Proton-Conducting Ceramic Electrolyzers for High-Temperature Water Splitting

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2019 DOE Hydrogen and Fuel Cells Program Review

Project ID# p177

Overview

Timeline

- Project Start Date: 10/01/2018
- Project End Date: 09/30/2020

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*: $ 75,000

* Estimated as of 3/1/19

Partner

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

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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:

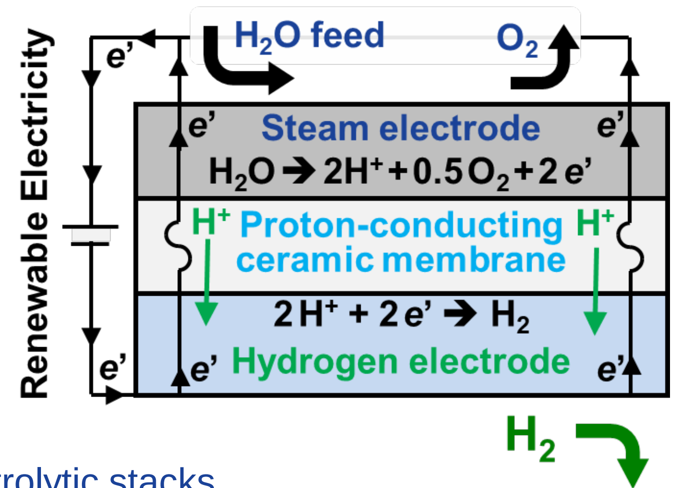
- Increase PCEC performance by achieving Faradaic efficiency > 95%, electrical efficiency > 95%, and area-specific resistance <0.15 Ω-cm^2 at 1 A / cm^2 and 550ºC
- Reduce PCEC degradation < 1% / 1000 hours
- Scale-up cell area (up to 10x10 cm) and develop manufacturing process
- Demonstrate operation 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

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 P-SOEC technology scale-up and stack design.
- Develop manufacturing processes for P-SOEC cells 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 P-SOEC stack design and specifications for stack components including seals, interconnects, compression plates, manifolds, and contact media.
- Develop stack manufacturing process including factory conditioning and acceptance tests.
- Develop a flow sheet and process flow diagram for a P-SOEC system.
- Design and build a P-SOEC 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 P-SOEC system for DOE's H2A analysis.
- Complete DOE H2A analysis for P-SOEC system to verify achievement of program cost target of less than \$2/kg H_2 for hydrogen production.

Approach

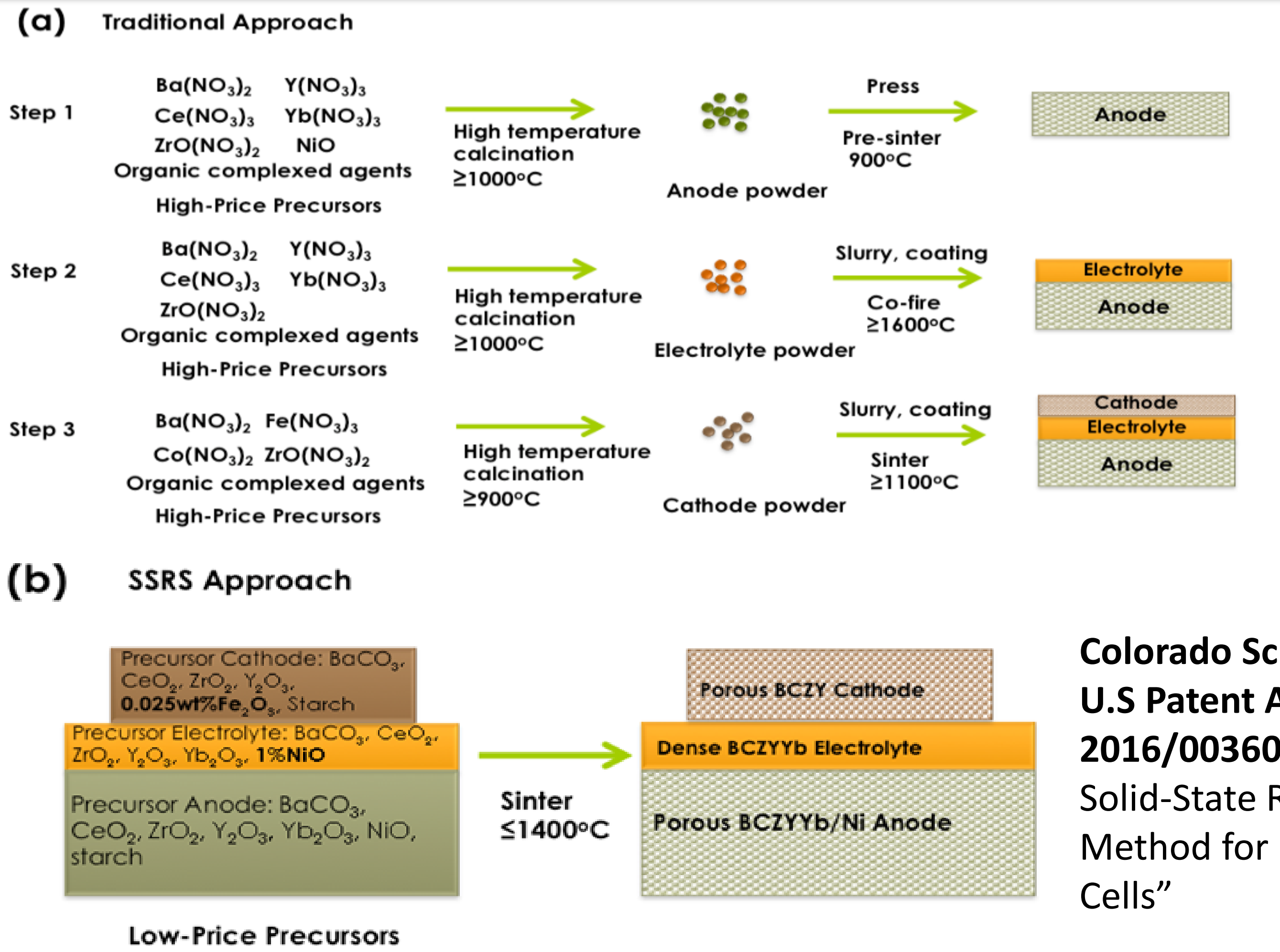
FY2019 & FY2020 Milestones

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter) Original Planned	Revised Planned	Actual	Percent Complete	Progress Notes
1.1.1	Down-select PCEC electrolyte	Milestone	6/30/19			75%	
1.1.2	Demonstrate Faradaic efficiency > 85%, Electric efficiency > 75% at 1 A / cm2	Milestone	9/30/19		12/31/18	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	Milestone	12/31/19			50%	
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	Milestone	6/30/20			5%	
1.2.1	Initiate 1000-hour PCEC fuel- and steam-electrode baseline degradation tests	Milestone	12/31/18		12/31/18	100%	Complete
1.2.2	Initiate 1000-hour PCEC MEA baseline-degradation tests	Milestone	3/31/19			10%	
	Demonstrate P-SOEC MEA with degradation rate of <5%/1000 hr and Faradaic efficiency of >95% at 1 A/cm^2 at ≤550°C	Go-No-Go	9/30/19				Not started
1.2.3	Demonstrate PCEC electrode degradation rates < 2% / 1000 hours	Milestone	12/31/19			0%	Not started
1.2.4	Demonstrate PCEC MEA degradation rates < 2% / 1000 hours	Milestone	3/31/20			0%	Not started
1.2.5	Demonstrate PCEC electrode degradation rates < 1% / 1000 hours	Milestone	6/30/20			0%	Not started
1.2.6	Demonstrate PCEC MEA degradation rates < 1% / 1000 hours	Milestone	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	Milestone	9/30/19			0%	Not started
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	Milestone	12/31/19			0%	Not started
2.1.1	Stack modeling complete and determining the effects of operating conditions	Milestone	9/30/19			0%	Not started
.2.1	Manufacture a tall stack for ≥ 1 kg H_2 / day	Milestone	6/30/20			0%	Not started
2.3.1	Achieve PCEC stack performance >95% eff (LHV) at ≥1A/cm^2 and degradation <3%/1khr	Milestone	9/30/20			0%	Not started
3.1.1	Develop a process flow diagram based on the selected PCEC system design.	Milestone	12/31/19			0%	Not started
3.3.1	Complete H2A analysis and determine the cost of hydrogen production with a target of \$2/kg H_2	Milestone	9/30/20			0%	Not started

Approach

Proton Conducting Cell Fabrication

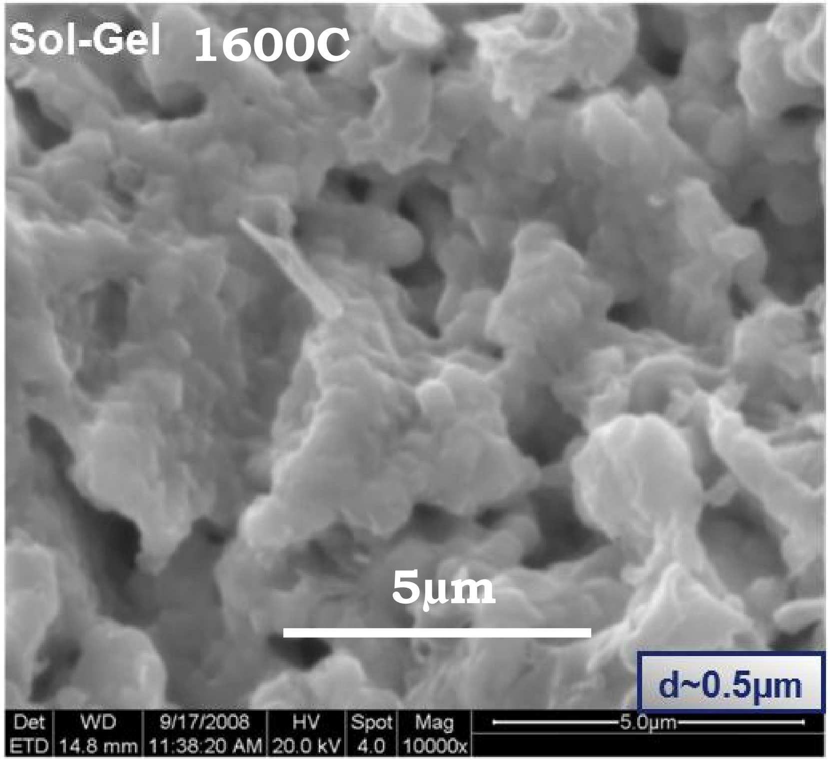
Simple, cost-effective cell fabrication using Solid-State Reactive Sintering (SSRS) developed for Proton Conducting Fuel Cells (PCFC) will be applied in this project to fabricate electrolytic cells (PCEC)

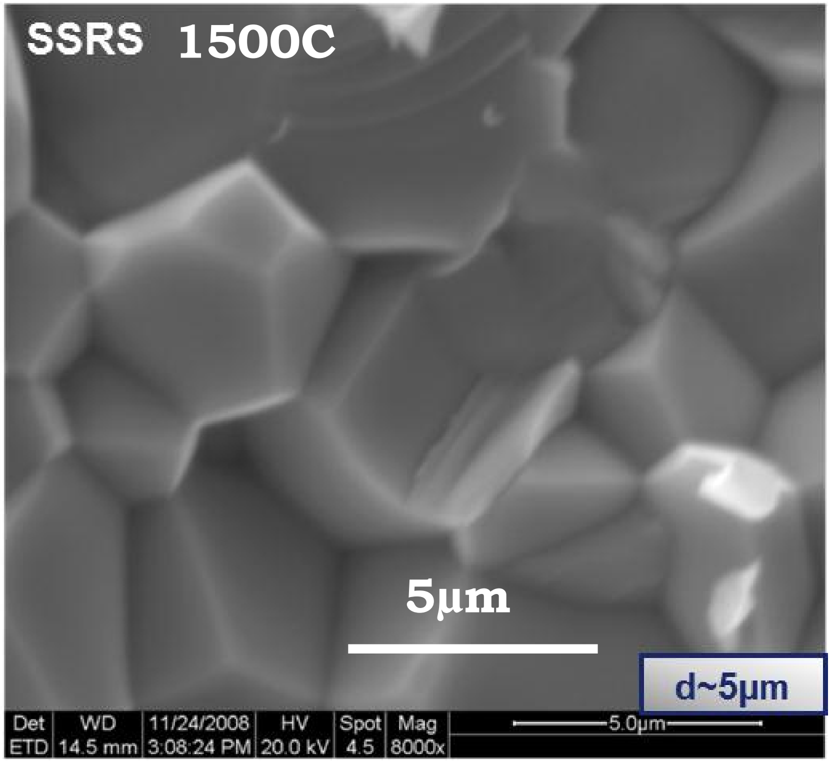


Colorado School of Mines (CSM) U.S Patent Application: US 2016/0036064 A1 "Cost Effective Solid-State Reactive Sintering Method for Protonic Ceramic Fuel Cells"

SSRS vs. Sol-gel Comparison

SSRS produces denser, larger-grained BZY20 at significantly lower sintering temperatures than the more complex and expensive sol-gel process alternative



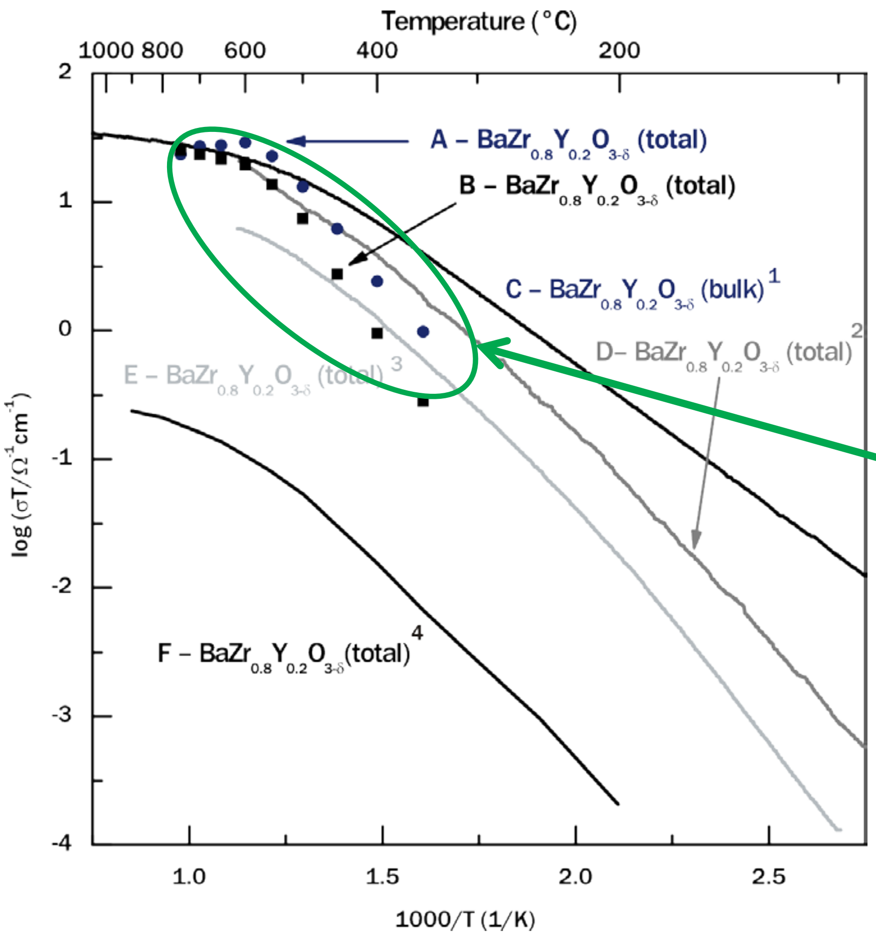


SSRS with 1wt% NiO sintering aid, both samples sintered for 24 hours

SSRS-derived materials demonstrate high conductivity

Technical Accomplishments and Progress

Arrhenius plots of total conductivity for BZY20 pellets obtained by SSRS method with 2wt% NiO as sintering aid by sintering at 1500°C for 24 hrs, and compared with total or bulk conductivities for recent reported BZY20 pellets



Conductivities at 600°C

A. Wet Ar – 33 mS/cm

B. Dry Ar – 22 mS/cm

SSRS materials meet or exceed best literature reports

[1] K.D. Kreuer et al, Solid State Ionics, 2001, 145, 295

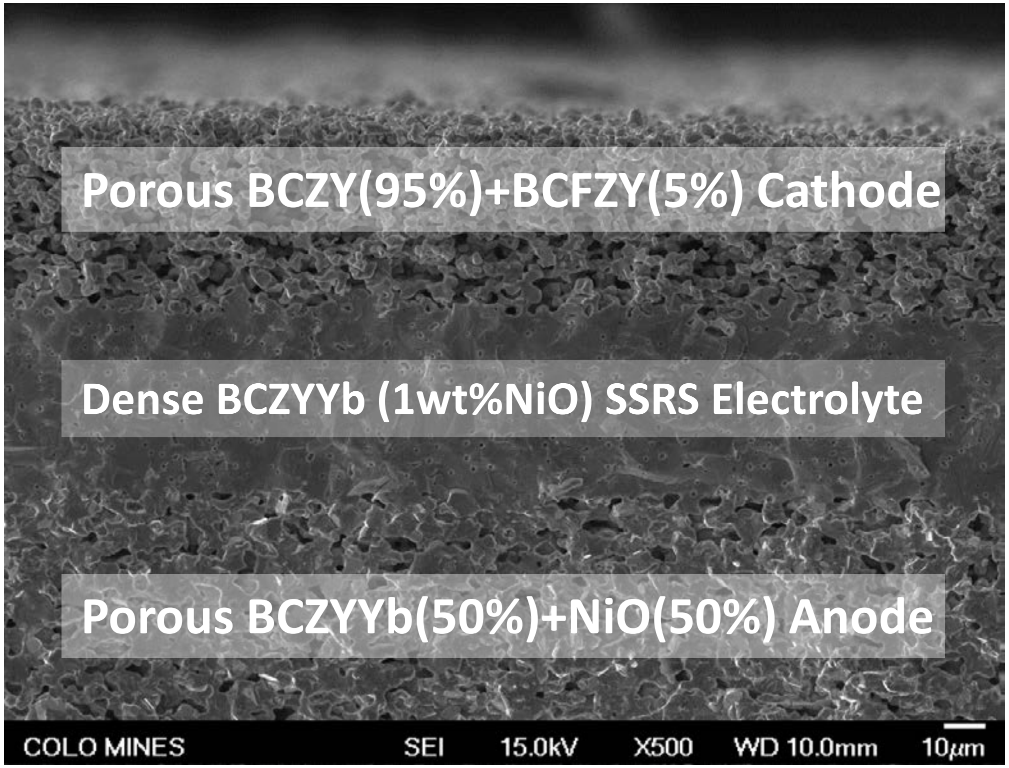
[2] Y. Yamazaki et al, Chem. Mater., Articles ASAP

[3] P. Babilo et al, J. Mater. Res., 2007, 22(5), 1322

[4] S.W. Tao et al, Journal of Solid State Chemistry, 2007, 180, 3493

Example SSRS PCFC Cross-Section

Produced from raw unreacted powder precursors of $BaCO_3$, CeO_2, ZrO_2, Y_2O_3, Yb_2O_3, and NiO, CeO_2, and Fe_2O_3 in a single-step via SSRS (1350°C for 12hrs)



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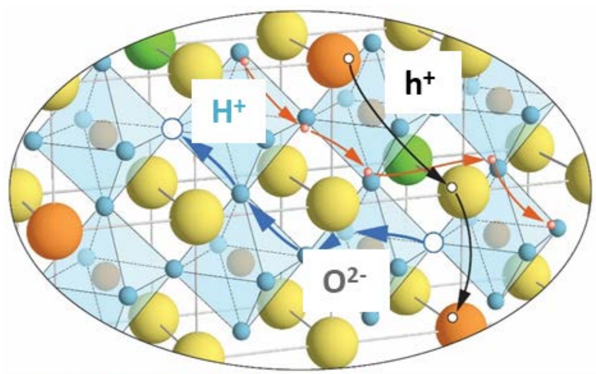
The Solution to Lack of Good Anode for PCEC

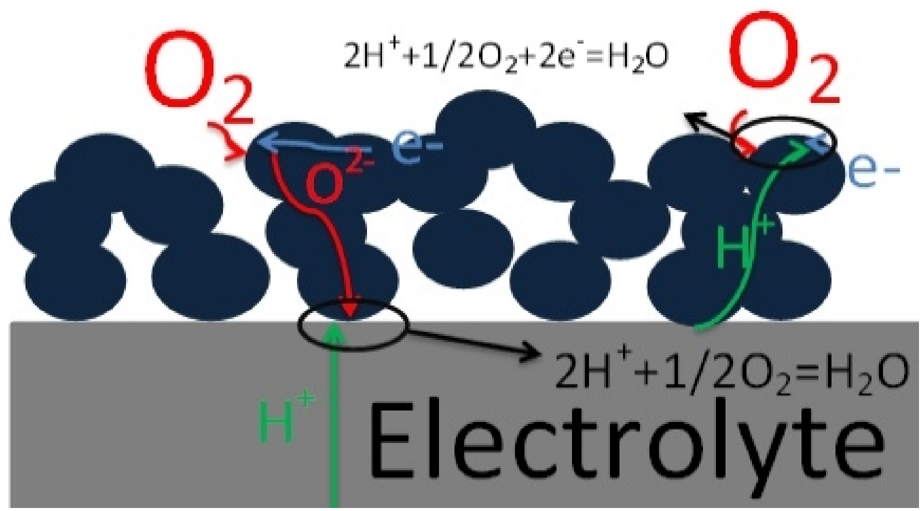
CSM Team has developed a triple conducting oxide based on BCFZY material. Co/Fe doping has enabled hole conduction within BZY structure

$BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ = BCFZY



A-site cation: Ba
B-site TM dopants: Co, Fe
B-site acceptor dopant: Y

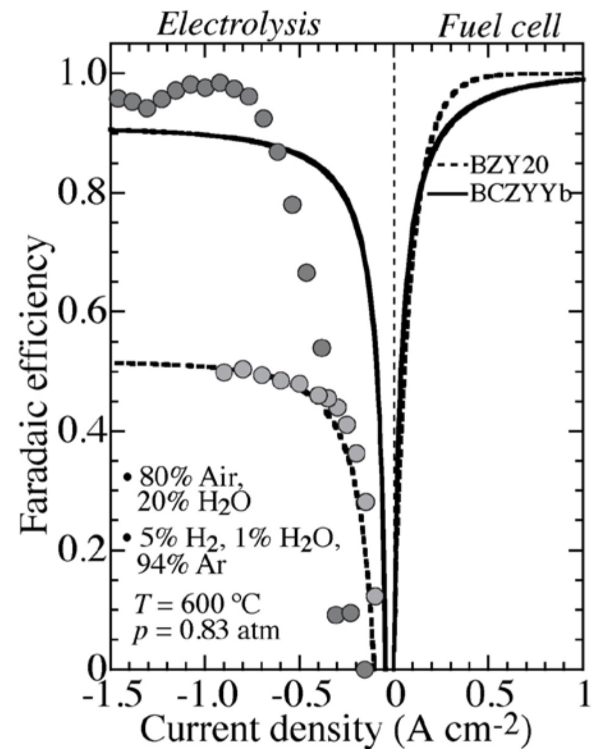
$H^{+}\downarrow \quad h^{+}\downarrow \quad O^{2-}\uparrow$

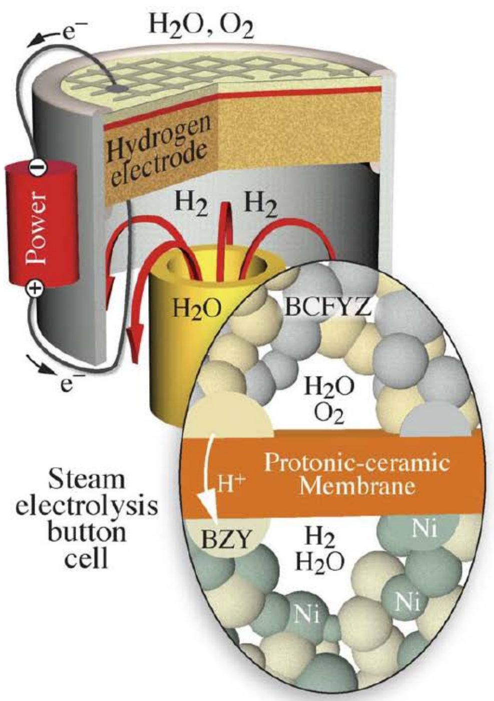


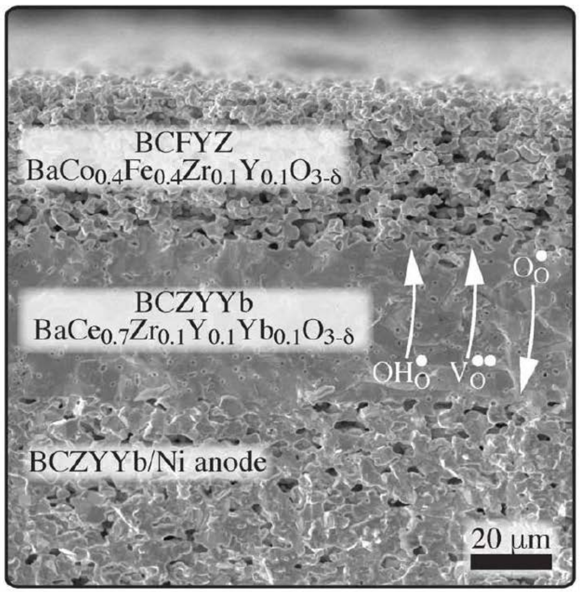
CSM U.S. Provisional Patent Application US 14/991027 "Triple Conducting Cathode Material for Intermediate Temperature Proton Conducting Electrochemical Devices"

Key Breakthrough: The Electrolyte Matters for Electrolysis Performance!

Test results have confirmed modeling work that at temperatures below 600°C, BCZYYb can achieve high faradaic efficiencies (i.e., low electronic leakage) as an electrolyzer membrane.







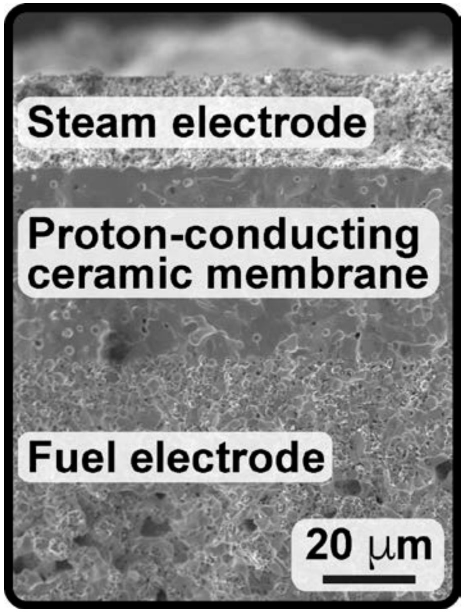
Protonic-ceramic membrane-electrode assembly

H. Zhu, S. Ricote, C. Duan, R. P. O'Hayre, and R. J. Kee, Defect Chemistry and Transport within Dense $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) Proton-Conducting Membranes, JES, volume 165, issue 10, F845-F853

Electrolyte Optimization

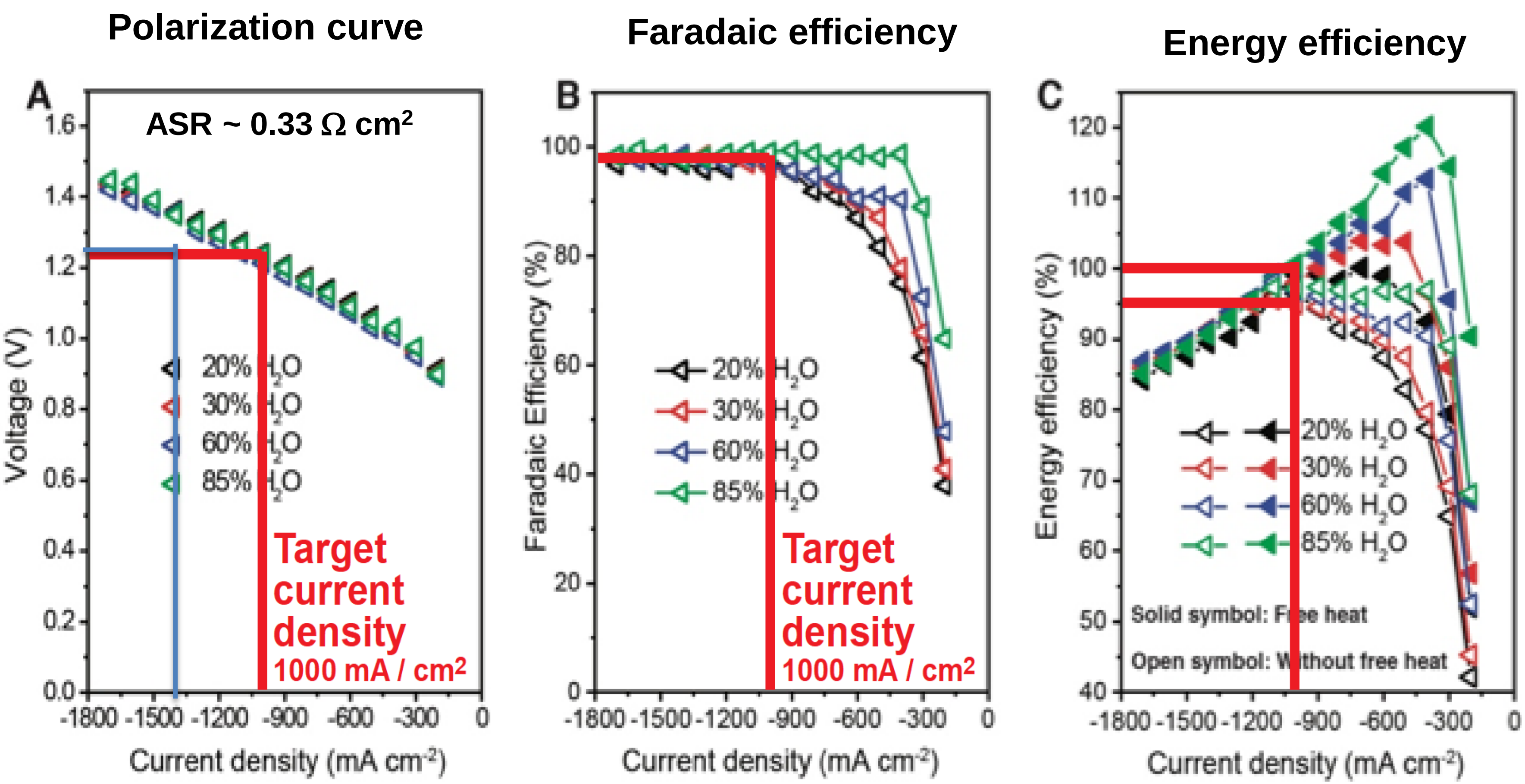
Milestone M1.1.1: Downselect electrolyte composition has progressed (75% complete)

- Electrolyte Layer
  - $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-d}$ (BCZYYb-7111)
    - Minimal electronic leakage at target operation
    - Also exploring BCZYYb-4411 composition
- Composite fuel electrode:
  - Ni + BCZYYb-7111 "cermet"
  - Mechanical support
- Composite steam electrode:
  - $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Yb_{0.1}O_{3-d}$
    - 80 wt-% BCFZY-44111
  - 20 wt-% BCZYYb-7111



Intermediate Cell Performance Targets

Milestone M1.1.2: Faradaic efficiency > 85% and electrical efficiency > 75% at 1 A / cm^2 were achieved

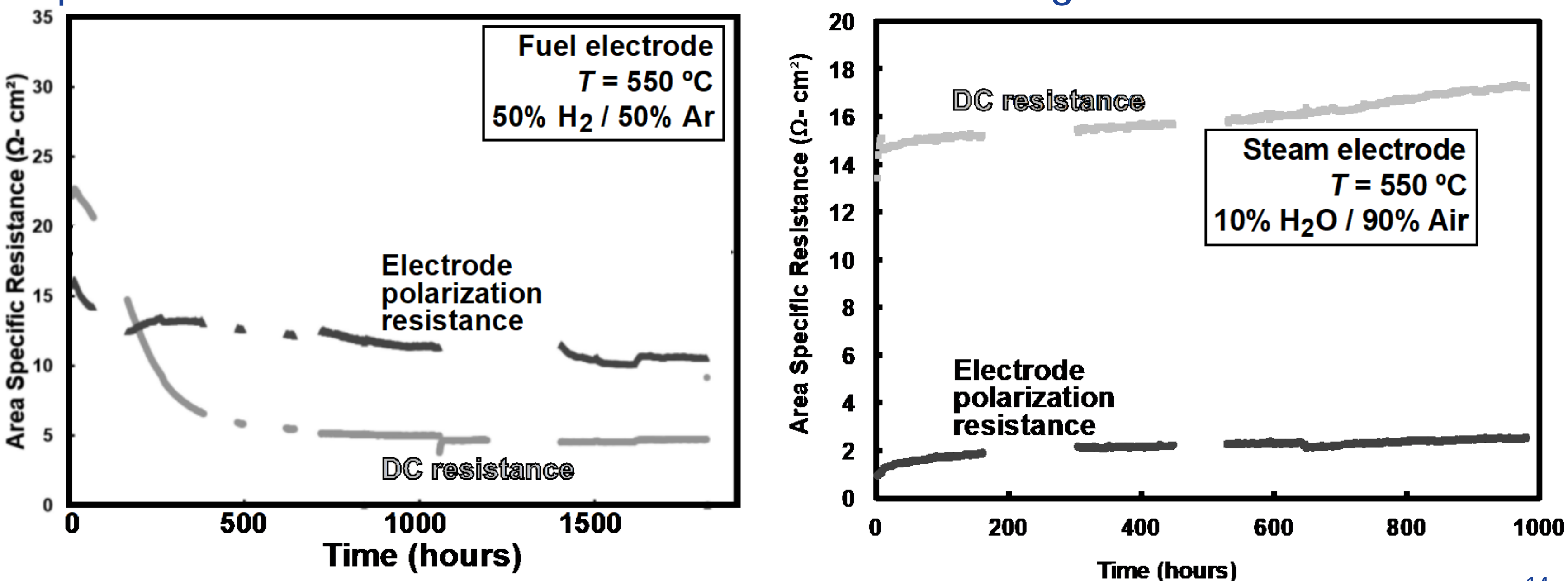


Technical Accomplishments and Progress

Cell Performance Degradation Studies

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

- Symmetric button cells 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 and electrode-polarization resistance over the 1000 hours of testing



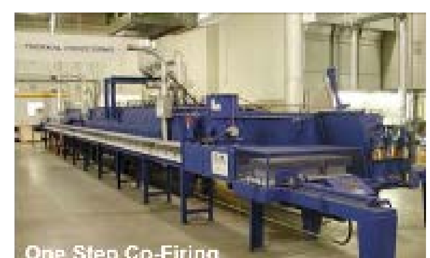
Degradation in fuel (left) and steam (right) electrodes over time

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaborations 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 providing the following 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), Operating as FuelCell Energy**
  - VPS is providing the following expertise in the project:
    - Cell materials & components
    - Stack design
    - Cell/stack pilot manufacturing and QC
    - Cell/stack testing



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

Collaboration and Coordination

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
  - Develop stack models predicting the PCEC performance and temperature profiles
  - 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)

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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
- Continue design of system process flow diagram and complete modeling of stack and sizing of the balance-of-equipment equipment:
  - Develop single-cell PCEC model
  - Update model and extend to stack design as cell materials/architecture become available
  - Validate cell model

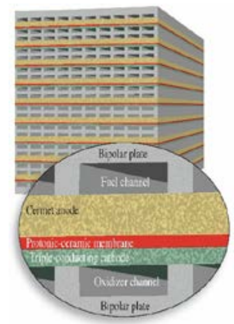
Any proposed future work is subject to change based on funding levels

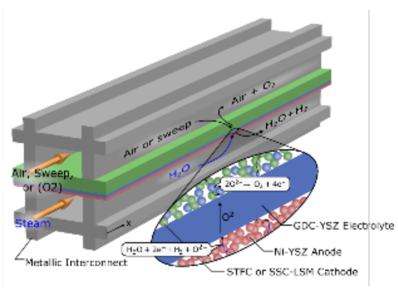
Proposes Future Work

Technology to Market Analysis (TEM)

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

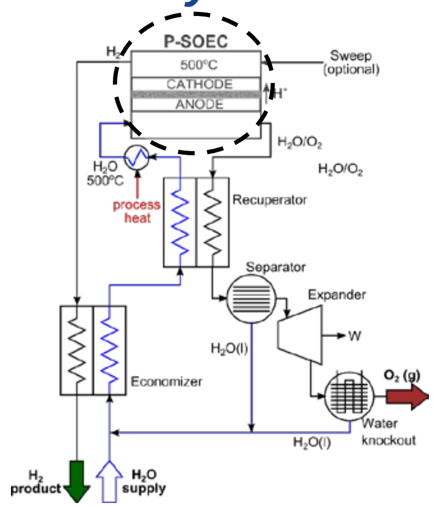
Stack Modeling



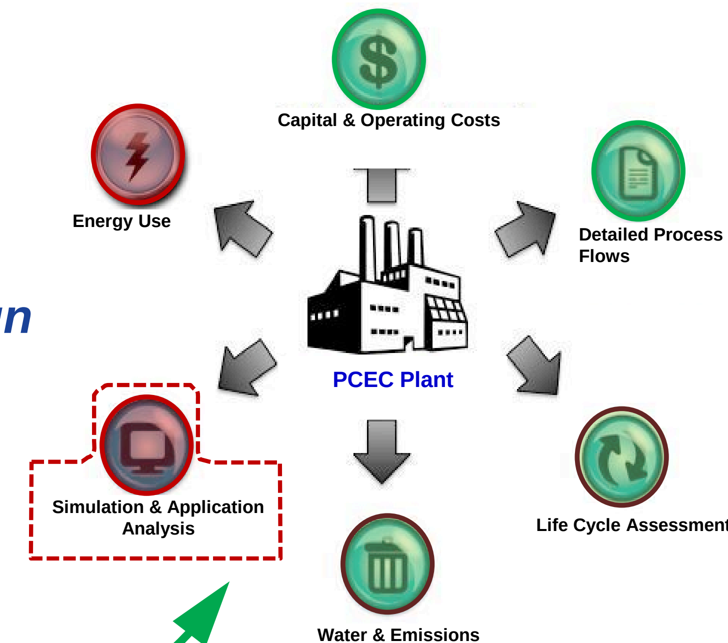


Cell Modeling

Process System Design



Systems-level TEA & LCA



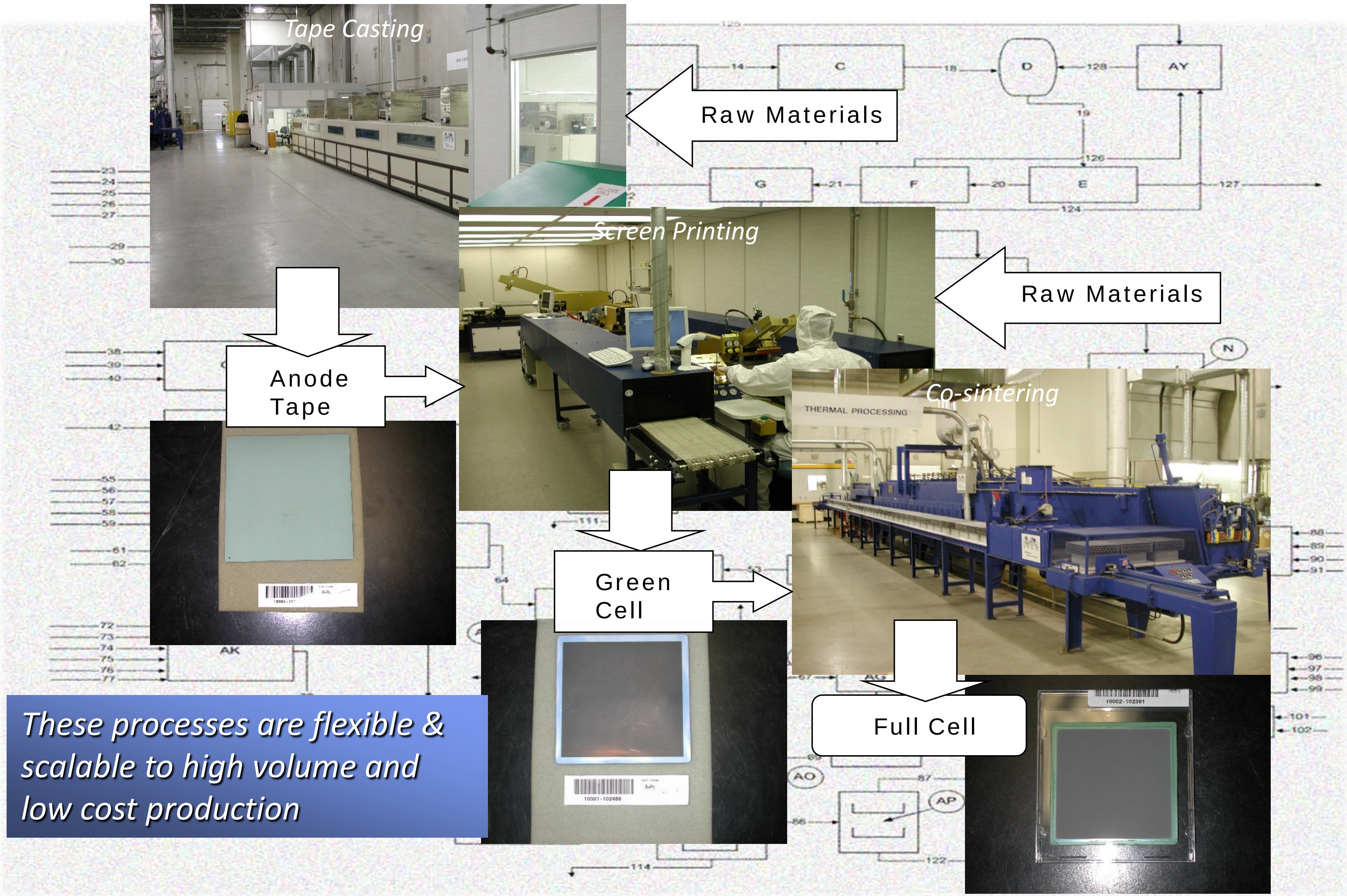
Technology Transfer Activities

Summary

- Work was initiated to identify key degradation issues by testing in symmetric cells
- Project's First Quarter (Q1) Milestone was achieved by completing tests of H_2 & steam electrodes over 1000 hours
- Q3 Milestone was completed ahead of time by showing Faradaic efficiency > 85% and electric efficiency > 75% at 1 A / cm^2 in testing of button cells
- Development of cell area scale up and manufacturing process was initiated
- Activities related to the stack components and design were begun

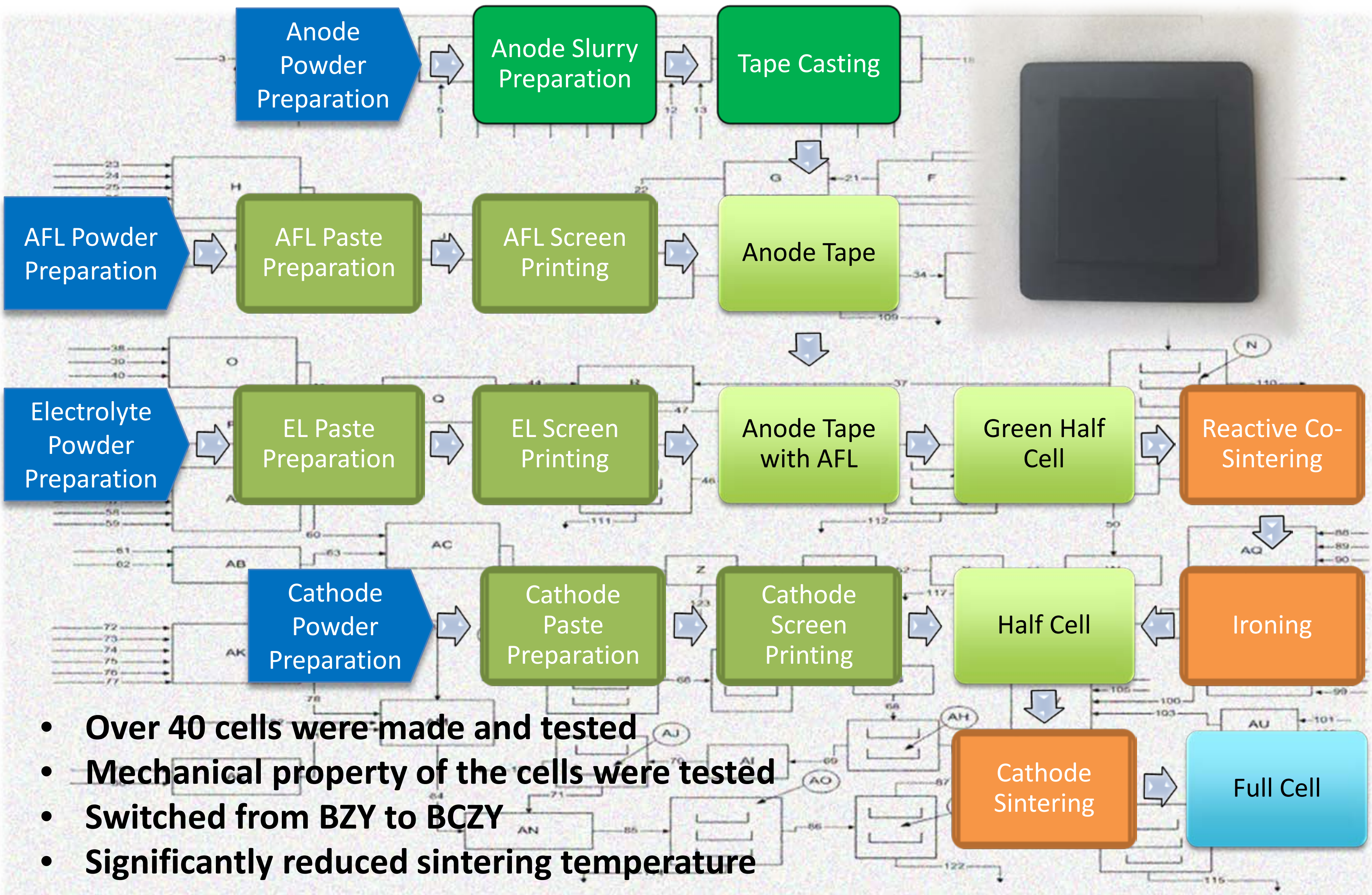
TECHNICAL BACK-UP SLIDES

Pilot Manufacturing at FCE



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

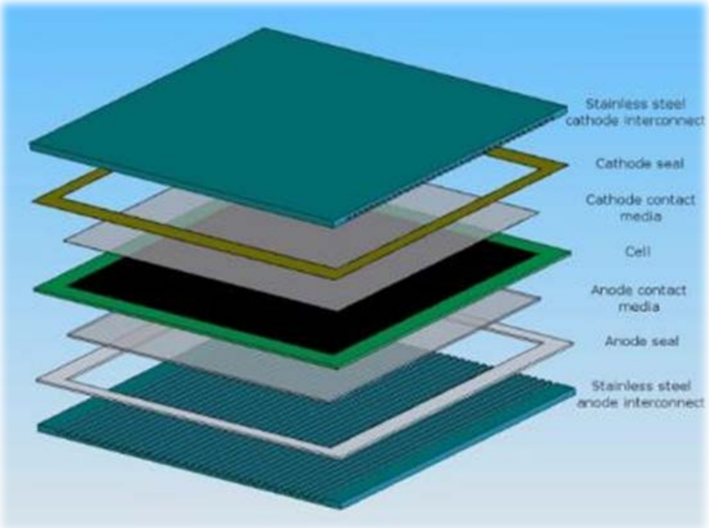
Proton Conducting Cell Process Development

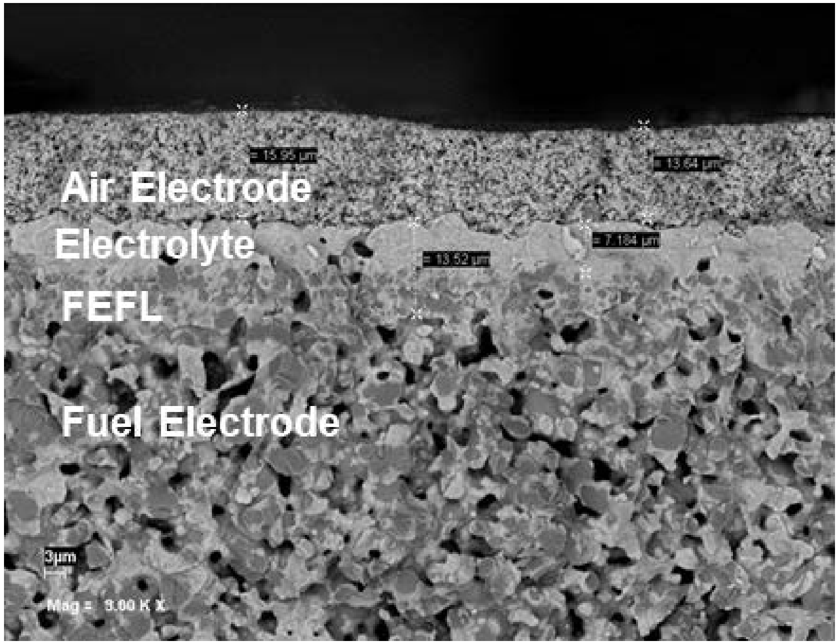


- **Over 40 cells were made and tested**
- **Mechanical property of the cells were tested**
- **Switched from BZY to BCZY**
- **Significantly reduced sintering temperature**

Proton Conducting Fuel Cell 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



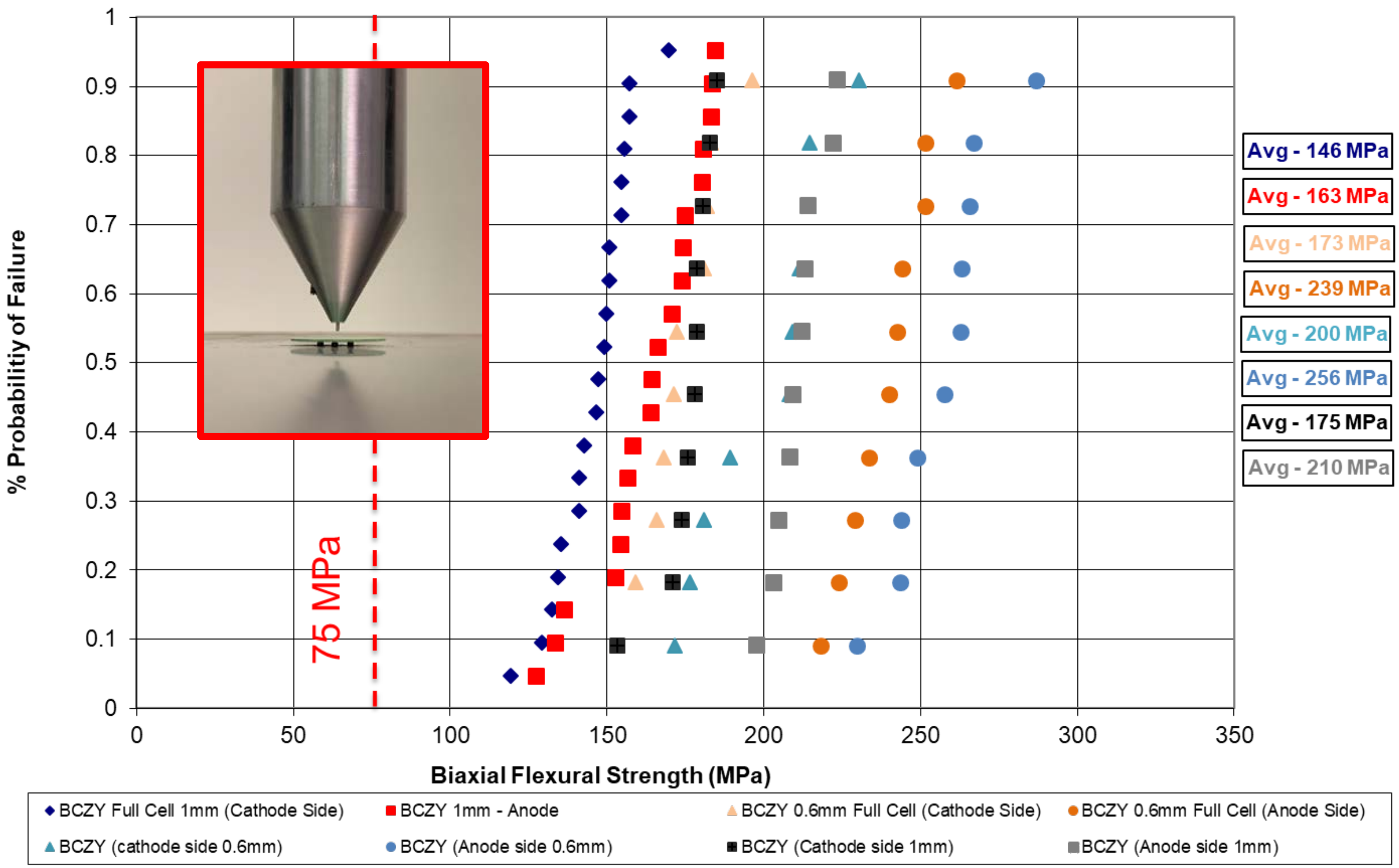


- Cell testing uses same materials and interfaces found in a stack repeat unit
- Cross-flow geometry
- Ferritic stainless steel current collection
- Seal and contact materials same as stack

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

Failure Probabilities of Proton Conducting Cells



PCFC Performance

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