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

Heli Wang: Phillips 66
Meilin Liu: Georgia Tech

DE-FE0031975

DOE FY23 FECM Spring R&D Project Review
April 18, 2023

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Acknowledgments

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Outline

- Project Overview
  - Phillips 66 and R&D
  - Fabrication and Testing Facilities
- Project Objective
- Project Progress
  - Air Electrode Development
  - Development of CeO2 Based Catalyst
  - Large Cells: Tackle the Cell Flatness for Stacking
  - Stack Test Station
- Summary
- Work in Progressing
- Acknowledgements

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

Heli Wang (PI) David Ingram Byunghyun Min Amin Baghalian Jordan Daniels	Junsung Hong Sarah Bushyhead Keri Collins Rob Kelly	• Powder synthesis • Large cell manufacturing • Stack fabrication and testing • System design, integration and operation
Meilin Liu (Co-PI) Zhijun Liu Jerry Luo Chanho Kim	Xueyu Hu Nikhil Govindarajan Gyutae Nam	• Cell materials development • Catalyst development • Button cell evaluation & advanced characterization • Combined theory & experimental validation

Phillips 66 and R&D

Overview

- Diversified 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
- Long history in R&D at ERI
- Emerging energy: solid oxides, hydrogen, decarbonization, renewables etc

PHILLIPS 66

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Fabrication and Testing Facilities

Tape Caster

Spray Coater

High Power Laser Cutter

High Temp Furnace

System Testing Enclosure

- Cost-effective fabrication methods
- Full spectrum of cell/stack manufacturing and testing facilities
- >10,000 sq. ft. floor space
- Fuel (H_2, CH_4, pipeline NG), processing and treatment, DI/steam generation and control
- Large load banks and power supplies.
- Fully automated control systems and stack test stations
- System instrumentation, control and communication

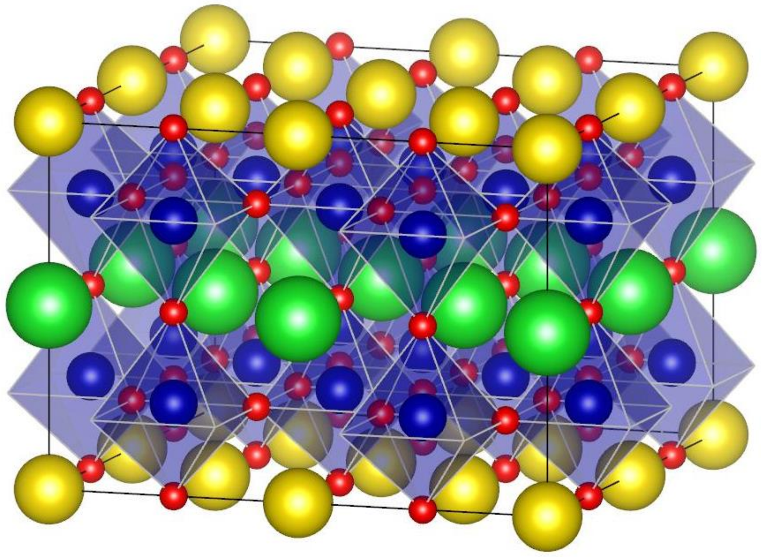
Project Progress

Date	Milestone (BP2)	% Complete
09/2022	Complete the stack design and components development	100%
05/2023	Complete the fabrication and evaluation of up to 3 short stacks (< 0.25 kW).	60%
09/2023	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.	20%
09/2023	Complete the system design and integration, complete a thermodynamic analysis.	20%
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

Accomplishments to Date

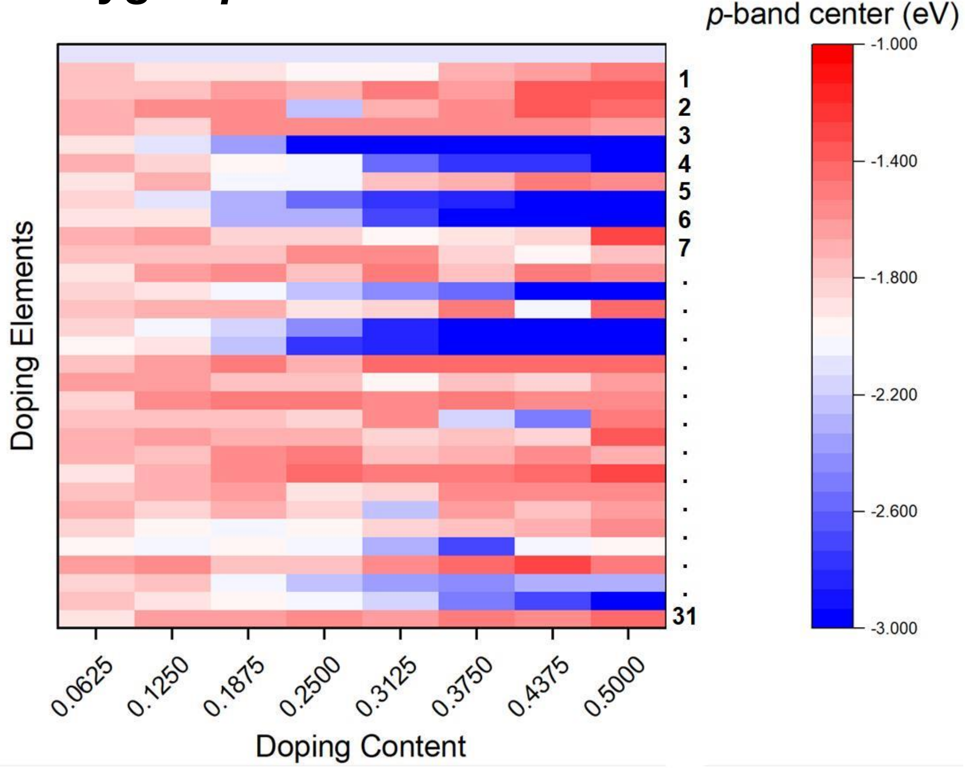
- ✓ **Air electrode**:
  - Based on high-throughput calculation and experimental validation, PBCX air electrode shows low polarization resistance in air (3% H_2O). In BZCYYb symmetrical cell, PBCX air electrode demonstrated **excellent stability in air with 3% and 30% steam (over 500h).**
- ✓ **Air electrode with catalyst:**
  - Complete the $PrBa_{0.8}Ca_{0.2}Co_2O_{6-\delta}$ air electrode with CeO_2 based catalyst development with a polarization resistance of **<0.15 Ω cm²** at 600 ºC in Air (3% H_2O).
  - The **$A_{0.4}Ce_{0.6}O_{2-\delta}$ catalyst** shows a degradation rate of **<2% per 1000 h** at 600 ºC under the presence of **3%H_2O and Cr contaminants** for **over 500 h.**
- ✓ **Large cell fabrication and stacking:**
  - Developed strategies to tackle the flatness of 10 cm x 10 cm cells.
  - With significant modifications (processes, starting powders, sinter profiles etc), we successfully fabricated 10 cm cells with flatness in the range of **≤ 500 μm**.
  - Using 10 cm YSZ cells, we evaluated follow-up air electrode fabrication and sealing for reduced flatness of cells/stacks, and developed optimal procedure for air electrode processing and sealing.
- ✓ **1 kW Test station:** Test station installed, with 3-segments heating/cooling. Successful dry runs.

Air Electrode Development: High-throughput calculations



$Pr_8Ba_8M_{16-x}M'_xO_{48}$
M = Co
M' = 31 different elements
x = 1, 2, 3, 4, 5, 6, 7, 8

Oxygen *p*-band center value

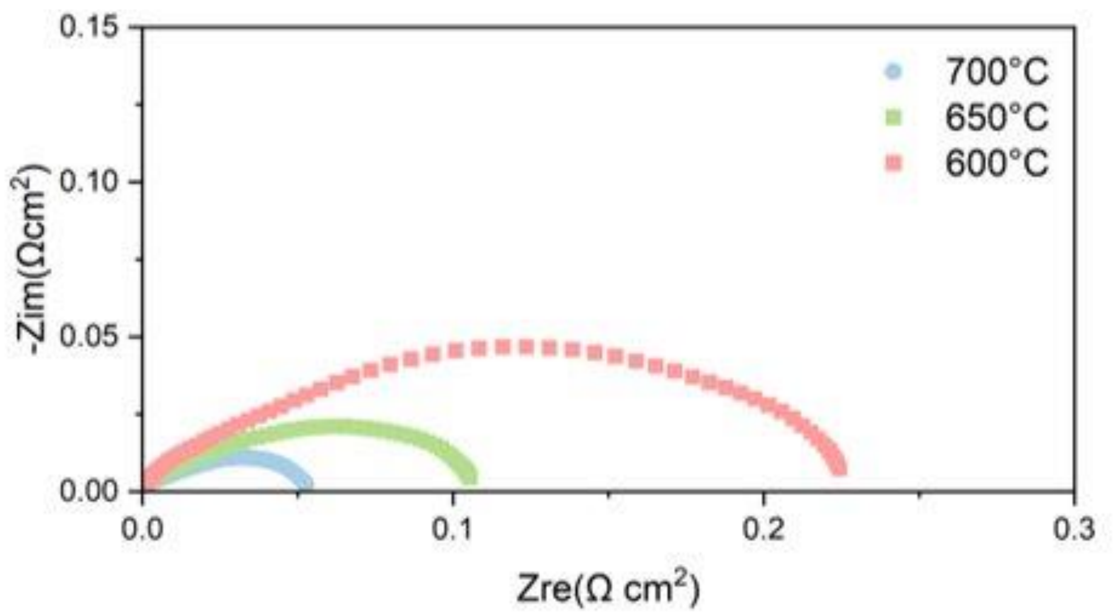


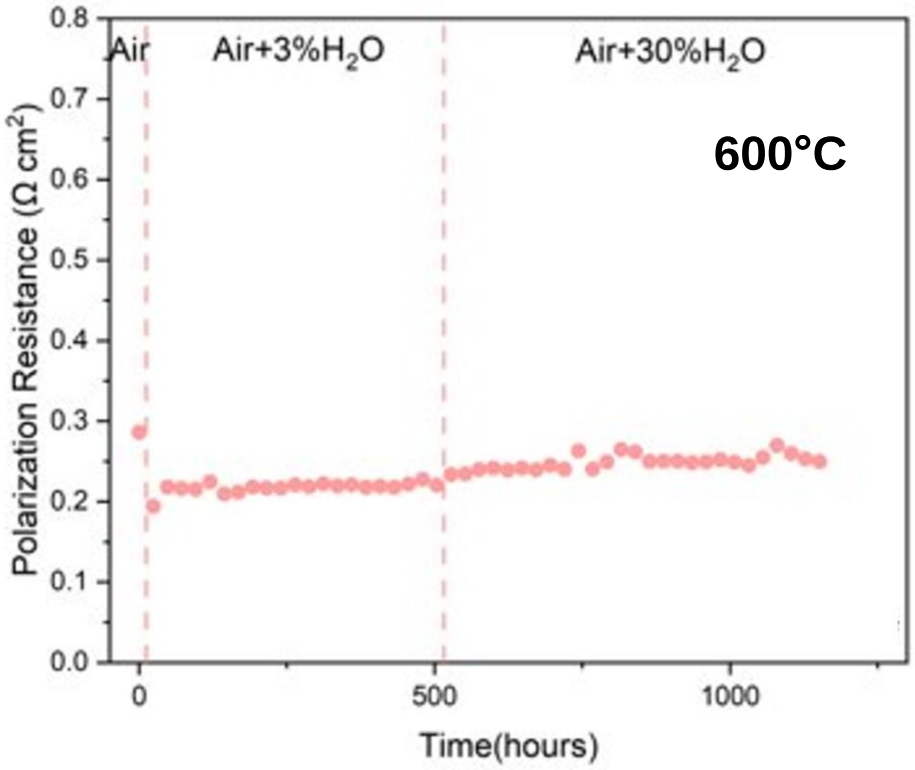
- ✓ **Oxygen *p*-band center value** represents the charge transfer activity, which is generally regarded as the rate-determining step of oxygen reduction reaction (ORR)
- ✓ **Warmer color with less negative *p*-band center** should have good performance with ORR

Air Electrode Development: Validation

$PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ /BZCYYb1711/$PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ symmetrical cells

Rp of PBCX Air Electrode Based on BZCYYb1711

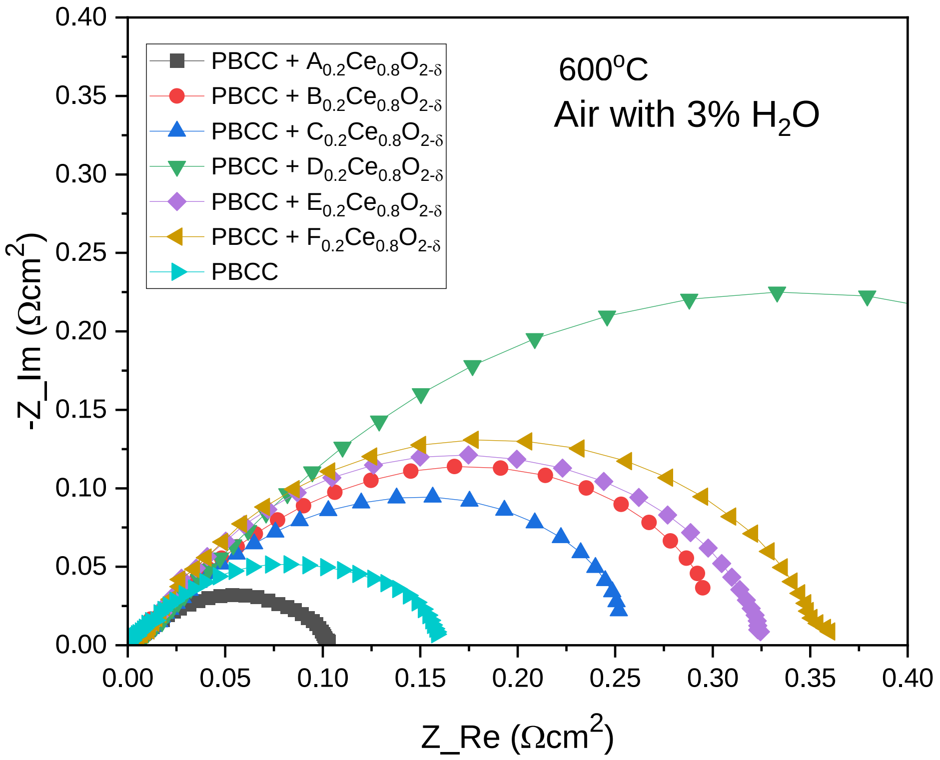




- ✓ A low polarization resistance of **0.22 Ω cm²** is achieved **at 600°C**
- ✓ $PrBaCo_{1.9}X_{0.1}O_{5+\delta}$/BZCYYb/ $PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ symmetrical cell also showed **good stability** under air with **3% and 30% H_2O at 600 °C**

Development of CeO_2 Based Catalyst

- **Enhancing the performance of $PrBa_{0.8}Ca_{0.2}Co_2O_{6-\delta}$ (PBCC) air electrode to achieve polarization resistance < 0.15 Ω cm^2 at 600 °C**

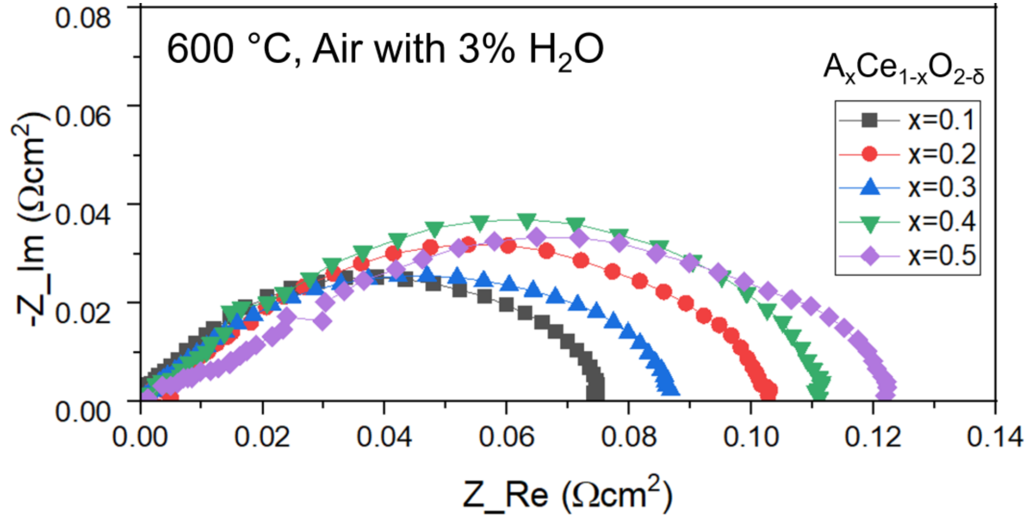


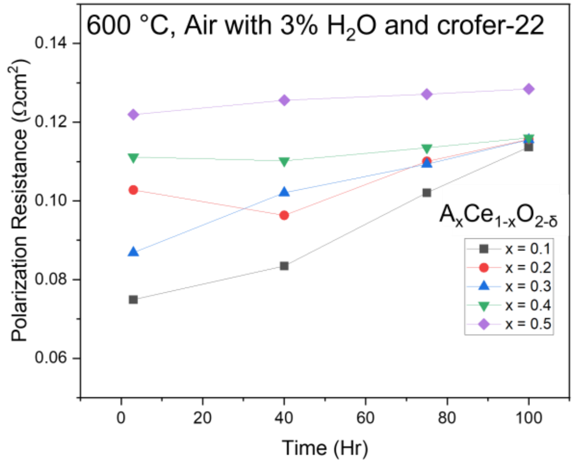
Catalyst	R_p (Ω cm^2)
Bare PBCC	0.158
$A_{0.2}Ce_{0.8}O_{2-\delta}$	**0.102**
$B_{0.2}Ce_{0.8}O_{2-\delta}$	0.295
$C_{0.2}Ce_{0.8}O_{2-\delta}$	0.252
$D_{0.2}Ce_{0.8}O_{2-\delta}$	0.522
$E_{0.2}Ce_{0.8}O_{2-\delta}$	0.324
$F_{0.2}Ce_{0.8}O_{2-\delta}$	0.360

✓ **CeO_2 based catalyst was screened for $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC) air electrode by the solution infiltration process**

Development of CeO_2 Based Catalyst

Enhancing $PrBa_{0.8}Ca_{0.2}Co_2O_{6-\delta}$ (PBCC) and stability of PBCC w/ catalysts





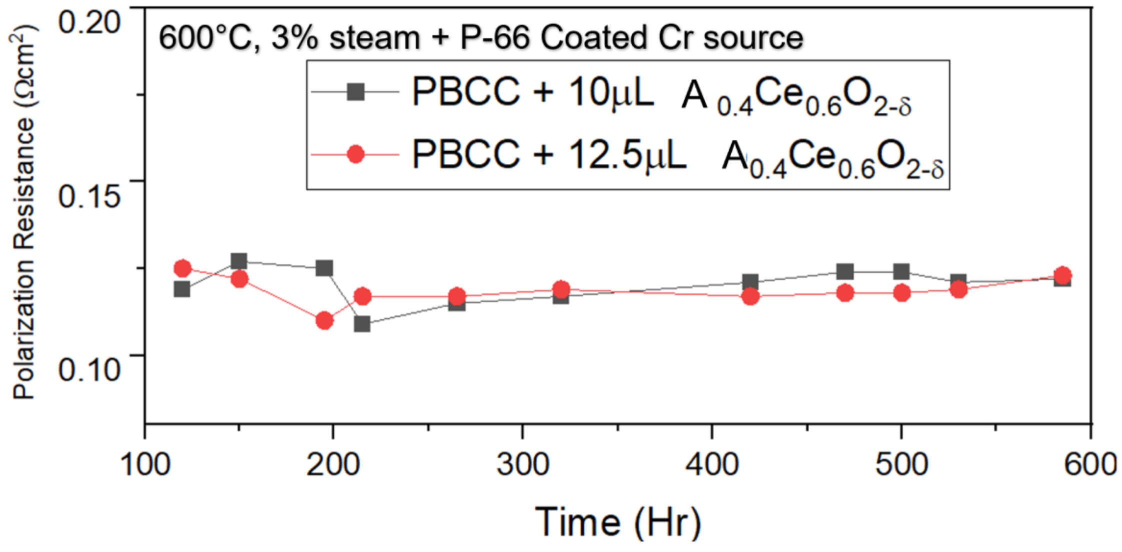
A content in $A_xCe_{1-x}O_{2-\delta}$ catalysts

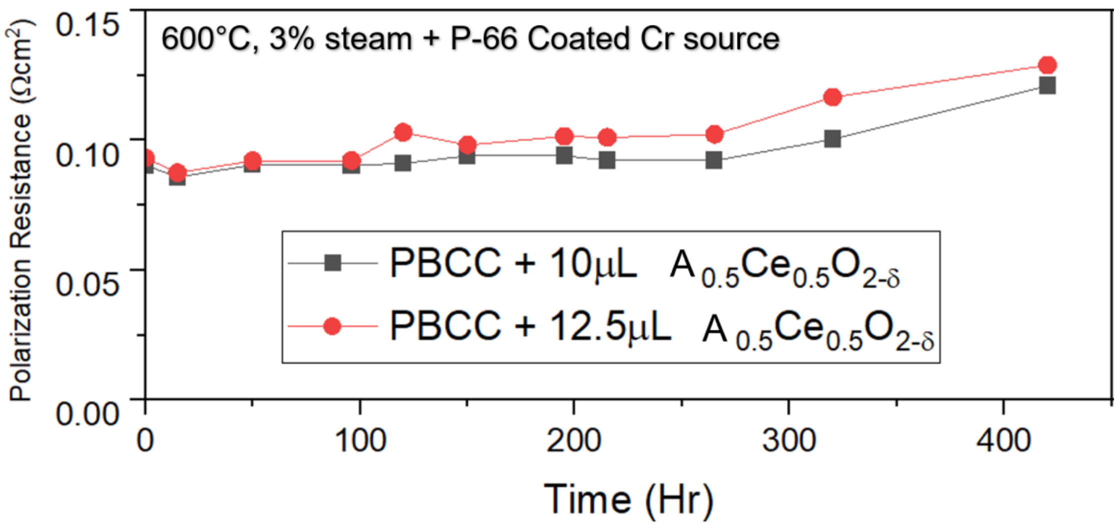
A Content	R_p (Ωcm^2)	% degradation
10%	0.0749	51%
20%	0.10276	12.5%
30%	0.08683	33%
40%	**0.11116**	**4.3%**
50%	**0.12194**	**5.3%**

- ✓ Enhancing performance of PBCC air electrode to achieve polarization resistance <0.15 Ω cm^2 at 600°C and 3% steam
- ✓ $A_xCe_{1-x}O_{2-\delta}$ catalysts demonstrated the required performance enhancement
- ✓ CeO_2 doped 40 and 50 % A catalysts showed lower degradation in Crofer-22 at 600 °C

Development of CeO_2 Based Catalyst

Long-term stability of $A_{0.4}Ce_{0.6}O_{2-\delta}$ and $A_{0.5}Ce_{0.5}O_{2-\delta}$ catalysts





- ✓ **PBCC with $A_{0.4}Ce_{0.6}O_{2-\delta}$** catalyst catalyst showed excellent stability **without degradation for 500h** in **3% steam + P66 coated Cr at 600 °C**

Large Cells: Tackle the cell flatness for stacking

Starting powders

Tape casting
BHCYYb/functional layer/Ni-BHCYYb

Drying and **flattening**

Cutting
15x15 cm^2 (6x6 in^2)

Burnout
(staged temperatures)

Sintering
(HT treatment)

Flattening
(HT processing)

Half cell > 10x10 cm^2
Laser-cut into desired size

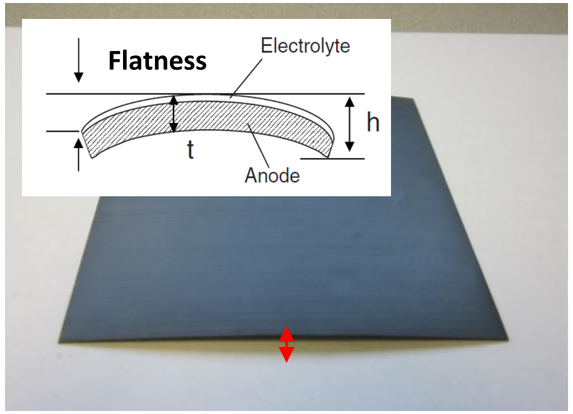
Interlayer spray coating and sintering

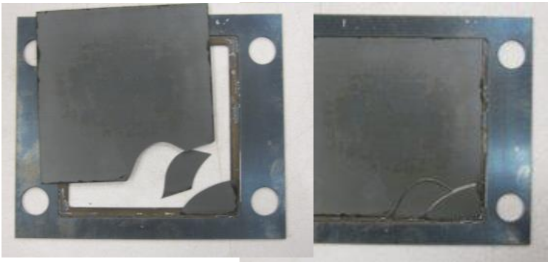
Screen printing of air electrode

Air electrode

Sealing

Stacking



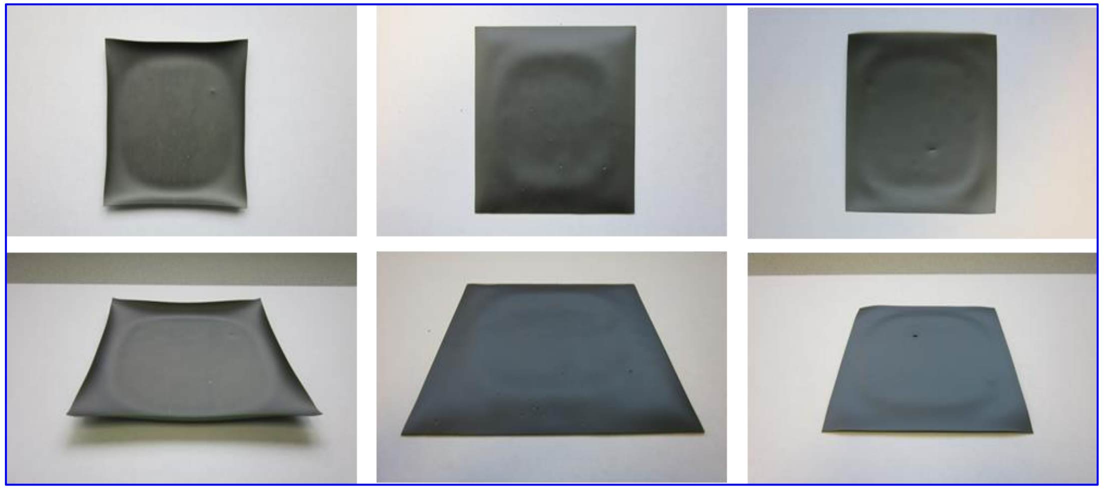


Strategies to reduce the residual stress:

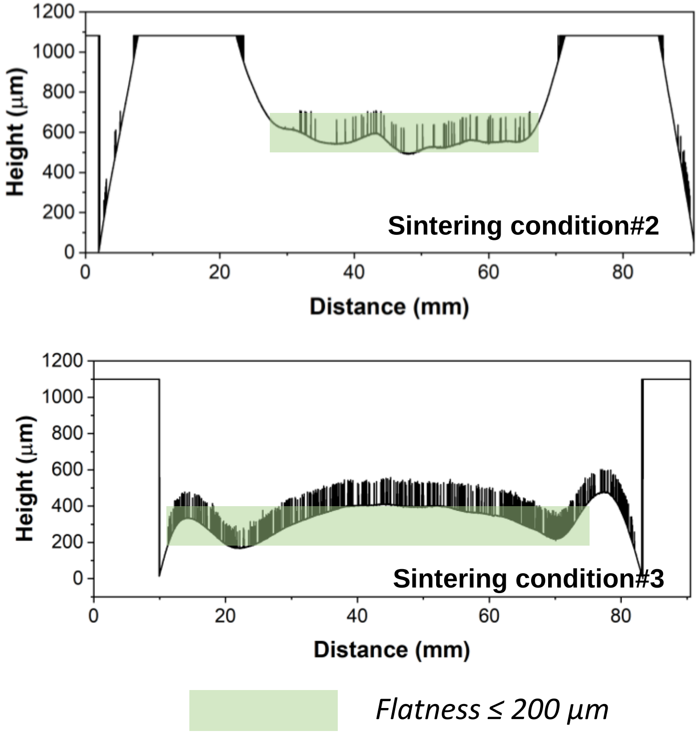
- ✓ Shape and size of the green tape
- ✓ *Optimize sintering temperature, ramping rate, and time*
- ✓ *Fine tune the microstructure (Starting powder particle size, fuel electrode porosity, and pore size)*
- ✓ Mechanical flattening
- ✓ *Combination*

- *Sealing/framing*
- *Air electrode fabrication then sealing*

Tackle the Cell Flatness: Effect of sintering profile



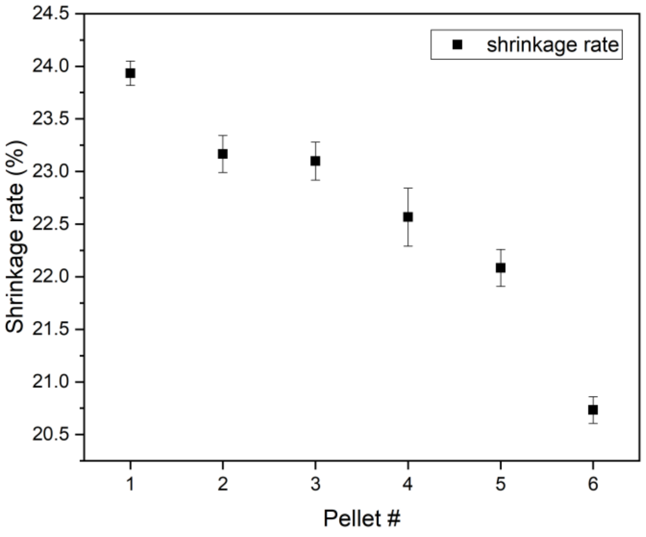
Sintering condition#1 Sintering condition#2 Sintering condition#3



Warping of the cell can be minimized to some degree by optimizing sintering profile

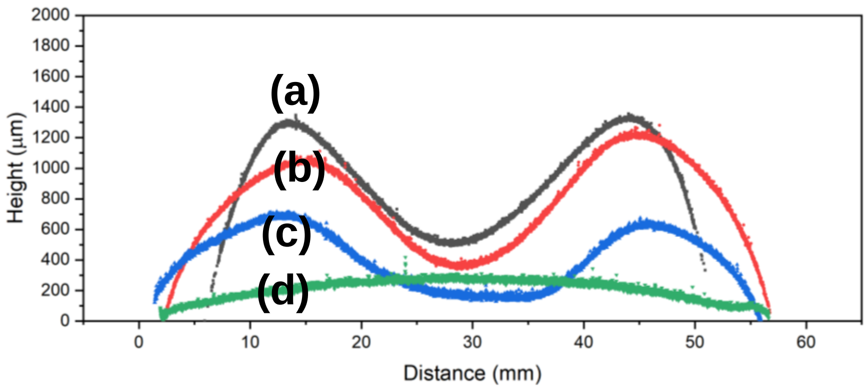
Tackle the Cell Flatness: NiO powder, combination

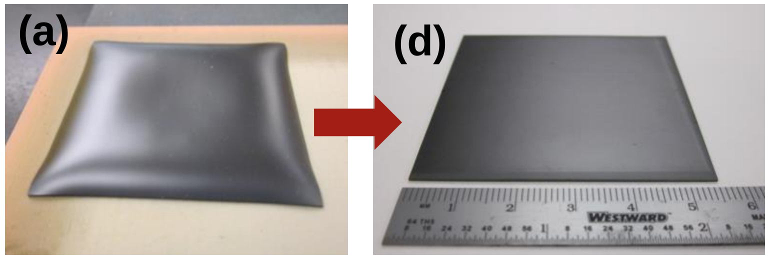
A. Study on the effect of NiO powder types



- ✓ Shrinkage rate of the support layer can be significantly reduced by adjusting NiO starting powder types
- ✓ Less shrinkage is preferred

B. Tape casting & sintering & mechanical flattening





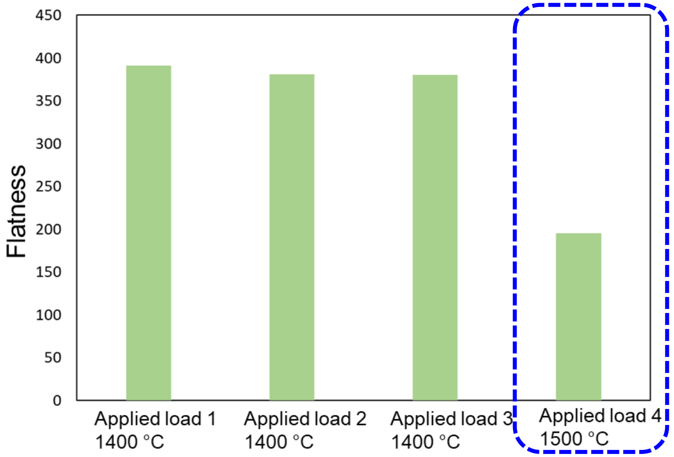
Flatness > 1 mm

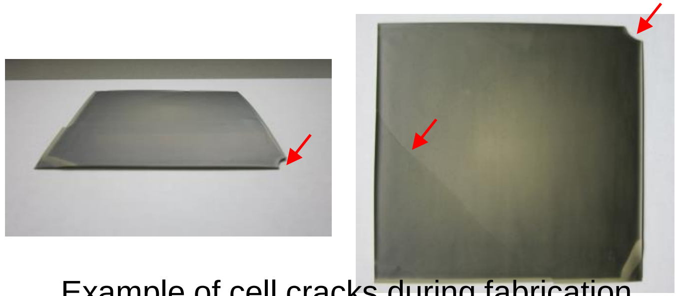
≤ 200 μm flatness
(*met target flatness*)

- ✓ (a) → (b) : optimized NiO powder types restrained the warpage
- ✓ (b) → (c) : optimized sintering profile
- ✓ (c) → (d) : mechanical flattening w/o defects
- ➢ Same approach is for fabricating 10 x 10 cm^2 cell

Tackle the Cell Flatness: Larger cells

Then

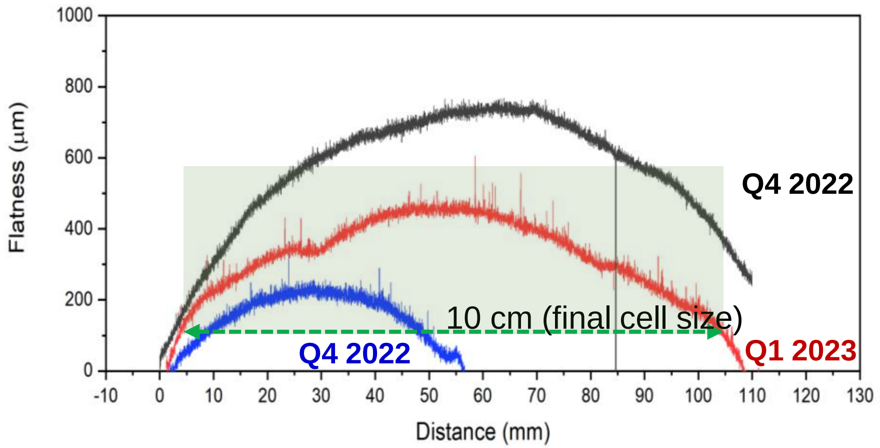




Example of cell cracks during fabrication

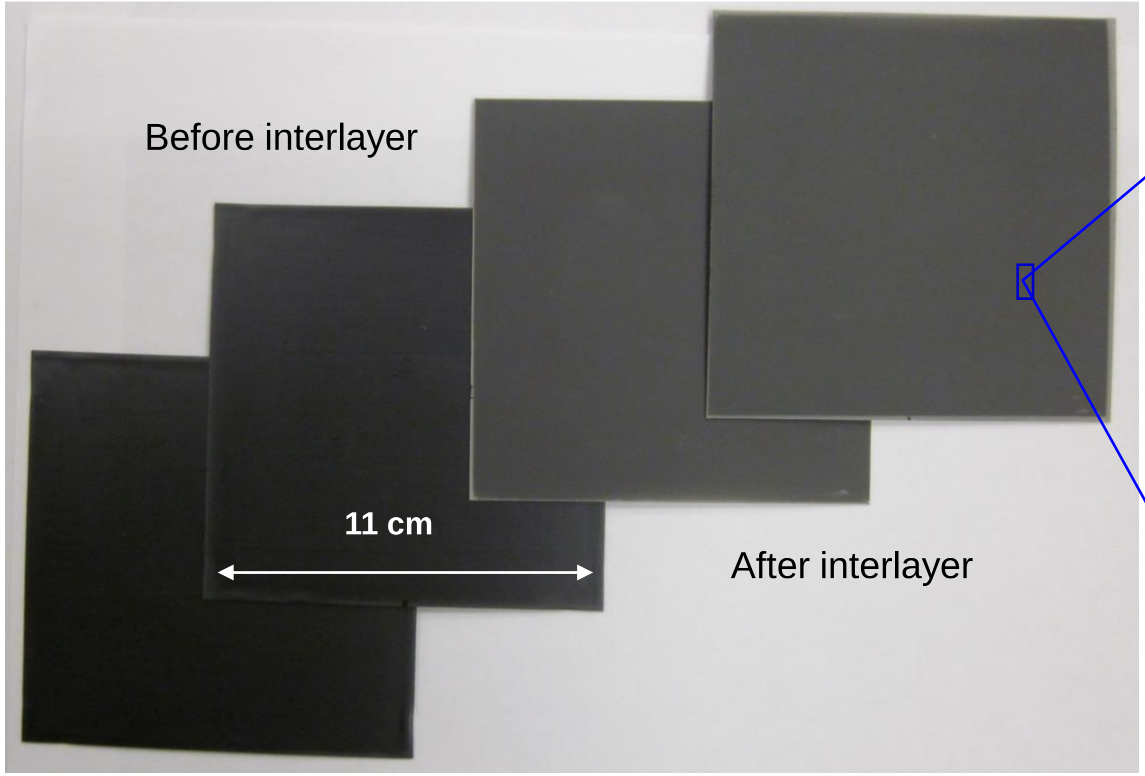
- ✓ 2022: Reasonable good flatness
- ✓ Low yield due to cells cracking associated

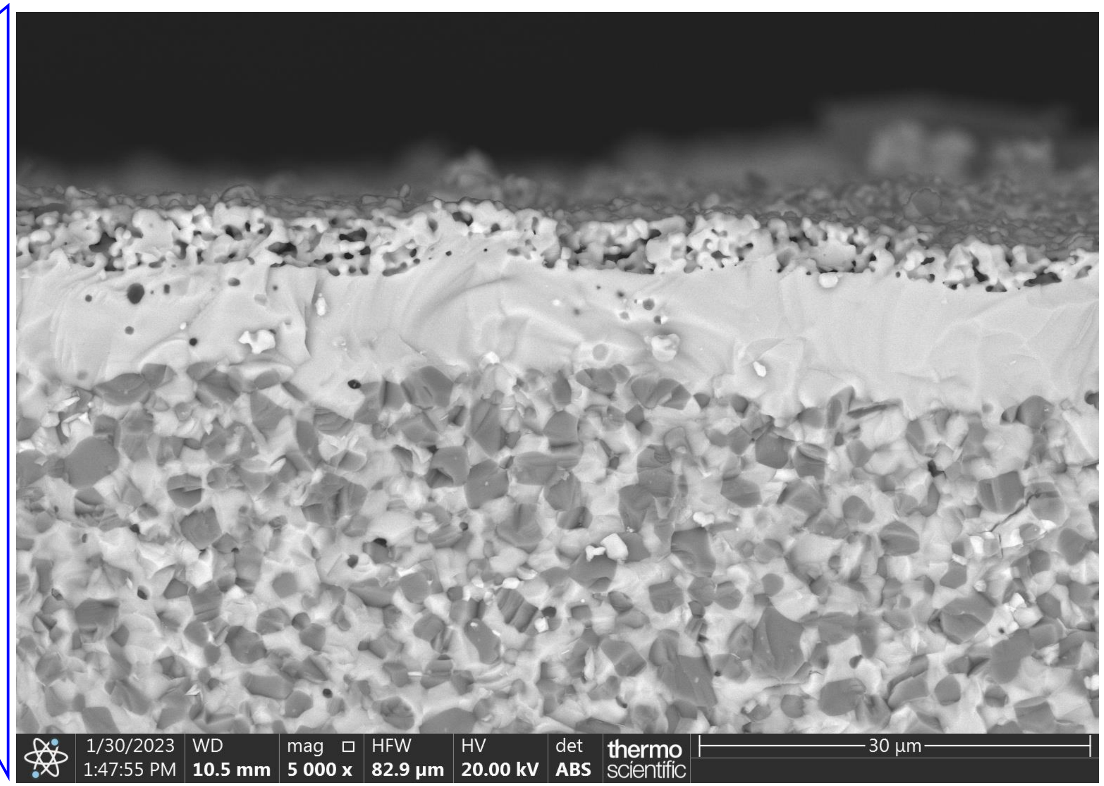
Now



- ✓ Q4 2022: Reduced cracking, but more cell bending compared to Q1 2022
- ✓ Q1 2023: Significantly improvement. The flatness is acceptable for bigger cell, and was controlled in the ≤ 500 µm range.

Tackle the Cell Flatness: Flat cells fabrication

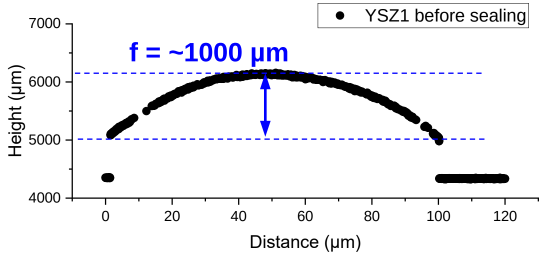


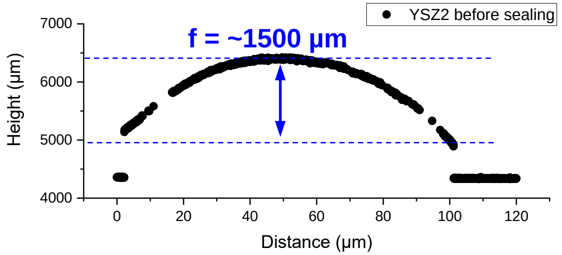


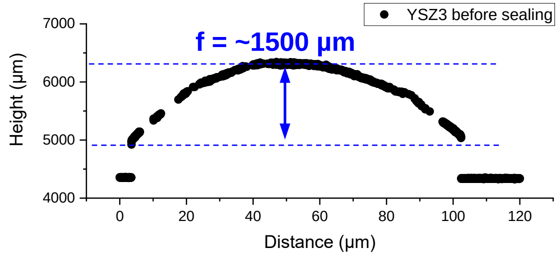
- ✓ **Good cells fabricated, with acceptable flatness and dense structure.**
- ✓ **QC of cell fabrication is underway including (cell-to-cell) variations in thickness, flatness, cracks etc. Working on improving yield.**

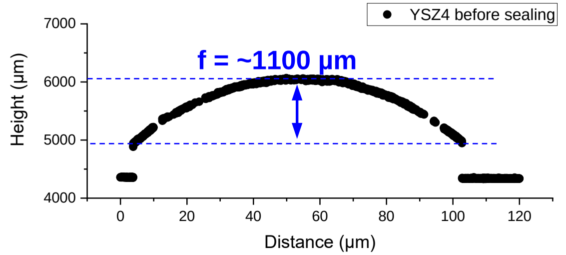
Tackle the Cell Flatness for Stacking: Sealing (YSZ cells)

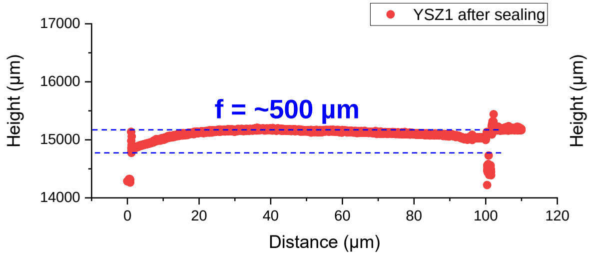
Sealing on frames

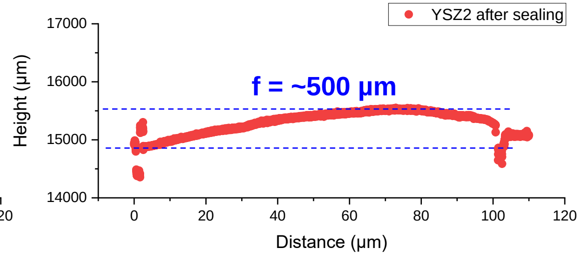


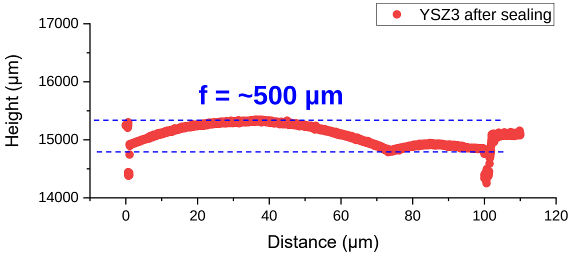


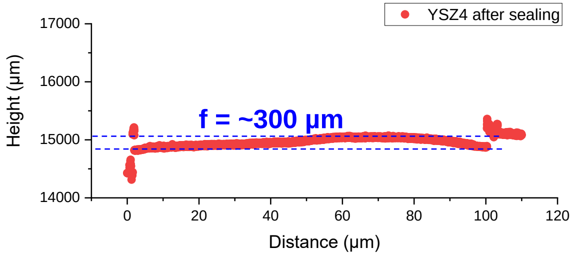


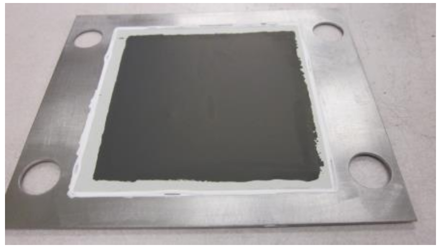


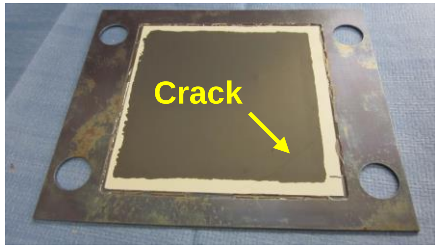


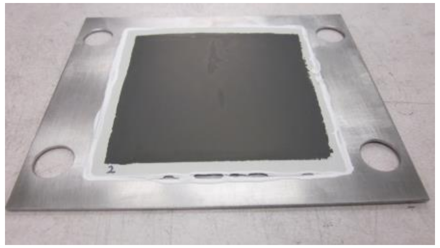


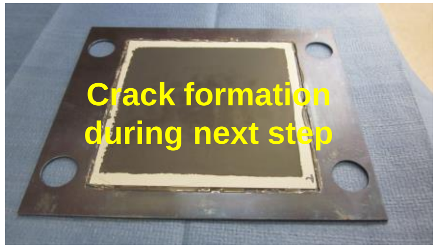


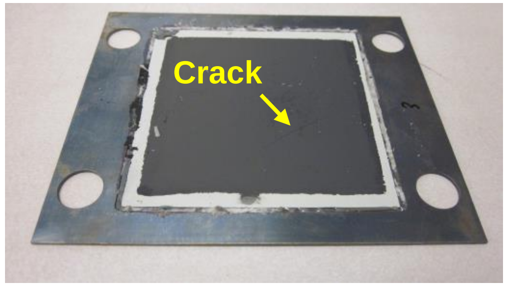


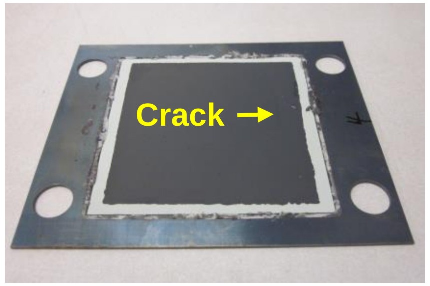










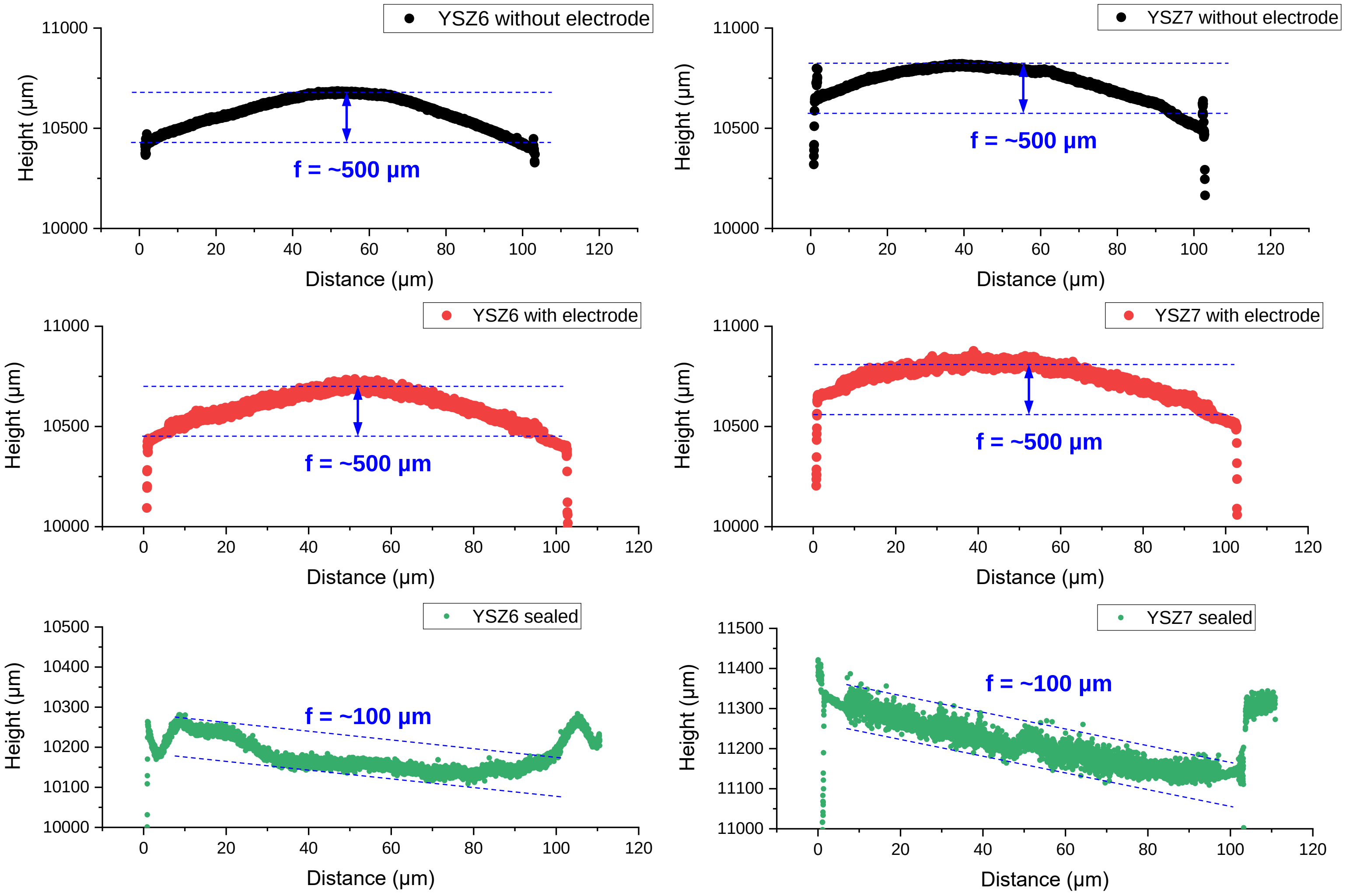


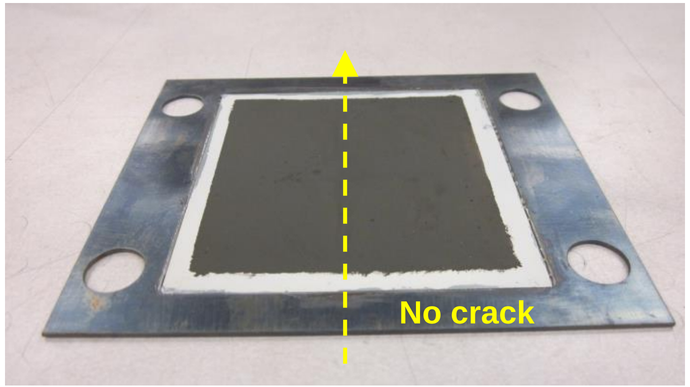
➢ **Sealing could reduce YSZ cells Flatness (f) from 1000 - 1500 µm → 300 - 500 µm, cracking an issue**

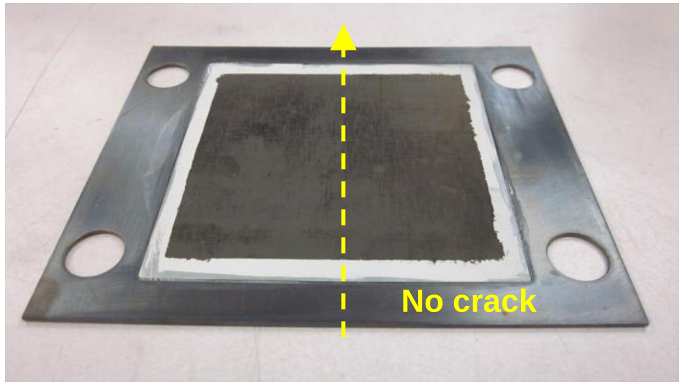
Tackle the Cell Flatness for Stacking: Air electrode & sealing

Air-electrode fabrication

Sealing on the frame

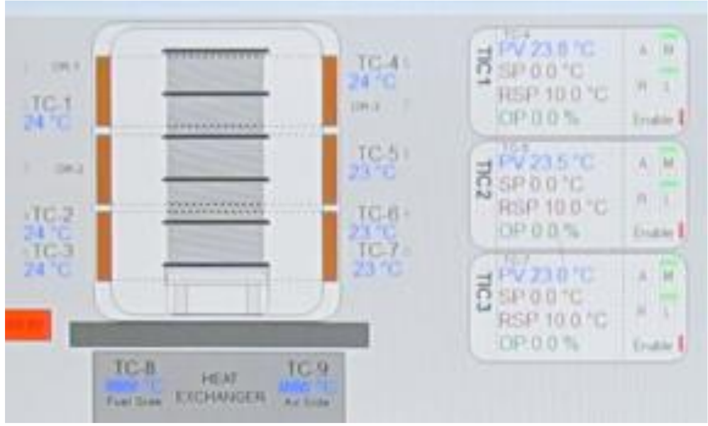


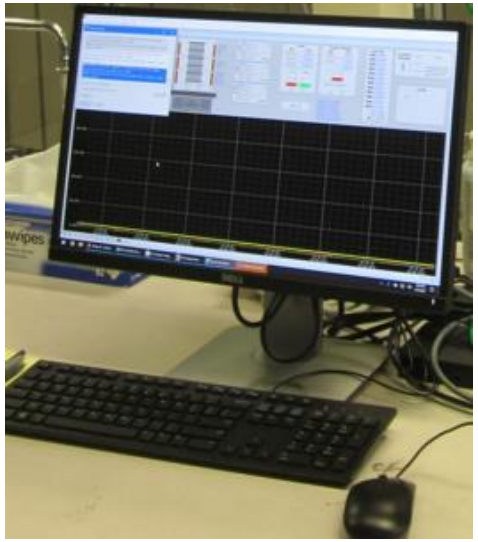


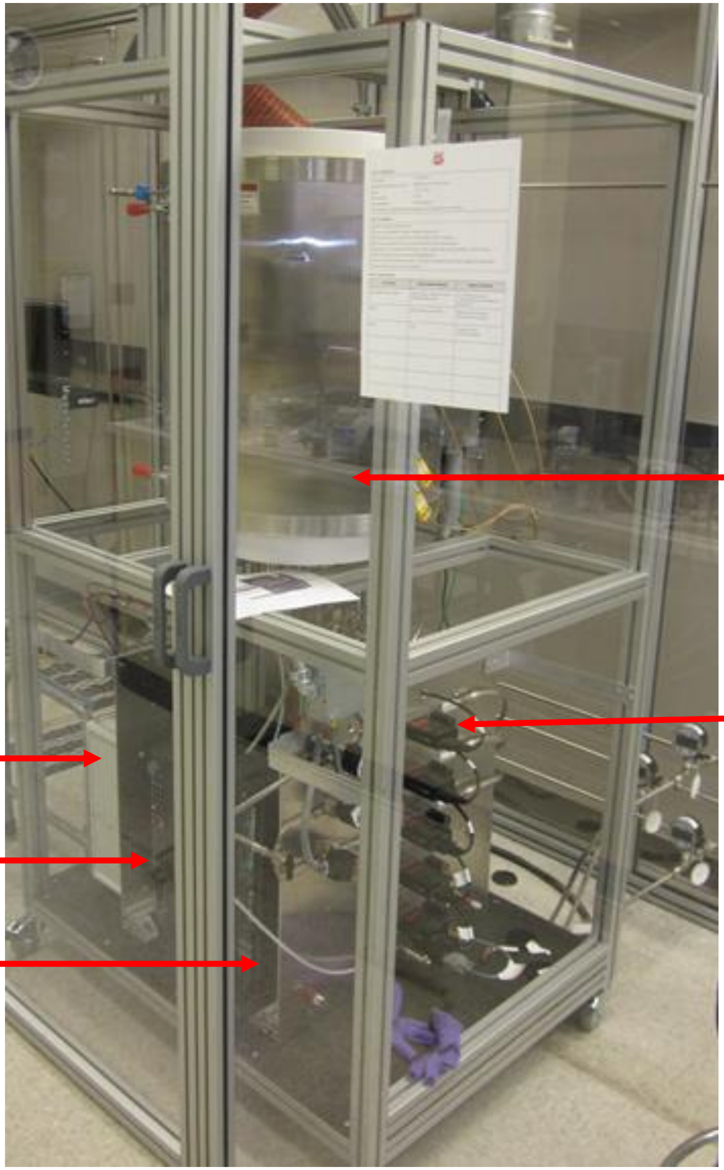


- ➢ No change in the flatness (f) by air-electrode fabrication at 950 ^{o}C: ~500 μm → ~500 μm
- ➢ The cells were further flattened from ~500 μm to ~100 μm without any fracturing.

Stack Test Station







- ✓ **3-segments heating/cooling**
- ✓ **Programable profiles vis PC control**
- ✓ **Successful dry-runs**
- ✓ **Location for long-term stack/system operations**

Summary

- Based on high-throughput calculation and experimental validation, we developed low resistance and highly stable PBCX air electrode. (500 h operation in 3% H_2O & additional 500 h in 30% H_2O at 600 °C)
- Developed highly active and stable $A_{0.4}Ce_{0.6}O_{2-\delta}$ catalyst-coated PBCC air electrode (0.12 Ω cm^2 at 600 °C, degradation rate of <1% per 1,000 h in 3% H_2O and Cr)
- With modifications in processes, starting materials, sintering profiles etc, we successfully fabricated 10 cm x 10 cm cells with acceptable flatness range (≤ 500 μm)
- Developed follow-up optimal procedures for air electrode processing and sealing, with YSZ cells.
- Installed 1kW stack test station, with successful dry runs.

Work in Progressing

Date	Milestone (BP2)	% Complete
09/2022	Complete the stack design and components development	100%
05/2023	Complete the fabrication and evaluation of up to 3 short stacks (< 0.25 kW).	60%
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Acknowledgements

US DOE-Solid Oxide Fuel Cell Program
Under Award No. DE-FE0031975

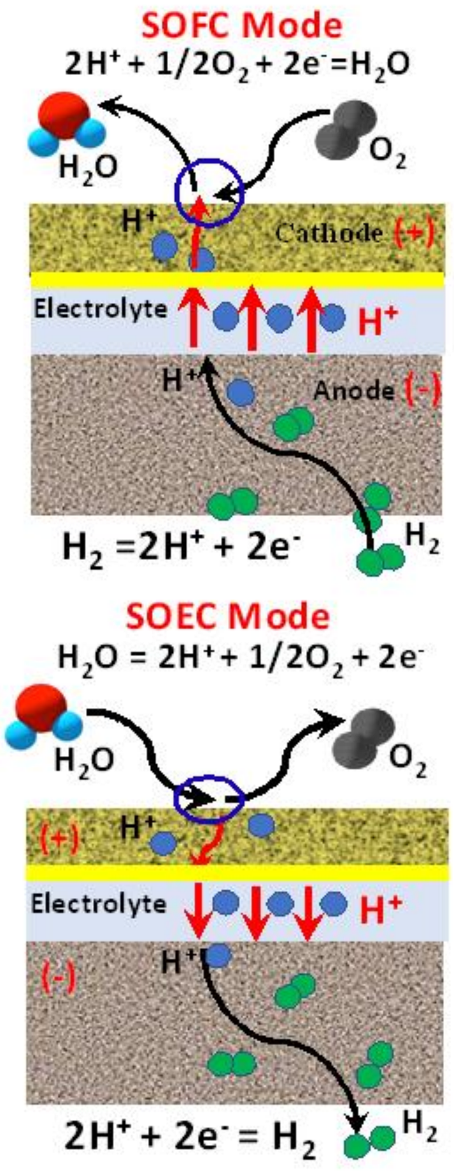
Thank you for your support!

Thank you!

Project Objectives (re-cap)

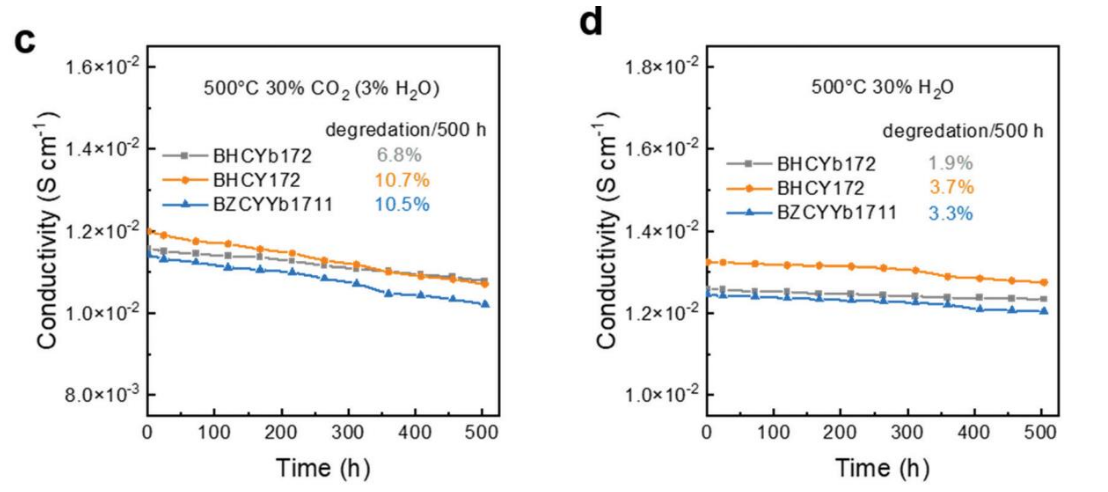
- To design, fabricate, and demonstrate a robust, highly efficient, and affordable reversible solid oxide cell (rSOC) system based on a proton conducting electrolyte membrane for hydrogen and power generation.

- 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.



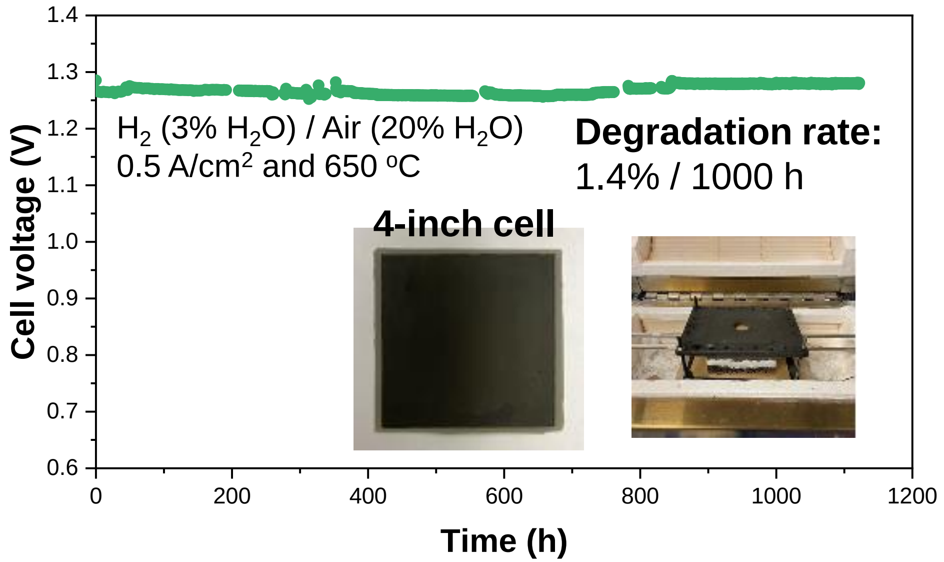
Electrolyte Development (re-cap)

Stability



- ✓ **Y- and Yb-doped electrolytes** show desirable conductivity of **~0.02 S cm^{-1}** at 600 ºC, making them good candidates for ReSOCs
- ✓ **BHCYb172** showed high chemical stability against CO_2 and H_2O
- ✓ BHCYb172 demonstrates excellent chemical compatibility with NiO *(not shown)*

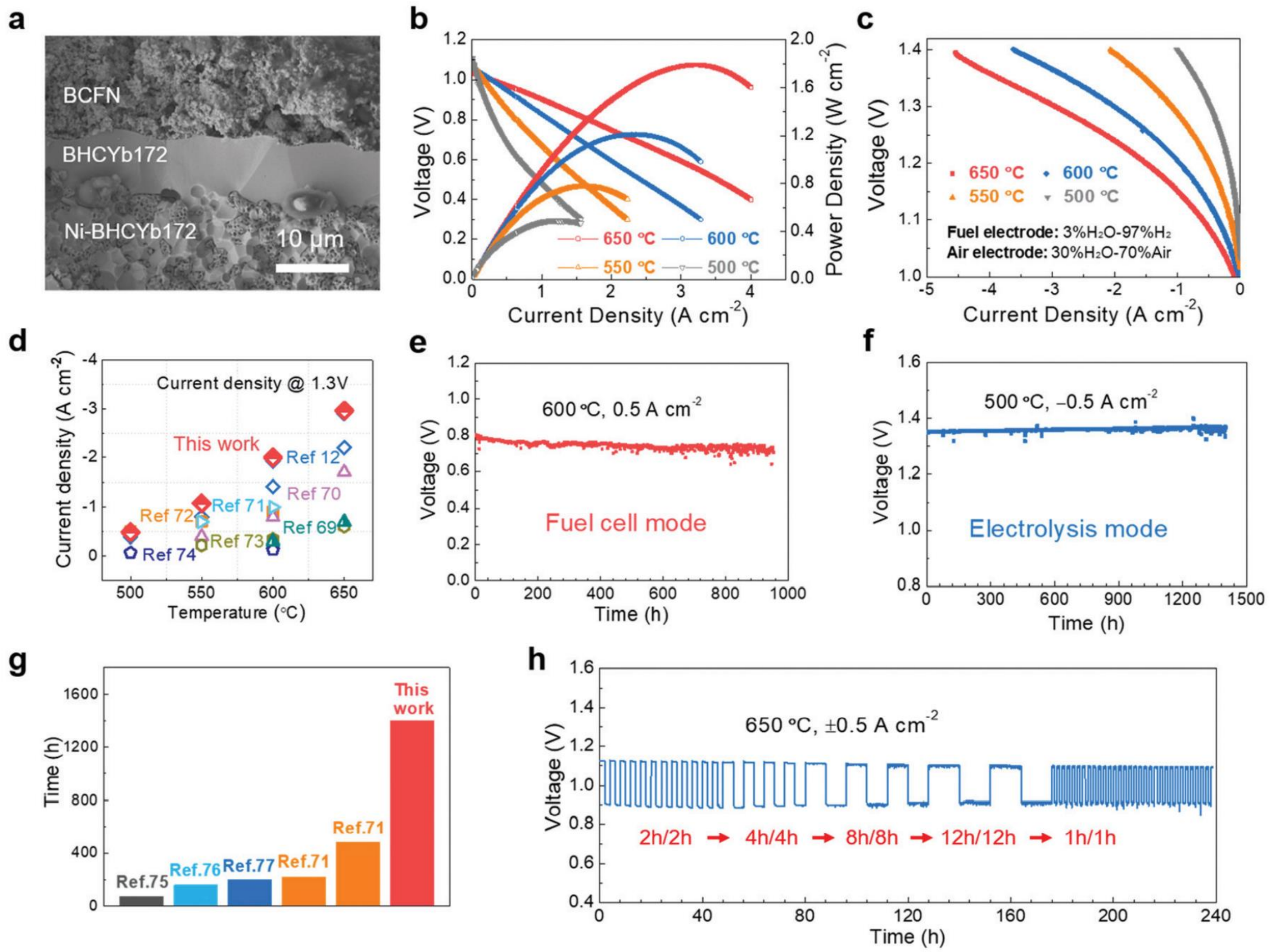
Long term testing



- ✓ The 1100-h EC mode operation of Ni-BHCYYb/BHCYYb/PB9CN cells show high durability, degradation rate <1.4%ΔV/1kh, achieving the target (<2% per 500 h).
- ✓ 84% efficiency in EC mode and 68% in FC mode, with roundtrip efficiency of 76%

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

High-Performance BHCYb172-based Cell and H_2O Electrolysis (re-cap)

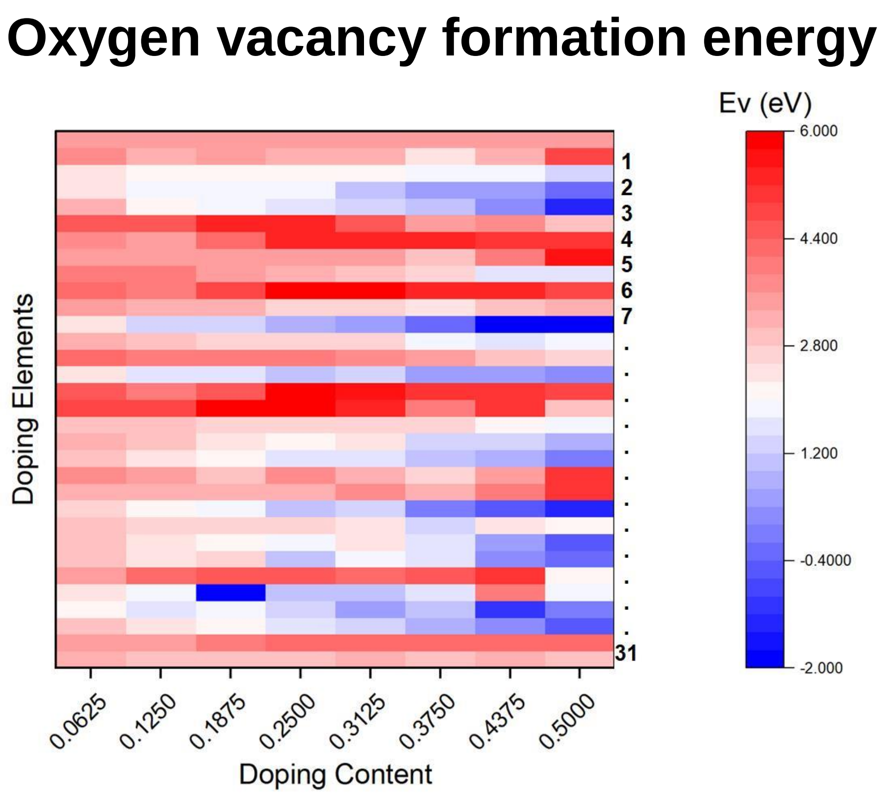


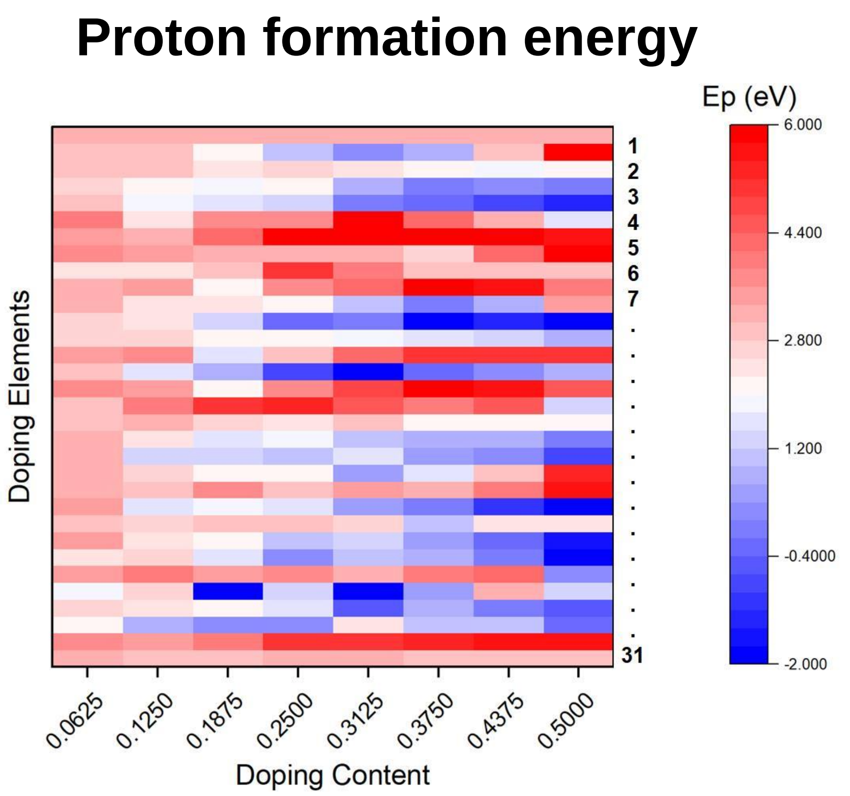
- ✓ At 600 °C, FC mode: **PPD=1.21 W cm^{-2}**; EC mode: 1.3 V, **current density= 2.0 A cm^{-2}**
- ✓ Roundtrip electric efficiencies of **84% and 79%** at 650 and 600 °C, respectively
- ✓ A low degradation rate of **0.8% /1000 h**

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

Backup page

Air electrode development: high-throughput calculations

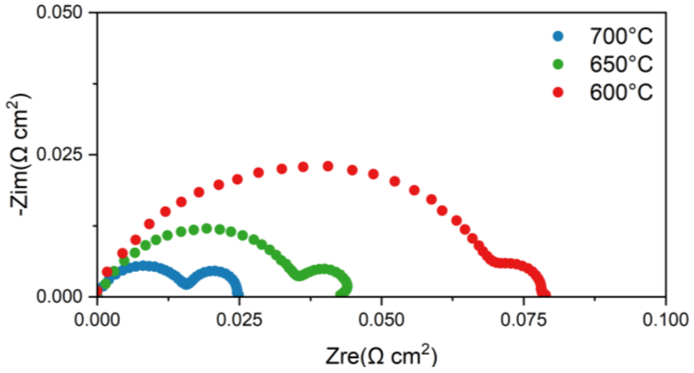


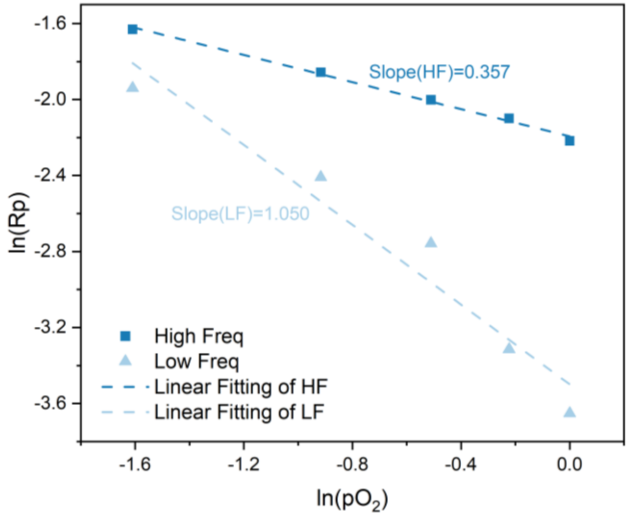


- **Oxygen vacancy formation energy (Ev)** represents the ability of materials in generating oxygen vacancies, which is **the active sites for ORR**
- **Proton formation energy (Ep)** represents the ability of materials in **generating protons, which provide the protonic conductivity**
- The performance of **X-doped $PrBaCo_2O_{5+\delta}$** are predicted to be promising in PCFCs

Air Electrode Development: Validation

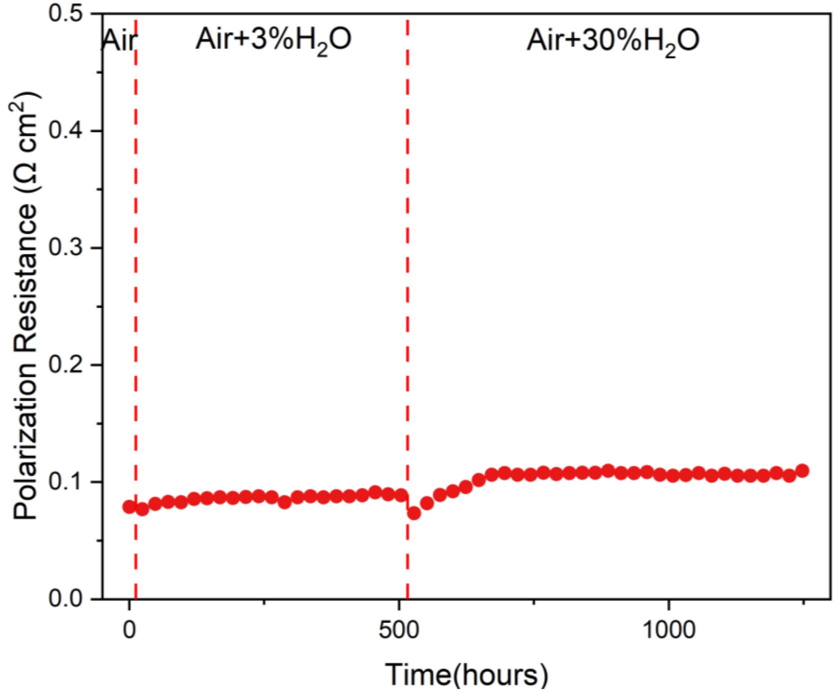
$PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ /SDC/$PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ symmetrical cells





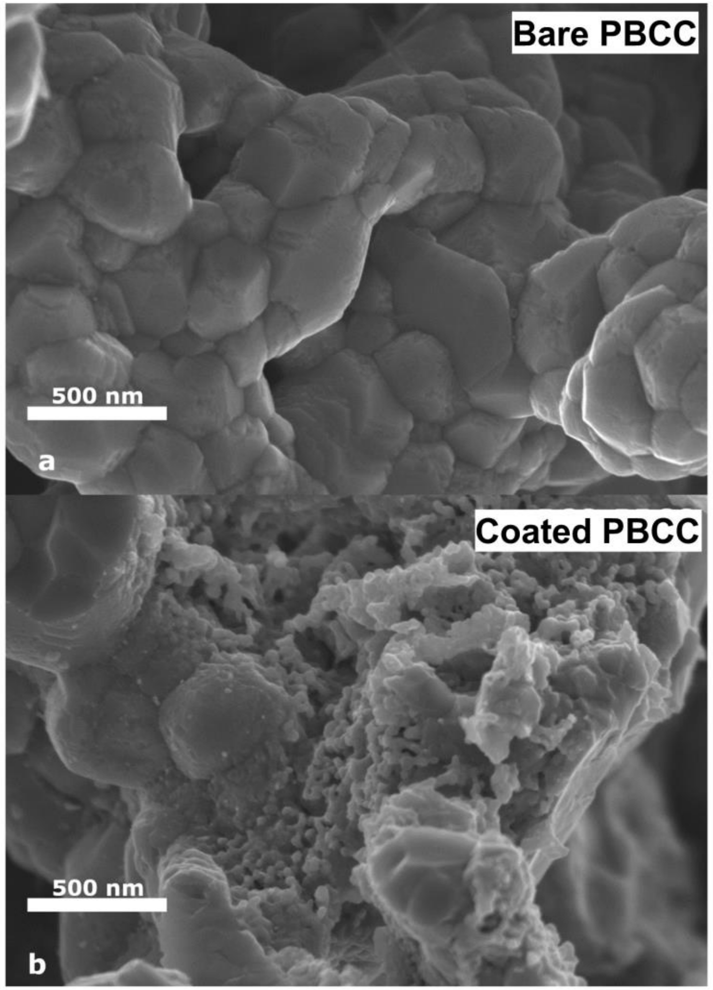
- A low polarization resistance of **0.077 Ω cm² is achieved at 600 °C.**
- **The rate determining process** for $PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ is **charge transfer ($R_p \propto p_{O_2}^{-0.375}$).**

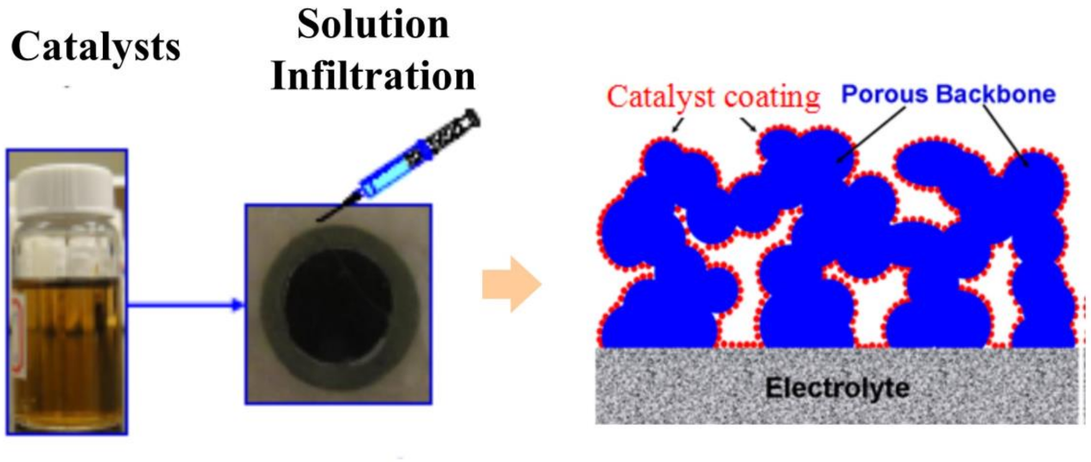
Stability of PBCX air electrode

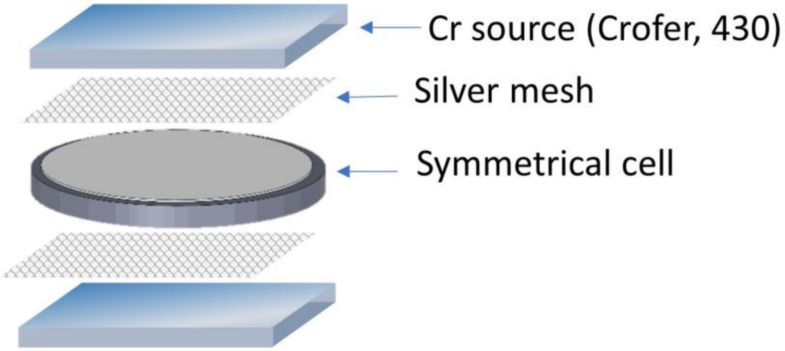


- $PrBaCo_{1.9}X_{0.1}O_{5+\delta}$/SDC/ $PrBaCo_{1.9}X_{0.1}O_{5+\delta}$ symmetrical cell shows outstanding stability under air with 3% and 30% H_2O at 600 °C

Catalyst Development (re-cap)







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