Proton-Conducting Ceramic Electrolyzers for High-Temperature Water Splitting

fuelcellenergy

PI: Hossein Ghezel-Ayagh

Co-PIs (CSM): Neal Sullivan, Ryan O'Hayre, Robert Braun

May 30, 2020

2020 DOE Hydrogen and Fuel Cells Program Review

Project ID# p177

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

fuelcellenergy

Overview

Timeline

- Project Start Date: 10/01/2018
- Project End Date: 03/31/2021

Barrier

- Key barriers addressed in the project are:
  - F. Capital Cost
  - G. System Efficiency and Electricity Cost
  - J. Renewable Electricity Generation Integration

Budget

- Total Project Budget: $1,875,000
- Total Recipient Share: $ 375,000
- Total Federal Share: $1,500,000
- Total DOE Funds Spent*: $ 901,219

* Estimated as of 4/30/2020

Partner

- FuelCell Energy (FCE) – Project Lead
- Colorado School of Mines (CSM)
- Versa Power Systems (VPS)

fuelcellenergy

Project Background

Objective:

Development of efficient and durable high-temperature water splitting (HTWS) systems for production of hydrogen at a cost less than \$2/kg H_2, using proton conducting ceramic electrolytic cell (PCEC) technology at a temperature ≥500ºC. Technical performance targets for the electrolysis stack include:

- Specific resistance of ≤0.30 Ω-cm^2
- Stack electrical efficiency >95% LHV H_2 at current density >1 A/cm^2
- Stack lifetime of ≥7 years

Project Goals:

- Increase PCEC performance by achieving Faradaic efficiency > 95%, electrical efficiency > 95%, and area-specific resistance <0.15 Ω-cm^2 at 1 A / cm^2 and 550ºC
- Reduce PCEC degradation < 1% / 1000 hours
- Scale-up cell area (up to 10x10 cm) and develop manufacturing process
- Demonstrate operation of a PCEC stack for ≥ 1 kg / day H_2 production, >95% electric efficiency (LHV) at ≥1A/cm^2 with degradation <3%/1 khr
- Perform Techno-Economic analysis and determine cost of hydrogen production with a target of \$2/kg

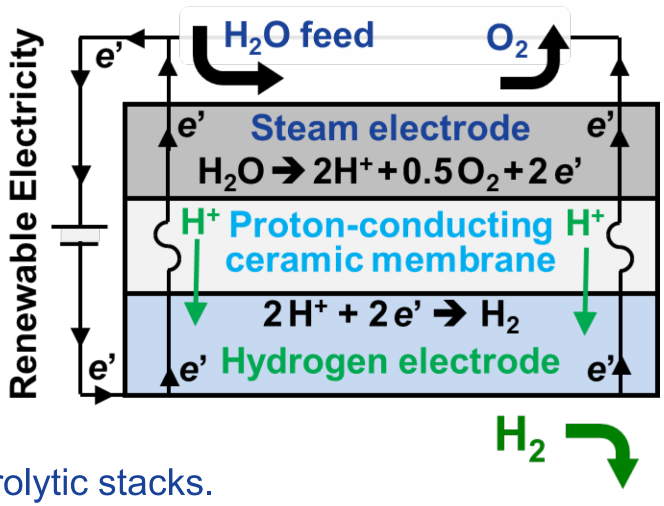
Relevance

fuelcellenergy

Technology Development Approach

The project seeks new protonic-ceramics to drive down operating temperature

- Conduct optimization of the air electrode under electrolysis operation, both from performance and degradation standpoints.
- Perform optimization of the electrolyte composition and morphology to establish long-term stability and mitigate current leakage.
- Develop database of physical and mechanical properties to be used in PCEC technology scale-up and stack design.
- Develop manufacturing processes using high-yield ceramic processing technologies including tape casting and screen printing.



- Scale cell active area up to 100 cm^2 suitable for commercial electrolytic stacks.
- Develop PCEC stack design and specifications for its components including seals, interconnects, compression plates, manifolds, and contact media.
- Develop stack manufacturing process including factory conditioning and acceptance tests.
- Develop flow sheet and process flow diagram for a PCEC system.
- Design and build a PCEC stack with capacity of at least 1 kg H_2/day for validation of project objectives' performance targets.
- Complete the Factory Cost estimate of the PCEC system.
- Complete DOE H2A analysis for PCEC system to verify achievement of program cost target of less than \$2/kg H_2 for hydrogen production.

Approach

FY2019 & FY2020 Milestones

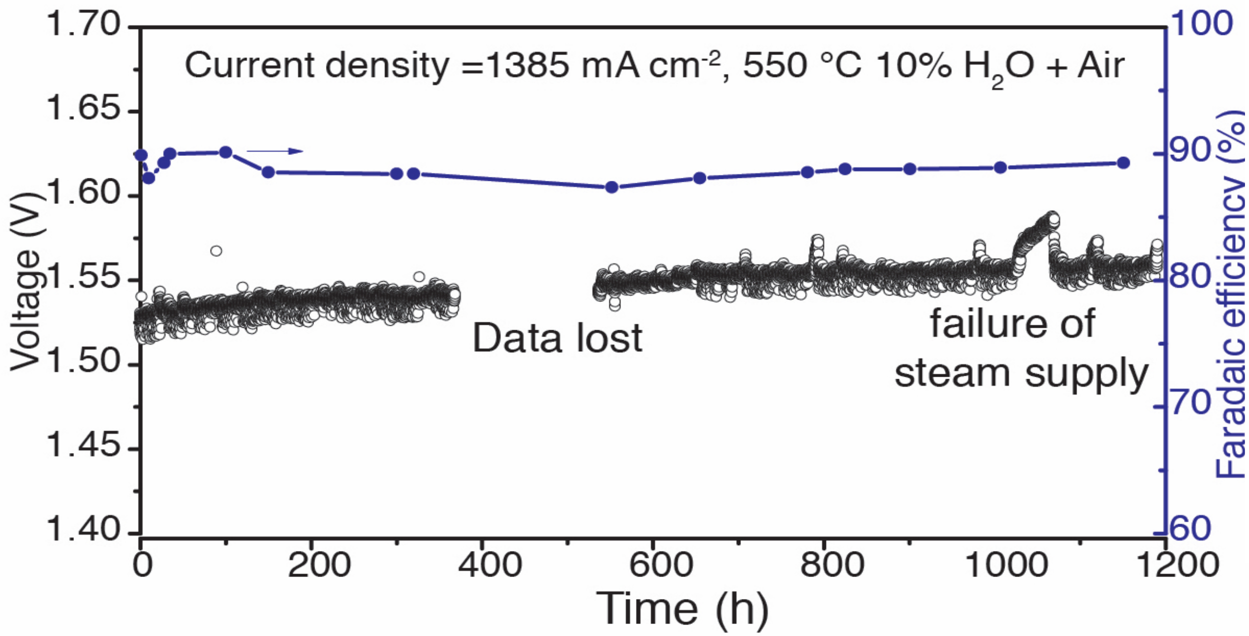
Milestone #	Project Milestones	Completion Date	Percent Complete	Progress Notes
1.1.1	Down-select PCEC electrolyte	6/30/19	100%	Complete
1.1.2	Demonstrate Faradaic efficiency > 85%, Electric efficiency > 75% at 1 A / cm2	9/30/19	100%	Complete
1.1.3	Demonstrate Faradaic efficiency > 90%, electrical efficiency > 80%, and area-specific resistance < 0.3 Ω-cm2 at 1 A / cm2 at 550 ºC	12/31/19	95%	Complete
1.1.4	Demonstrate Faradaic efficiency > 95%, electrical efficiency > 85%, and area-specific resistance <0.15 Ω-cm^2 at 1 A / cm^2 at 550 ºC	6/30/20	5%	On-going
1.2.1	Initiate 1000-hour PCEC fuel- and steam-electrode baseline degradation tests	12/31/18	100%	Complete
1.2.2	Initiate 1000-hour PCEC MEA baseline-degradation tests	3/31/19	100%	Complete
Go/No-Go	Demonstrate P-SOEC MEA with degradation rate of <5%/1000 hr and Faradaic efficiency of >95% at 1 A/cm^2 at ≤550°C	9/30/19	100%	Complete
1.2.3	Demonstrate PCEC electrode degradation rates < 2% / 1000 hours with a minimum steam feedstock concentration of 40%	12/31/19	90%	On-going
1.2.4	Demonstrate PCEC MEA degradation rates < 2% / 1000 hours with a minimum steam feedstock concentration of 40%	3/31/20	90%	On-going
1.2.5	Demonstrate PCEC electrode degradation rates < 1% / 1000 hours with a minimum steam feedstock concentration of 40%	6/30/20	0%	Not started
1.2.6	Demonstrate PCEC MEA degradation rates < 1% / 1000 hours with a minimum steam feedstock concentration of 40%	9/30/20	0%	Not started
1.3.1	Establish baseline performance of industrially manufactured protonic ceramic electrolytic cell with ≥ 16 cm^2 active area	9/30/19	100%	Complete
1.4.1	Performance validation of large-area cell (at least 5x5 cm and up to 10x10 cm) equal to or better than the baseline and demonstrate Faradaic efficiency >95% at current density of 1 A/cm2 at 550 °C	12/31/19	80%	On-going
2.1.1	Stack modeling complete and determining the effects of operating conditions	9/30/19	100%	Complete
.2.1	Manufacture a tall stack for ≥ 1 kg H_2 / day	6/30/20	0%	Not started
2.3.1	Achieve PCEC stack performance >95% eff (LHV) at ≥1A/cm^2 and degradation <3%/1khr	9/30/20	0%	Not started
3.1.1	Develop a process flow diagram based on the selected PCEC system design.	12/31/19	100%	Complete
3.3.1	Complete H2A analysis and determine the cost of hydrogen production with a target of \$2/kg H_2	9/30/20	30%	On-going

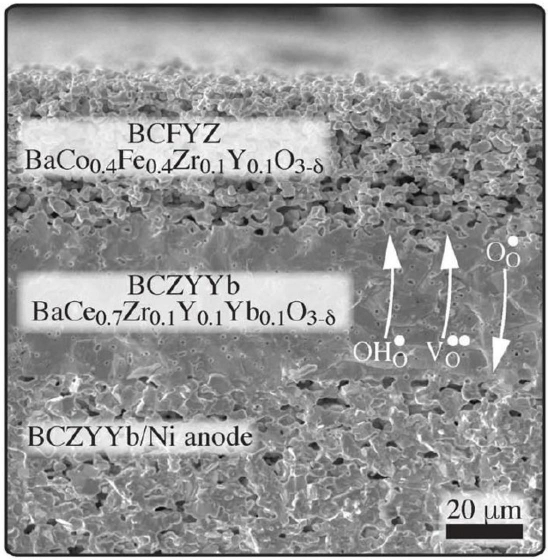
Approach

Button Cell Long-Term Stability

Milestones M1.2..2 & M1.2.4: Initiate 1000-hour PCEC MEA baseline-degradation tests. Demonstrate PCEC MEA degradation rates < 2% / 1 khr ✓

Go / No-Go Milestone: Demonstrate PCEC degradation rate < 5% / 1000 hrs at < 550 °C and Faradaic Efficiency (FE) > 95% at 1 A/cm2 ✓

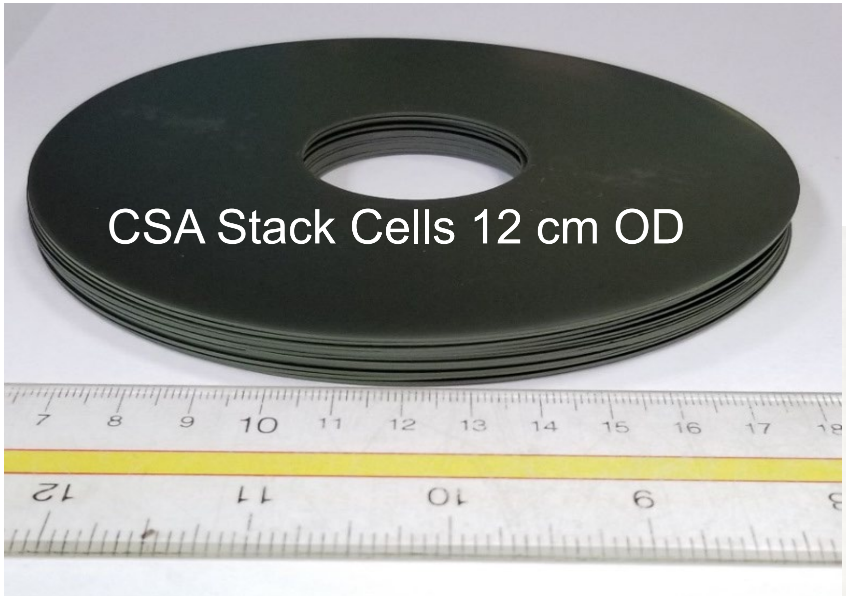


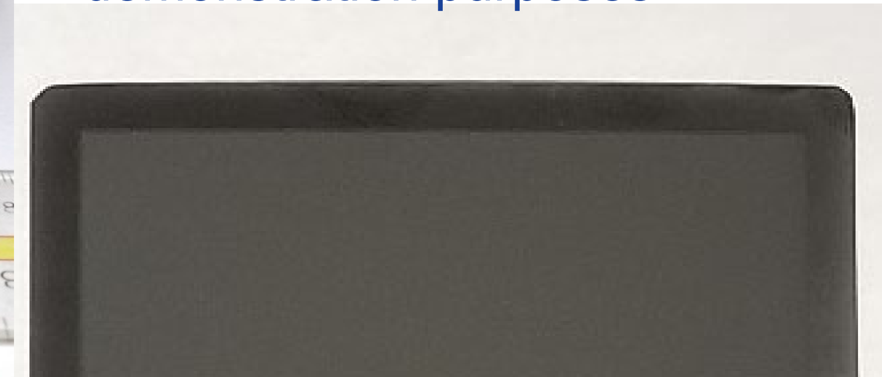


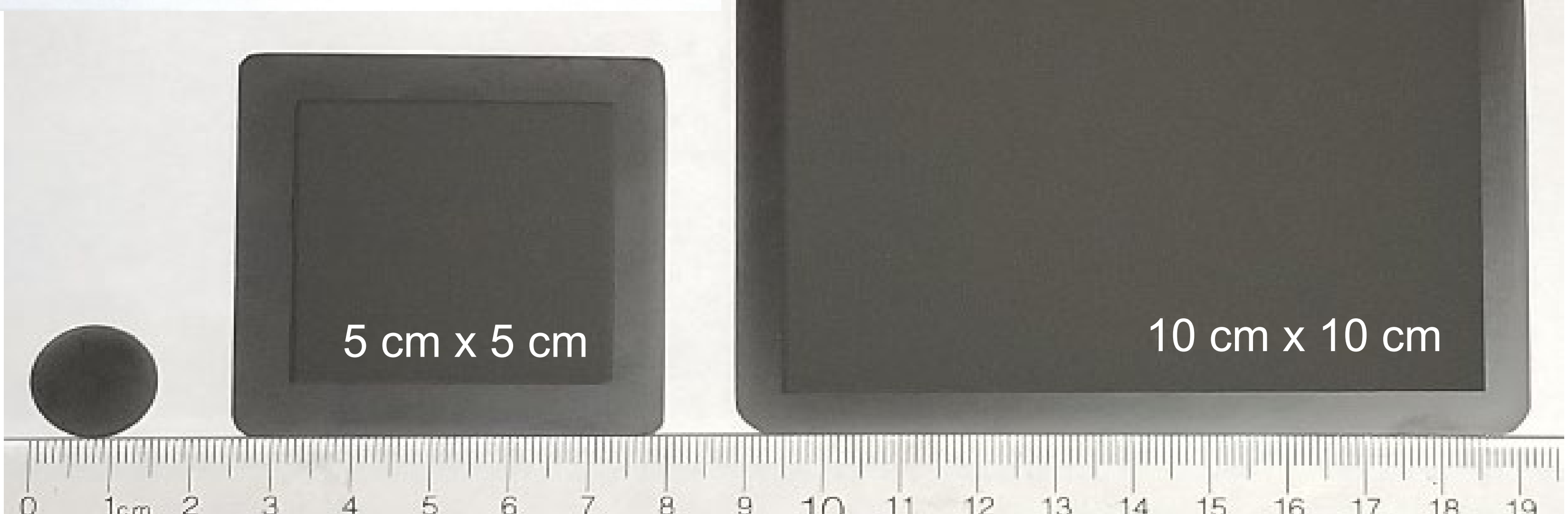
- Achieved performance degradation ~ 1.6%/1000 and FE> 89% hrs over 1200 hours of testing at 550°C and 1.385 A /cm^2
- The modification to the scope of work with >40% steam concentration requires the repeat of Milestone M1.2.4

Proton-Conducting Cell Scale-Up

- Cells have been successfully scaled up to 10 cm x 10 cm single-cell and stack cells have been prepared for demonstration purposes

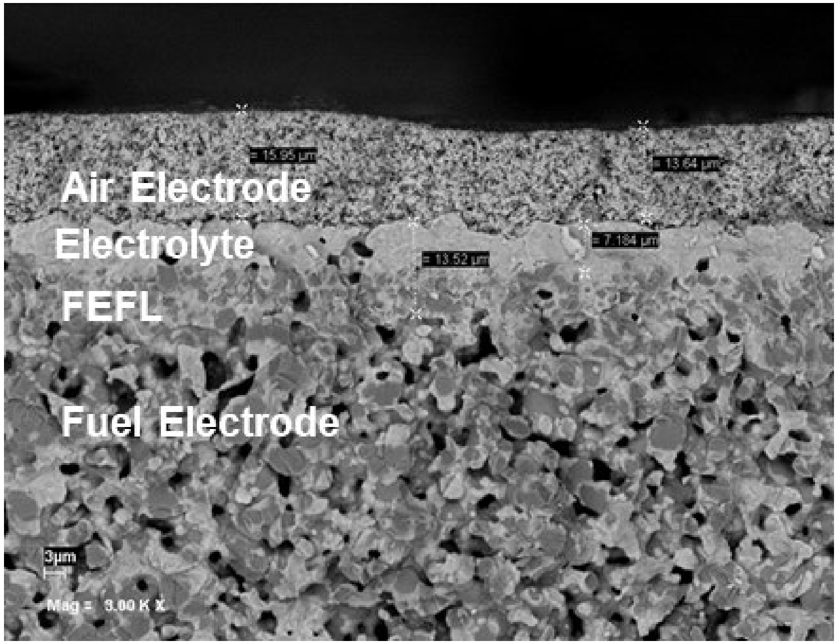


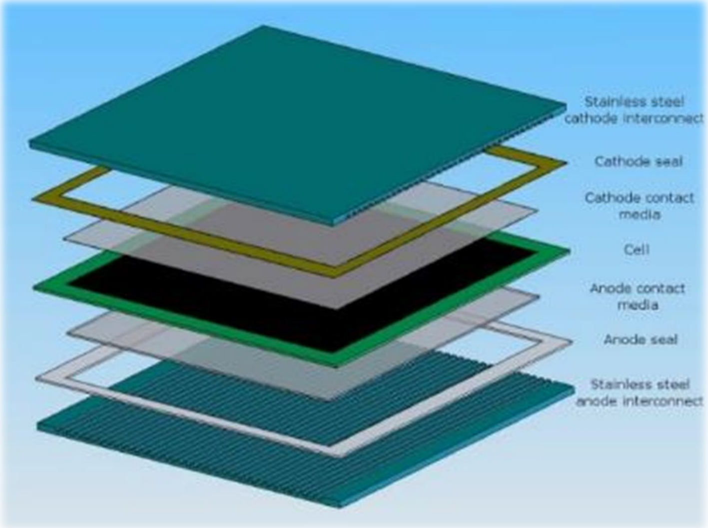




Sacled-up Cell Fabrication and Testing

- Fuel electrode-supported cell
- 0.5 to 1.5 mm fuel electrode (BCZYYb4411/Ni)
- ~15 micron fuel electrode functional layer (BCZYYb4411/Ni)
- ~10 micron electrolyte (BCZYYb4411)
- 10 - 50 micron air electrode
- 16 to 81 cm^2 active area



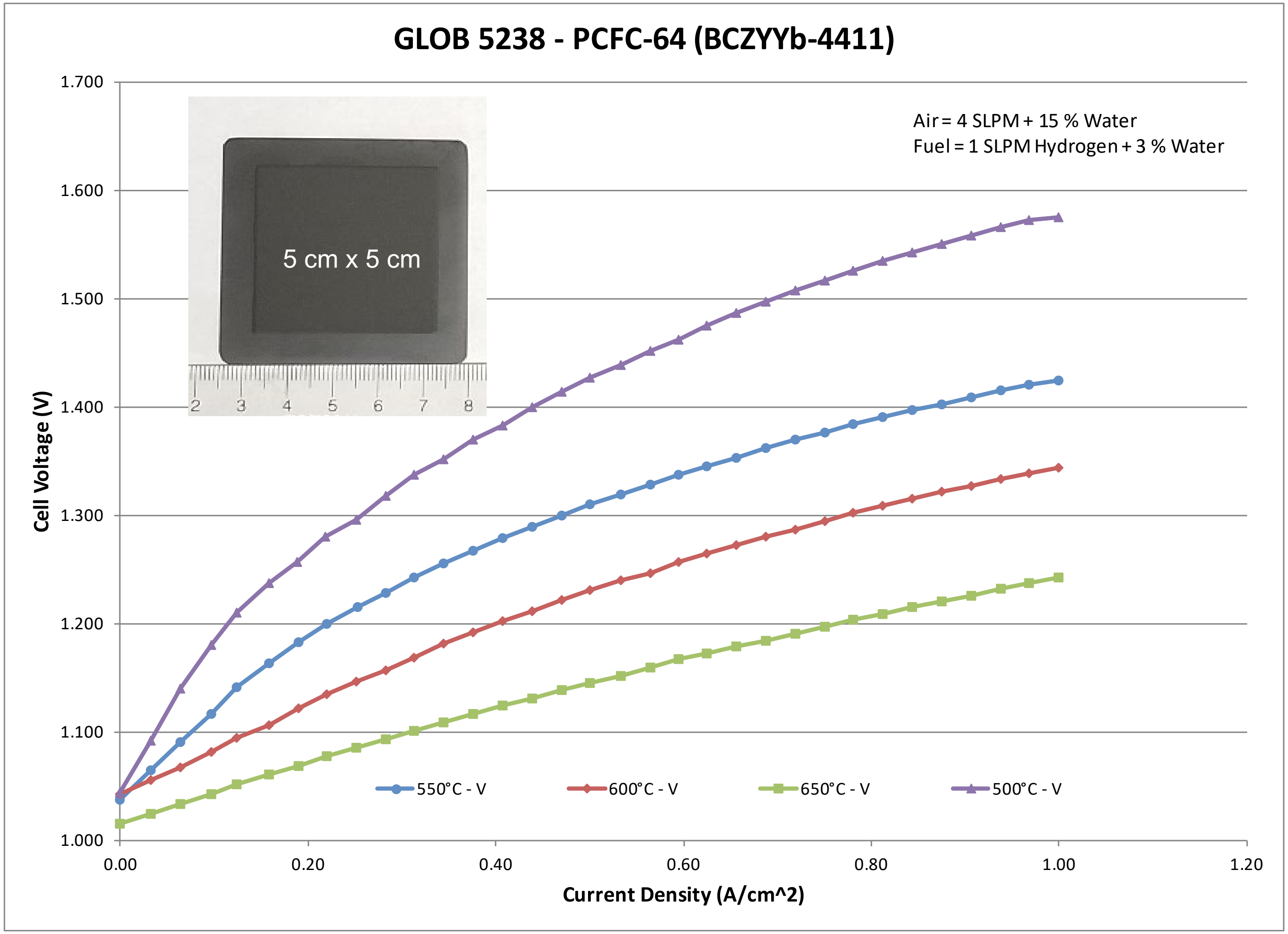


- Cell testing uses same materials and interfaces found in a stack repeat unit
- Cross-flow geometry
- Ferritic stainless steel current collection
- Seal and contact materials same as stack

Technical Accomplishments and Progress

PCEC – BCZYYb-4411 Cell 16 cm^2

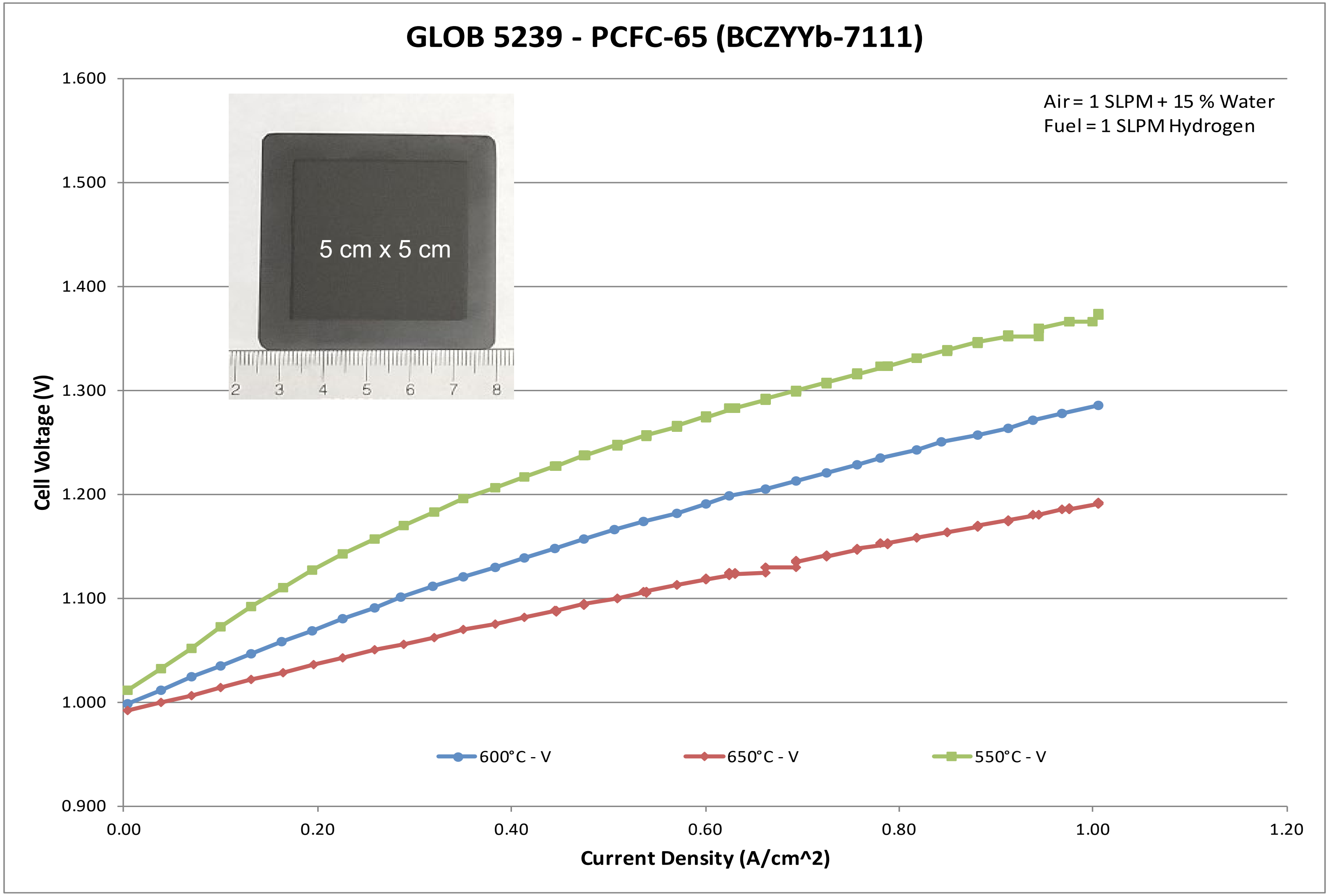
Milestone M1.3.1: Establish baseline performance of industrially manufactured protonic ceramic electrolytic cell with ≥ 16 cm2 active area ✓



Technical Accomplishments and Progress

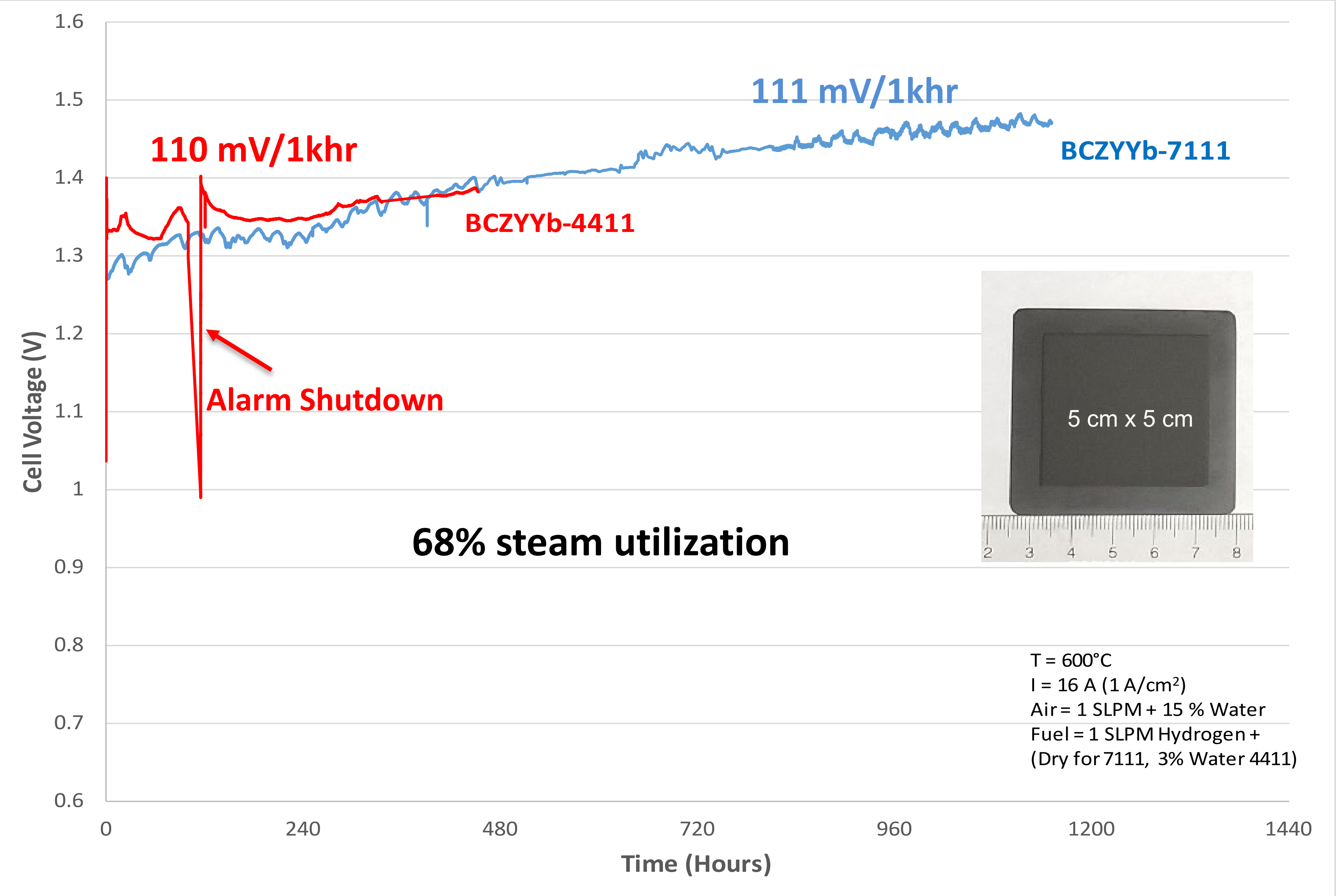
PCEC – BCZYYb-7111 Cell 16 cm^2

Milestone M1.3.1: Establish baseline performance of industrially manufactured protonic ceramic electrolytic cell with ≥ 16 cm2 active area ✓



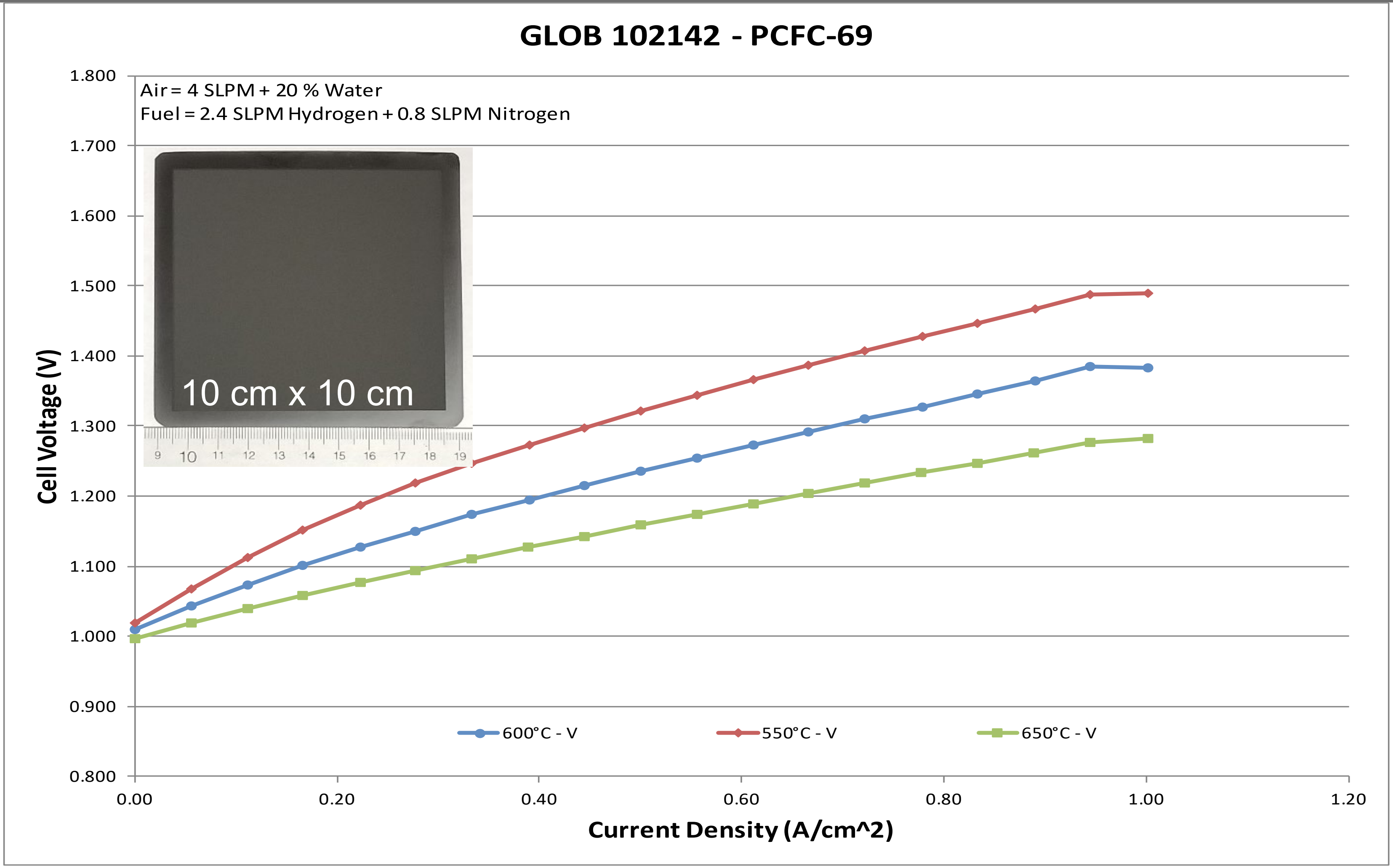
Technical Accomplishments and Progress

Cell Degradation Results



10cm x 10cm BCZYYb-4411 PCEC

Milestone M1.3.1: Performance validation of large-area cell (at least 5x5 cm and up to 10x10 cm) equal to or better than the baseline and demonstrate Faradaic efficiency >95% at current density of 1 A/cm2 at 550 °C ✓

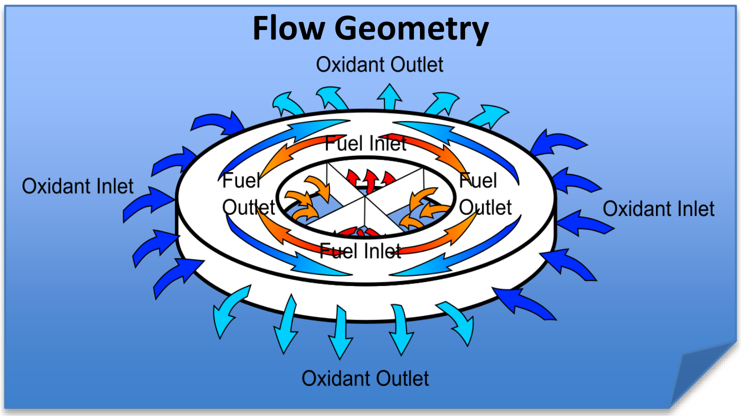


Technical Accomplishments and Progress

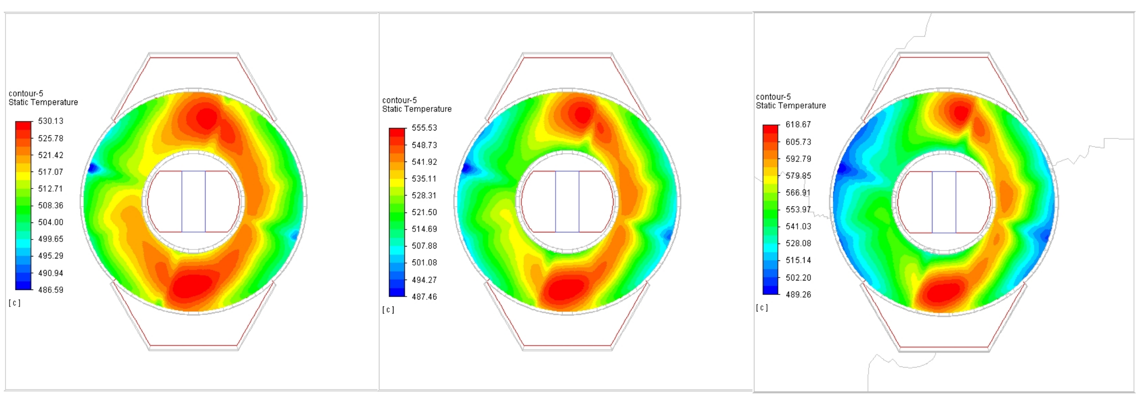
fuelcellenergy

PCEC Modeling

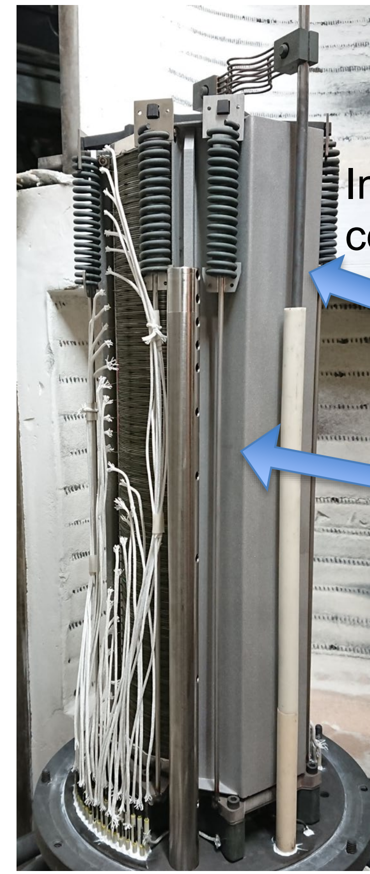
Milestone M2.1.1: Stack modeling complete and determining the effects of operating conditions ✓



- CFD model of the PCEC stack based on FCE's CSA design was developed using Fluent software platform



PCEC CSA on-cell thermal profiles at 0.75, 1.0, 1.5 A/cm^2 and Inlets temperatures of 500°C



Integrated compression

Oxidant outlet manifold

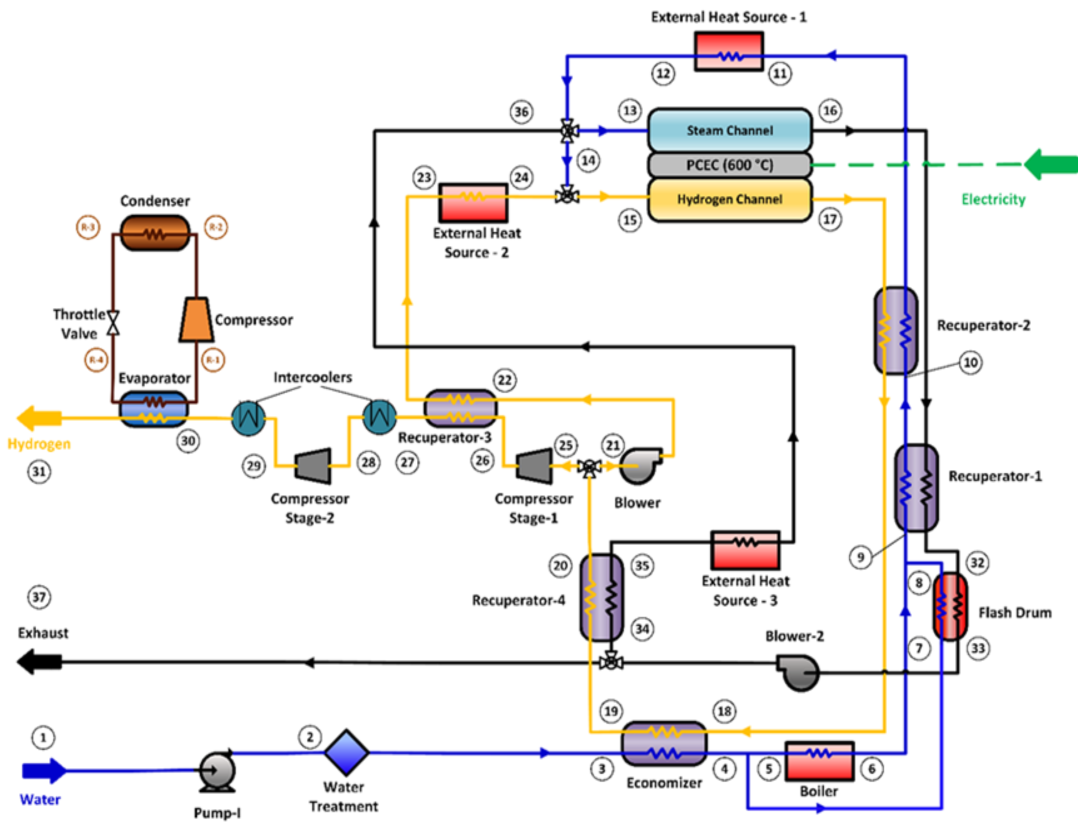
CSA Full Size Stack
350 cells - 17” tall

Technical Accomplishments and Progress

PCEC Modeling

Milestone M3.1.1: Develop a process flow diagram based on the selected PCEC system design. ✓

Hydrogen Production: 50,000 kg/day (99.9% @20 bar, 10 °C)	
Water Supply (kg/day)	514,734
Stack Electricity Consumption (MW_{AC})	78.3
Parasitic Power Consumption (MW)	6.2
Utility Heating Requirement (MW_{th})	16.5
Utility Cooling Requirement (MW_{th})	5.6
Average Faradaic Efficiency	92.4%
Average Current Density (A/cm^2)	0.70
Average Power Density, @1.28V (W/cm^2)	0.90
Steam concentration in feed gas (%)	50%
Cathode (positrode) Recycle (mass %) [$\boldsymbol{RE_{po}}$]	0.8
Anode (negatrode) Recycle (mass %) [$\boldsymbol{RE_{ne}}$]	77.8
Stack LHV Efficiency (%)	93.2
System LHV (Excl. heating) (%)	82.2
Overall System Efficiency (%-LHV) [η_{sys}]	68.8
Estimated System Cost ($/kW)	548



System flow diagram

Responses to Previous Year Reviewers' Comments

Reviewers' Recommendations:

1. The steam electrode degradation needs to be addressed. Project focus on this issue should be increased before expending resources on other project activities

- Project activities were focused on the steam electrode degradation including protective coating of interconnect resulting in mitigation of chromium poisoning of the electrode. Further work in reducing degradation of the steam electrode is underway hinged upon post-test analysis of long-term data.

2. A greater focus on cell leaks, stack leaks, and source tracking is recommended

- The leakage of current through the electrolyte layer was reduced via increasing Zr/Ce ratio, which also resulted in a higher Faradaic efficiency. The challenge of large thermal expansion coefficient of electrolyte possibly causing high gas leakage from stacks is being addressed in the upcoming quarters.

3. Investigators' anticipated future testing lacks thermal cycling. Thermal cycling should be included in future testing

- The focus has been on the reduction of steady-state degradation rates down to acceptable values. Few involuntarily thermal cycles resulting from test facility mishaps have not shown significant loss of performance. Future tests will include more rigorous studies on thermal cycling effect on PCEC performance.

Collaborations and Cooredination

Collaboration and Coordination

- **Colorado School of Mine (CSM)**
  - R&D activities at CSM are led by Professors Neal Sullivan, Ryan P. O'Hayre, and Robert Braun. The CSM team is … expertise:
    - Fundamental solid Ionics and materials science
    - Cell and multi-cell stack testing
    - Performance optimization
    - System and Techno-Economic Analysis (TEA)
- **Versa Power Systems (VPS), <u>Operating as FuelCell Energy</u>**
  - VPS is providing the following expertise in the project:
    - Cell materials & components
    - Stack design
    - Cell/stack pilot manufacturing and QC

Cell Pilot Manufacturing Processes at VPS: (Tape Casting, Screen Printing, and Co-sintering)

Remaining Challenges and Barriers

- Cell Performance
  - Develop understanding of cell performance degradation mechanisms
  - Develop degradation mitigation strategies and reduce cell performance degradation to <1%/1000 hours
  - Reduce specific cell resistance to < 0.15 ohm-cm^2
  - Scale up of cell and manufacturing process to fabricate cells up to 10 x 10 cm in size and meeting the target electric efficiency of >95% (based on LHV)
- Stack Development
  - Fabricate a commercial porotype PCEC stack sized for 1 kg/day of H_2 production, meeting the performance targets of >95% efficiency (LHV) at ≥ 1 A/cm^2 and performance degradation of <3%/1000 hours
- Techno-economic Analysis
  - Develop cost-optimized system to meet \$2/kg H_2 target while meeting the overall system efficiency goal of 75% (LHV of H_2)

Future Work

- Investigate cell performance degradation mechanisms and develop mitigation strategies to reduce cell performance loss with time to < 1%/1khr
- Fabricate and build cells with active area up to >100 cm^2
- Complete stack design and initiate fabrication of stack hardware components for building a stack for 1 kg/day H_2 production
- Work on design of system process flow diagram and modeling of stack:
  - Develop single-cell PCEC model
  - Update model and extend to stack design as cell materials/architecture become available
  - Validate cell model
- Techno-economic Analysis
  - Develop cost-optimized system to meet \$2/kg H_2 target while meeting the overall system efficiency goal of 75% (LHV of H_2)

Proposes Future Work

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

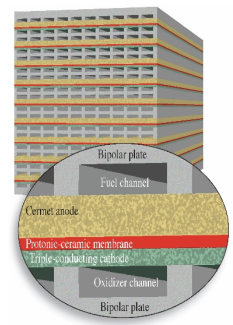
fuelcellenergy

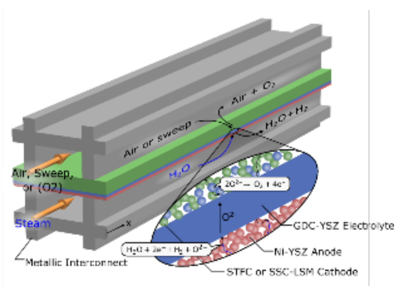
Technology to Market Analysis (TEM)

Technology Transfer Activities

Planned multi-scale modeling will move from physical models to process systems to TEA and Life-Cycle-Analysis (LCA)

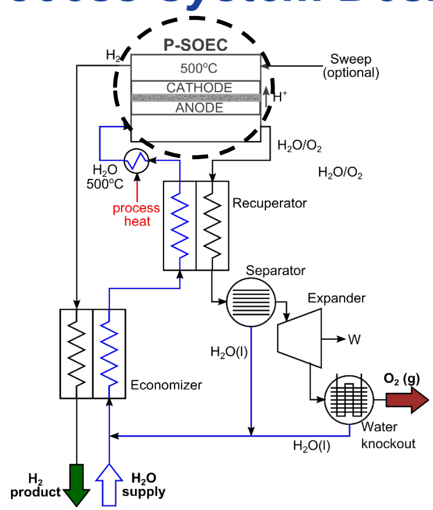
Stack Modeling



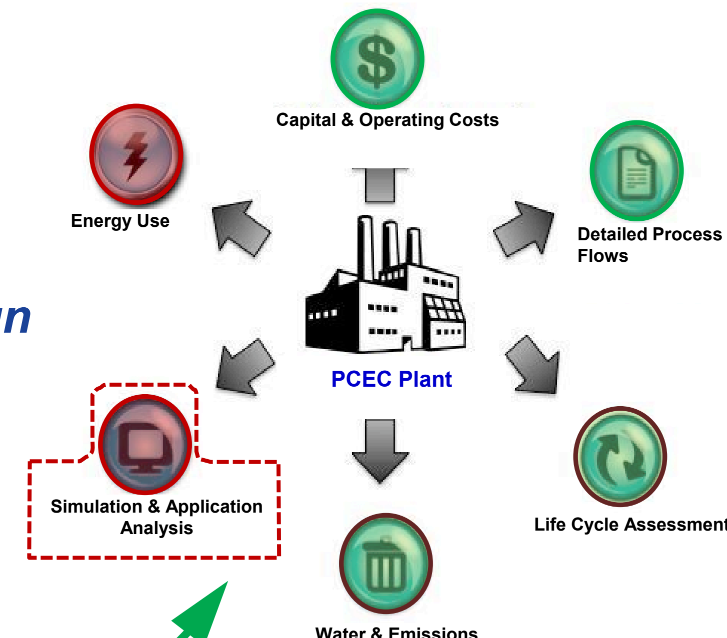


Cell Modeling

Process System Design



Systems-level TEA & LCA

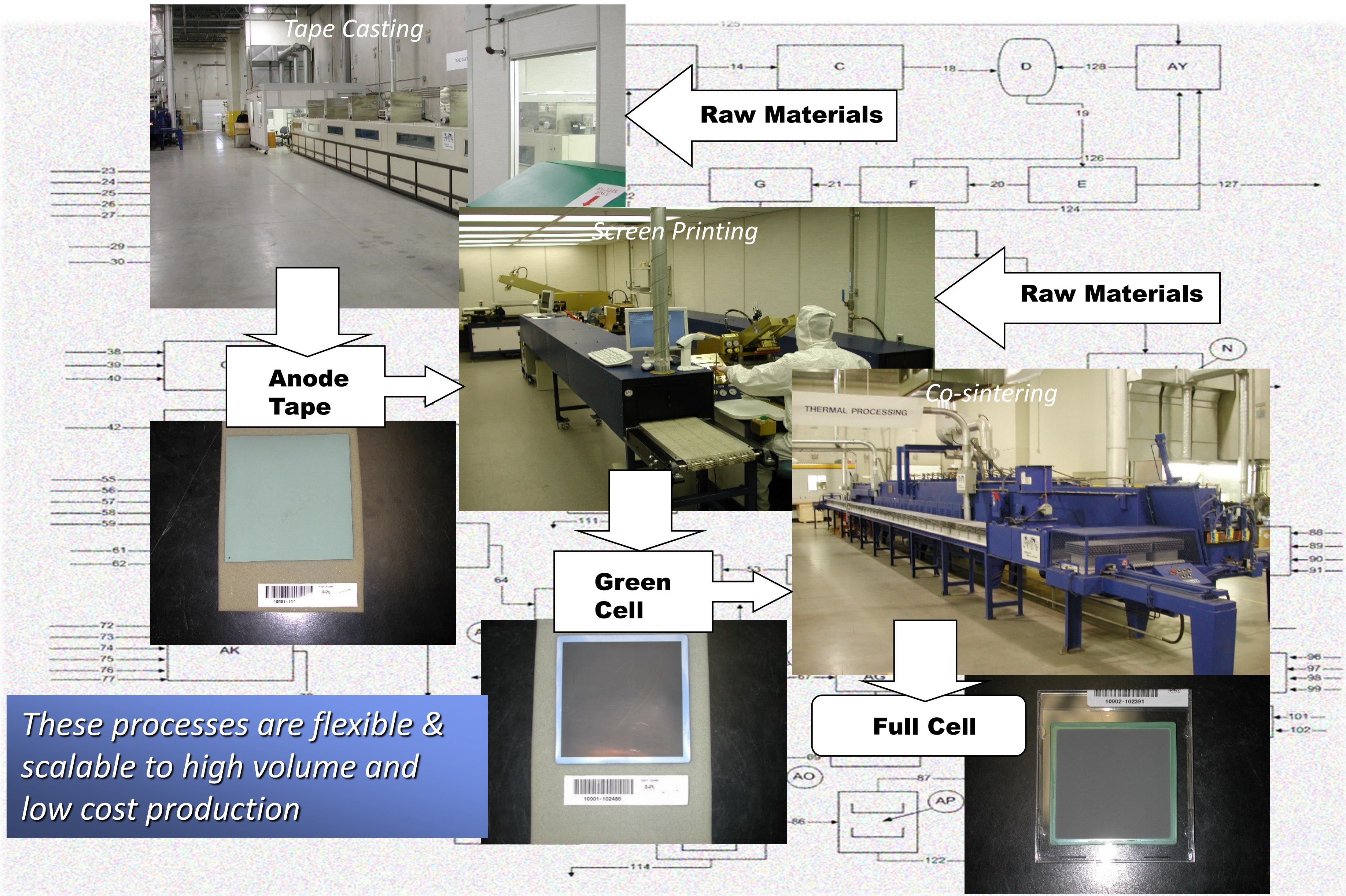


Summary

- Achieved performance degradation ~ 1.6%/1000 and FE> 89% hrs over 1200 hours of testing at 550 °C and 1.385 A /cm^2
- Developed manufacturing processes suitable for fabrication of scaled-up cells
- Accomplished scale-up and testing of 100 cm^2 PCEC size cells with 81 cm^2 active area
- Developed stack models predicting the PCEC performance and temperature profiles
- Completed process flow sheet of PCEC-based hydrogen production systems

TECHNICAL BACK-UP SLIDES

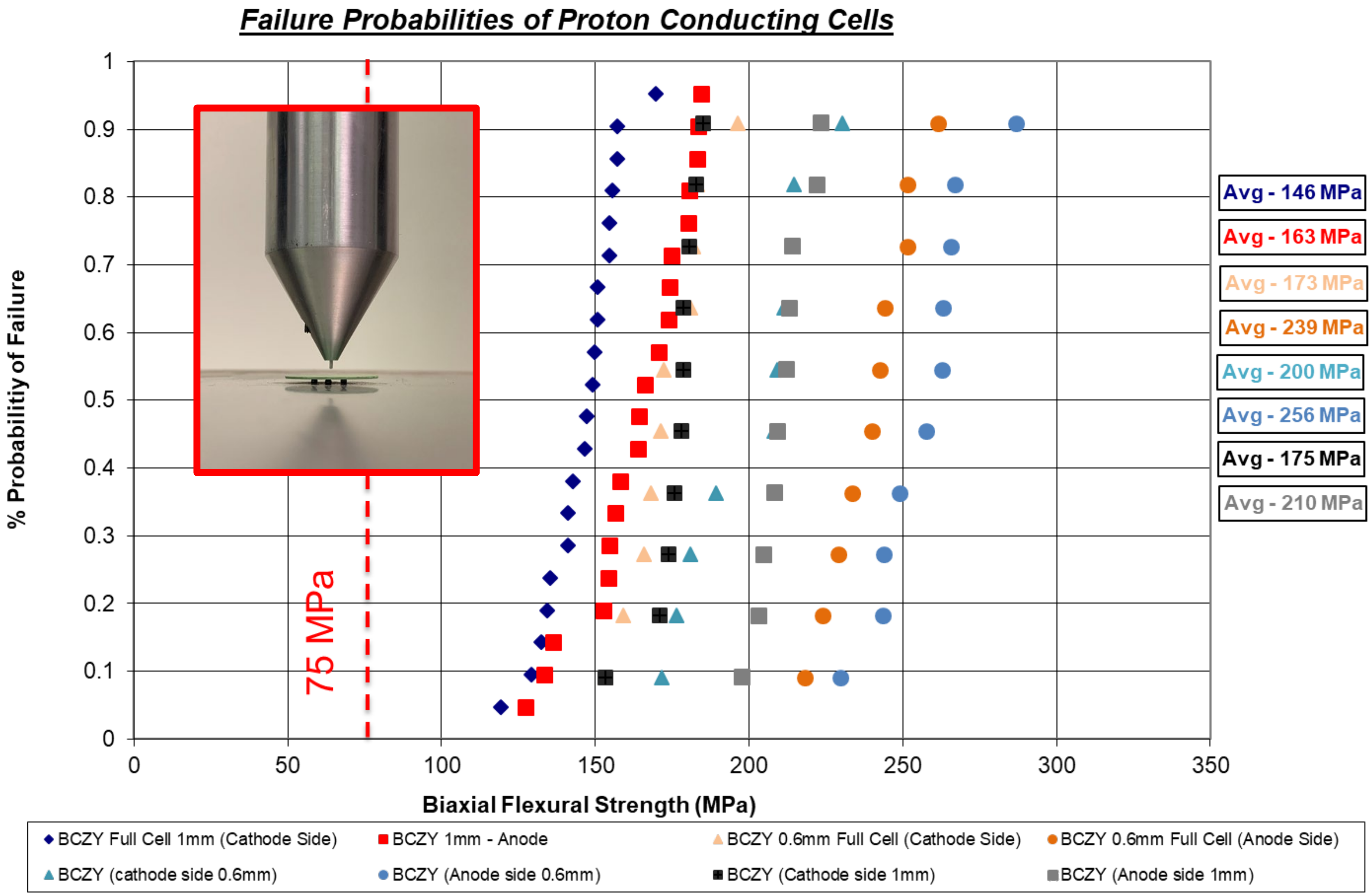
Pilot Manufacturing at FCE



These processes are flexible & scalable to high volume and low cost production

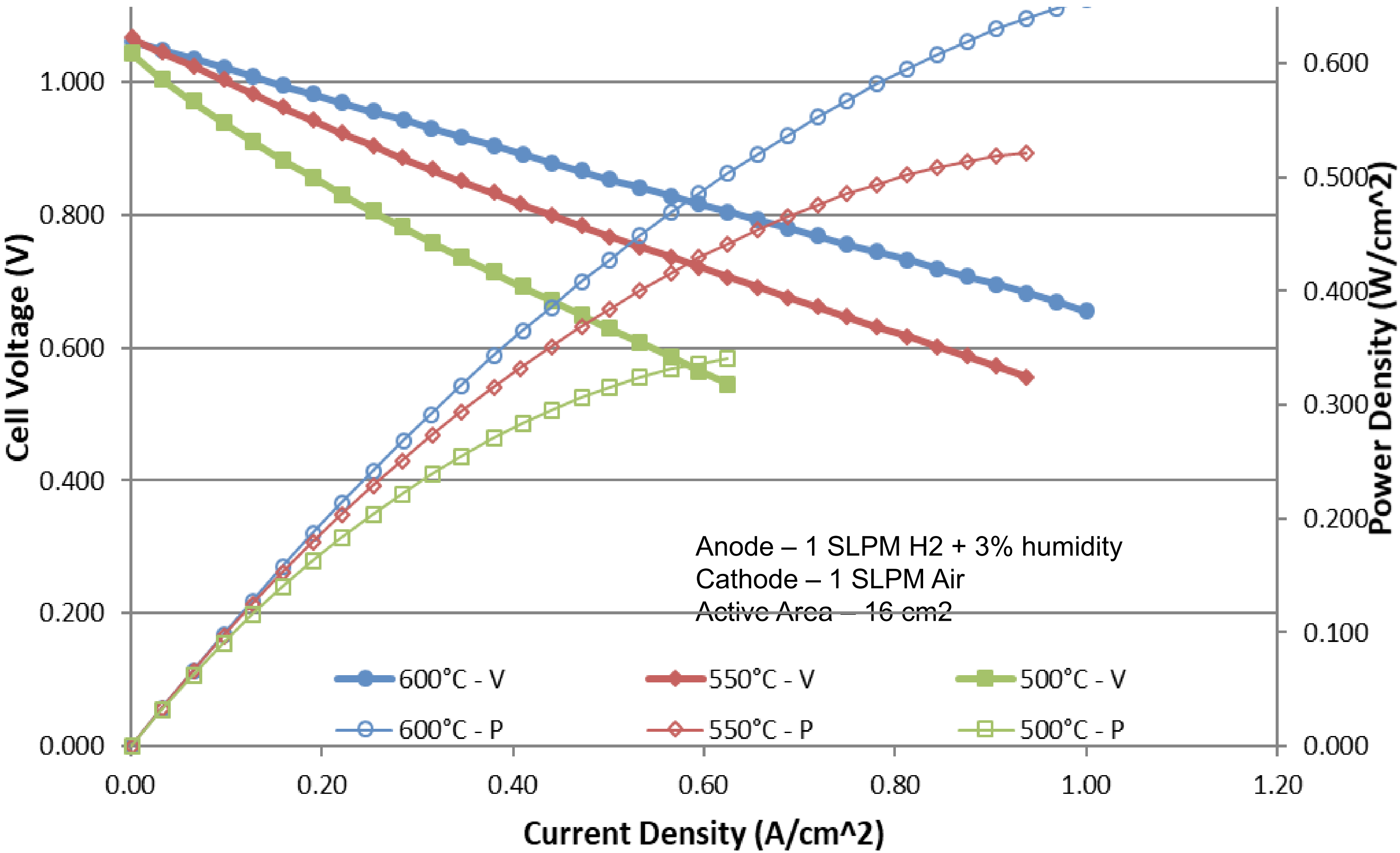
Proton Conducting Cell Biaxial Flexural Strength

Test results have shown that BCZY based cells have biaxial flexural strength higher than the targeted 75 MPa value



PCFC Performance

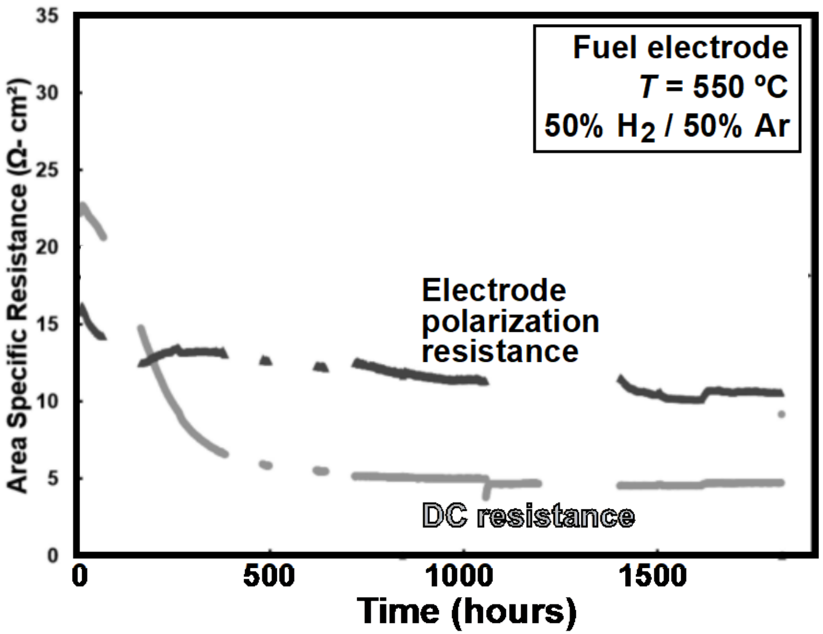
Excellent performance has been achieved by the proton conducting fuel cells in the temperature range of 500-600°C

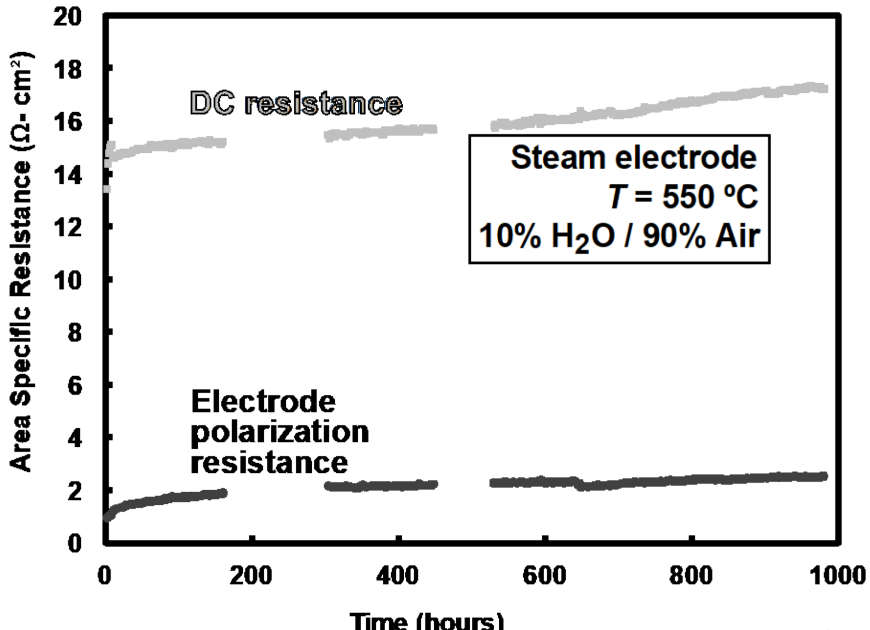


Electrode Degradation Studies

Milestone M1.2.1: Initiate 1000-hour PCEC fuel- and steam-electrode baseline degradation tests ✓

- Symmetric button cells with thick BCZYY7111 electrolyte were fabricated to measure the electrode performance degradations by AC impedance spectroscopy
- Negligible degradation was observed in the fuel electrode at the testing conditions of 550 ºC and 50% H_2O / 50% Ar over a period of 1800 hours
- Steam electrode showed a measurable increase in both the DC but stable electrode-polarization resistances over the 1000 hours of testing





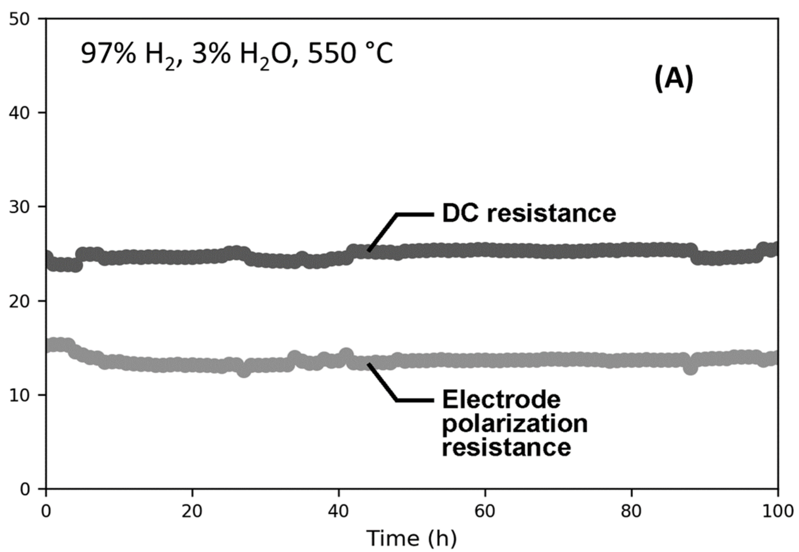
Degradation in fuel (left) and steam (right) electrodes over time

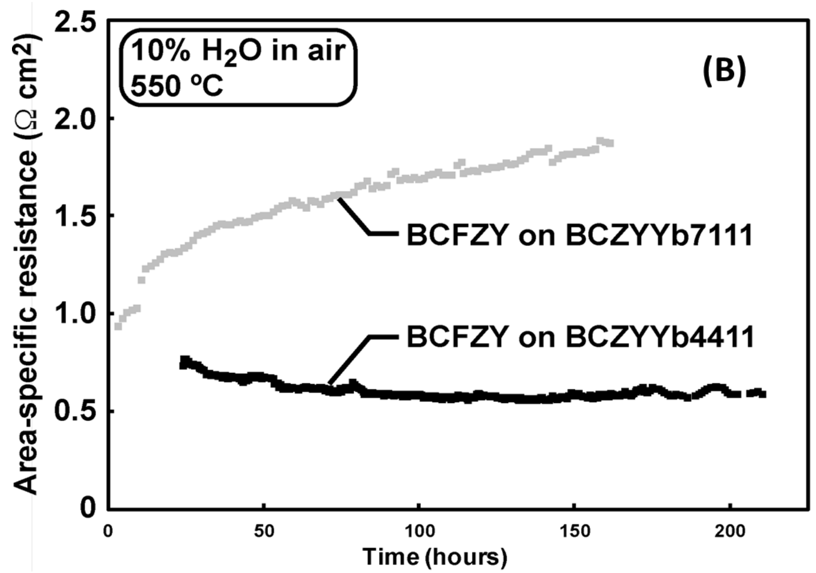
Technical Accomplishments and Progress

Long-Term PCEC Electrodes Stability Tests

Milestone M1.2.3: Demonstrate PCEC electrode degradation rates < 2% per 1000 hours ✓

- Achieved less than <2%/khr degradation in symmetric cells for both the steam as well as the fuel electrodes





Tests of ~ 1-mm thick BCZYYb4411electrolyte in symmetric button cells:

(A) DC and polarization resistances of fuel electrode at 550 ºC showed ~ 1%/khr degradation.

(B) Steam electrode composed of BCZYYb4411 electrolyte showed a stable performance as compared to the steam electrode made of BCZYY7111

Publications / Presentations

C. Duan, R.J. Kee, H. Zhu, N.P. Sullivan, L. Zhu, L. Bian, R. O'Hayre, "Highly efficient reversible protonic ceramic electrochemical cells for power generation and green fuels production," *Nature – Energy*, DOI: 10.1038/s41560-019-0333-2 **4** (3) 230-240 (2019).

Ryan P. O'Hayre, "The Perovskite Playground: Engineering defect chemistry in doped perovskite and perovskite-related oxides for high-temperature redox-active chemical and electrochemical applications," *2019 Spring Meeting of the Materials Research Society*, Phoenix, Arizona, USA, April 22 – 26, 2019.

L.Q. Le, H. Ding, L. Zhu, C. Herradon Hernandez, N.P. Sullivan, "Development of solid-oxide fuel cell stacks based on proton-conducting ceramics," *2019 Spring Meeting of the Materials Research Society*, Phoenix, Arizona, USA, April 22 – 26, 2019.

M. Hernandez Rodriguez, L.Q. Le, L. Zhu, C. Herradon Hernandez, M. Pisciotta, N.P. Sullivan, "Electrode degradation in proton-conducting ceramic fuel cells and electrolyzers," *2019 Spring Meeting of the Materials Research Society*, Phoenix, Arizona, USA, April 22 – 26, 2019.