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

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Georgia Institute of Technology

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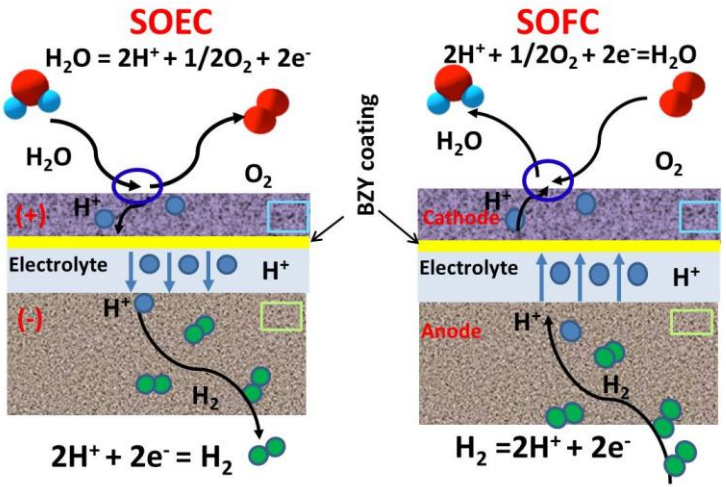


DE-EE0008439

Project ID: **FC316**

Overview

Timeline

- ✓ Project Start Date: Oct 1, 2018
- ✓ Project End Date: Dec. 31, 2021
- ✓ Percent complete: ~10 %

Barriers

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

Budget

- ✓ Total Project Budget: $937,500
  - ✓ Total Recipient Share: $187,500
  - ✓ Total Federal Share: $750,000
  - ✓ Total DOE Funds Spent: $12,000*

*As of 3/1/19

Partners

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

Relevance

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

- ✓ To gain a profound understanding of the ***degradation mechanism*** of electrolyte, electrode, and catalyst materials,
- ✓ To ***integrate nanostructured components*** into cell design and the interfaces between electrodes, and
- ✓ To develop a roll-to-roll manufacturing concept for ***mass production*** of URFCs

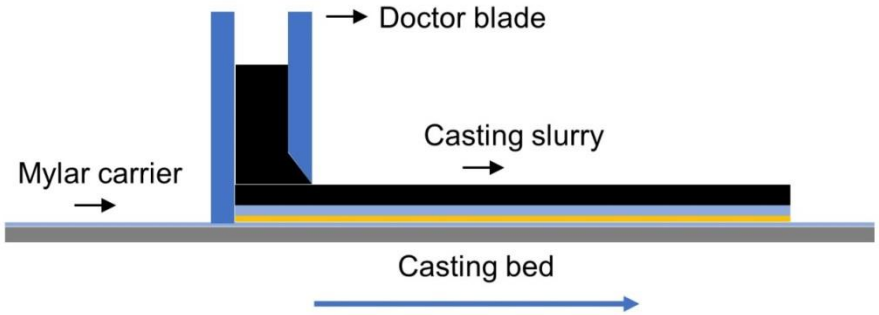
Impact: Our URFC based on a proton conductor can produce pure/dry H_2 without needs for downstream separation/purification, greatly enhances negative electrode durability, and reduces ASR due to high conductivity of the electrolytes and the highly-active electrodes. It has the potential to significantly advance energy storage and power generation technology.

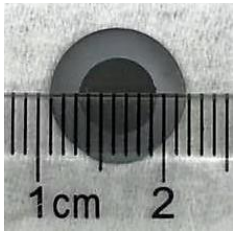
Approaches: Materials Development

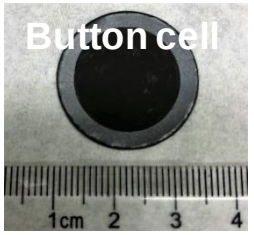
- ✓ Unravelling the ***mechanism*** of charge and mass transfer processes associated with reversible operation of fuel cells using various *in situ, ex situ*, and *operando* tools guided by theoretical analysis
- ✓ Modifying electrode and electrolyte surface with active bi-functional catalysts and/or protection coatings in order to achieve >70% roundtrip efficiency at 1 A/cm^2 in both operating modes while maintaining required durability

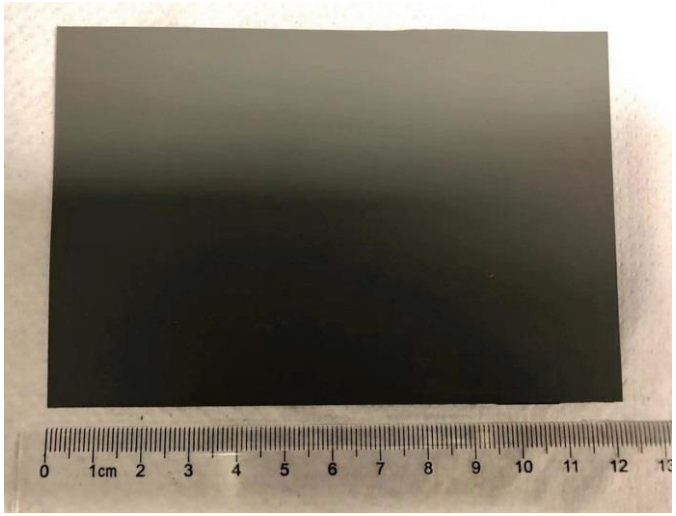
Approach: Cell Fabrication

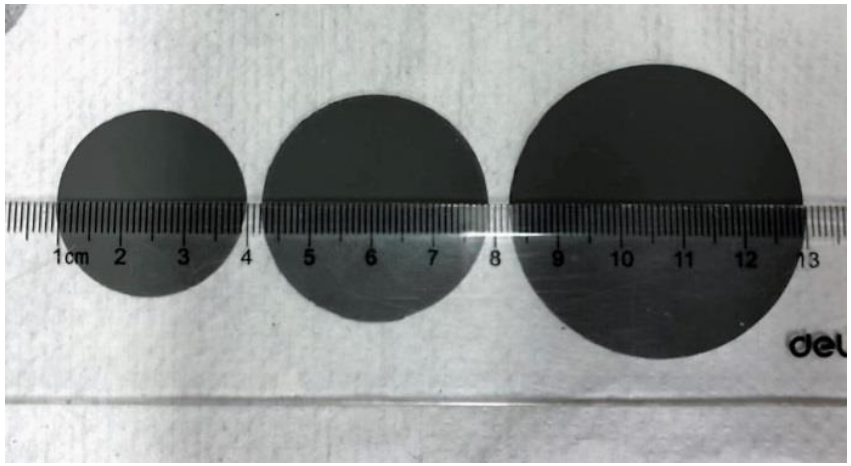
Developing cost-effective processes for cell fabrication, (e.g., tape-casting and printing) and for surface modification (e.g., sol-gel and ALD)





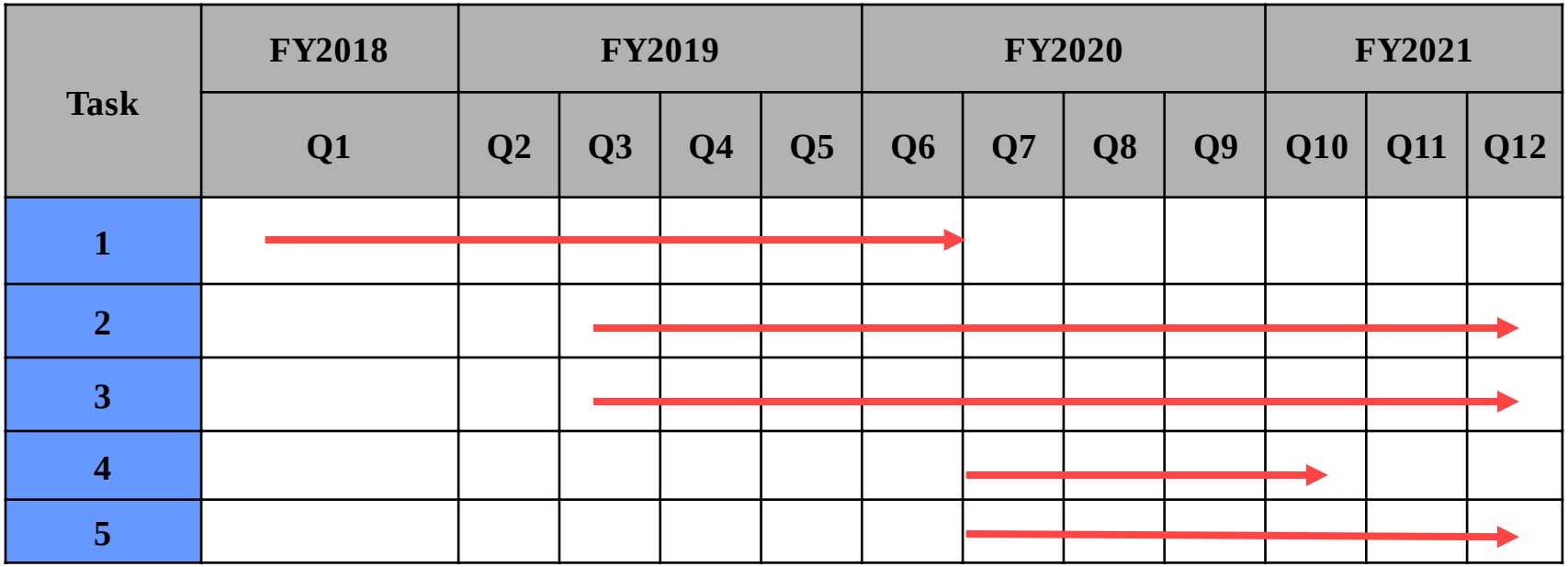






Tasks and Schedule of Project

Task 1: Design, synthesis, & fabrication of electrolytes & electrodes
Task 2: Understanding the degradation mechanism and development of materials-based solutions for enhancing performance and durability
Task 3: Assembly and testing of URFCs with improved performance and durability
Task 4: Development of conceptual roll-to-roll mass production processes
Task 5: Fabrication of prototype large URFCs



Milestones

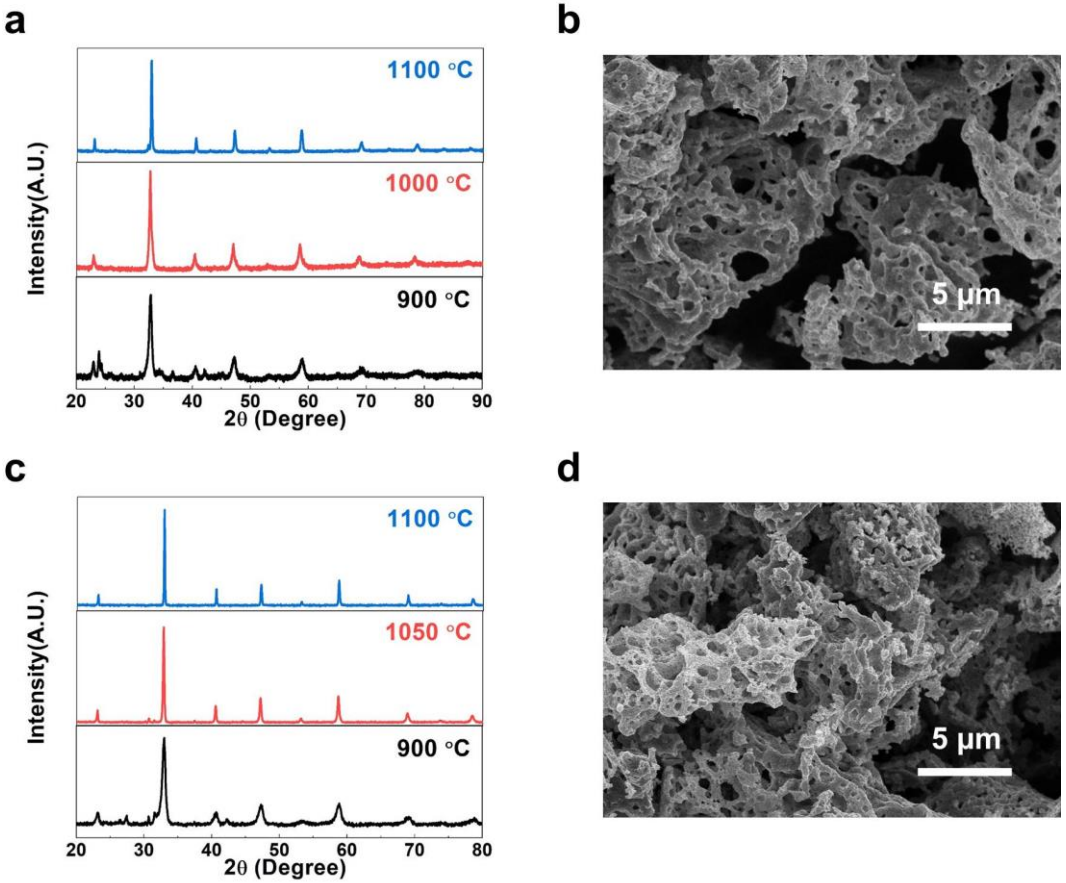
Date	Milestone as of 05/01/19	Completion
01/19	Complete literature survey and select state-of-art electrodes and electrolyte for URFCs;	100%
04/19	Complete the fabrication of electrodes and electrolyte powders of desired properties : Homogeneous nanoparticles (50-200 nm diameters) with spherical shape through optimizing the parameters of synthesis.	100%
07/19	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.	50%
10/19	Complete the chemical compatibility study of air electrode and OER catalysts; Complete the baseline study of ASR of air electrode ($0.06\Omega cm^2$ under a bias of +0.2V at 750^oC with a durability test of 200 h)	10%

Go/No-Go Decision Point 1	**Demonstrate 200 h operation of a button cell at ≤700 °C with >60% roundtrip efficiency at 1 A/cm² in both SOFC and SOEC modes with degradation rate <2% per 500h.**	**FY20**
End of Project Goal	**Demonstrate 500 h continuous operation of a large cell (6 cm x6 cm) with >70% roundtrip efficiency at 1 A/cm² in both SOFC and SOEC modes with degradation rate <2% per 1000h.**	**FY21**

Accomplishments and Progress

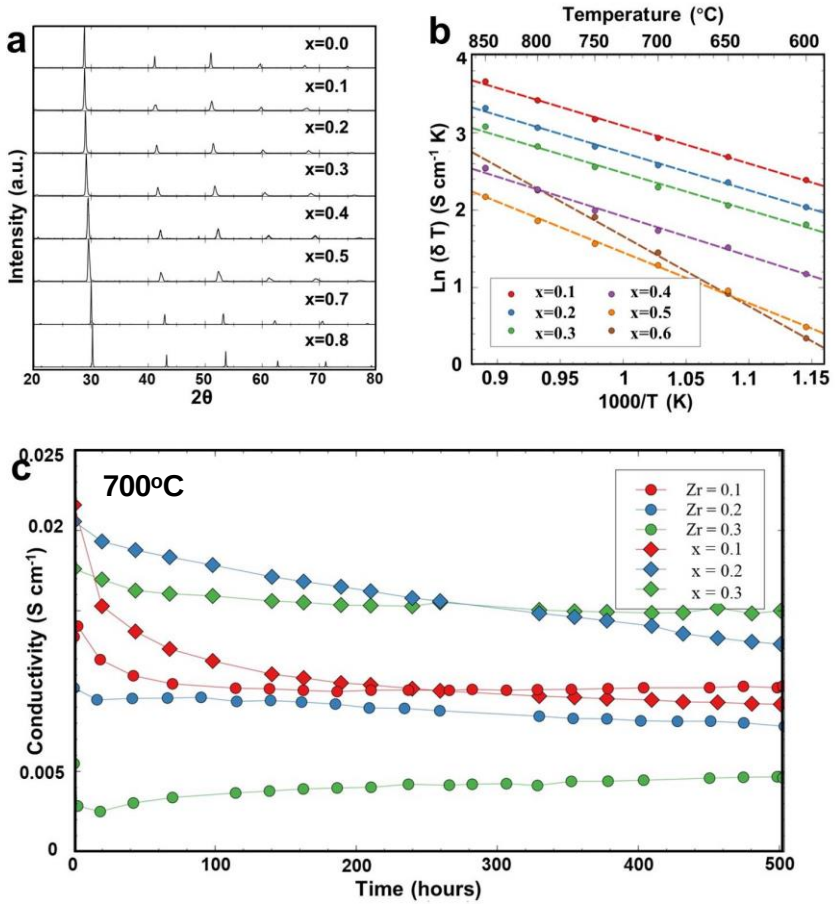
- Synthesized the electrode and electrolyte materials with desired particle size and morphology;
- Fabricated the symmetrical cells and single cells**;**
- Developed a new coating material (on electrolyte) with higher conductivity and better stability against water and CO_2;
- Evaluated the electrochemical performance of single cells;
- Demonstrated a roundtrip efficiency of ~72% at 1Acm^{-2} at 700^{o}C;

Structure and morphology of the positive electrode materials



- Positive electrodes (NBSCF, and PBSCF) with desired perovskite phase has been synthesized by solution combustion method;
- The particle size of powder (calcined at 1050°C for 2h) is within 100nm.

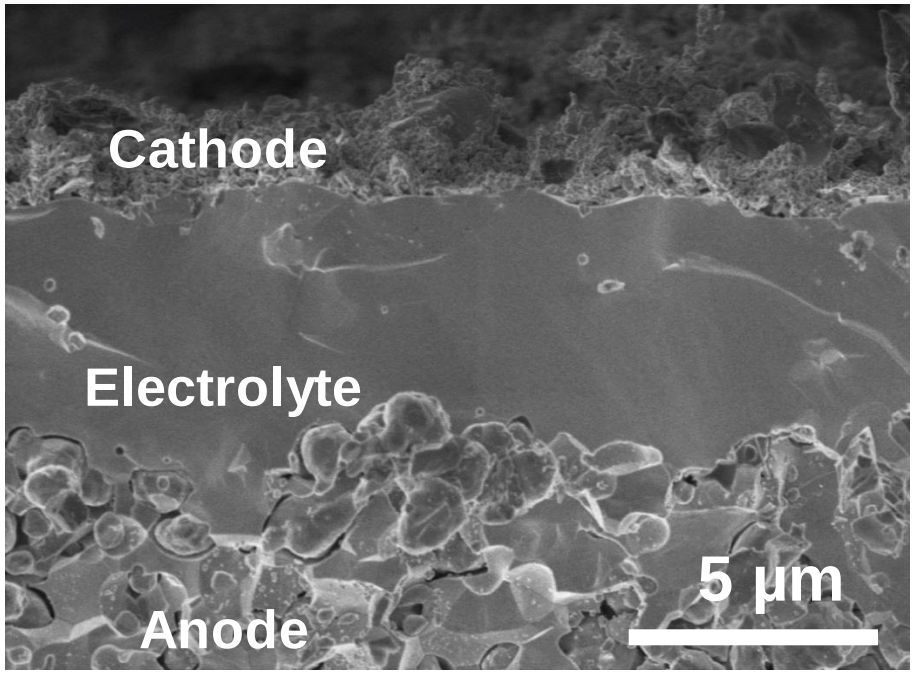
Structure, conductivity and stability of the proton conducting electrolytes

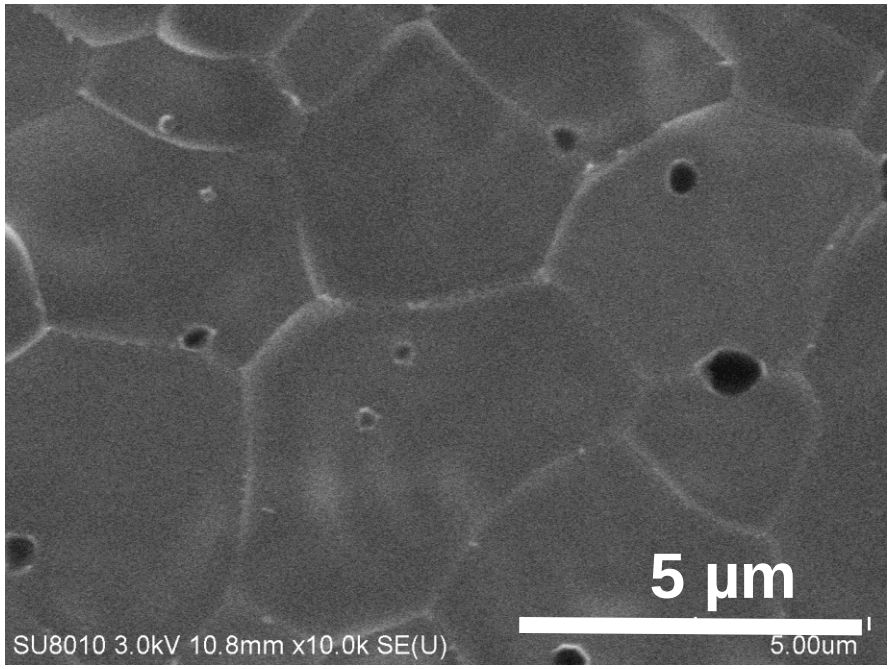


(**a)** XRD patterns at room temperature obtained for the synthesized $BaM_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_3$ powders; **(b)** conductivities of the $BaM_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_3$ measured at 600 to 850 °C in wet argon (3 vol% H_2O); **(c)** evolution of the conductivities of the $BaM_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_3$ and $BaZr_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_3$ electrolytes as the function of time measured at 700 °C in 25% CO_2, 25% H_2O and 50% H_2

- **Identified a new coating material with higher conductivity and better stability against water and CO_2 (25% CO_2, 25% H_2O and 50% H_2);**
- **Transfer number of BMCYYb system will be identified in the future;**

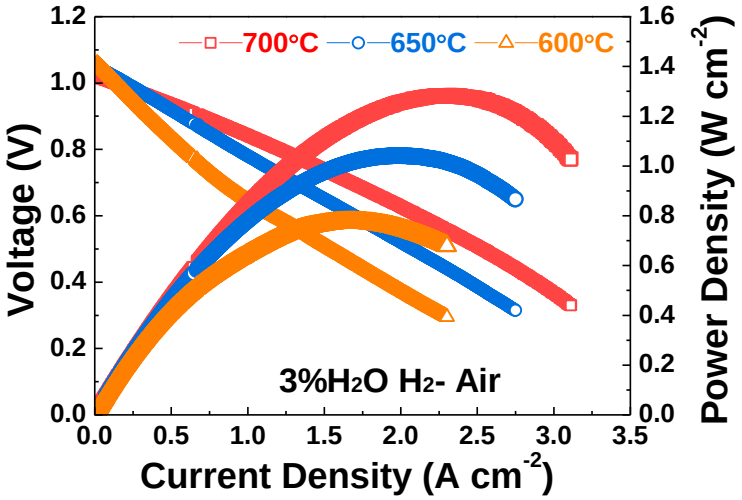
Microstructure of a single cell

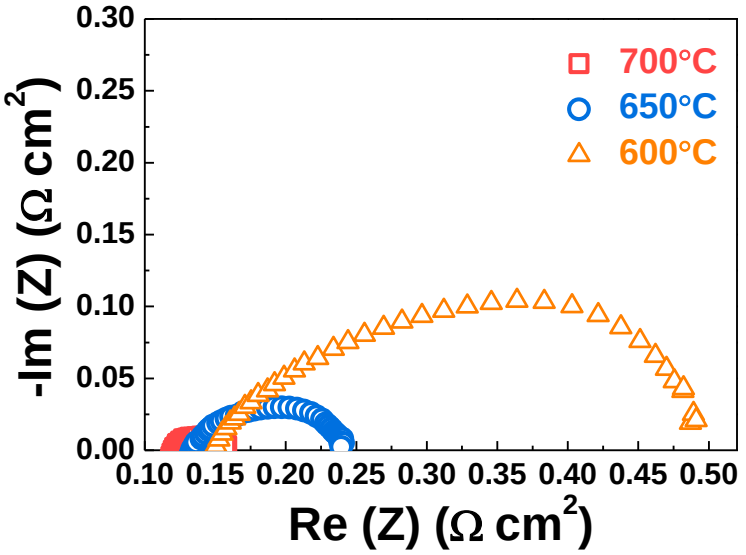


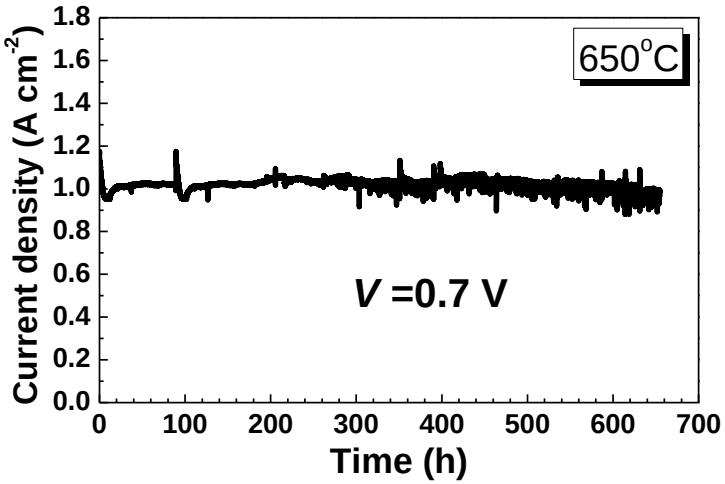


- A dense electrolyte with a thickness of ~8 um;
- Grain size of ~5 um

Fuel cell performance



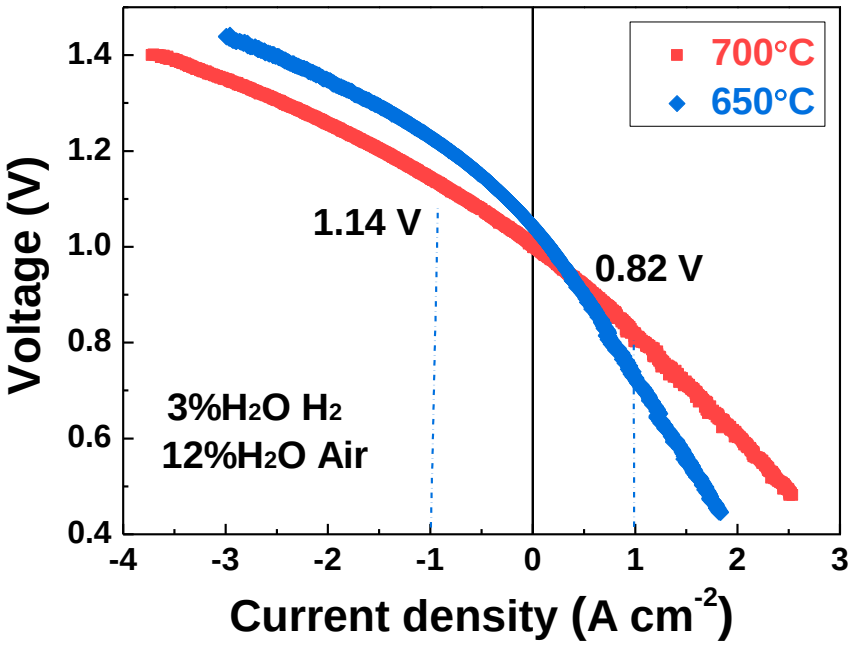


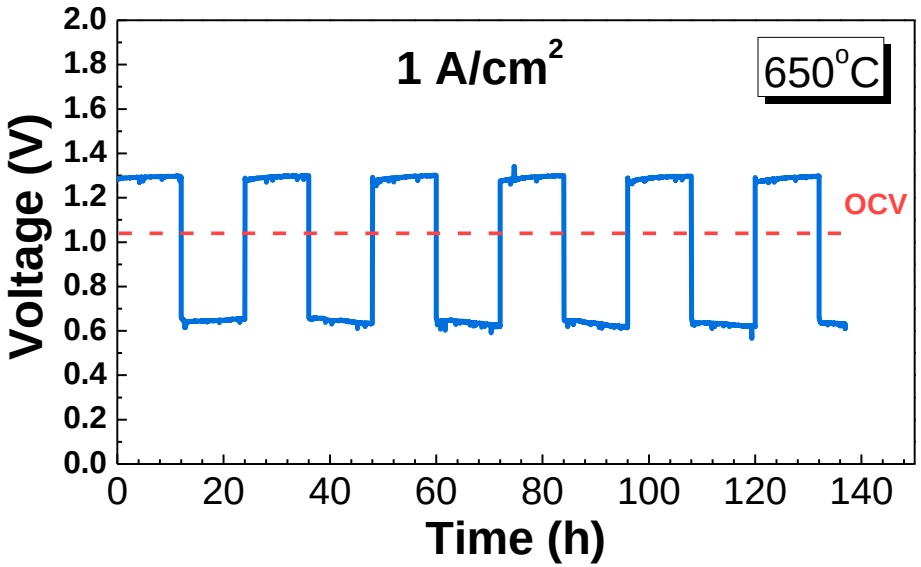


Button cells: Ni-BZCYYb /BZCYYb/cathode

- A peak power density of ~1.3Wcm^{-2} at 700 °C has been obtained;
- Cell shows reasonable durability in fuel cell mode

Reversible fuel cell performance





Reversible fuel cell: Ni-BZCYYb /BZCYYb/Cathode

- **Roundtrip voltage efficiency of ~72% at 700°C at current density of 1 A cm^{-2}**
- **Cell shows reasonable durability during cycle**

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- Not applicable; this project started in January 2019

Collaboration & Coordination

- This project does not yet have a formal partner.
- Georgia Tech will identify an industrial partner for implementation of the developed processes for enhancing electrode performance and durability through surface modification with an efficient catalyst.

Remaining Challenges and Barriers

Challenges:

- Understanding the degradation mechanism in order to enhance long-term durability while maintaining high performance (power output and efficiency);
- Minimizing the electronic conduction of electrolyte under operating conditions while maintaining required performance;
- Achieving complete control of the morphology, composition, and thickness of the catalyst layer; developing flat URFCs (6 cm x 6 cm) with defect-free, dense and thin electrolyte (< 10 μm) toward the end of the project.

Plans:

- Investigate into the surface electrochemical processes using various in situ and operando tools to unravel the degradation mechanism and formulate effective approaches to mitigate the problems
- Enhance the Faradaic efficiency through surface coating of protective layers
- Develop well controlled powder synthesis process (to control the particle morphology and size), co-tape casting process (to control the viscosity, flowability and thickness of the slurry), and co-sintering process (to control the porosity and shrinkage of the half cell) to fabricate defect-free large cells (6 cm x 6 cm) with controlled mechanical strength, thickness and porosity.

Proposed Future Work

M	Brief Description	Complete
2.0	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.	80%
3.0	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.	50%

Go/No-Go Decision Point	**Go/No-Go # 1**	**Demonstrate 200 h operation of a button cell at ≤700 °C with >60% roundtrip efficiency at 1 A/cm² in both SOFC and SOEC modes with degradation rate <2% per 500 h.**	**FY20**

To optimize the synthesis conditions for preparation of electrodes and electrolyte powders with desired properties for cell fabrication

To determine transfer numbers of electrolytes with or without protective coatings

To unravel the mechanism of electrode processes and characterize cell performance under various operating conditions

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

Technology Transfer Activities

- Invention disclosure on new materials will be filed shortly.
- Inquiries 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)

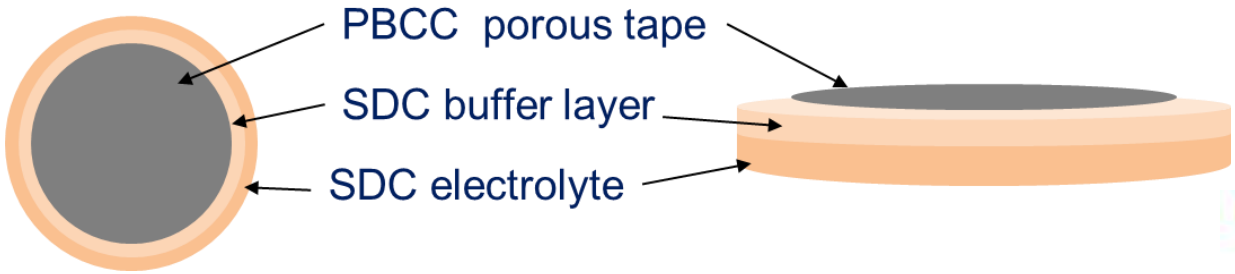
Summary- Progress and Accomplishments

- Synthesized mixed proton-electronic conducting materials (NBSCF and PBSCF) as positive electrode
- Developed novel proton conducting electrolytes with enhanced stability against H_2O and CO_2
- Developed high-performance reversible fuel cells based on proton conductors

Technical Back-Up Slides

Cell configurations and testing conditions

- ✓ PBCC I SDC I PBCC
- ✓ SDC: dry-pressed & fired at 1450°C
- ✓ PBCC on SDC fired at 1080°C/2h
- ✓ Infiltrate catalysts into porous cathode backbones to mitigate the effect of contaminants;
- ✓ Rp was determined from EIS of cells at OCV

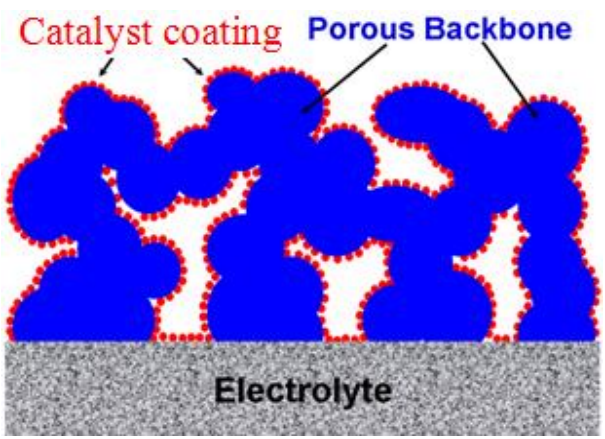


SDC pellet
10 mm diameter
0.8 mm thick

SDC buffer layer
5 µm thick

PBCC
Tape casting
¼ inch diameter
50 µm thickness

Catalysts Solution Infiltration



Surface Modified Cathode

Critical Assumptions and Issues

- Inadequate understanding of electro-catalytic and degradation mechanisms due largely to
  - ✓ Inability to probe/map *incipient* surface species/phases under operating conditions
  - ✓ Poor knowledge of surface topography and its evolution under operating conditions
  - ✓ Little information on the local properties of hot spots on heterogeneous surfaces
- Precise control of the morphology, composition, and thickness of the catalyst coatings remains a challenge;
- Faradaic efficiency may have to be improved under realistic operation conditions.