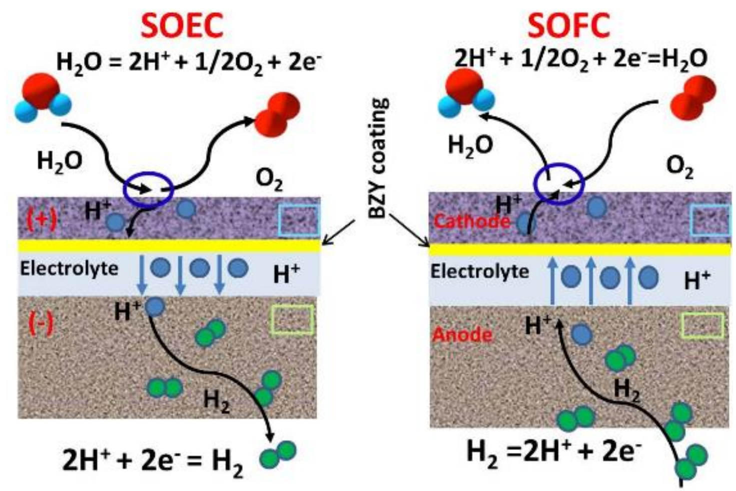
Durable, High-Performance Unitized Reversible Fuel Cells Based on Proton Conductors

PI: Meilin Liu

Team: Yucun Zhou, Nick Kane, and Weilin Zhang

Georgia Institute of Technology

May. 30, 2020



DE-EE0008439

Project ID: **FC316**

Overview

Timeline

- ✓ Project Start Date: Jan 1, 2019
- ✓ Project End Date: Dec. 31, 2021
- ✓ Percent complete: ~50 %

Barriers

- ✓ F. Capital cost
- ✓ G. System Efficiency and Electricity Cost
- ✓ L. Operations and Maintenance

Budget

- ✓ FY19 DOE Funding: $375K
- ✓ Planned FY20 DOE funding: $375K
- ✓ Total funding received to Date: $375K

Partners

- ✓ Georgia Tech (prime)
- ✓ No sub-contactor for this project

Relevance

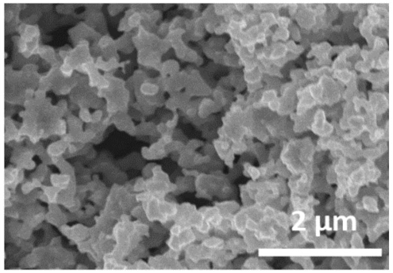
Objectives: To develop robust, highly efficient, and economically viable H^+-conducting membrane based, unitized **high-temperature reversible** fuel cell (URFC) technology for large-scale co-located energy storage and power generation.

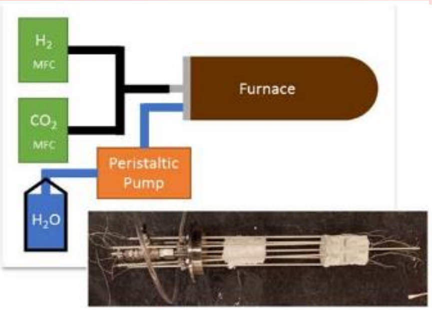
- ✓ To gain a profound understanding of the ***degradation mechanism*** of cell materials and interfaces, using various *in situ, ex situ*, and *operando* measurements guided by theoretical analysis;
- ✓ To ***integrate nanostructured components (through solution infiltration)*** into cell design and the interfaces between electrodes, and to modify the electrolyte with active bi-functional catalysts and protection coatings, in order to achieve >60% roundtrip efficiency at 1 A/cm^2 in both operating modes;
- ✓ To develop a roll-to-roll manufacturing concept for ***mass production*** of URFCs.

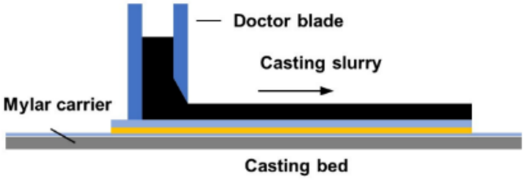
Impact: Our URFC system has the potential to be transformative and disruptive in advancing energy storage and power generation technology. Our URFCs can produce pure/dry H_2 without needs for downstream separation/purification, greatly enhance negative electrode durability, and dramatically reduces ASR due to high conductivity of the electrolytes and the highly-active electrodes.

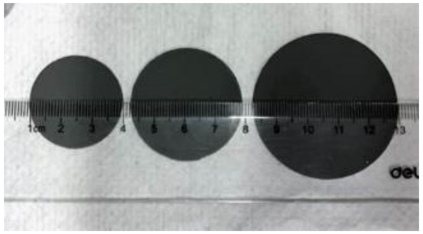
Approach

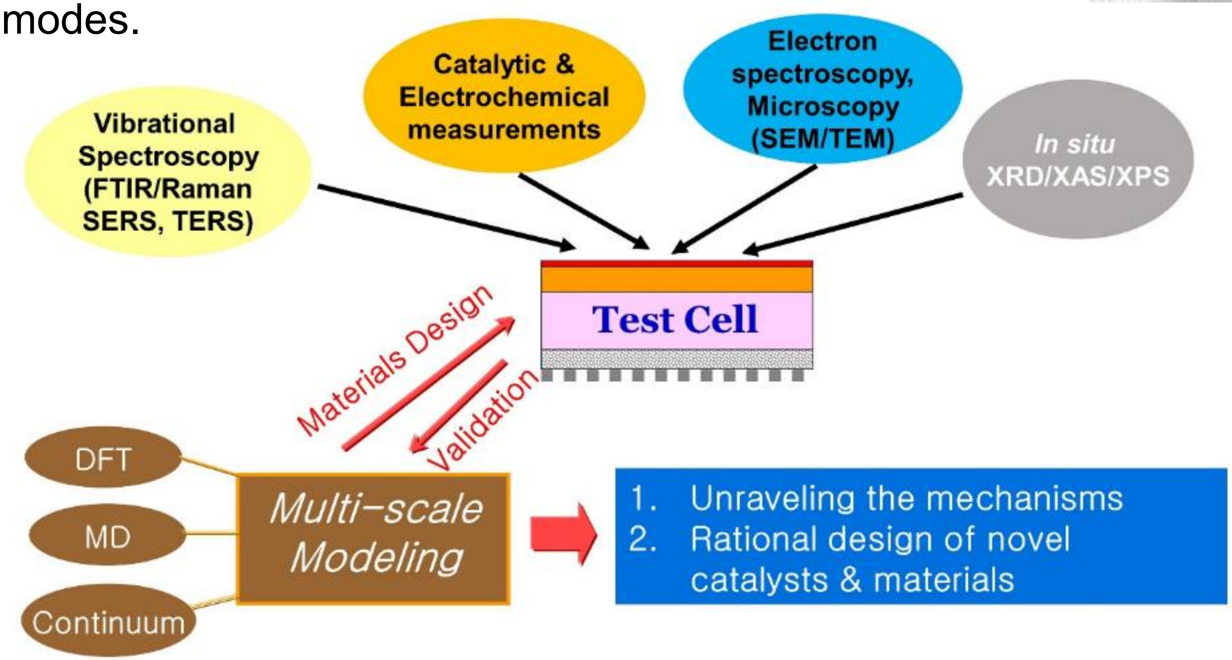
- ✓ Synthesize the electrode, electrolyte materials with desired particle size, and morphology;
- ✓ Fabricate the symmetrical cells and single cells;
- ✓ Integrate nanostructured components into cell design, and to modify the electrolyte with active bi-functional catalysts and protection coatings, in order to achieve >60% roundtrip efficiency at 1 A/cm^2 in both operating modes.











Milestones

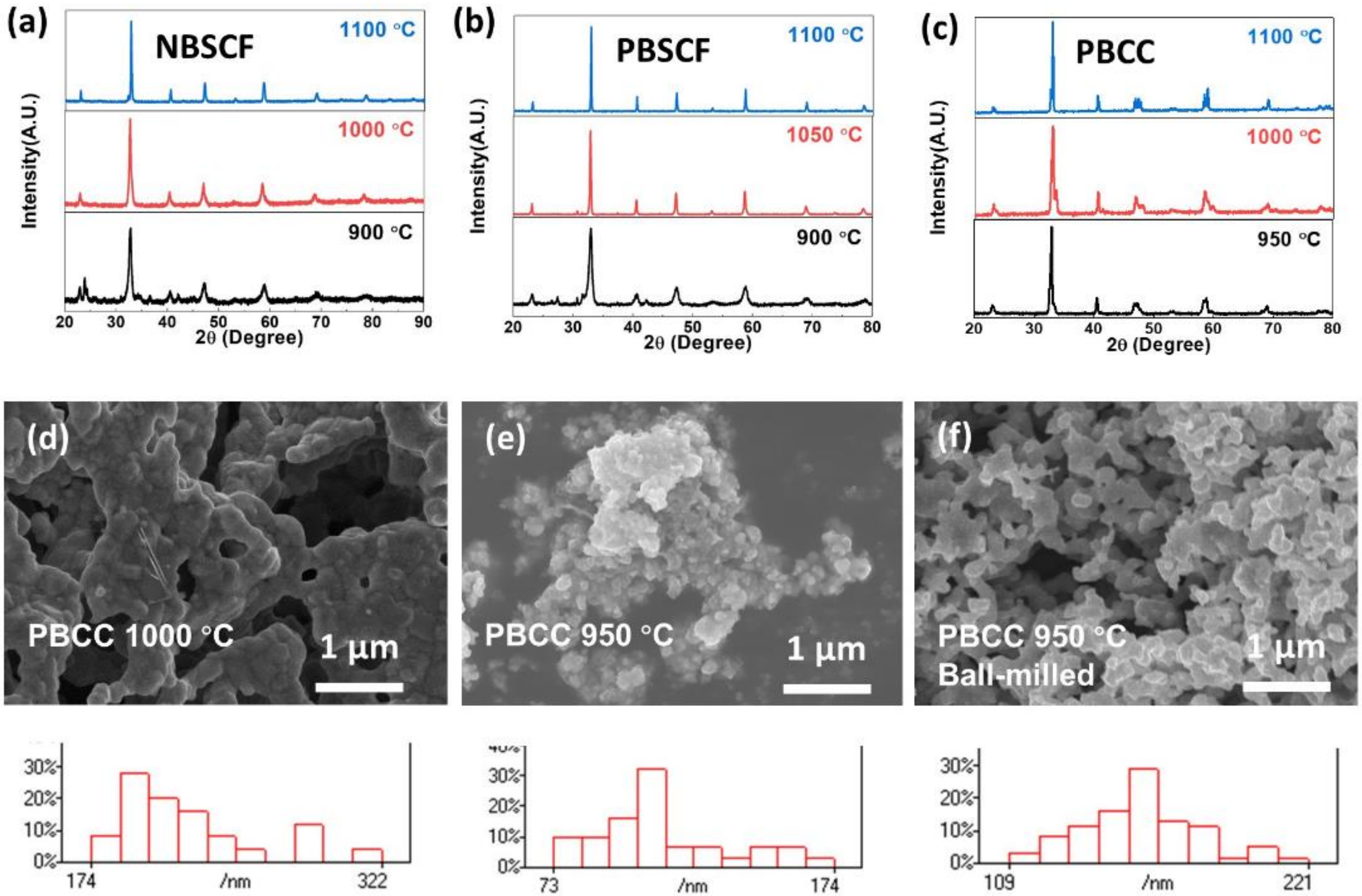
Date	Milestone as of 05/21/20	Complete
03/19	Complete literature survey & select state-of-art electrodes & electrolyte for URFCs.	100%
06/19	Complete the fabrication of electrodes and electrolyte powders of desired properties: Homogeneous nanoparticles (50-200 nm diameters) with spherical shape through optimizing the parameters of synthesis.	100%
09/19	Complete fabrication/microstructure modification of electrode support with diameter of 10 mm: Fabricate macroporous NiO-BZCYYb anode support with target porosity of 30% to 40% before reduction.	100%
12/19	Complete the chemical compatibility study of air electrode and OER catalysts; Complete the baseline study of ASR of air electrode (0.06 Ω cm^2 under a bias of +0.2 V at 750 °C with a durability test of 200 h).	100%
03/20	Complete the modification of HER and HOR catalysts to achieve HOR/HER electrode polarization < 0.07 V at 1 A cm^{-2} while targeting an overall cell polarization of <0.2 V.	100%
06/20	Complete electrolyte protection layer development for enhanced durability of at least 200 h with a degradation rate of <2% per 1000 h under relevant reversible fuel cell operating conditions.	80%
06/20	Complete 200 h continuous operation of a button cell (ϕ = 1 cm) with >70% roundtrip efficiency at 1 A cm^{-2} in both modes.	80%

Go/No-Go Decision Point	# 1	**Demonstrate 200 h continuous operation of a button cell at ≤700 °C with >60% roundtrip efficiency at 1 A/cm^2 in both SOFC and SOEC modes with degradation rate <2% per 500 h.**	**FY20**

Accomplishments and Progress

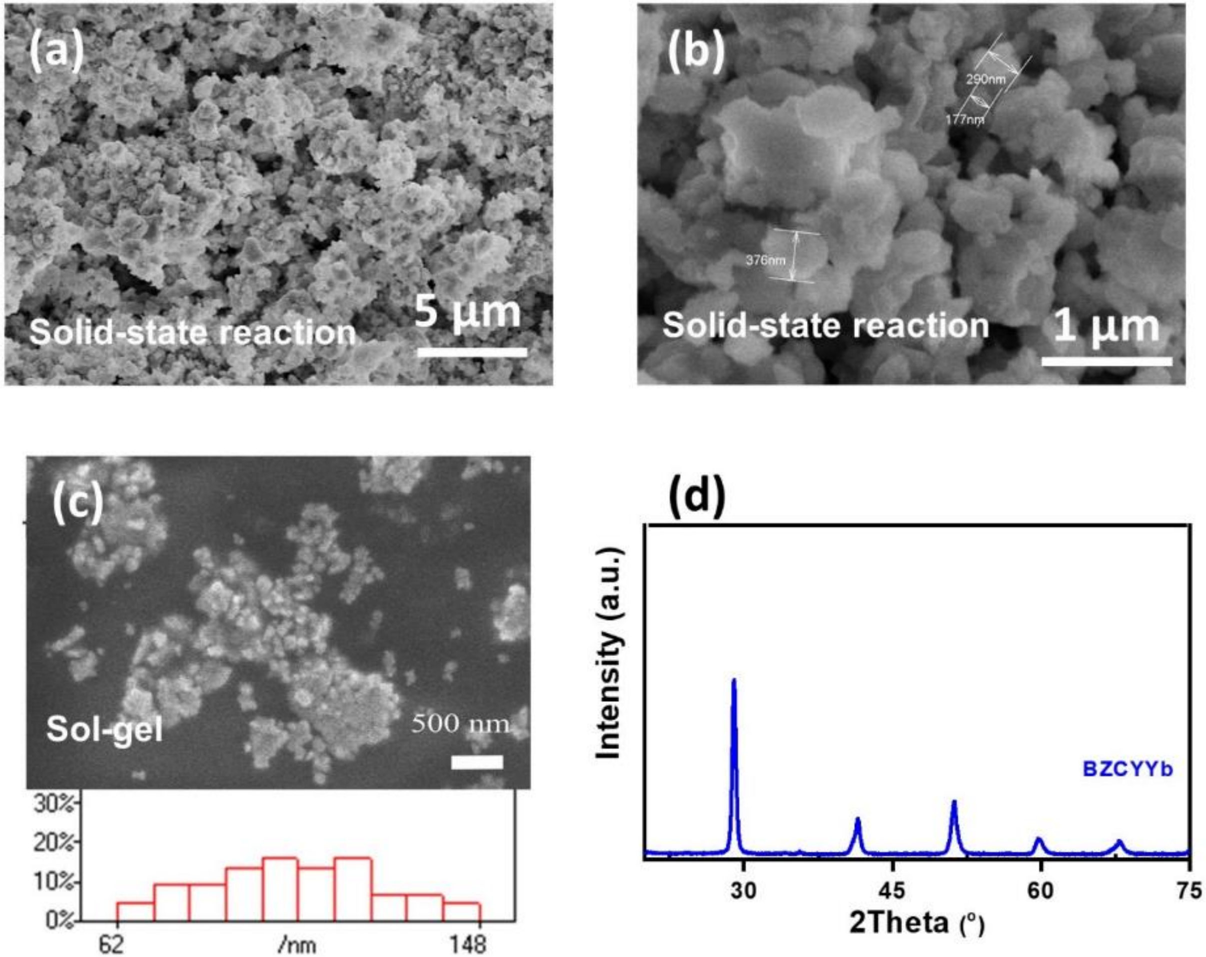
- Synthesized electrode and electrolyte materials with desired particle size (50-200 nm diameters) and spherical morphology;
- Fabricated porous NiO-BZCYYb anode support with target porosity of 30% to 40% before reduction;
- Completed baseline study of air electrodes (ASR=**0.02-0.03 Ωcm^2** under a bias of +0.2 V at 700 °C with a durability test of **200 h**);
- Developed fuel electrodes/catalysts with electrode polarization <0.07 V at 1 A cm^{-2};
- Completed the chemical compatibility study of air electrode and ORR/OER catalysts;
- Demonstrated roundtrip efficiency of **>60% at 1 A cm^{-2}** and 650^{o}C;
- Demonstrated 500 h operation of a button cell at 650^{o}C with a degradation rate of **<1% per 500 h**.

Structure and morphology of air electrodes



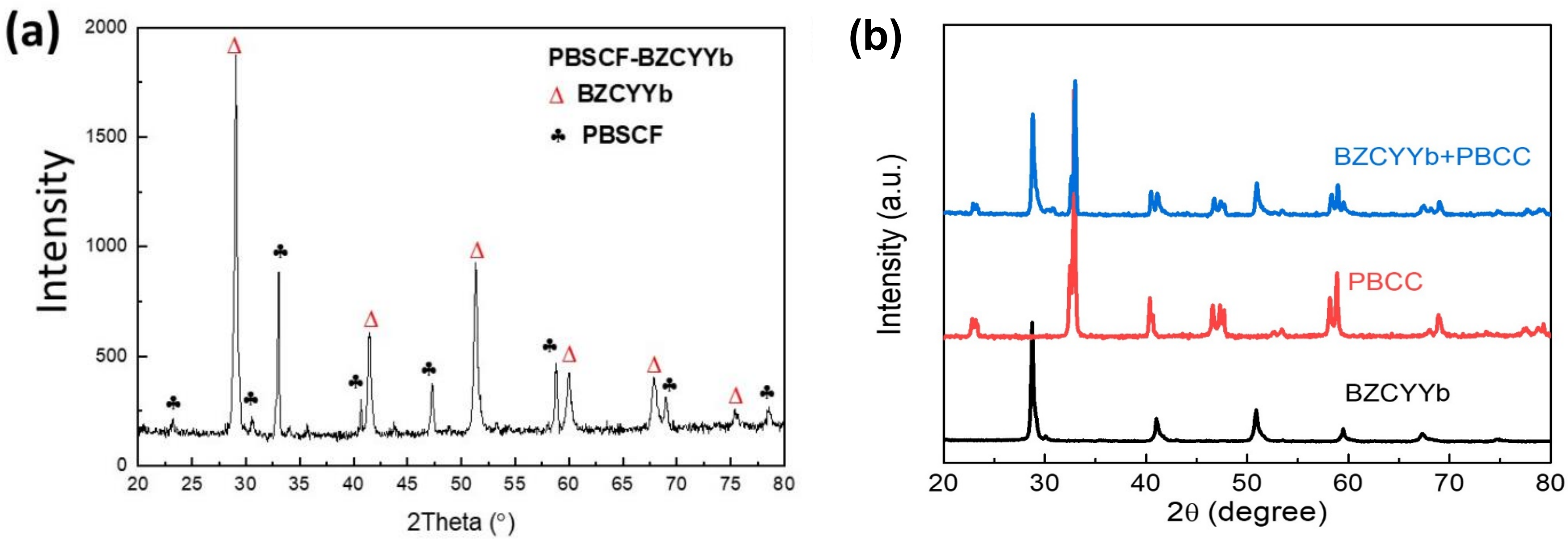
- ❑ Air electrodes (NBSCF, PBSCF, and PBCC) with desired perovskite phase have been synthesized by a sol-gel method;
- ❑ The particle sizes of powder (calcined at 950°C) are within 100-200 nm.

Structure and morphology of the electrolyte



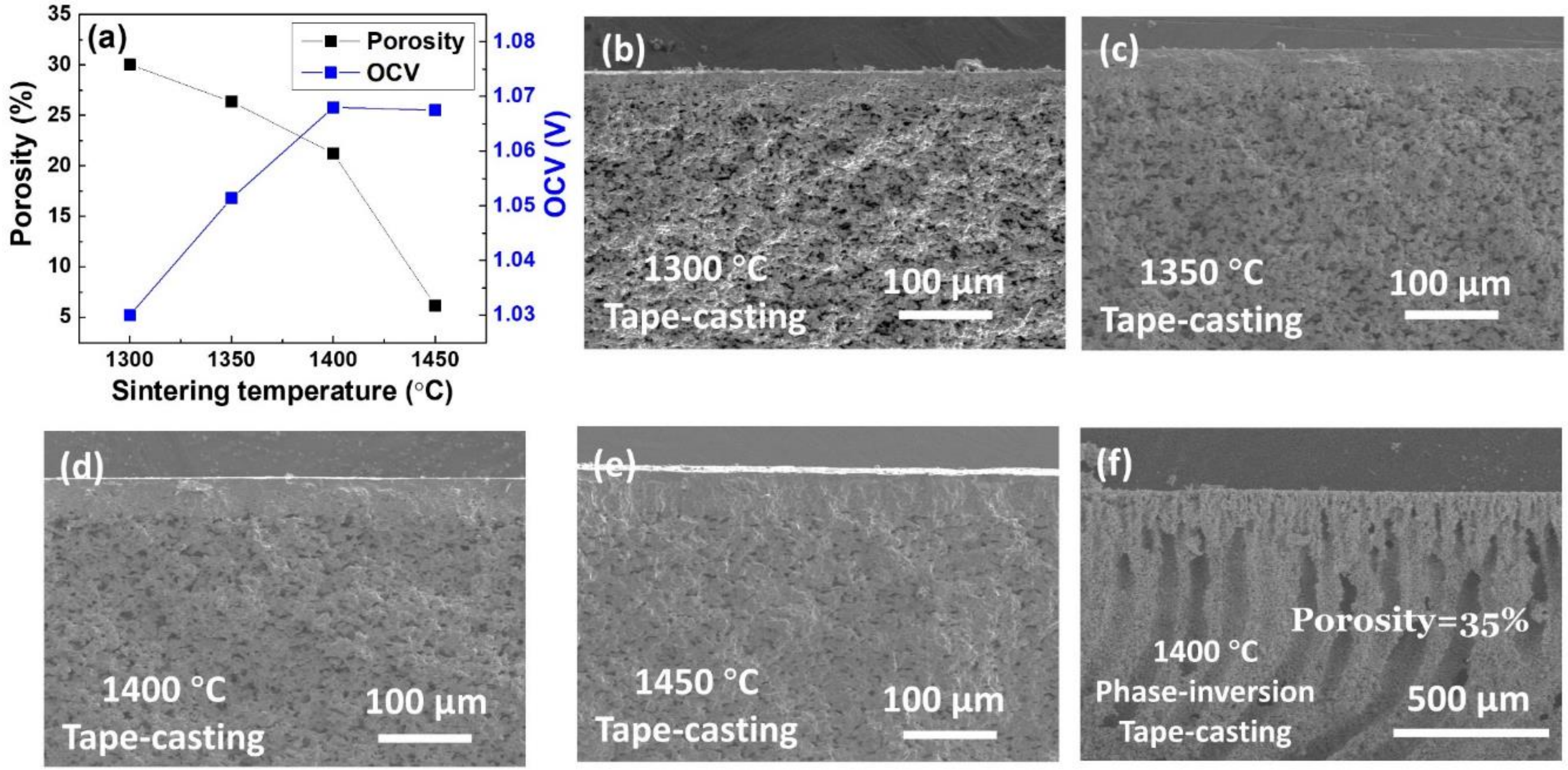
- ❑ BZCYYb was synthesized by solid-state reaction and a sol-gel process.
- ❑ Sol-gel derived powder has desired perovskite phase and particle size.

Chemical compatibility between air electrode and electrolyte materials



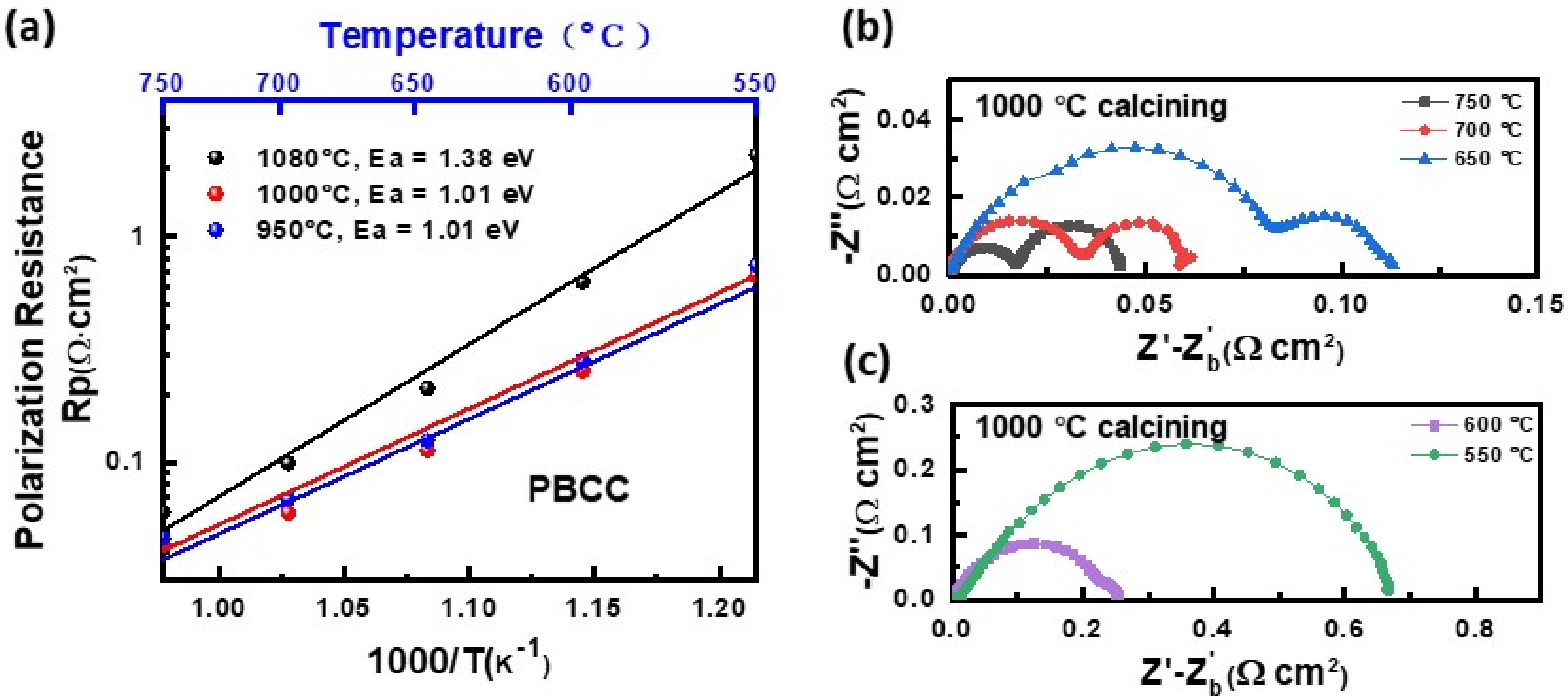
- **XRD patterns of the mixed air electrode and electrolyte powders were acquired after firing at 1000°C for 4 h.**
- **PBSCF and PBCC air electrodes are chemically compatible with the BZCYYb electrolyte.**

Fabrication and optimization of the NiO-BZCYYb anode support



- ❑ Traditional and phase-inversion tape casting and sintering were used to fabricate NiO-BZCYYb anode supports.
- ❑ Phase-inversion tape casting produced high porosity of 35%.

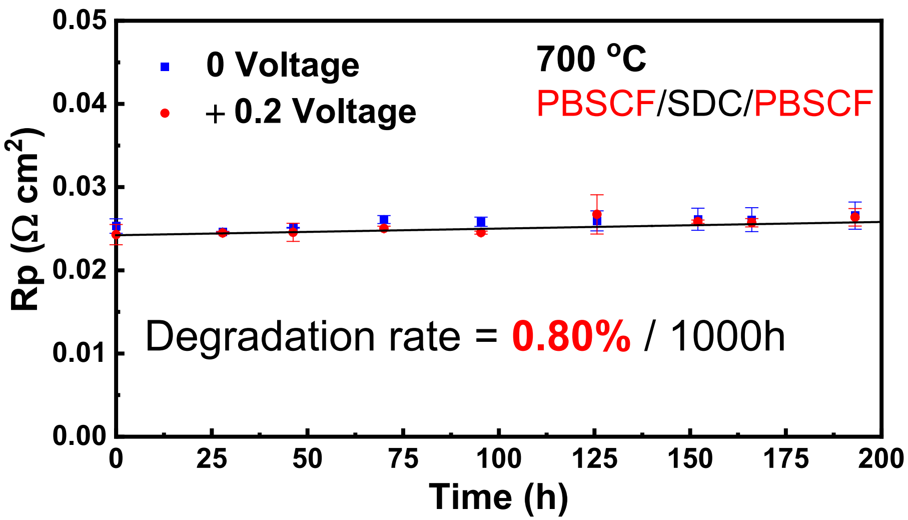
Performance of symmetrical cell with air electrode



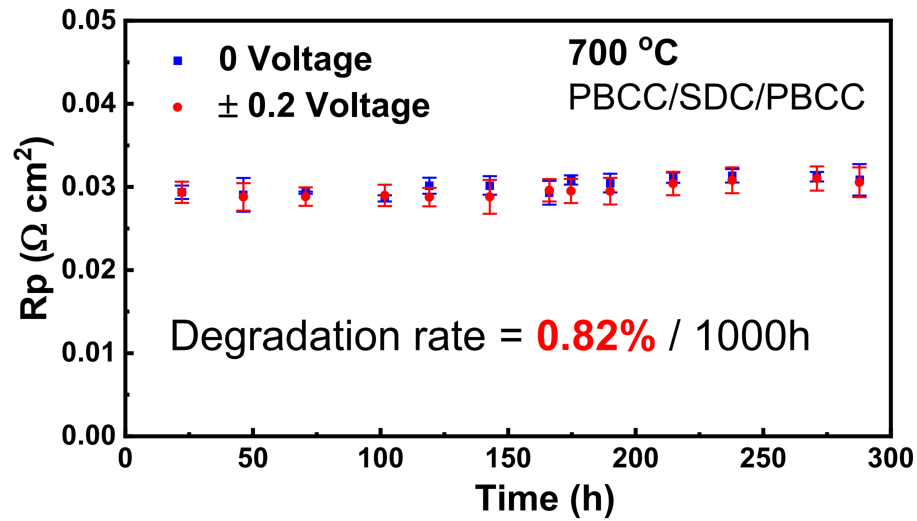
- Temperature dependence of the polarization resistances of PBCC electrodes fired at different temperatures were measured;
- PBCC electrode (fired at 1000°C) demonstrates a low polarization resistance of 0.04 Ω cm^2 at 750 °C.

Stability of air electrodes at 700°C

PBSCF:

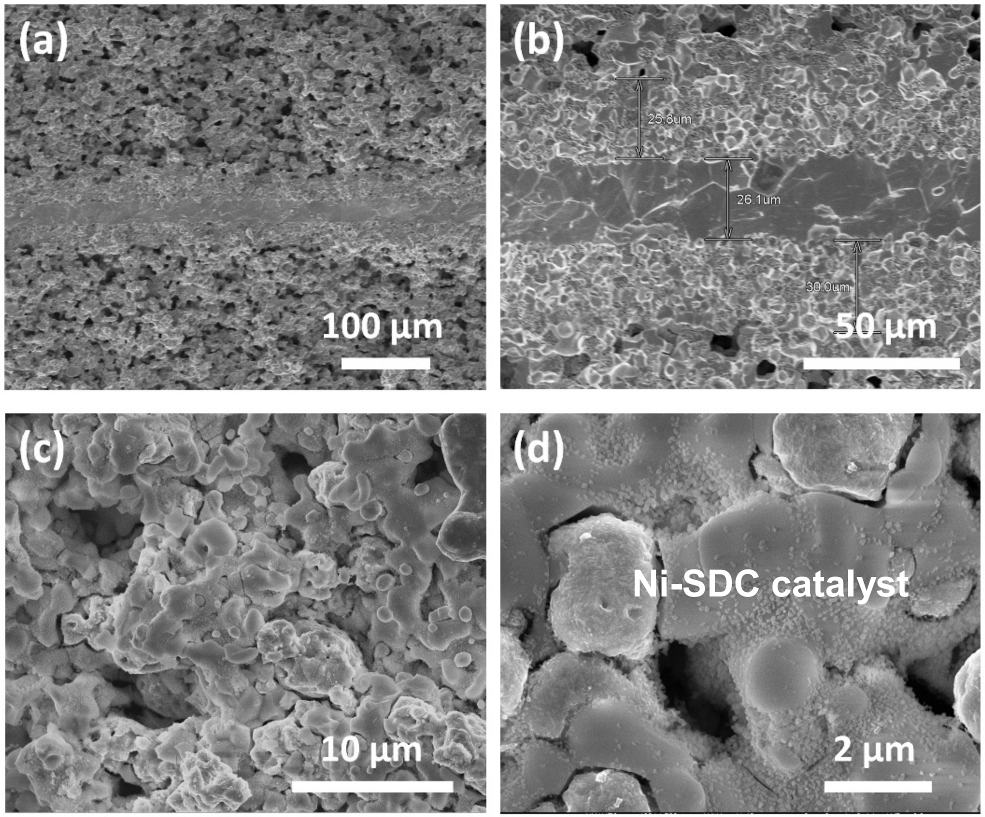


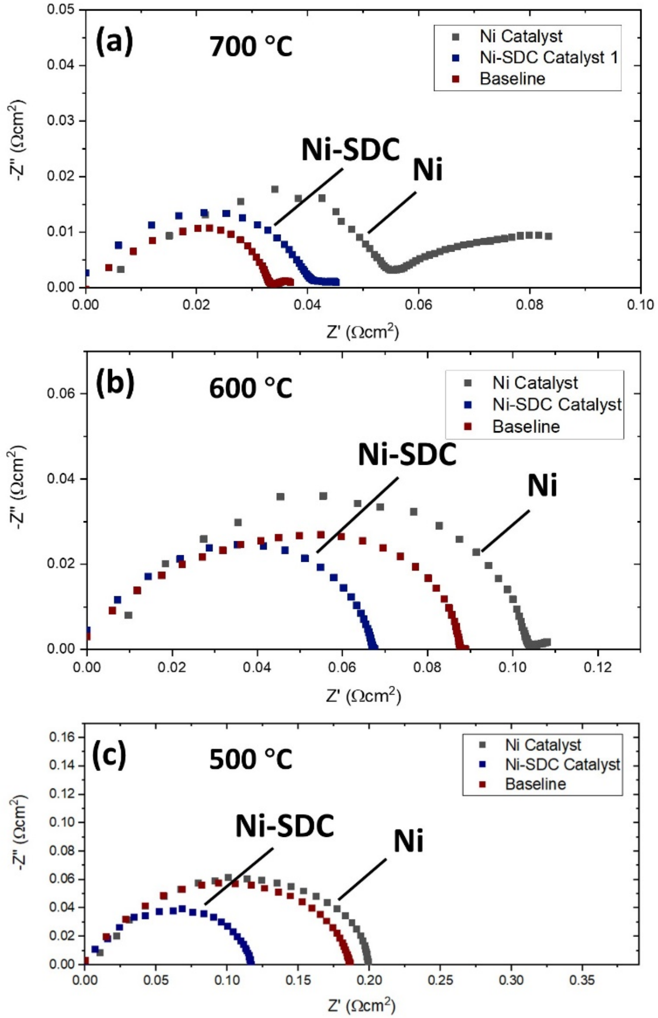
PBCC:



- **Both PBSCF and PBCC electrodes demonstrate low polarization resistances and excellent durability under OCV and bias at 700 °C.**

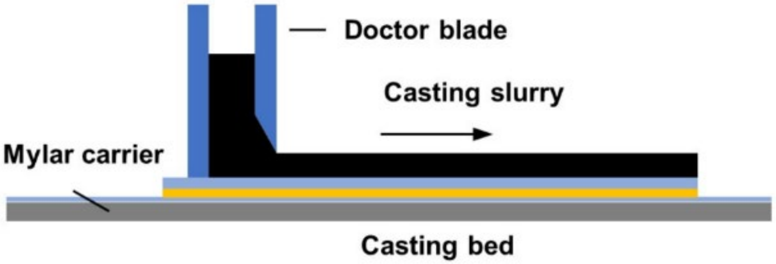
Symmetrical cells of fuel electrodes with catalysts

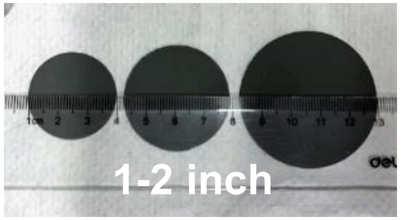


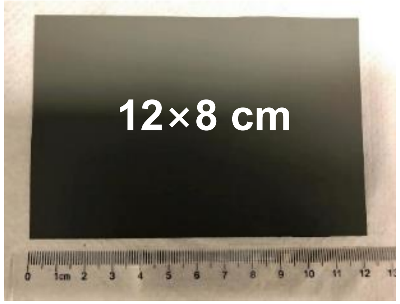


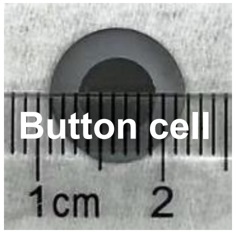
- ❑ Ni/Ni-SDC catalysts were infiltrated into NiO-BZCYYb electrode by infiltration;
- ❑ Ni-SDC modified fuel electrode shows a low R_p of 0.068 Ω cm^2 at 600 °C.

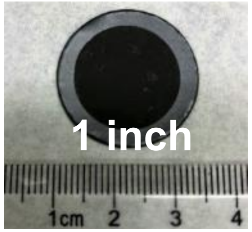
Single cell fabrication

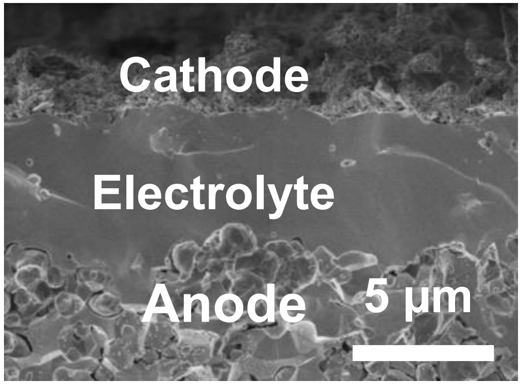


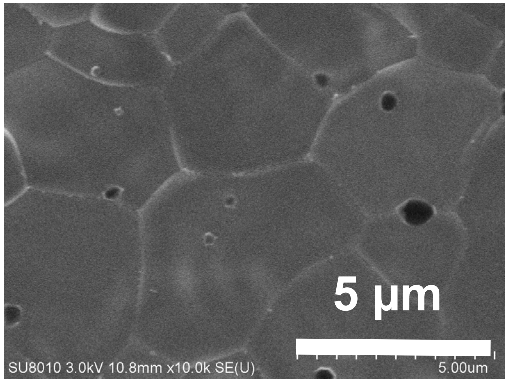






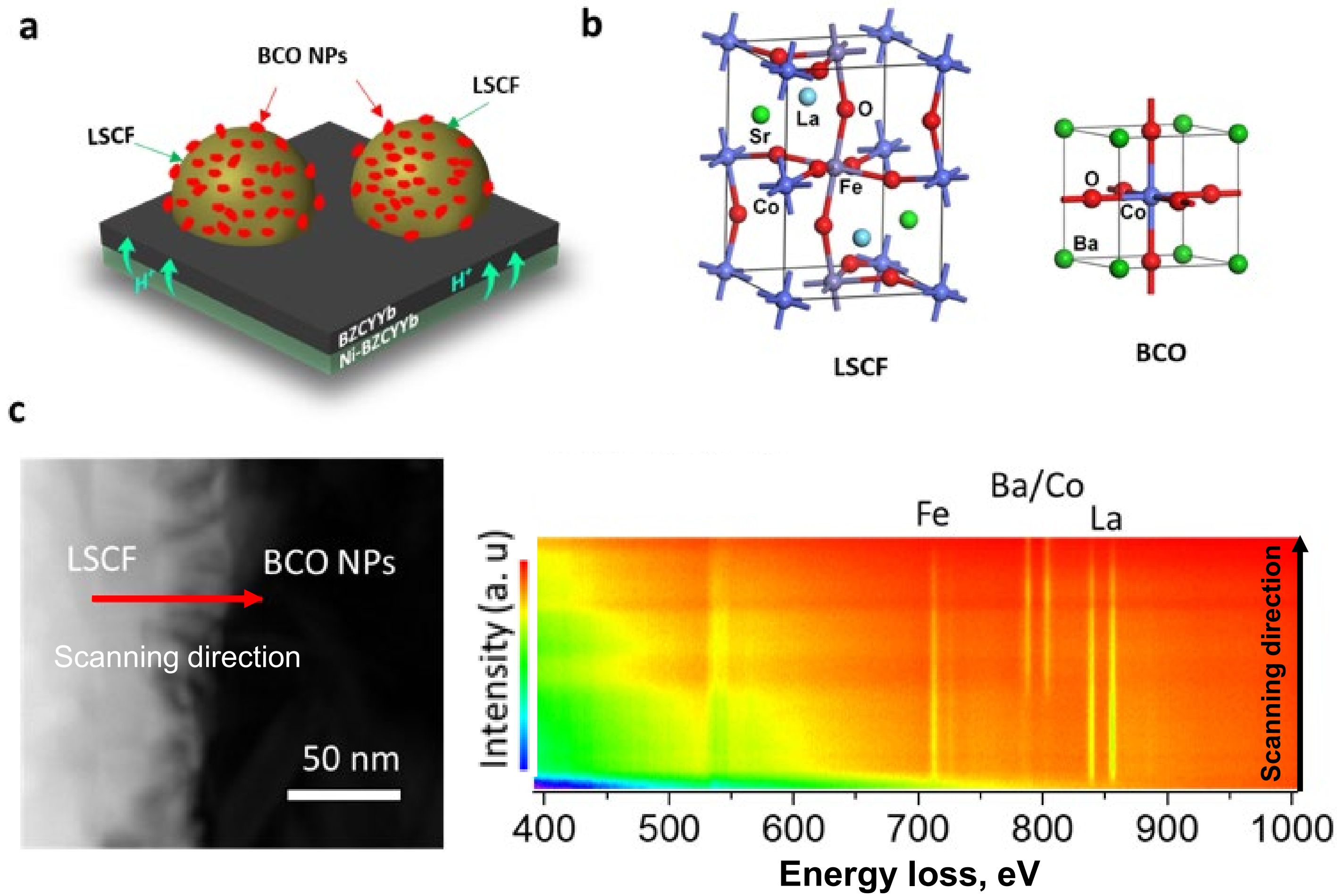






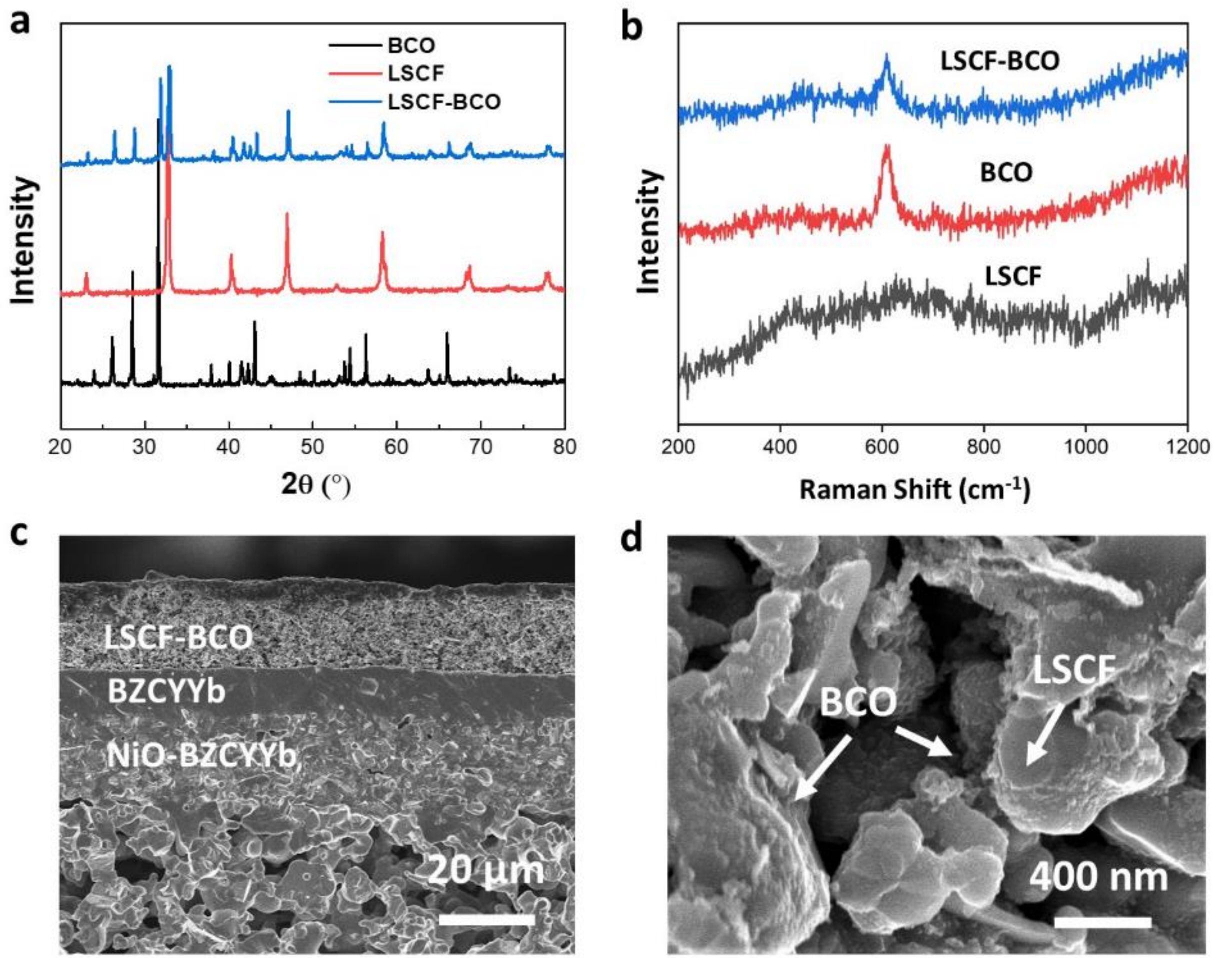
- ✓ Developed a robust co-tape casting and co-sintering process to fabricate single cells
- ✓ The thickness of the dense electrolyte is about **~8 μm.**

LSCF air electrode with ORR&OER catalysts



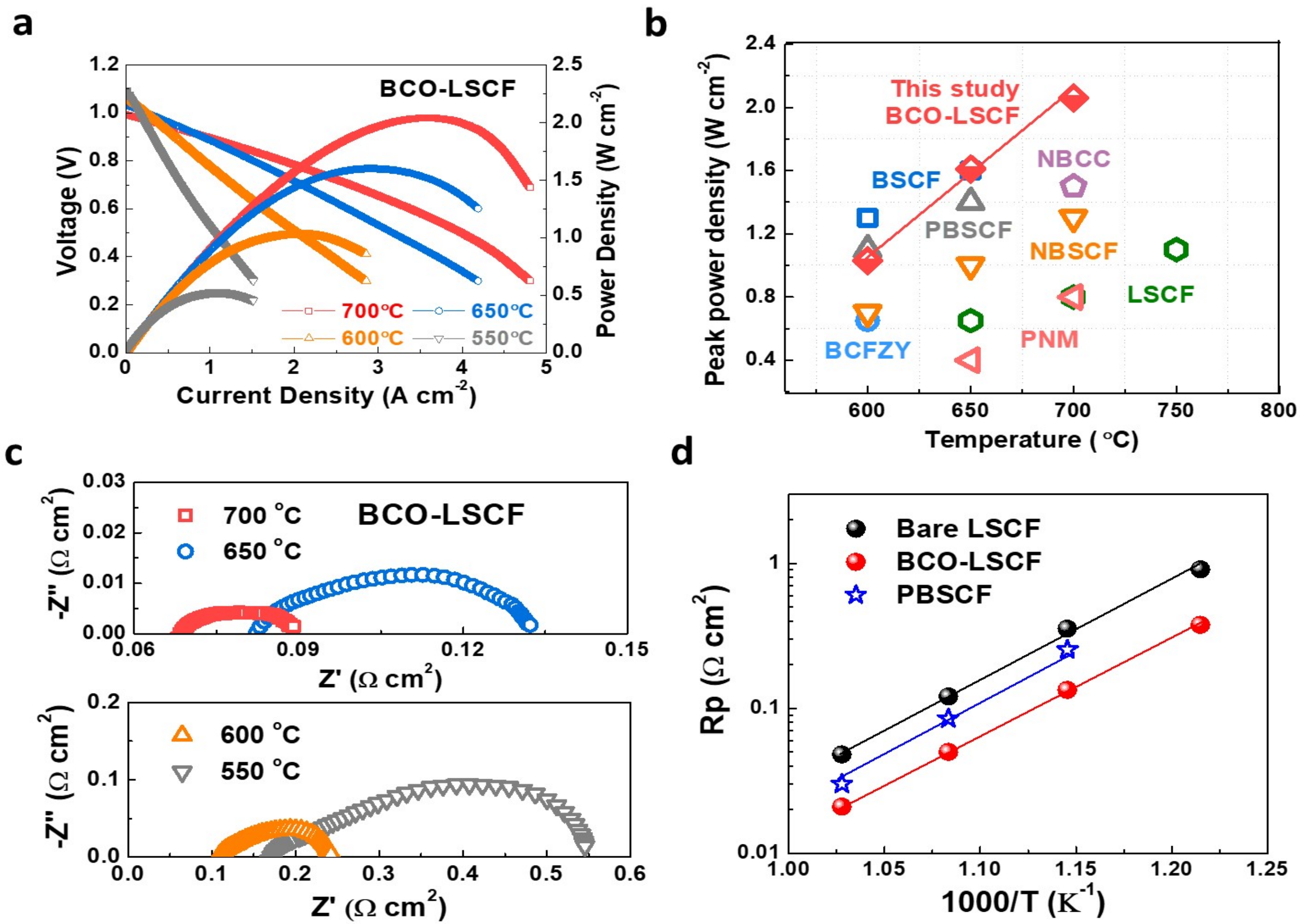
- ❑ **$BaCoO_{3-x}$ catalyst was coated on LSCF via a one-step infiltration method;**
- ❑ **$BaCoO_{3-x}$ coating was confirmed by EELS.**

Compatibility and Morphology of BCO-LSCF



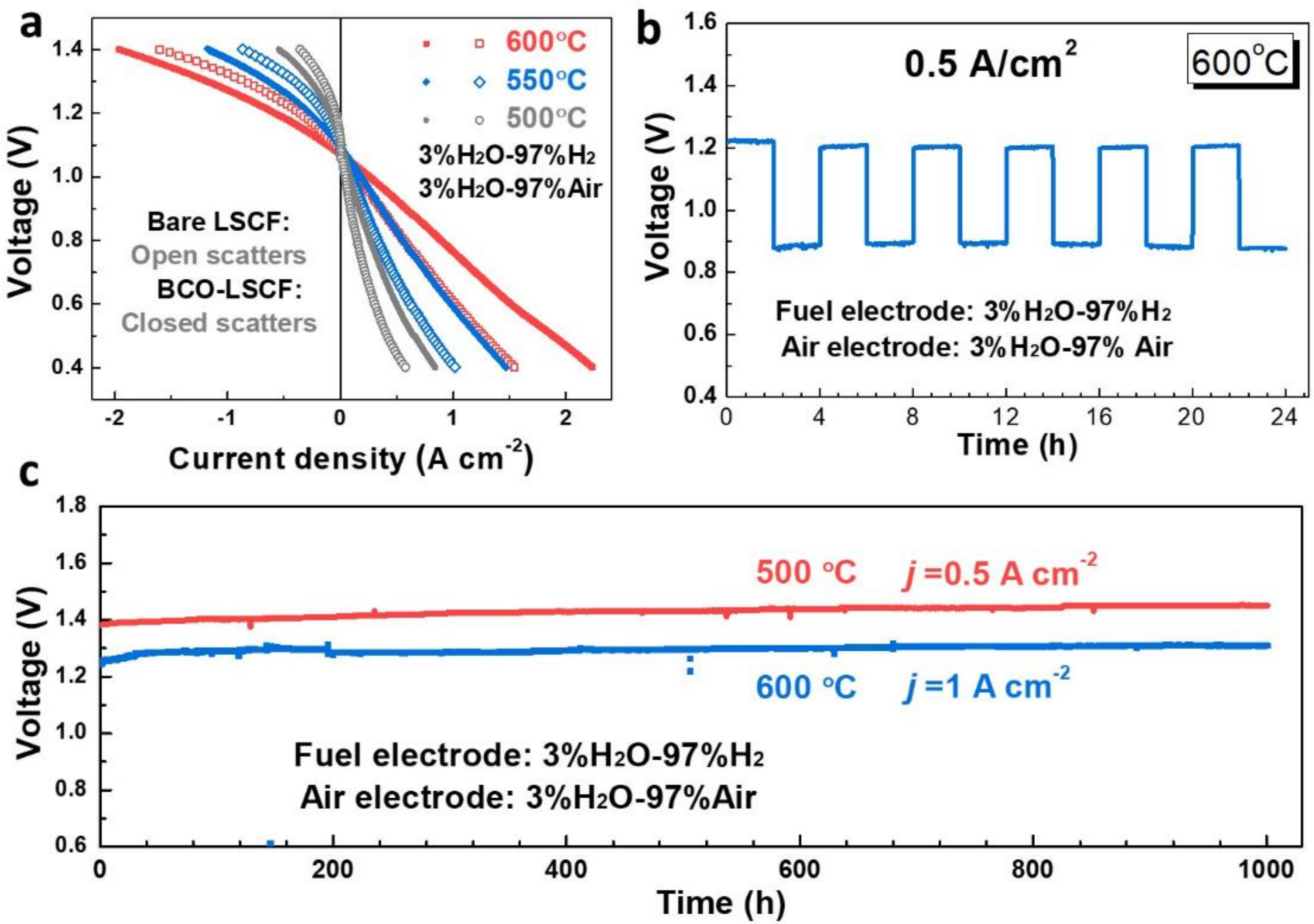
- BCO is chemically compatible with LSCF (after calcinating at 800 °C for 2 h) ;
- Nanosized BCO particles (~50 nm) are coated on LSCF.

Performance of Cells with BCO-LSCF Air Electrode



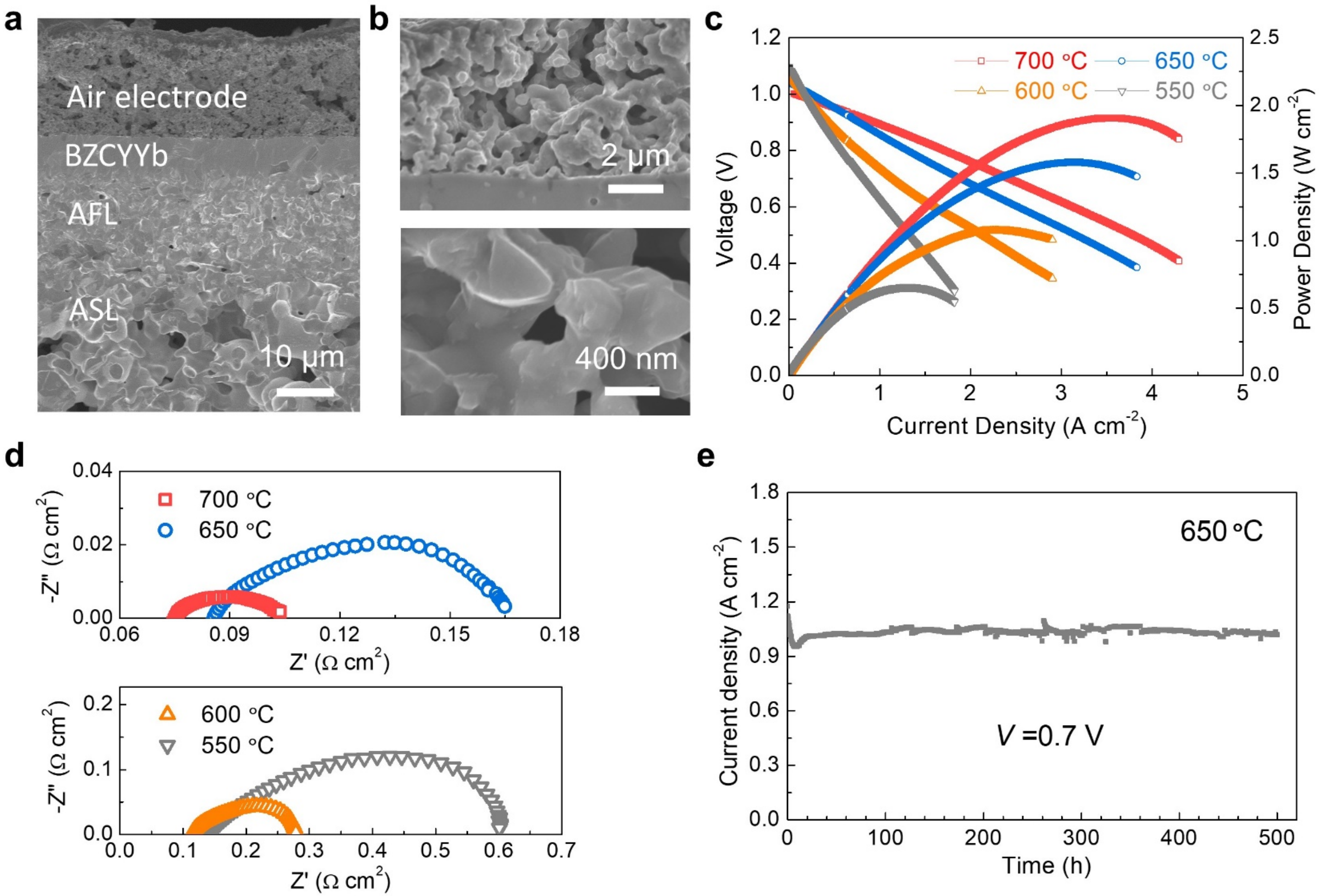
- Single cells with BCO-LSCF air electrode demonstrate peak power densities of 2 W cm^{-2} at 700 °C and 1 W cm^{-2} at 600 °C.

Reversible fuel cells performance



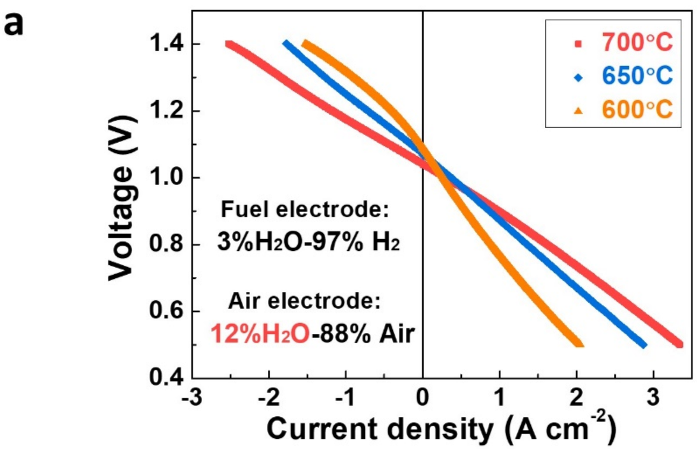
- ❑ BCO demonstrates high ORR & OER catalytic activity;
- ❑ Cells with BCO-LSCF air electrode show good durability.

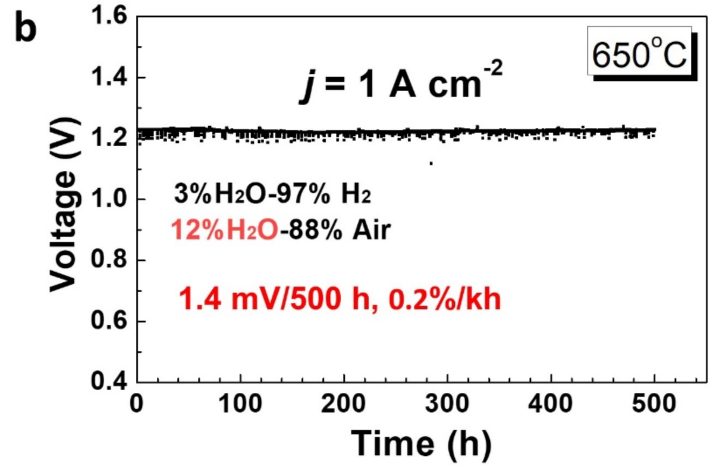
Performance of Cells with PBC based Air Electrode

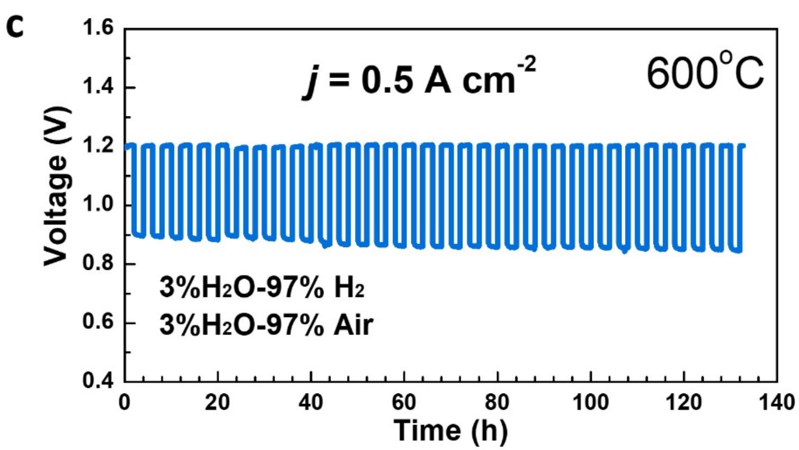


- Single cells demonstrate good durability and peak power densities of 2 W cm^{-2} at 700 °C and 1.1 W cm^{-2} at 600 °C.

Reversible fuel cells performance





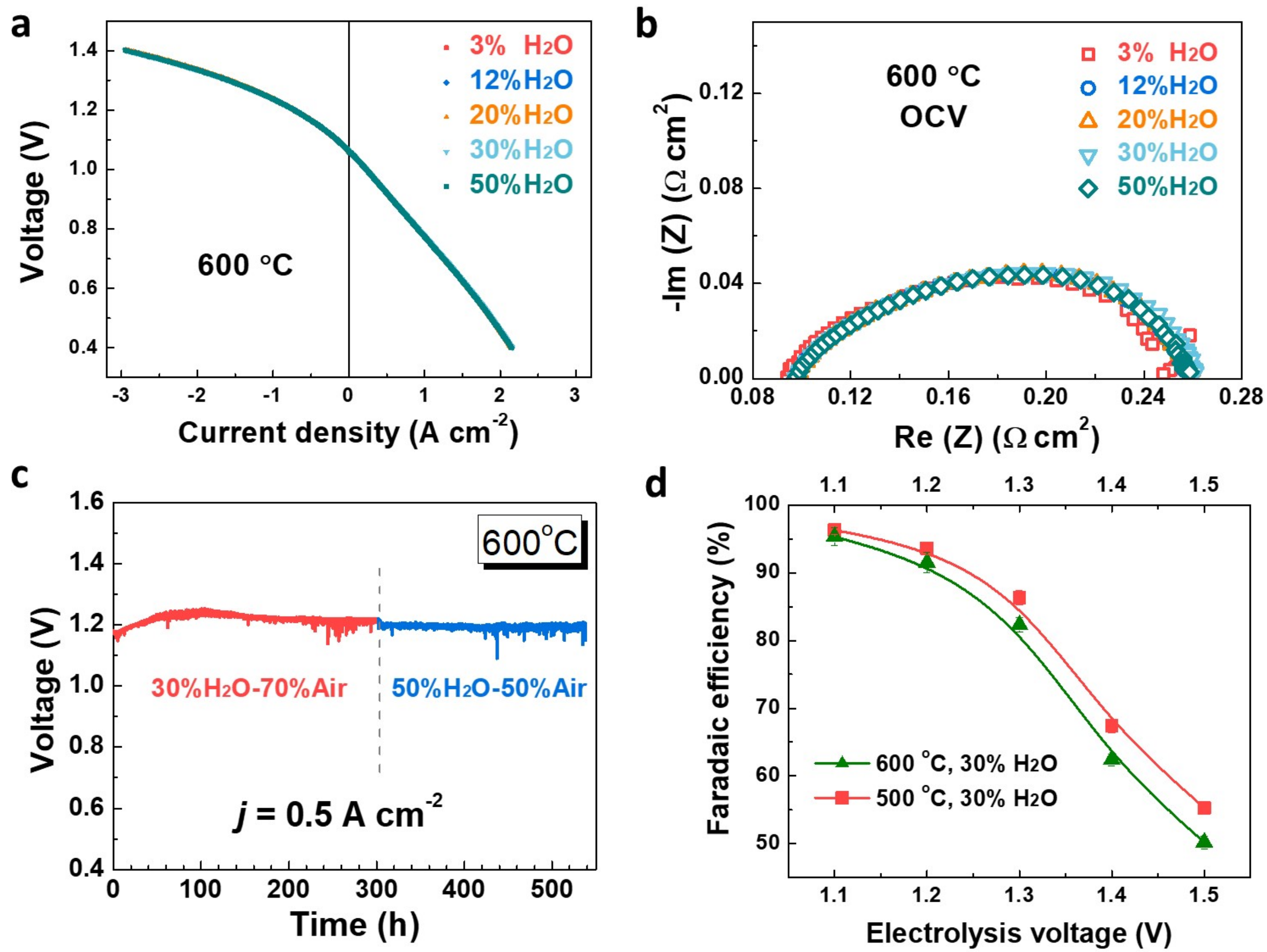


Temp (ºC)	Voltage at -1 A cm^{-2}	Voltage at 1 A cm^{-2}	Round Trip Voltage Efficiency	Ionic transference numbers	Energy efficiency
700	1.176	0.898	76%	~0.91	~69%
650	1.250	0.873	70%	~0.92	~64%
600	1.319	0.771	58%	~0.92	~53%

- ❑ **Roundtrip voltage efficiency of 76 and 70% at 700 and 650°C, respectively (at 1 A cm^{-2});**
- ❑ **Cells show good durability with a degradation rate of 0.3% per 500 h.**

Go/No-Go Decision: Demonstrate 200 h operation of a button cell at ≤700 °C with >60% roundtrip efficiency at 1 A/cm^2 in both SOFC and SOEC modes with degradation rate <2% per 500 h.

Cell Performance and & Faradic Efficiency



Temp (ºC)	Ionic transference numbers [1]
700	0.95
650	0.97
600	0.98

- ❑ pH_2O has no obvious effect on cell performance;
- ❑ Cell shows excellent durability under high pH_2O (~1% per 500 h);
- ❑ Faradic efficiency at cell voltage of 1.2 V >90% at 30% pH_2O.

[1]. Ryan Murphy, Ph.D. Thesis, Georgia Institute of Technology, **2019**.

Responses to Previous Year Reviewers' Comments

Main questions/comments and responses

Comment 1: What is the target operating temperature?

Response: ≤700^{o}C; preferably 500-650^{o}C.

Comment 2: The size of testing cells?

Response: Button cells (diameter of 10 mm and 1 inch) are used for materials development/performance evaluation.

Comment 3: Main project focus?

Response: Development of new materials and processes for enhancing electrode performance and durability.

Collaboration & Coordination

- Georgia Tech will focus on **development of new materials and processes** for enhancing electrode performance and durability against cycling through surface modification with an efficient catalyst.

- **Potential partners** for implementation:
  – INL
  – Phillips 66

Remaining Challenges and Barriers

Challenges:

- Achieving Faradaic efficiency of over 95% at ≤700 ºC and 1 A cm^{-2};
- Understanding the degradation mechanism in order to develop a highly-active and durable material/cell;
- Developing large-size flat URFCs (6 cm x 6 cm) with defect-free, dense and thin electrolyte (< 10μm);
- Pushing operation temperature lower in order to minimize the electronic conduction, while keeping the performance as required.

Plans:

- To fabricate high-performance cells with the developed catalysts to push operation temperature lower in order to minimize the electronic conduction of electrolytes while maintaining the required performance.
- To test long-term stabilities of the cells under various conditions (e.g., current density, H_2O concentration) and evaluate the evolution of cell performance, electrode morphology and structure, and electrolyte-electrode interfaces.
- To develop well controlled powder synthesis process, co-tape casting process, and co-sintering to fabricate defect-free large-sized URFCs (6 cm x 6 cm) with controlled mechanical strength, thickness, and porosity.

Future Milestones

M	Brief Description	Complete
7.0	Achieve Faradaic efficiency of over 90% at ≤700 ºC at 1 A cm^{-2} on small button cells with a diameter of 1 cm.	50%
8.0	Atomistic level prediction of novel materials with enhanced catalytic activity and understanding of underlying degradation mechanism.	30%

End of Project Goal:	**Demonstrate 500 hours of continuous operation of a large cell (6x6 cm) with >70% roundtrip efficiency at 1 A/cm^2 in both SOFC and SOEC modes. The degradation rate will be <2% per 1000 h.**	**FY21**

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- Inquires about our technologies have been received from a number of companies, including Nissan, HiFunda, MillenniTek, and Phillips 66
- Potential future funding: Nissan (high-temperature fuel cells), DOE-EERE (electrolytic cells for water splitting)

Summary- Progress and Accomplishments

- ❑ Synthesized the electrodes and electrolyte materials with desired particle size (50-200 nm diameters), and spherical morphology
- ❑ Fabricated porous NiO-BZCYYb anode support with target porosity of 30% to 40% before reduction
- ❑ Developed **ORR&OER** catalysts for air electrodes;
- ❑ Developed high-performance and durable reversible fuel cells based on proton conductors
  - **Roundtrip efficiency >60% at 1 A cm^{-2}, 650 °C**
  - **500 h operation at 650 °C with a degradation rate of <1% per 500 h**