Air Electrode and Catalyst Development
    - Button Cell Performance
    - Powder Synthesis Scale up and Large Cell Fabrication
- Summary and Future Work
- Acknowledgement

Overview

- **Project Title:** A Highly Efficient and Affordable Hybrid System for Hydrogen and Electricity Production
- **Award No.:** DE-FE0031975
- **Project Timeline:** 09/27/2020 – 02/26/2024
- **DOE/NETL Program Manager:** Andrew O'Connell

Organization	Team	Team	Roles
PHILLIPS 66	Heli Wang (PI) David Ingram Byunghyun Min Amin Baghalian	Junsung Hong Sarah Bushyhead Keri Collins	• Powder synthesis • Large cell manufacturing • Stack fabrication and testing • System design and operation
Georgia Tech	Meilin Liu (Co-PI) Zhijun Liu Yucun Zhou Jerry Luo Conor Evans	Nick Kane Humphrey Lin Xueyu Hu Gyutae Nam	• Cell materials development • Catalyst development • Button cell evaluation

Phillips 66 SOFC R&D

Company Overview

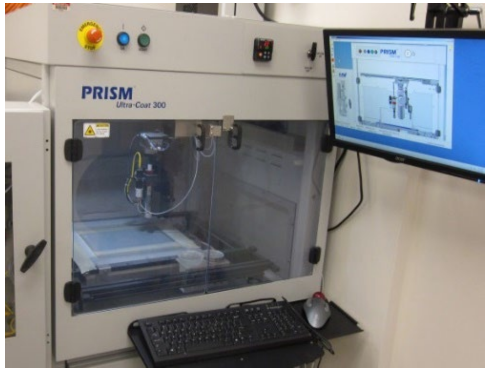
- Diversified energy manufacturing and logistics company
- Portfolio includes Midstream, Chemicals, Refining, and Marketing & Specialties businesses
- Process, transport, store, and market fuels and products globally
- #29 on the Fortune 500 list

SOFC Program

- Launched in 2010
- Proprietary high-performing materials
- Cost-effective fabrication methods
- Unique stack designs
- Fully automated control systems
- Full spectrum of cell/stack manufacturing and testing facilities

Fabrication and Testing Facilities

Tape Caster



Spray Coater

High Power Laser

High Temp Furnace

Stack Tester

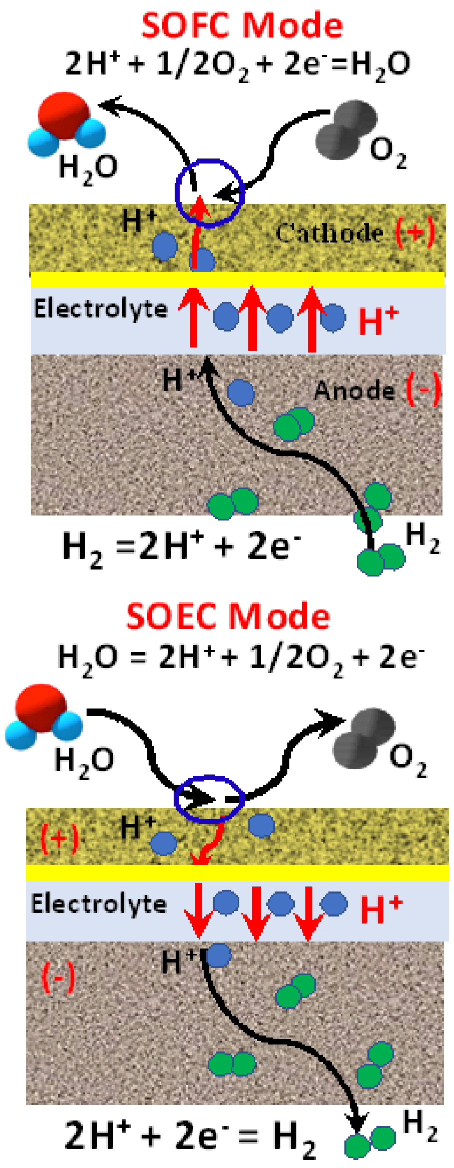
System Testing Enclosure

- >10,000 sq. ft. floor space
- 20+ fuel cell and stack test stations
- Fuel (H_2, CH_4, pipeline NG) processing and treatment
- Steam generation and control
- Large load banks and power supplies
- System instrumentation, control and communication

Project Objectives

- To design, fabricate, and demonstrate a robust, highly efficient, and affordable reversible solid oxide cell (rSOC) system based on a proton conducting electrolyte membrane for hydrogen and power generation.

- The 1-kW prototype system will meet the following technical specifications:
  - Operate the system in a real-world environment.
  - ≥50% electrical efficiency (LHV of H_2) at 0.5 A cm^{-2} in fuel cell mode on H_2 at 650 °C.
  - >85% electrical efficiency (LHV of H_2) in electrolysis mode at ≤ 650 °C.
  - Demonstrate the potential to < $2/kg hydrogen.



Technical Approach

Major Tasks	Action Plan
Materials Development	• Modify composition of state-of-the-art $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte • Develop air electrodes with high ORR/OER activities and excellent tolerance to H_2O and Cr-poisoning
Cell Fabrication	• Scale up powder synthesis to >1 kg /day • Fabricate button cells showing higher performance and good durability • Fabricate 10 cm × 10 cm cells by low cost and scalable methods
Stack Development	• CFD assisted stack design • QC for stack components and assembly • Demonstrate high stack performance in both SOFC and SOEC modes
System Demonstration	• Design a 1.0 kW autonomous system with cloud-based control and data communication • Evaluate system performance and achieve efficiency, lifetime and cost targets • Techno-economic analysis to demonstrate \$2/kg H2

Project Progress

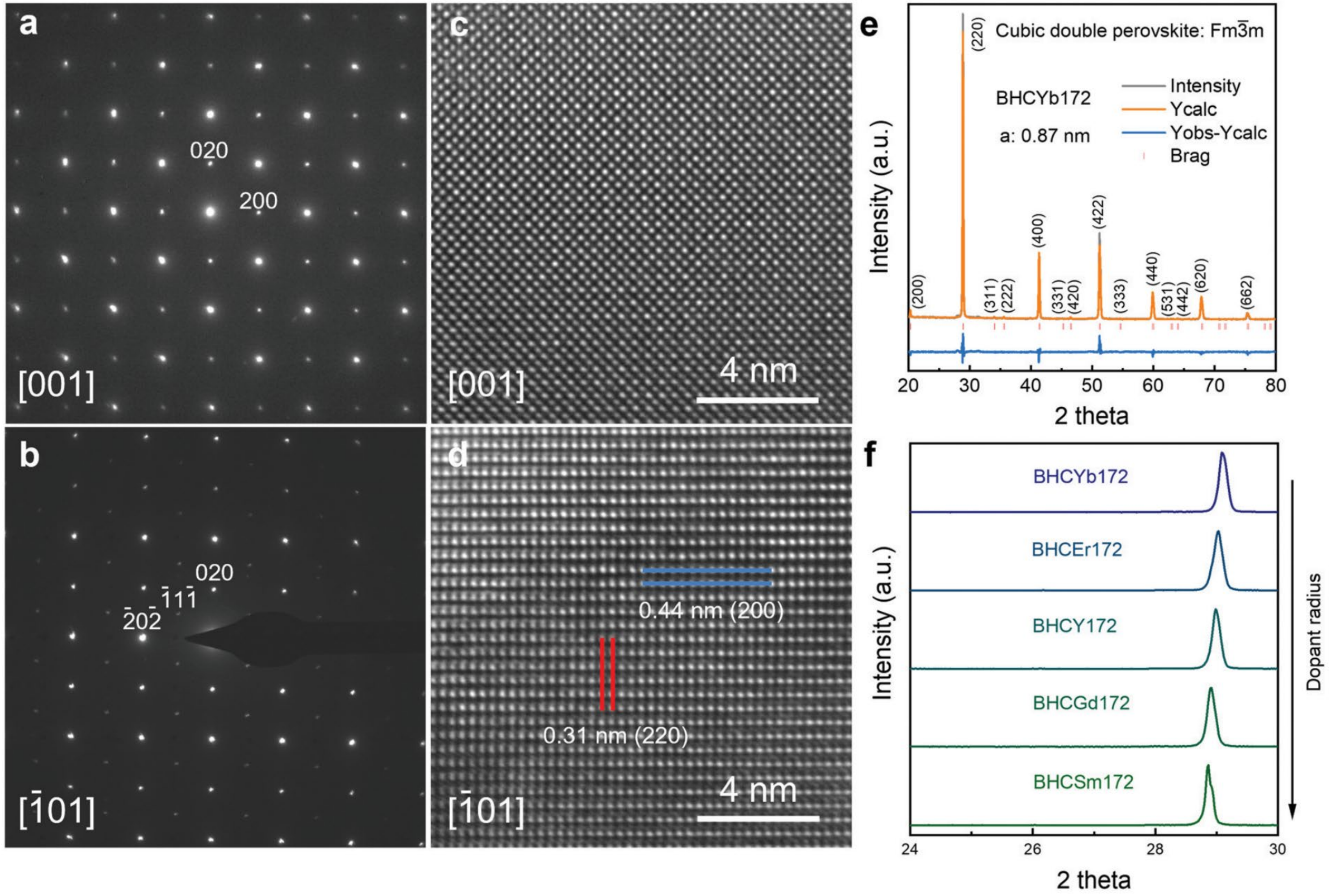
Timeline	Milestone (BP1)	% Complete
12/31/2020	Electrolyte conductivity >0.01 S cm^{-1} and ionic transference numbers >0.95 at 600 ºC.	100%
12/31/2020	Electrolyte degradation rate <2%/1000 h at 600 ºC.	100%
03/31/2021	Air electrode with catalysts polarization resistance <0.2 Ω cm^2 at 600 ºC.	100%
06/30/2021	Air electrode with catalysts degradation <2%/1000 h at 600 ºC under H_2O and Cr.	100%
07/30/2021	Scale up ceramic powder synthesis to > 1.0 kg per day	100%
09/30/2021	Button cells 1 W cm^{-2} at 0.7 V and 600 ºC in fuel cell mode, 1.5 A cm^{-2} at 1.3 V and 600 ºC in electrolysis mode, and a Faradaic efficiency of 95%.	100%
03/31/2022	Button cells degradation <2%/1000 h at ≤ 650 ºC	100%
06/30/2022	***Go/No-Go Decision Point*** 10x10 cm^2 cells with ≥70% roundtrip efficiency at 0.5 A cm^{-2}, <2% per 500 h at ≤ 650 ºC.	100%

Accomplishments to Date

- ✓ **Electrolyte**: Complete electrolyte development with conductivity **>0.01 S cm^{-1}** in Ar (3%H_2O), ionic transference numbers **>0.95** and degradation rate **<2% per 1000 h** in cell operating conditions at 600 ºC
- ✓ **Air Electrode with catalyst:** Complete air electrode with catalyst development with a polarization resistance of **<0.2 Ω cm^2** at 600 ºC in Air (3% H_2O) and a degradation rate of **<2% per 1000 h** at 600 ºC under the presence of H_2O and Cr contaminants for over 500 h
- ✓ **Button cell Performance:**
  - Fabricated high-performance button cells with the power density of **1.2 W cm^{-2} at 0.7 V** and 600 ºC in fuel cell mode, current density of **2.0 A cm^{-2} at 1.3 V** and 600 ºC in electrolysis mode, and a Faradaic efficiency of over 95%
  - Completed durability evaluation of the button cell for at least 1000 h with a degradation rate of **<2% per 1000 h** at ≤ 650 ºC
- ✓ **Powder synthesis:** Established in-house powder synthesis capability **> 1500 g/day**
- ✓ **Large cell fabrication:** Fabricated flat, robust 10 cm×10 cm cells, which demonstrated **77%** roundtrip electrical efficiency and a degradation rate of **1.3%/1000 h**

Electrolyte Development

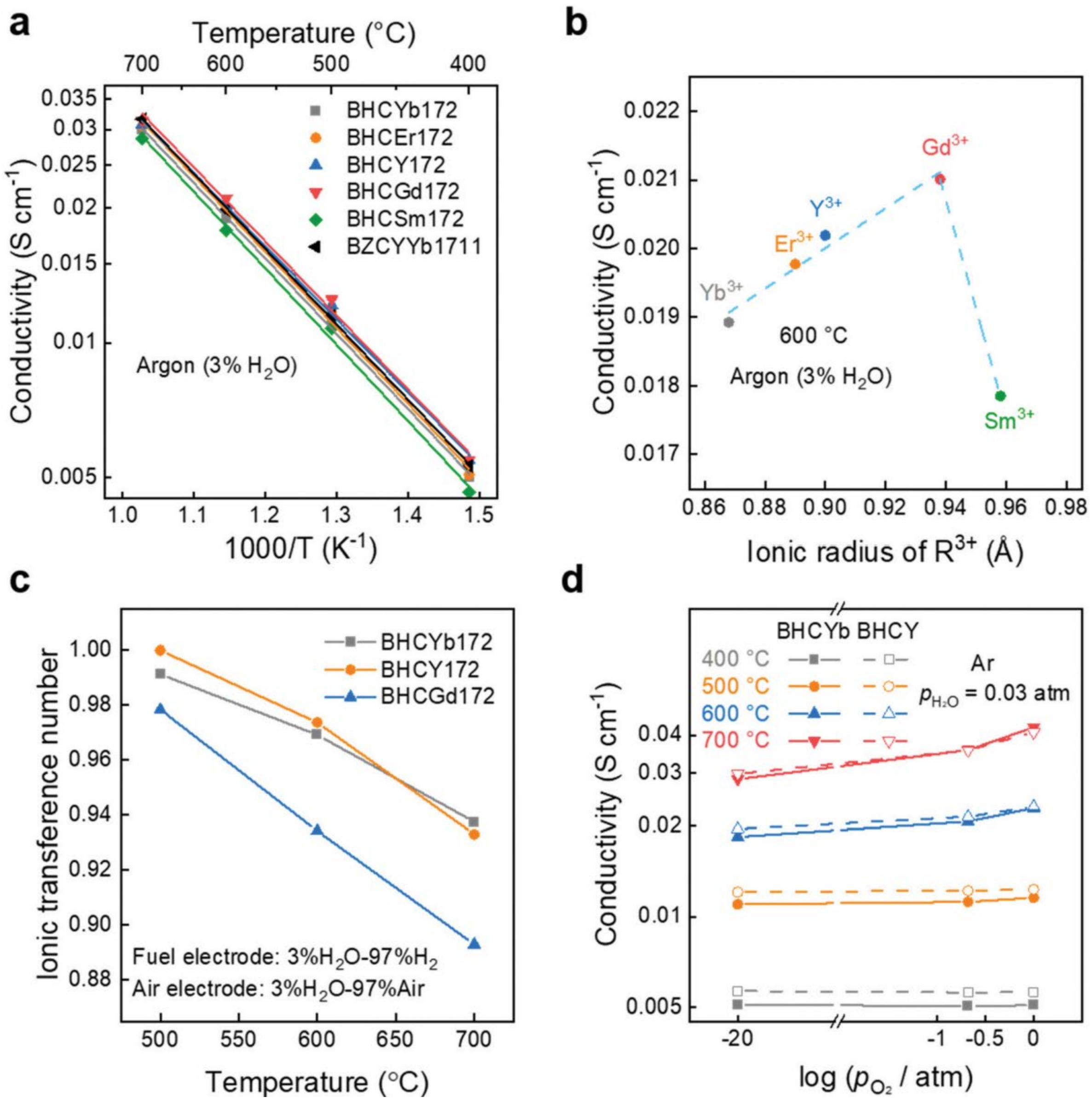
- $BaHf_{0.1}Ce_{0.7}R_{0.2}O_{3-\delta}$ **(BHCR172, R = Yb, Er, Y, Gd, Sm)**
- **The ordered dopant structures** could be beneficial to proton conductivity



- The SAED pattern of BHCYb172 is characteristic of a typical cubic perovskite lattice
- As the ionic radius of R increases, the peak positions shift to lower angles

Energy Environ. Sci., 15 (**2022**) 2992-3003.

Conductivity and Ionic Transference Number

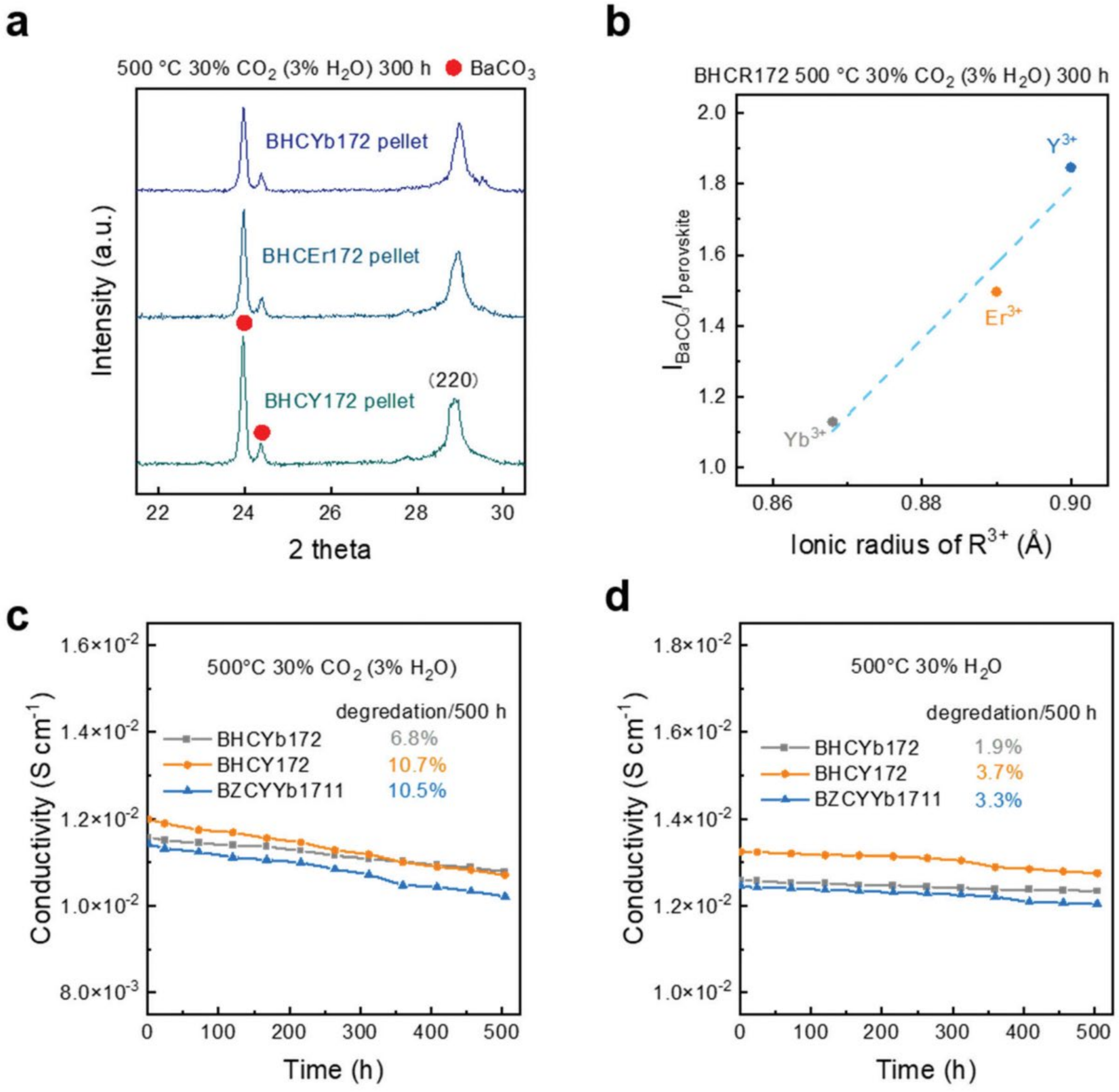


- Trivalent dopants with an intermediate **ionic radius can offer balanced lattice distortion and free volume**, giving the highest conductivity

- **Y- and Yb-doped electrolytes** show desirable conductivity of **~0.02 S cm^{-1}** and ionic transference number of >0.97 at 600 ºC, making them good candidates for ReSOCs

Energy Environ. Sci., 15 (**2022**) 2992-3003.

Chemical Stability Against CO_2 and H_2O



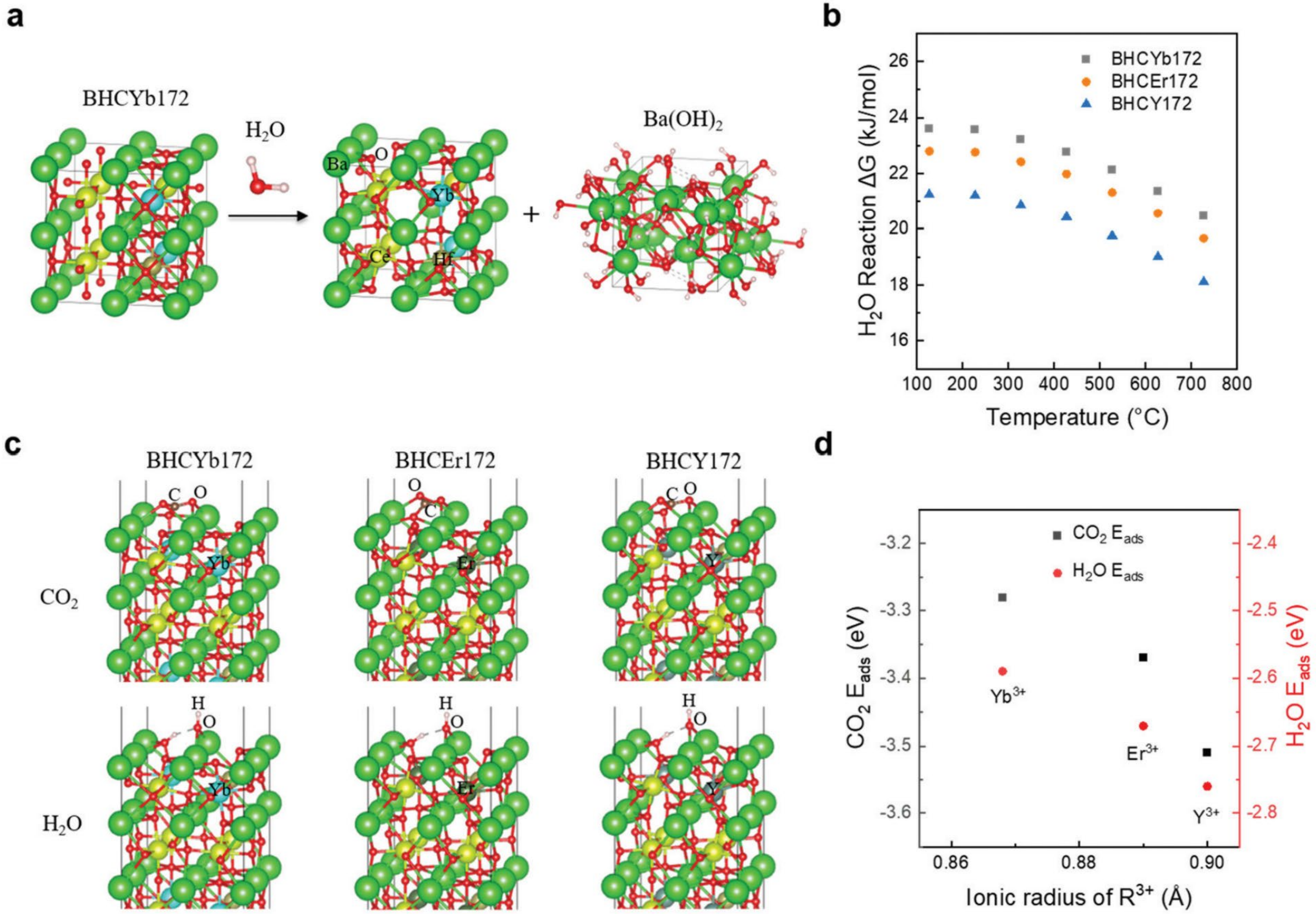
✓ **BHCYb172** showed high chemical stability against CO_2 and H_2O

- $Ba(Hf,Ce)O_3$-based proton conductors are more stable in high concentration of H_2O than CO_2

- **Yb-doping** positively affects the stability of the electrolyte materials

Energy Environ. Sci., 15 (**2022**) 2992-3003.

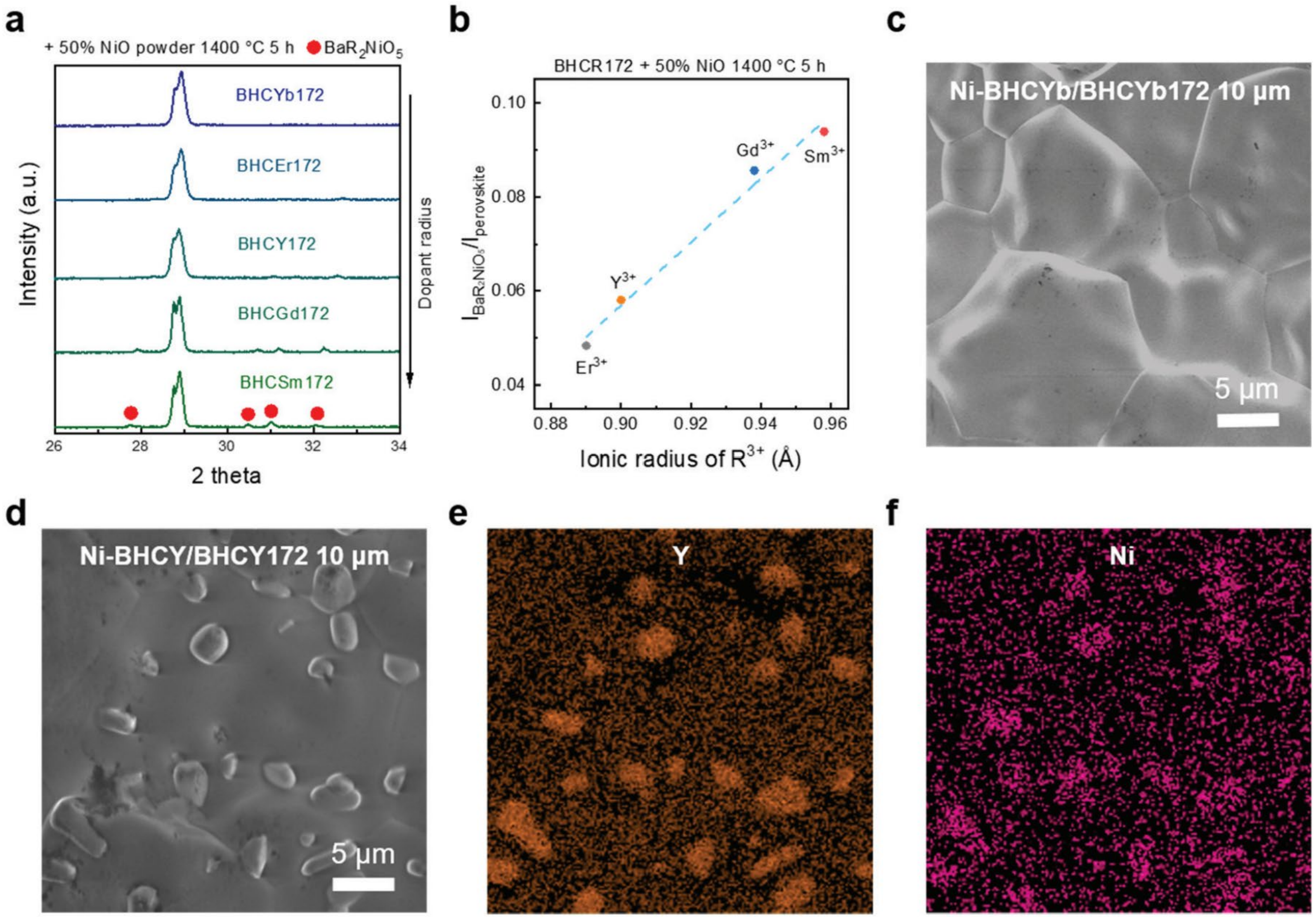
Understanding of the Enhanced Chemical Stability



- **Gibbs free energy (ΔG)** of the reaction between **BHCYb172 and H_2O is higher** than that of the Er- and Y-doped electrolytes
- The superiority of **Yb**-doping in **suppressing surface CO_2 and H_2O adsorption**.

Energy Environ. Sci., 15 (**2022**) 2992-3003.

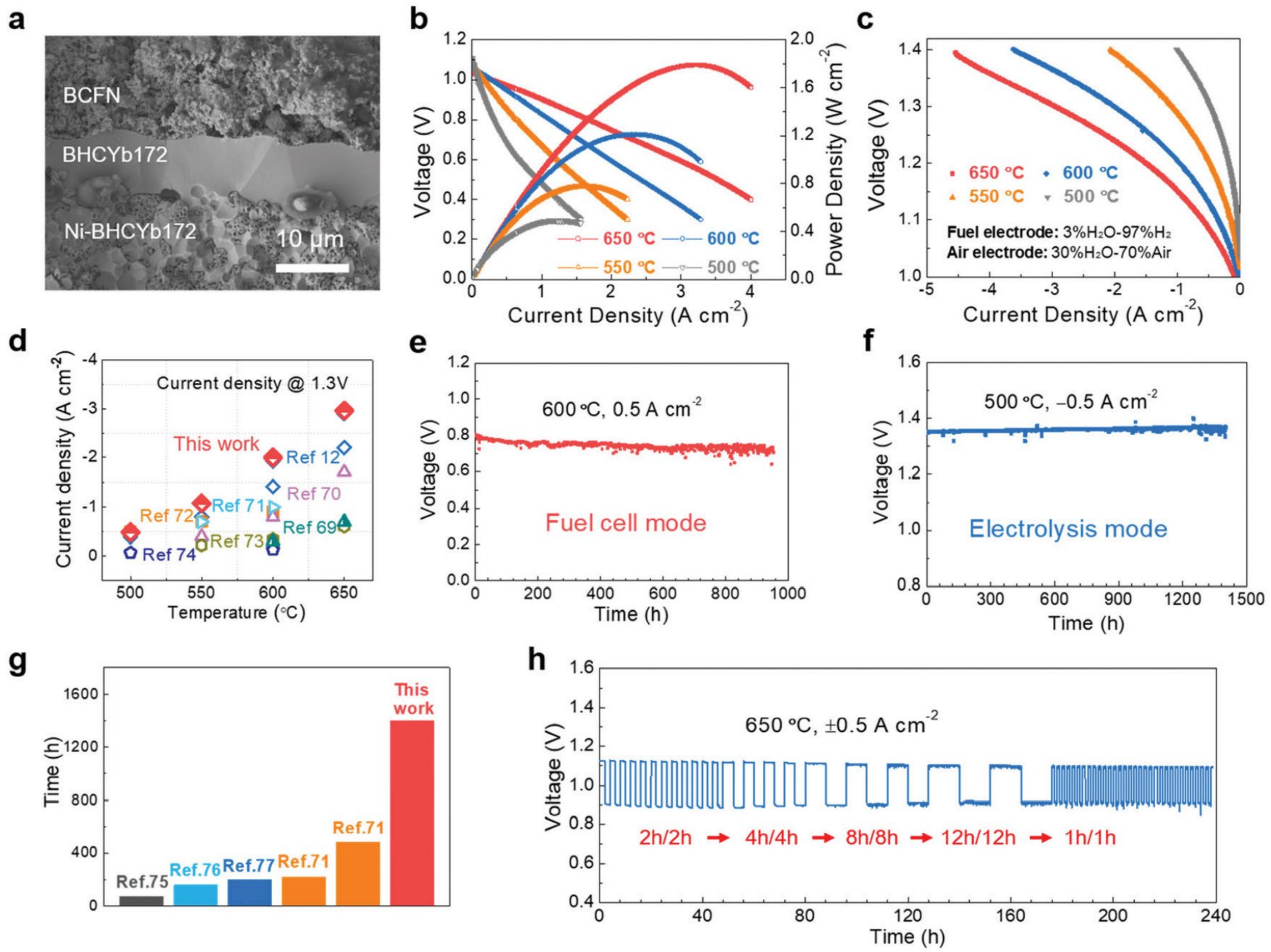
Chemical Compatibility with NiO



- **BHCYb172 demonstrates excellent chemical compatibility with NiO**
- **Larger dopants tend to react with NiO** at 1400 °C, forming BaR_2NiO_5 secondary phase.

Energy Environ. Sci., 15 (**2022**) 2992-3003.

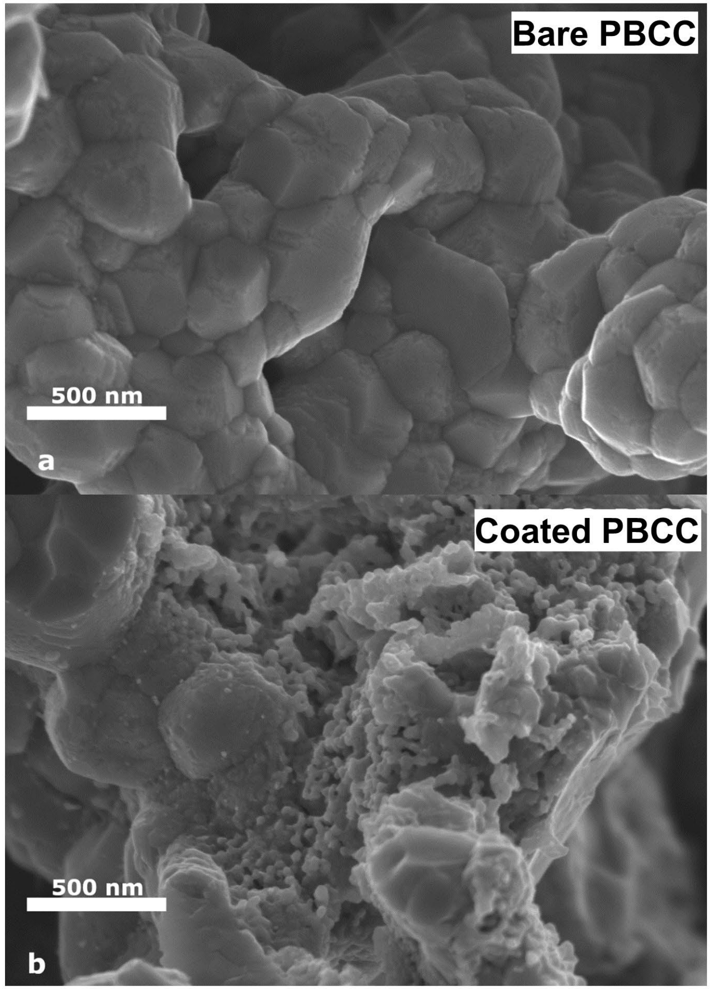
High-Performance BHCYb172-based Cell and H_2O Electrolysis

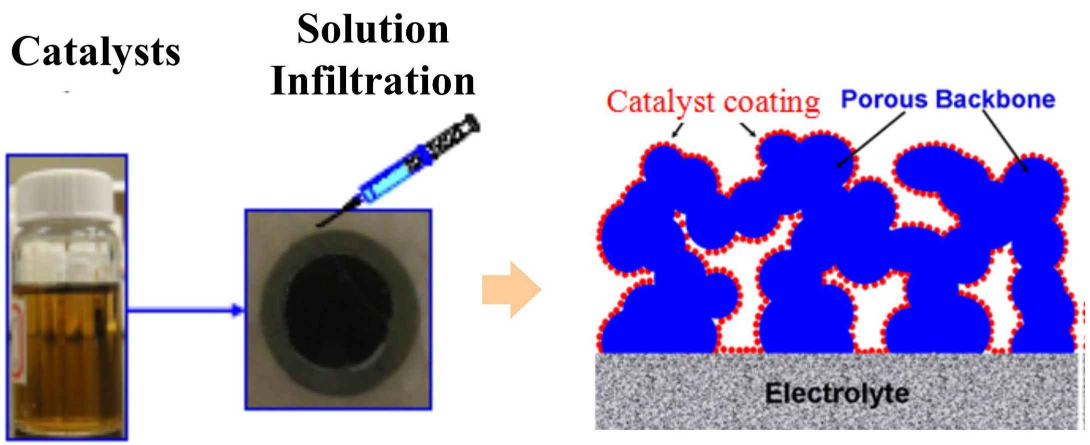


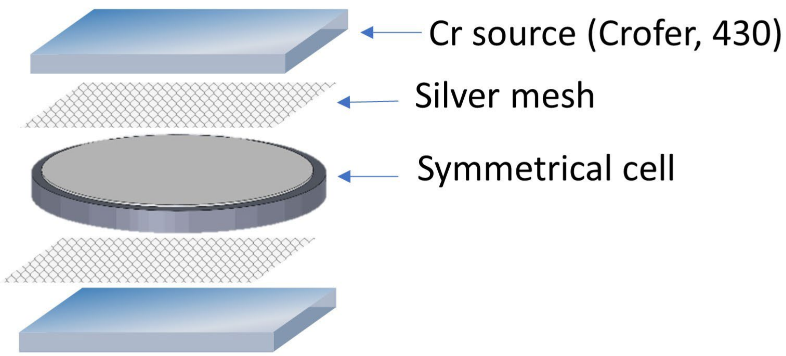
- ✓ At 600 °C, SOFC: **PPD=1.21 W cm^{-2}**; SOEC: 1.3 V, **current density= 2.0 A cm^{-2}**
- ✓ Roundtrip electric efficiencies of **84% and 79%** at 650 and 600 °C, respectively
- ✓ A low degradation rate of **0.8% /1000 h**

Energy Environ. Sci., 15 (**2022**) 2992-3003.

Catalyst Development

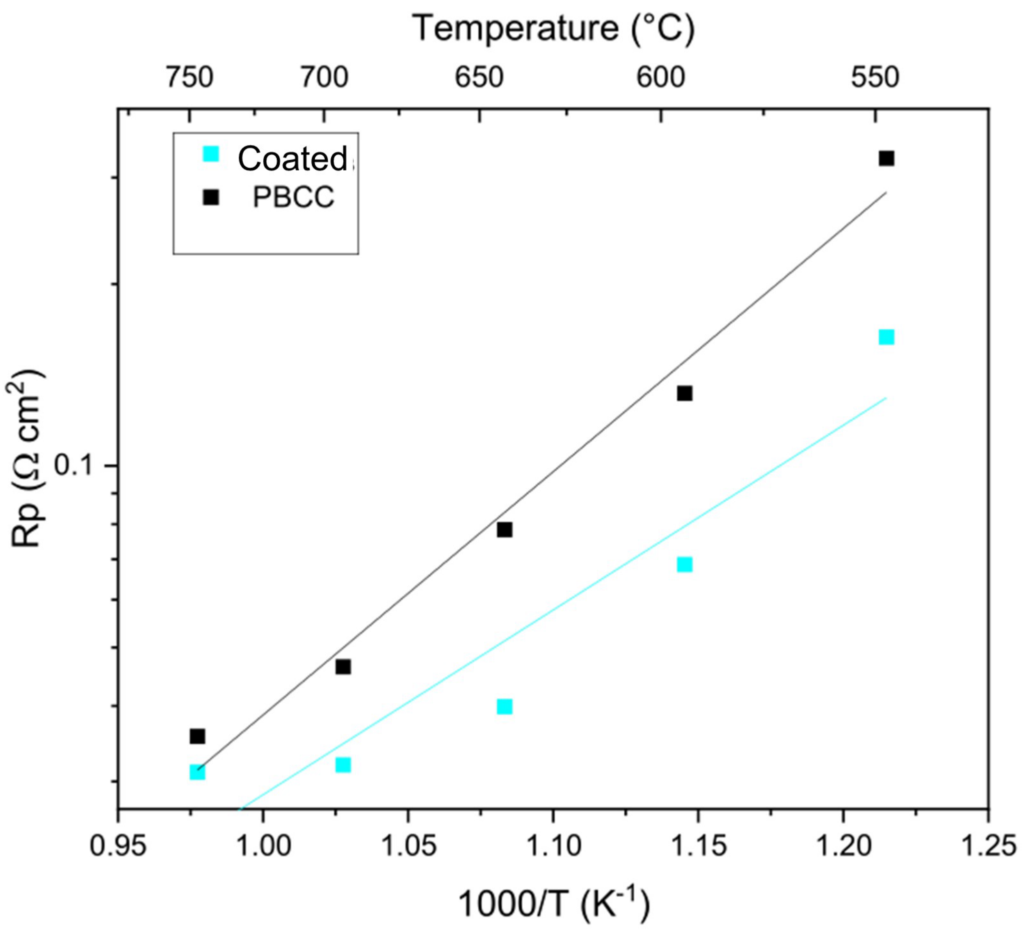


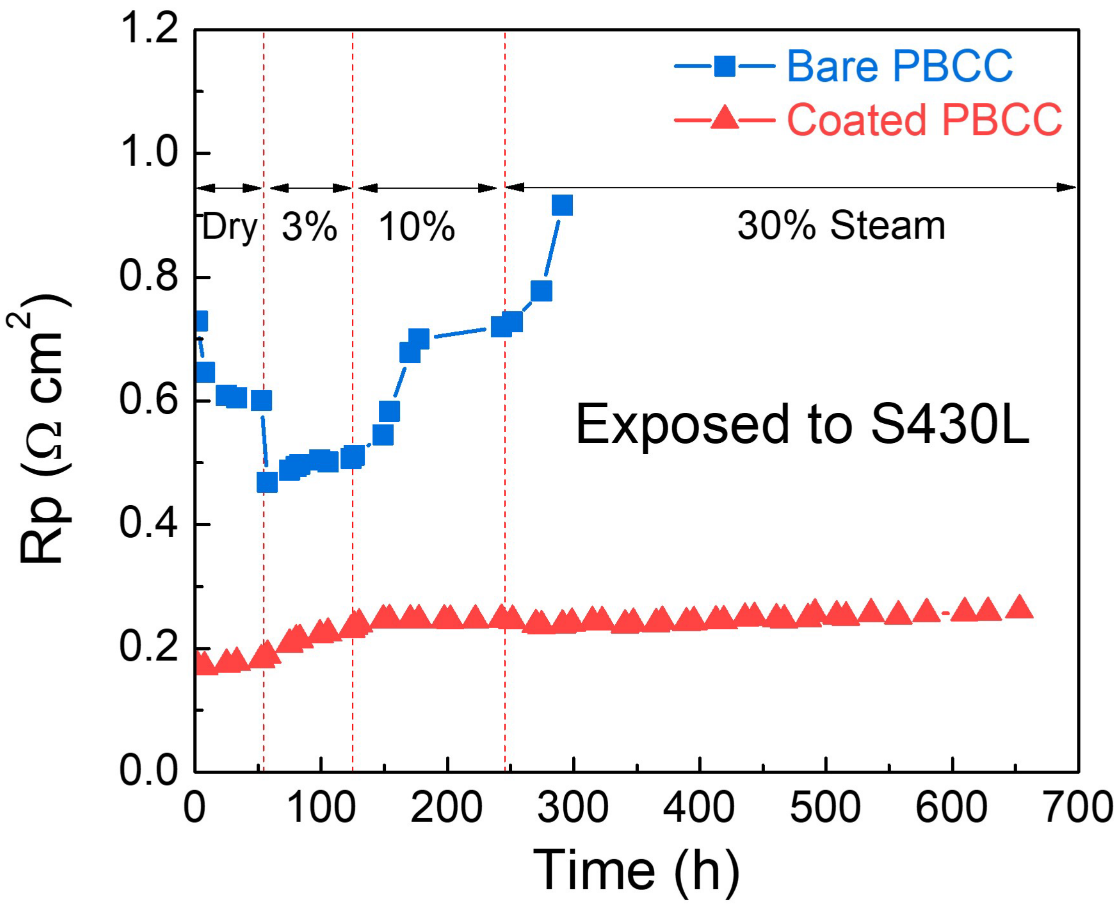




- Catalyst was developed for $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC) air electrode by the solution infiltration process

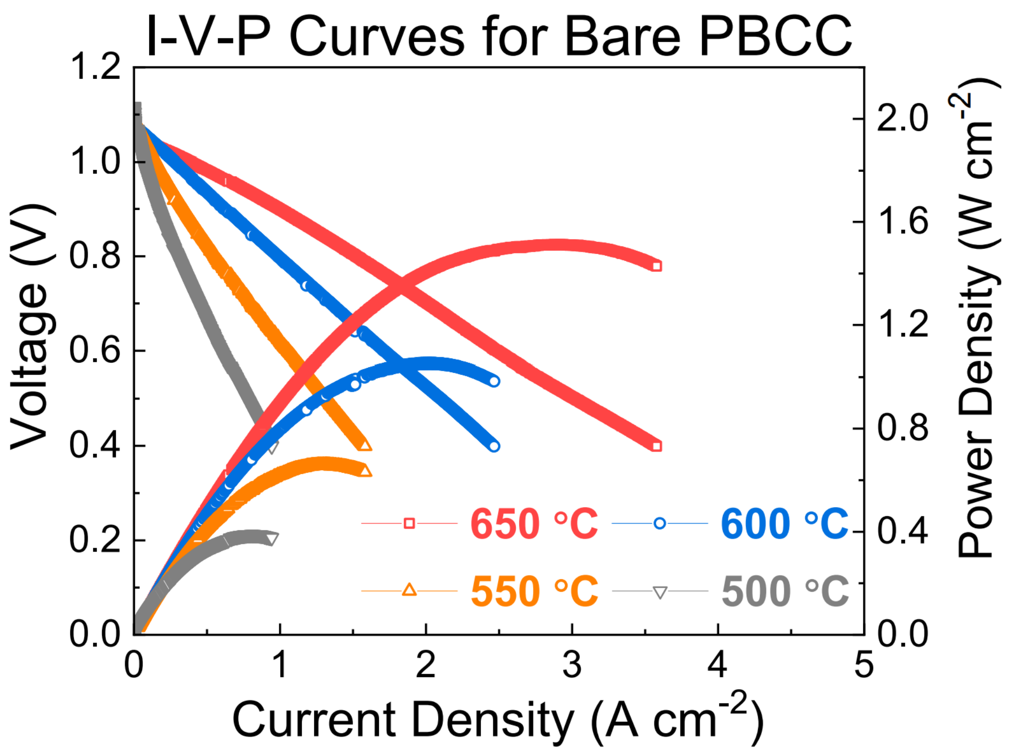
Enhanced Activity and Stability

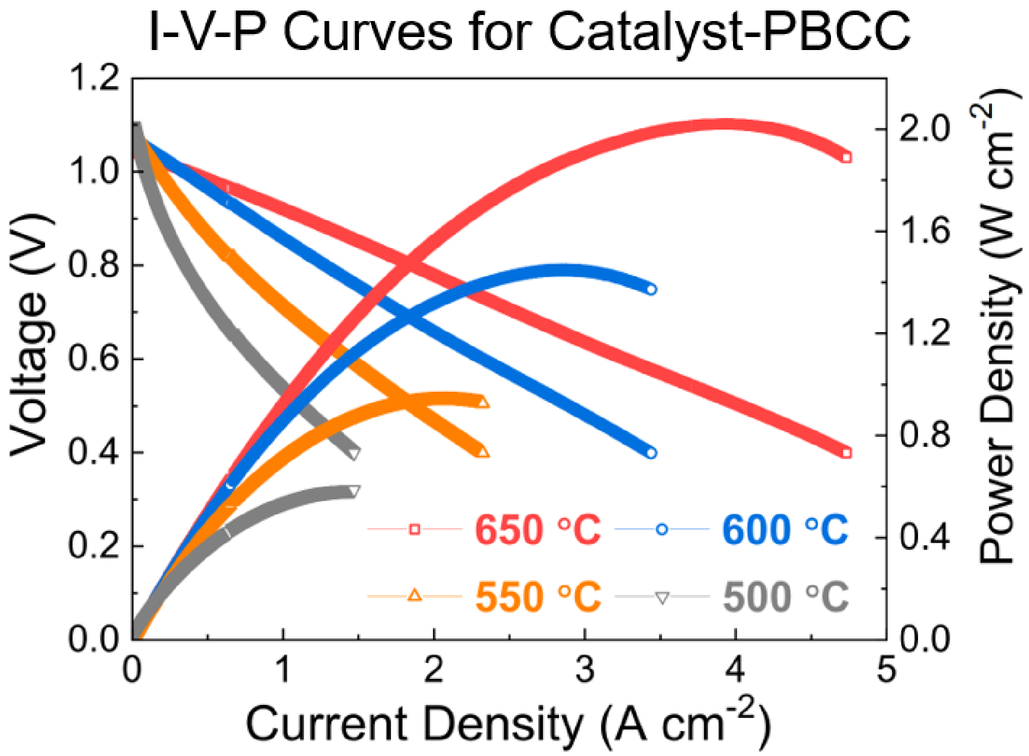




- Catalyst-coated PBCC air electrode shows enhanced activity and stability against H_2O and Cr

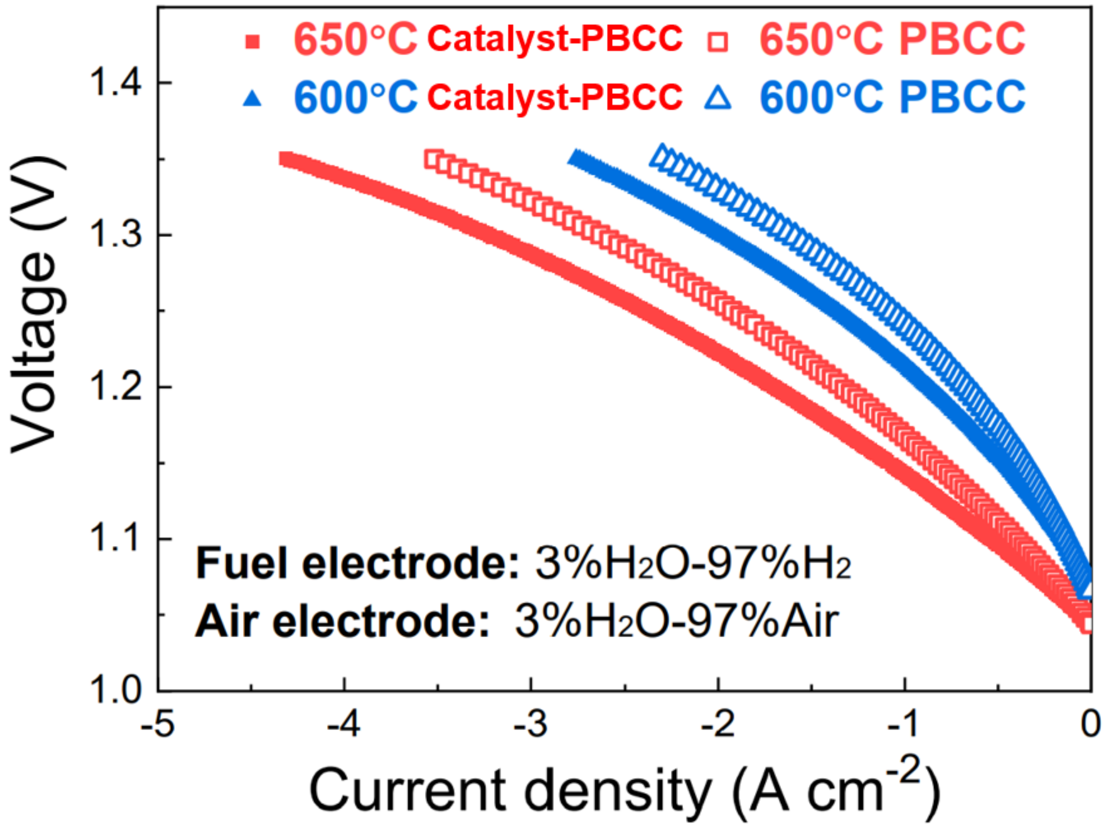
Enhanced Cell Performance

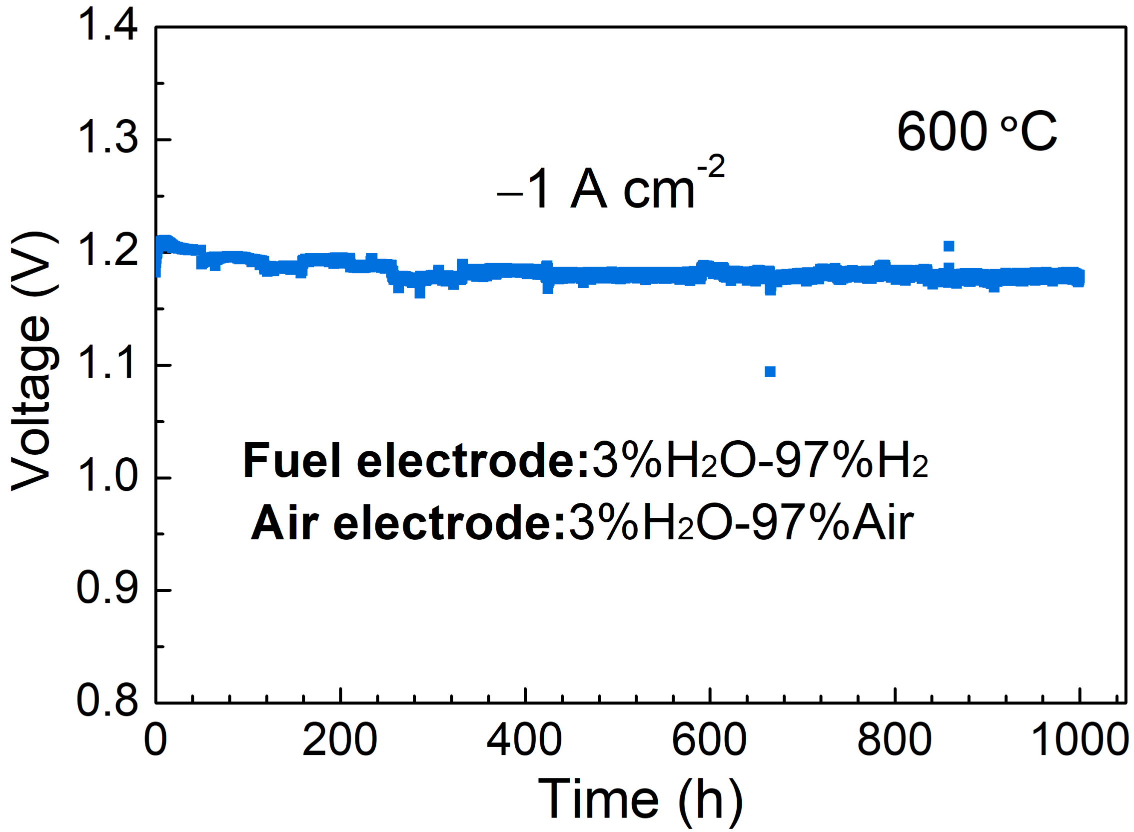




- The peak power density of catalyst-coated PBCC single cell is **2.02 W cm^{-2}** at 650 ºC , an over **35.5% improvement**.

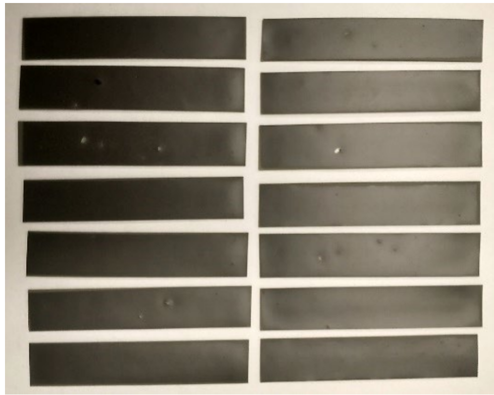
Enhanced Cell Performance and Stability

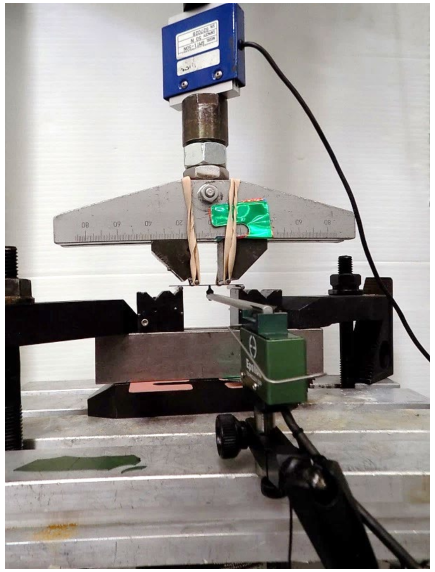


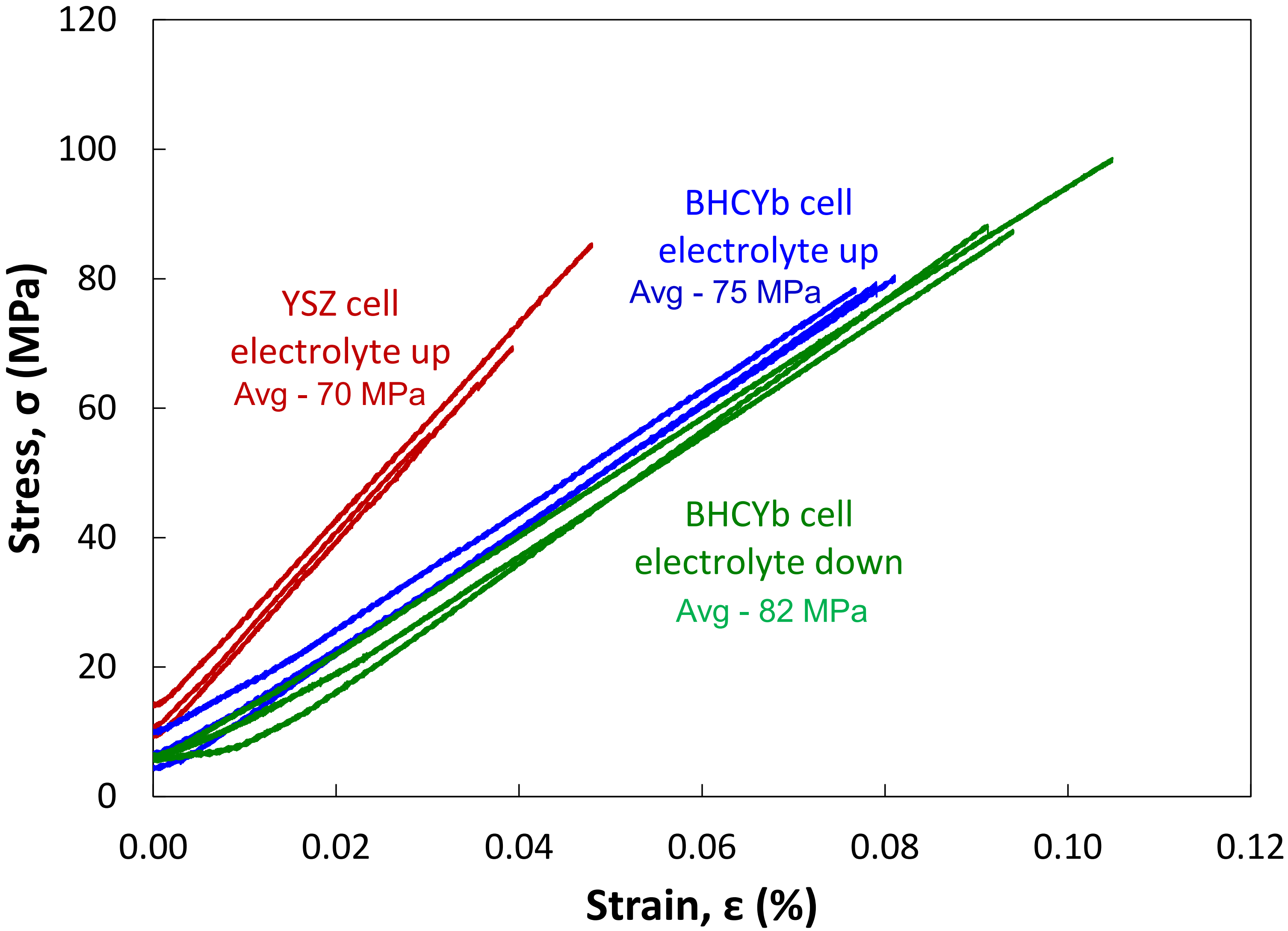


- Catalyst-coated PBCC single cell demonstrates a current density of **-3.22 A cm^{-2}** at 650 °C (**22.4% improvement**) and **-1.99 A cm^{-2}** at 600 °C (**22.3% improvement**)
- In SOEC mode, the single cell demonstrates **good stability.**

Flexural Strength of Proton Conducting Cells



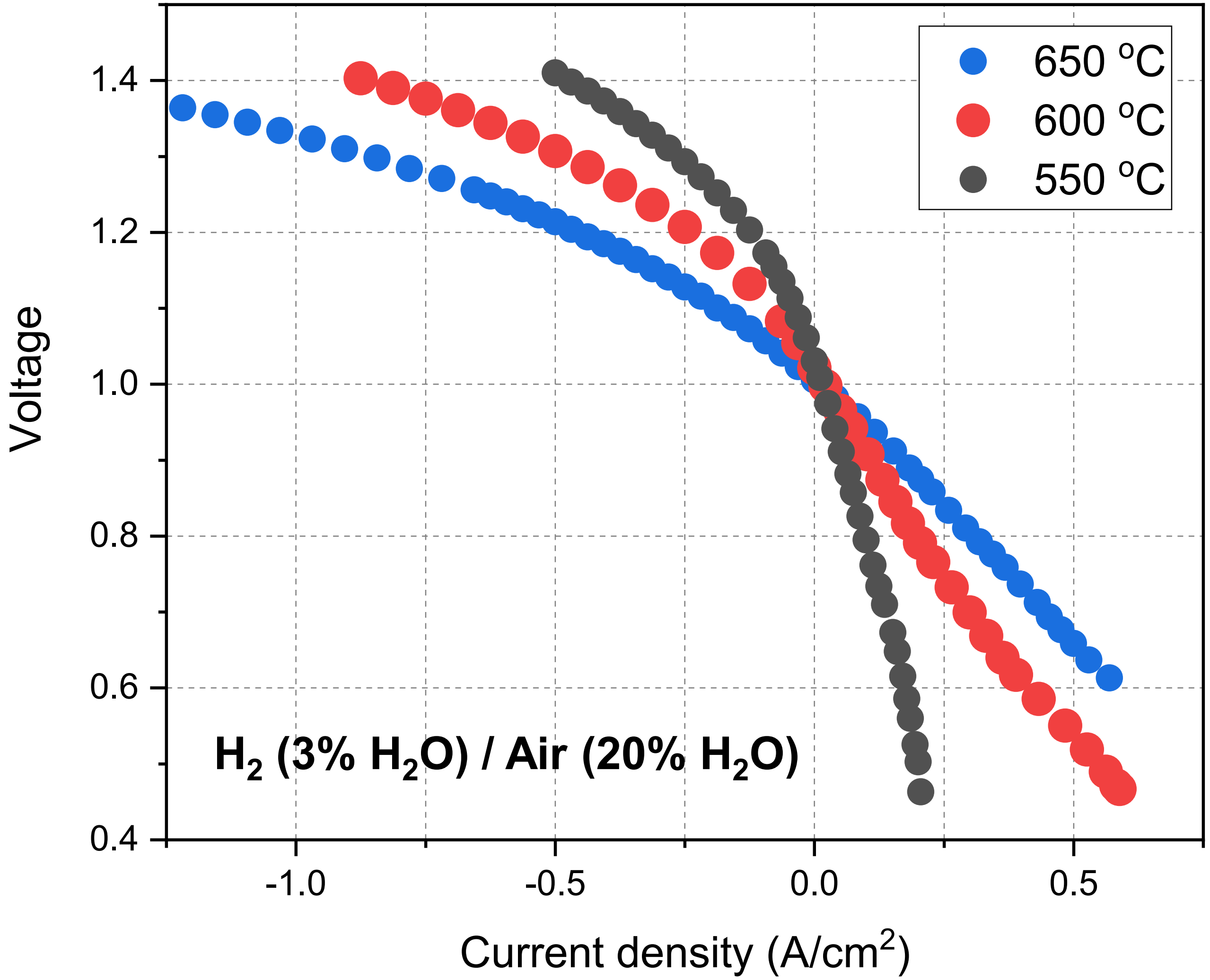




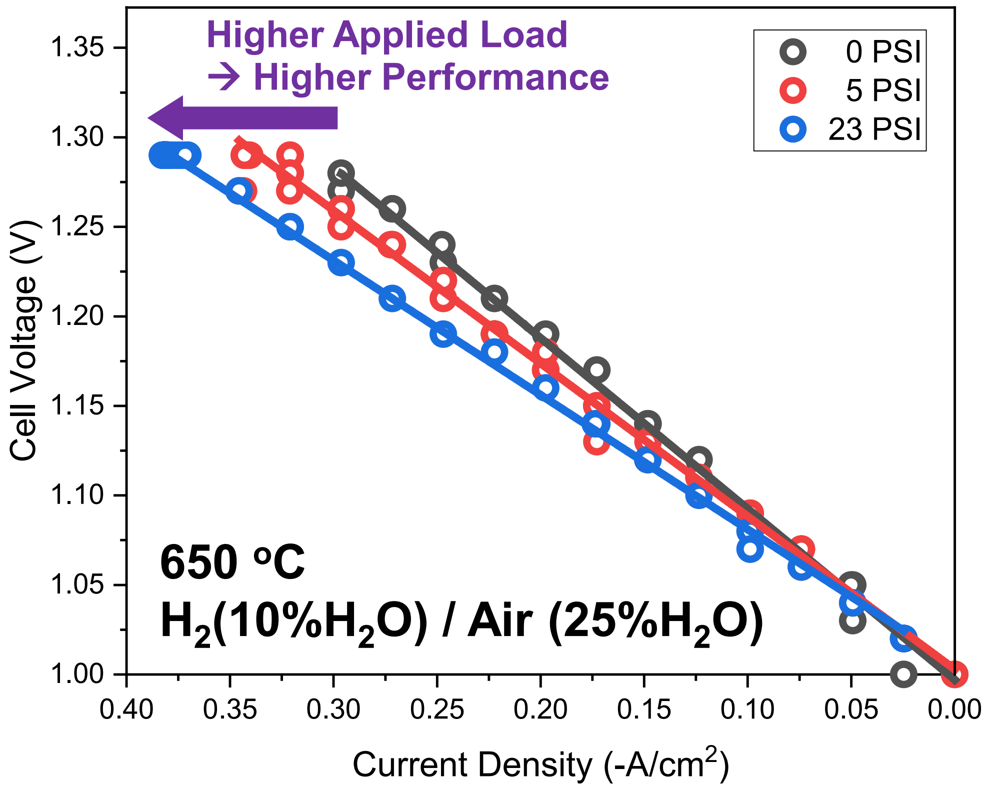
BHCYb cells meet the targeted 75 MPa value!

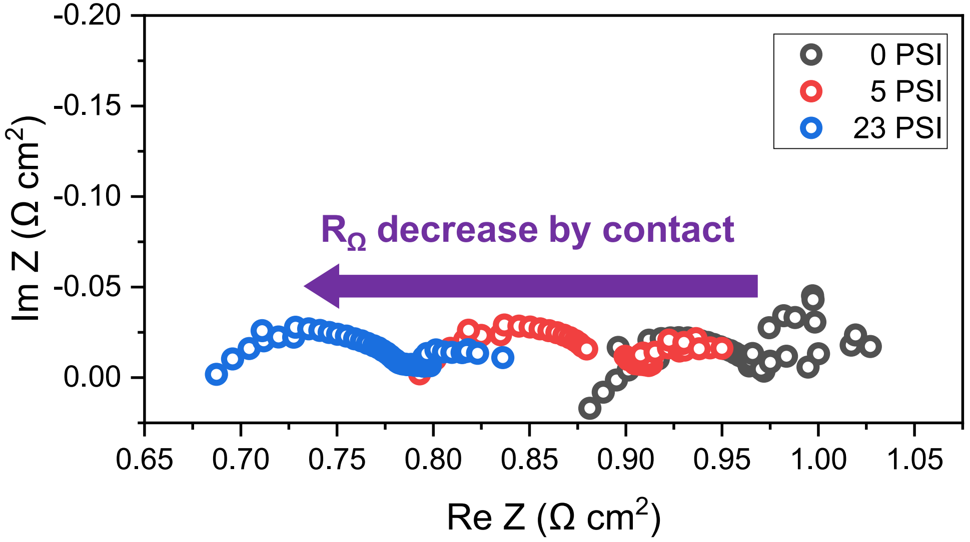
10cm x 10cm Cells

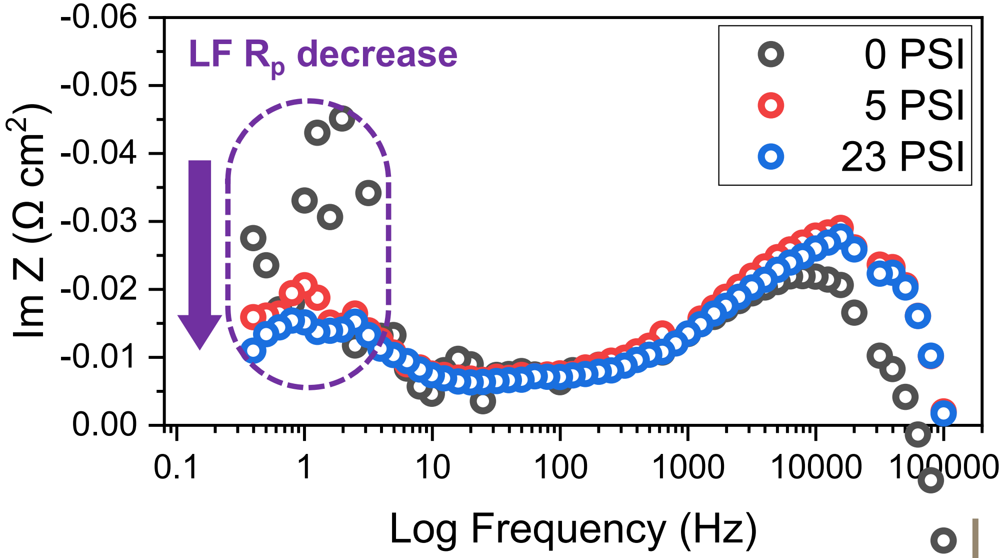
4-inch cell



Effect of Applied Load on the Cell

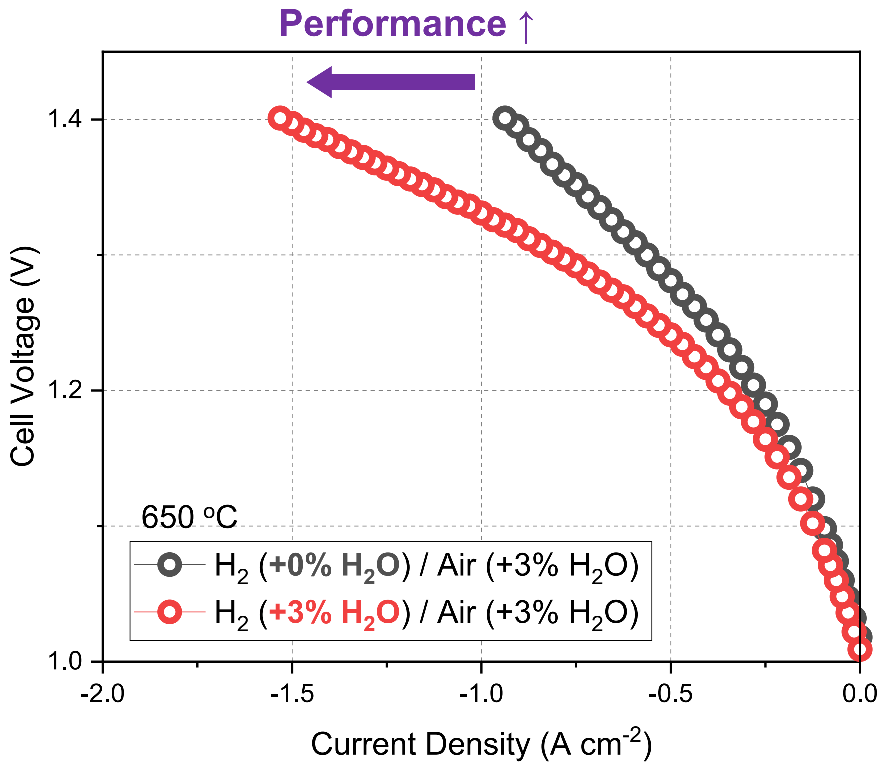


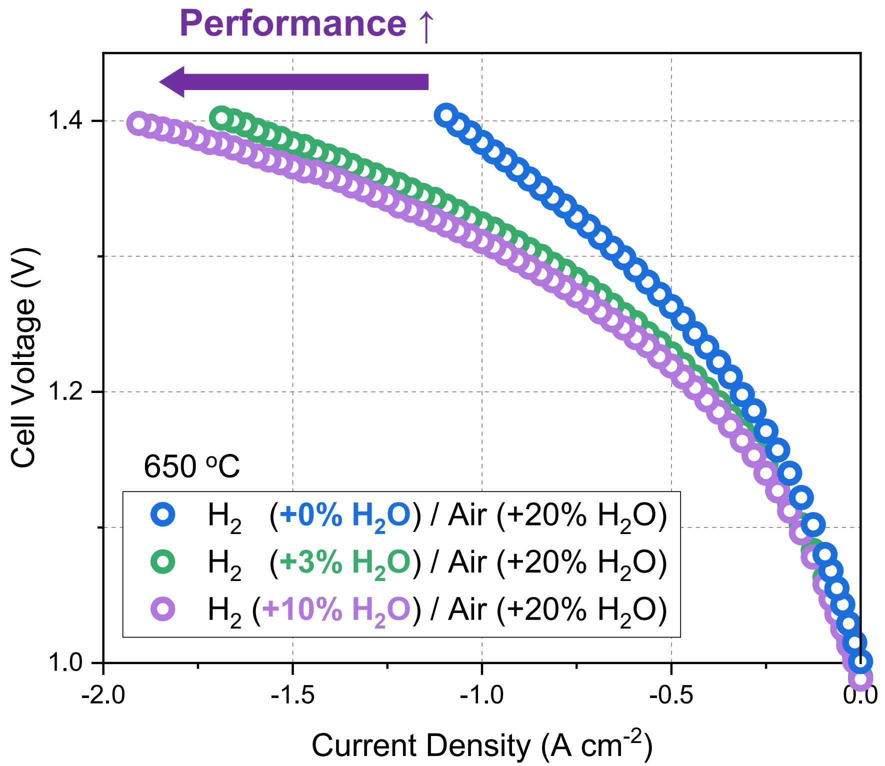




- With increasing applied load on the cell, the cell performance was enhanced.
- The reduced R_Ω and LF R_p indicate the improvement of (i) the contact between the interconnect and electrodes and (ii) sealing under the applied load.

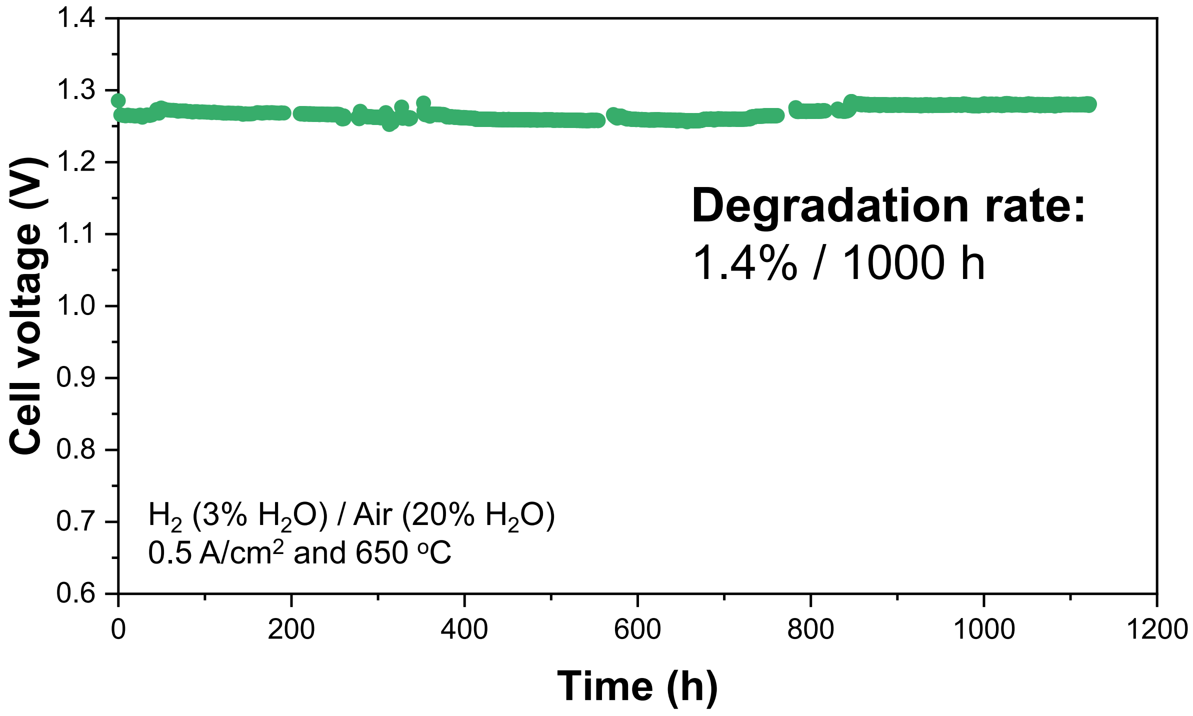
Effect of Steam Concentration

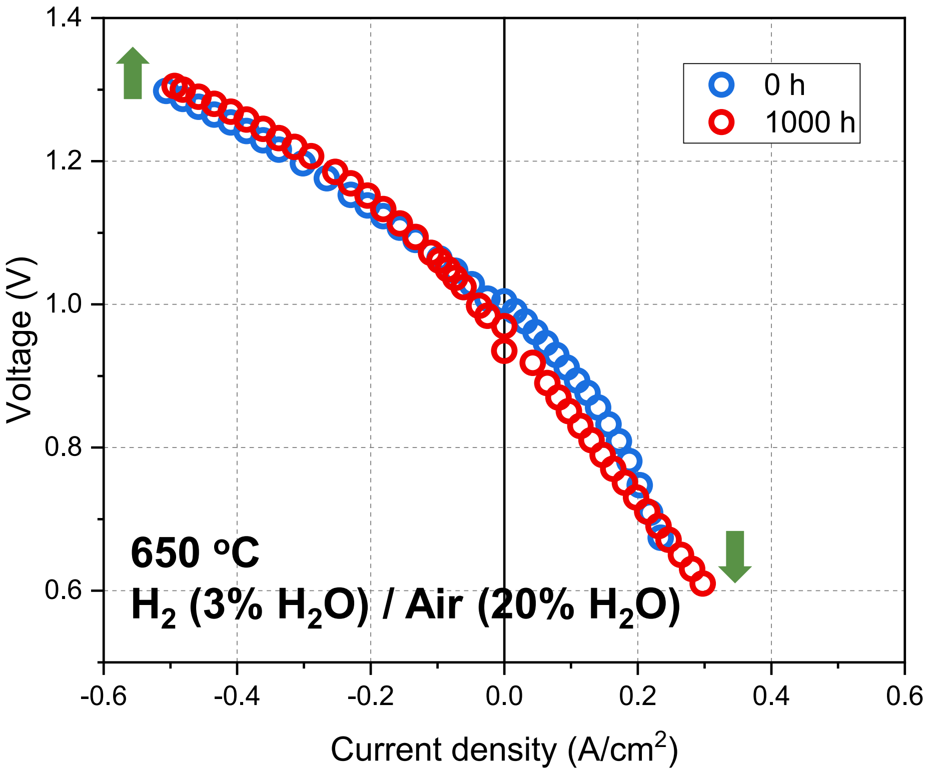




- With increasing H_2O concentration (in H_2), the SOEC mode performance was improved.
- The presence of steam further hydrates the electrolyte, improving the ionic conductivity and kinetics.

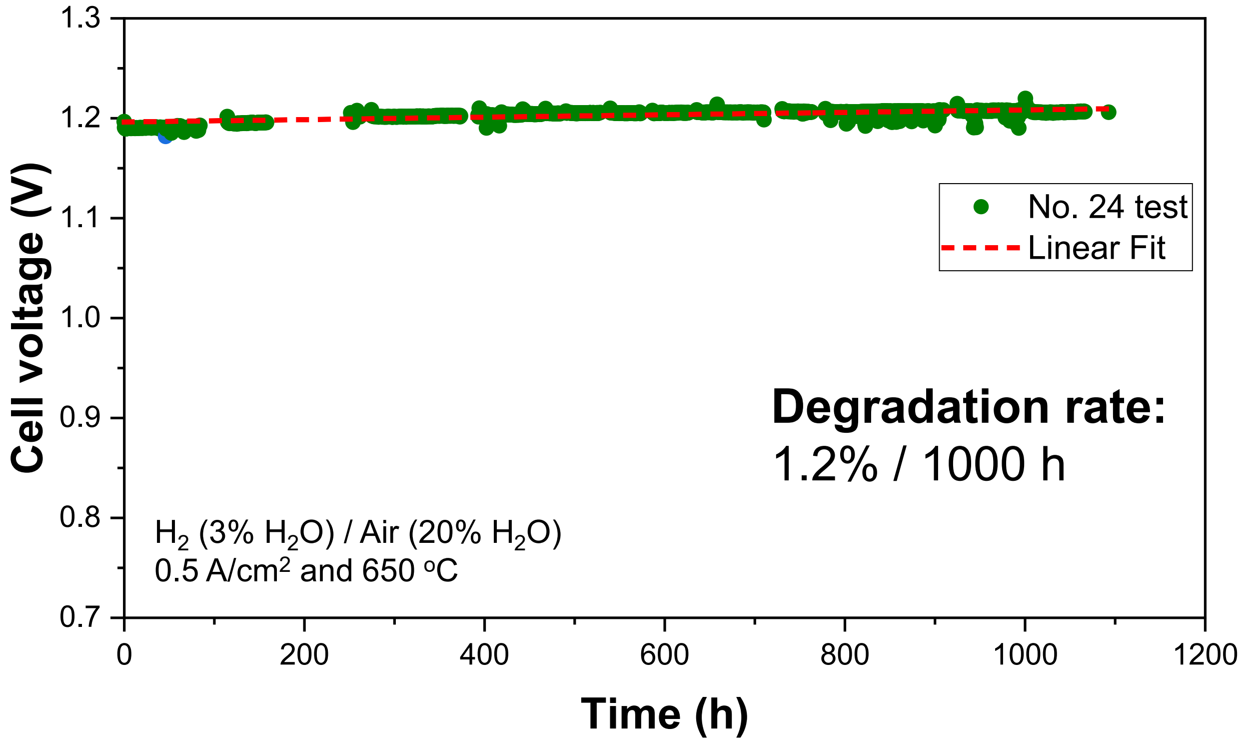
Long-Term Testing of 10cm x 10cm Cells - Cell #1

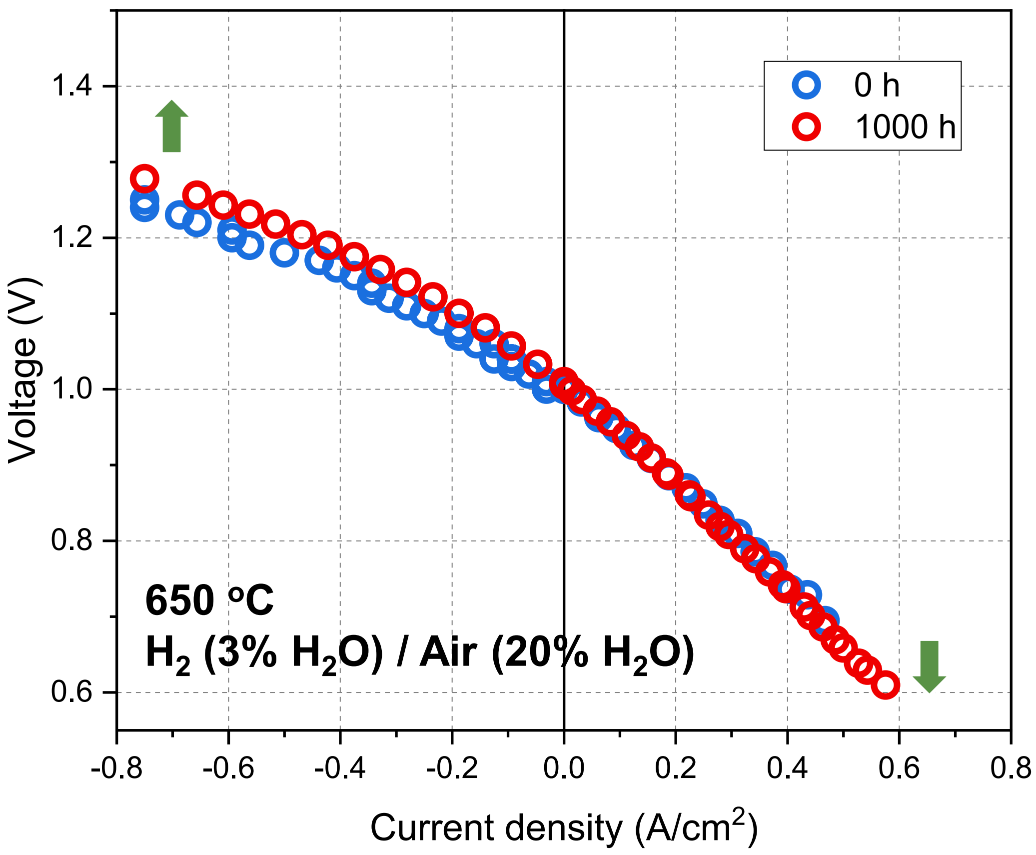




The 1100-h EC mode operation of BHCYYb cells shows very small degradation (1.4%ΔV/1kh), demonstrating high durability and achieving the targeted specification (<2% per 500 h)!

Long-Term Testing of 10cm x 10cm Cells - Cell #2





The 1100-h EC mode operation of BHCYYb cells shows very small degradation (1.2%ΔV/1kh), demonstrating high durability and achieving the targeted specification (<2% per 500 h)!

Summary

- Developed $BaHf_{0.1}Ce_{0.7}Yb_{0.2}O_3$ electrolyte with high conductivity and stability
- Developed highly active and stable catalyst-coated PBCC air electrode
- Developed high-performance and durable reversible cells based on proton conductors
  - Peak power density of 1.2 W cm^{-2} and electrolysis current density of 2 A cm^{-2} at 1.3 V and 600 °C
  - 1000 h operation at 600 °C with a low degradation rate of ~1% per 1,000 h
- Fabricated 10 cm × 10 cm cells
  - Roundtrip electrical efficiency of 77% at 0.5A/cm^2, 650 °C
  - 1000 h operation at 650 °C with a low degradation rate of ~1.3% per 1,000 h

Proposed Future Work

Date	Milestone (BP2)	% Complete
02/2023	Complete the stack design and components development	60%
05/2023	Complete the fabrication and evaluation of up to 3 short stacks (< 0.25 kW).	30%
08/2023	Complete 1 kW stack testing with ≥55% fuel cell at 0.5 A cm^{-2}, and >90% electrolysis at ≤ 650 °C, <2% per 1000 h degradation.	Not started
10/2023	Complete the system design and integration, complete a thermodynamic analysis.	Not started
12/2023	Complete evaluation of the 250 W system with ≥50% fuel cell efficiency at 0.5 A cm^{-2}, and >85% electrical efficiency at ≤ 650 °C.	Not started
02/2024	Demonstrate the potential to produce hydrogen at a cost of \$2 per kilogram based on a cost of electricity of \$30 per MWhr.	Not started
02/2024	Complete the establishment of a thermodynamic model to analyze the energy balance and global efficiency of the system.	Not started
02/2024	Evaluate 1.0 kW rSOC system performance at the relevant operating conditions and model: efficiency, durability, degradation, life of electrolysis cell.	Not started
02/2024	Complete a techno-economic analysis (TEA) based on test data on the rSOC system or components for the defined application	Not started

Thank you

DOE/NETL	Andrew O'Connell	
Phillips 66	Heli Wang (PI) David Ingram Byunghyun Min Amin Baghalian	Junsung Hong Sarah Bushyhead Keri Collins
Georgia Tech	Meilin Liu (Co-PI) Zhijun Liu Yucun Zhou Jerry Luo Conor Evans	Nick Kane Humphrey Lin Xueyu Hu Gyutae Nam