Intermediate-temperature Tubular Direct Ammonia Fuel Cells

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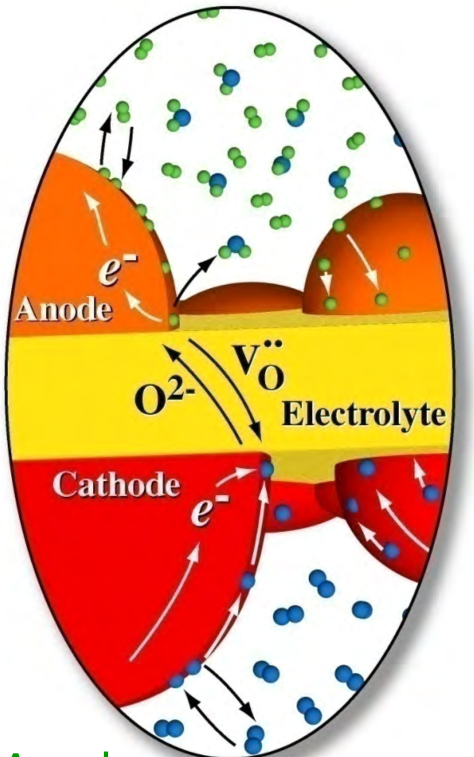
Presentation Outline

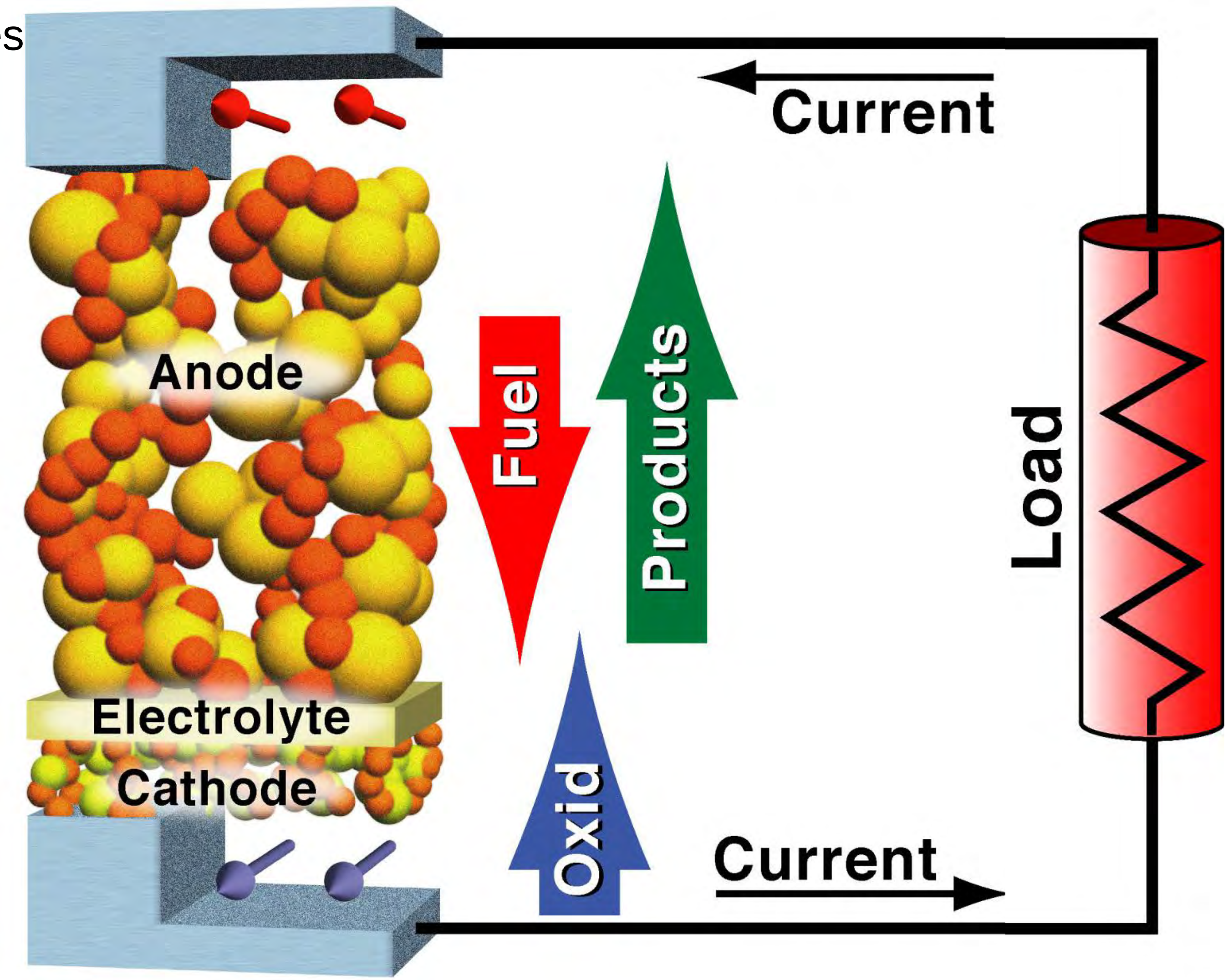
- **Introduction to Ceramic Fuel Cells**
  - Solid Oxide Fuel Cells (SOFCs) vs. Protonic Ceramic Fuel Cells (PCFC)
- **PCFC Materials and Fabrication Overview**
  - Barium zircontate and barium cerate
  - Solid-state reactive sintering
  - Cathode application
- **PCFC Experimental Setup and Results**
  - Test stand description
  - LSCF cathode
  - $LaCoO_3$ infiltrated cathode
- **Future Goals with Protonic Ceramic Fuel Cells**

Ceramic Fuel Cell Overview

Direct “harvesting” of electrons increases energy efficiency as compared to combustion

Three-Phase Boundaries





Anode:

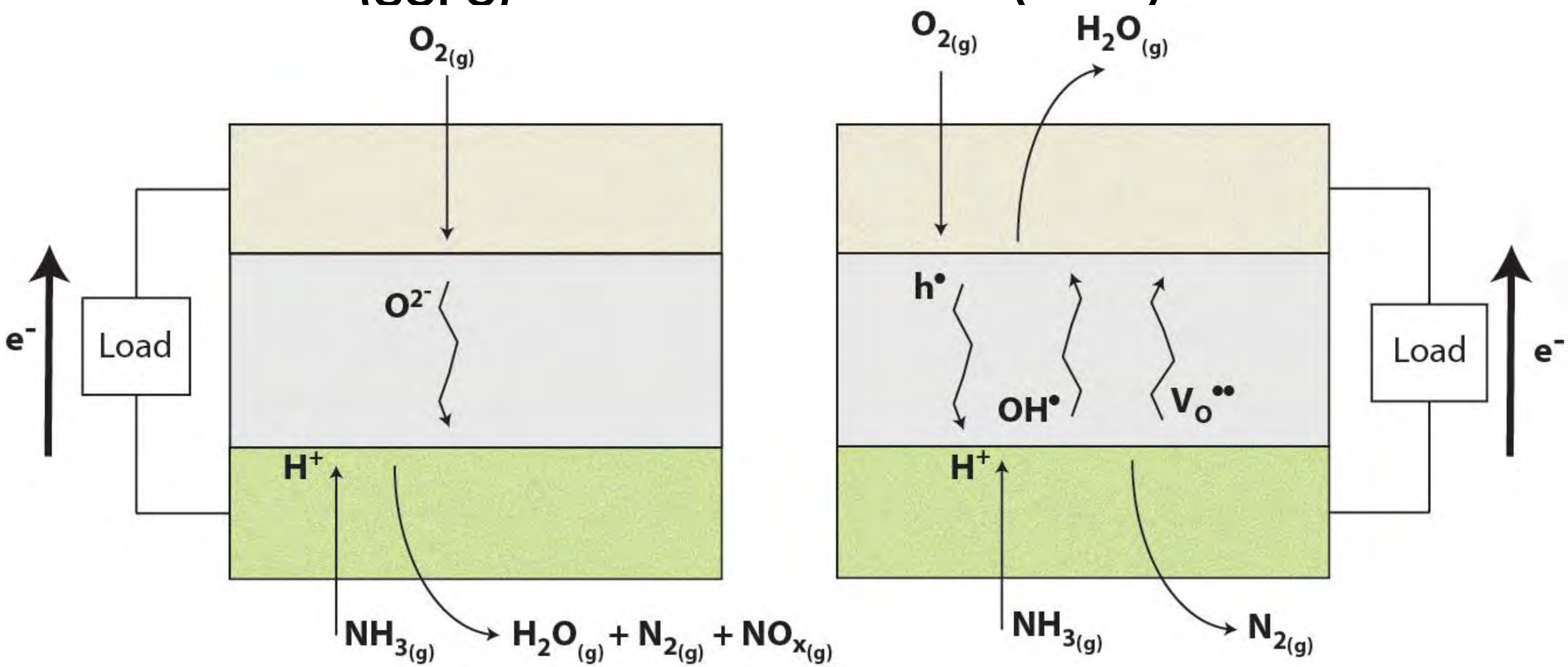
$H_2 + O^{-2} \rightarrow H_2O + 2e^{-1}$

Cathode:

$O_2 + 4e^{-1} \rightarrow 2O^{-2}$

Basic operation of SOFCs and PCFCs under ammonia fuel

Solid-oxide fuel cell (SOFC) | **Protonic-ceramic fuel cell (PCFC)**



- **The choice between oxygen ion or proton conductivity affects the product gas streams**

$$\mathrm{H_2O} + \mathrm{V_O^{\bullet\bullet}} + \mathrm{O_O^{\times}} = 2\mathrm{OH_O^{\bullet}}$$

$$\frac{1}{2}\mathrm{O_2} + \mathrm{V_O^{\bullet\bullet}} = \mathrm{O_O^{\times}} + 2\mathrm{h^{\bullet}}$$

$$\frac{1}{2}\mathrm{H_2} + \mathrm{O_O^{\times}} = \mathrm{OH_O^{\bullet}} + \mathrm{e'}$$

Key differences in SOFCs and PCFCs

- **SOFC**
  - **Higher power densities**
    - **Oxygen ion transport generally quicker than protonic transport**
  - **Well understood technology/processing**
  - **Product gasses occur on anode side**
    - **H_2O, N_2, and possible NO_x**

- **PCFC**
  - **Proton-conduction can create higher-quality product gasses**
    - **NH_3 Fuel : N_2 on anode side, H_2O on cathode side**
      - **No possible NO_x formation**
  - **Can be used as membrane reactor**
    - **Hydrogen separation/pumping**
    - **Fuel de-hydrogenation**
    - **Steam electrolysis**
      - **Ammonia synthesis**

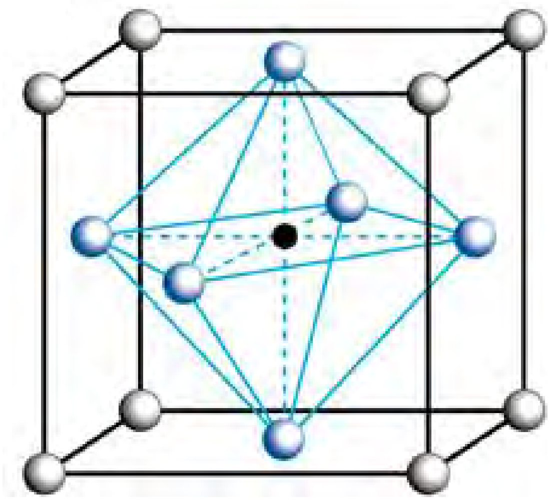
Both power generation and fuel synthesis!

Protonic Ceramic History & PCFC Fabrication

Protonic ceramics of interest: Perovskite ABO_3 structures

CFCC

- $BaCe_{(1-x)}Y_xO_{3-\delta}$ (BCY)
  - High protonic conductivity
  - Instability in CO_2 and H_2O environments
    - Can form barium carbonates/hydrates
    - Problematic for fuel cell operation



Perovskite structure
(Grey atoms: A, Black: B, Blue: O)
Image courtesy of Northwestern University

- $BaZr_{(1-x)}Y_xO_{3-\delta}$ (BZY)
  - Good chemical stability with CO_2 and H_2O
  - Lower protonic conductivity
    - Thought to be from high grain boundary resistance
- $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$ (BCZY)
  - Can have good chemical stability
    - Determined by dopant amounts
  - Generally better protonic conduction than BZY

$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95}$ (BCZY27)

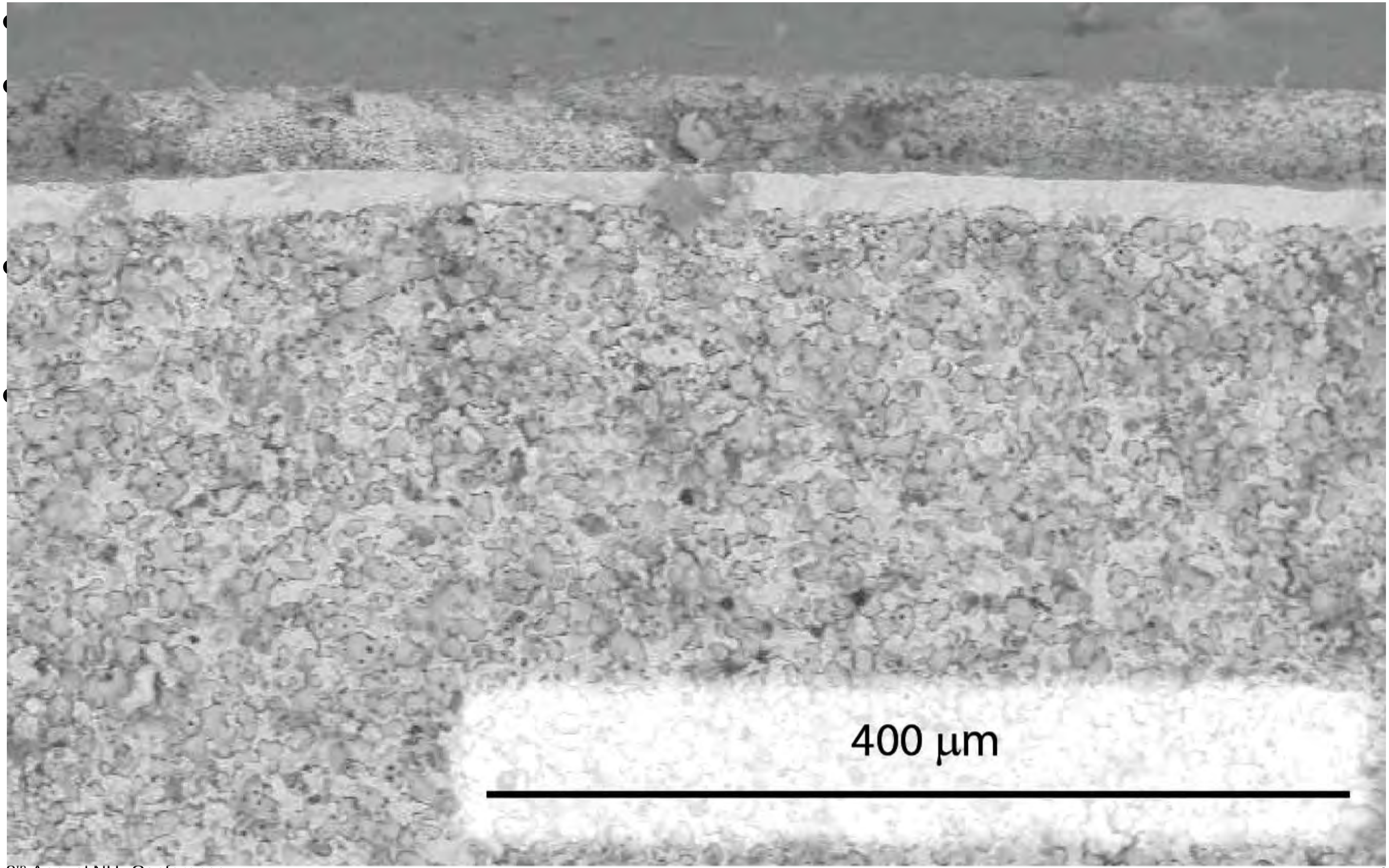
Synthesis of BCZY27 using solid-state reactive sintering

- **Normal sintering temperature of BCZY is far too high**
  - ~1700 °C, can cause Ba to volitize, creating Ba deficient phase
  - Creating dense ceramics very difficult

- **Transition metal oxides extensively shown to lower sintering temps**
  - NiO, ZnO, CuO
  - Lowers sintering temperature of dense BCZY27 to ~1575°C

- **Precursor powders mixed with 1 wt.% NiO**
  - “Green” ceramic shape formed
  - Calcination to desired phase happens simultaneously with sintering

Anode-supported anode-electrolyte membranes supplied by CoorsTek



Cell test preparation and test stand description

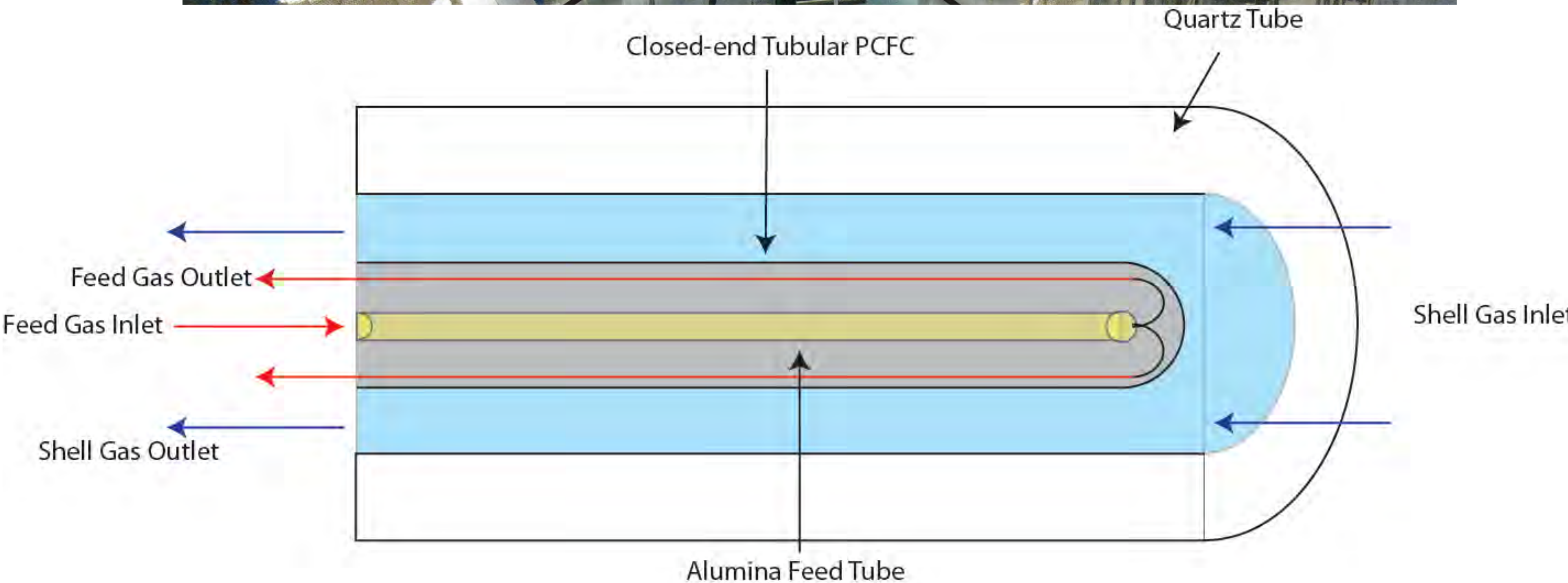
Cold zone sealing accomplished by Ultra-Torr fittings, 4-point wiring accomplished

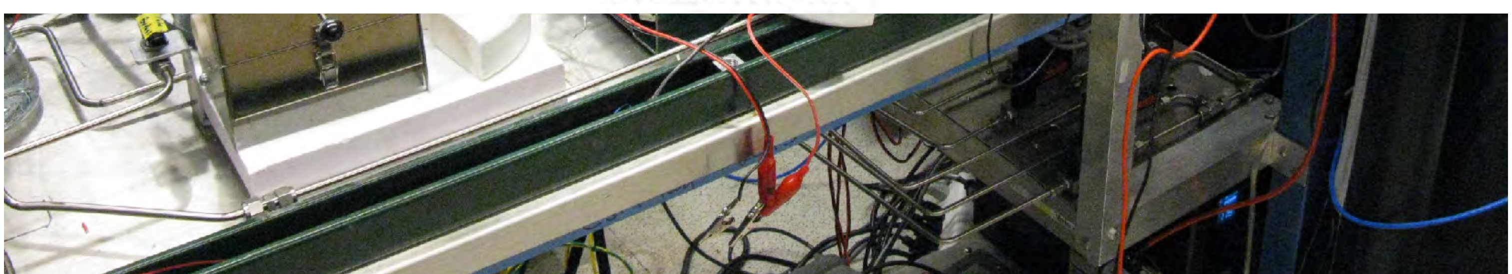
Gas feed tube/anode current collection

Cathode current collection and voltage sense

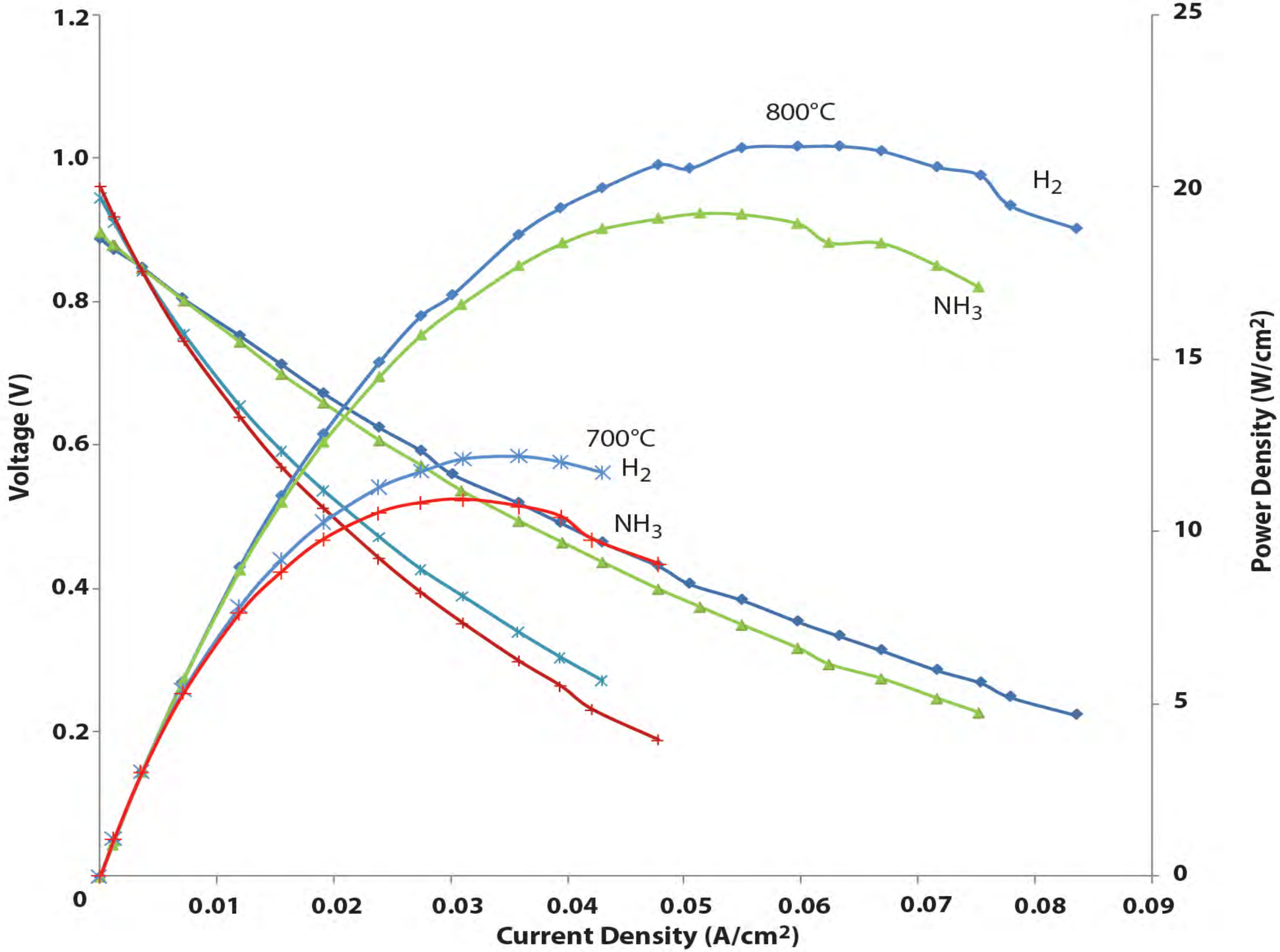
Anode voltage sense

Tube-in-shell reactor allows control over gas compositions for each electrode

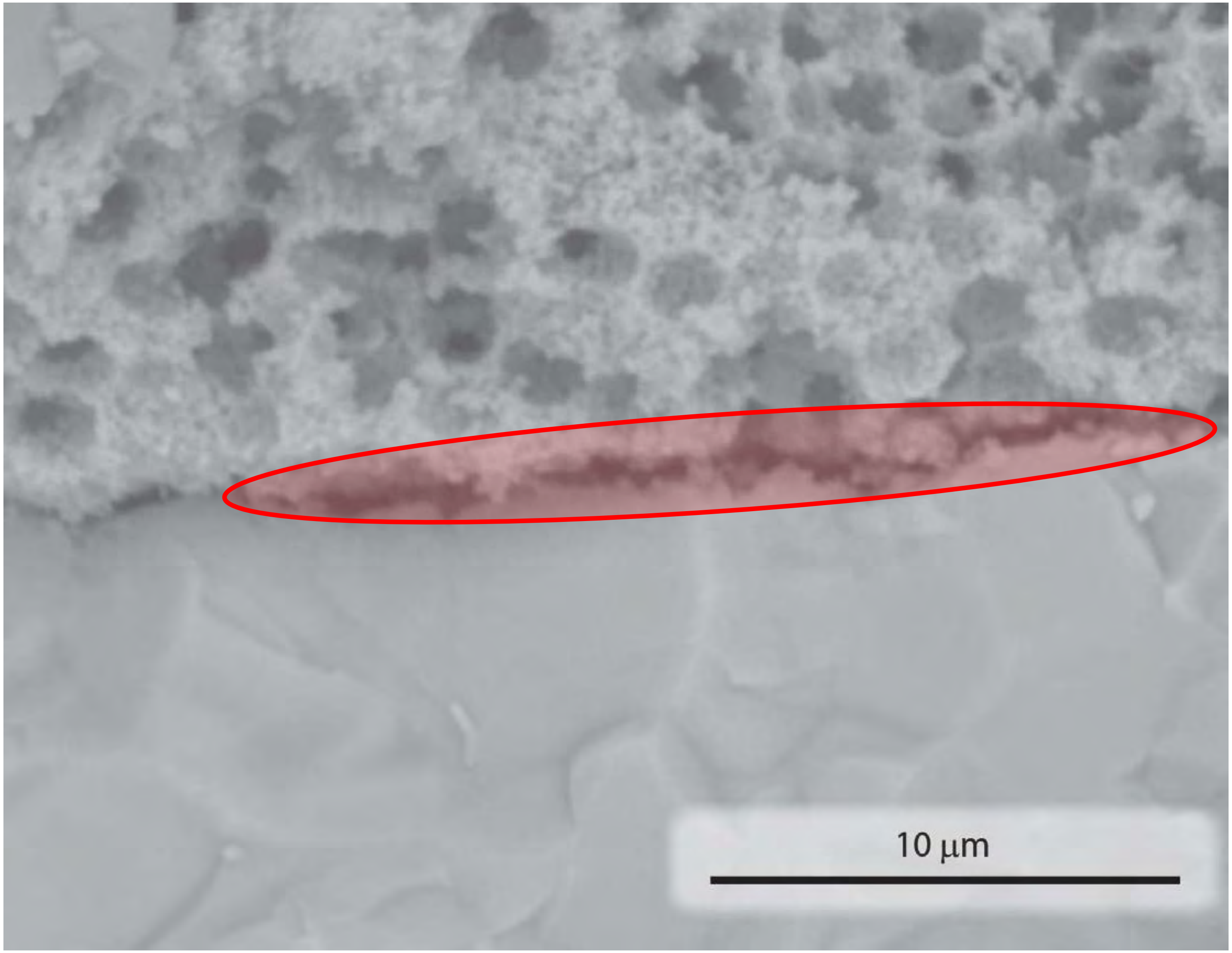




PCFC with LSCF cathode exhibits poor performance on H_2 and NH_3 fuels

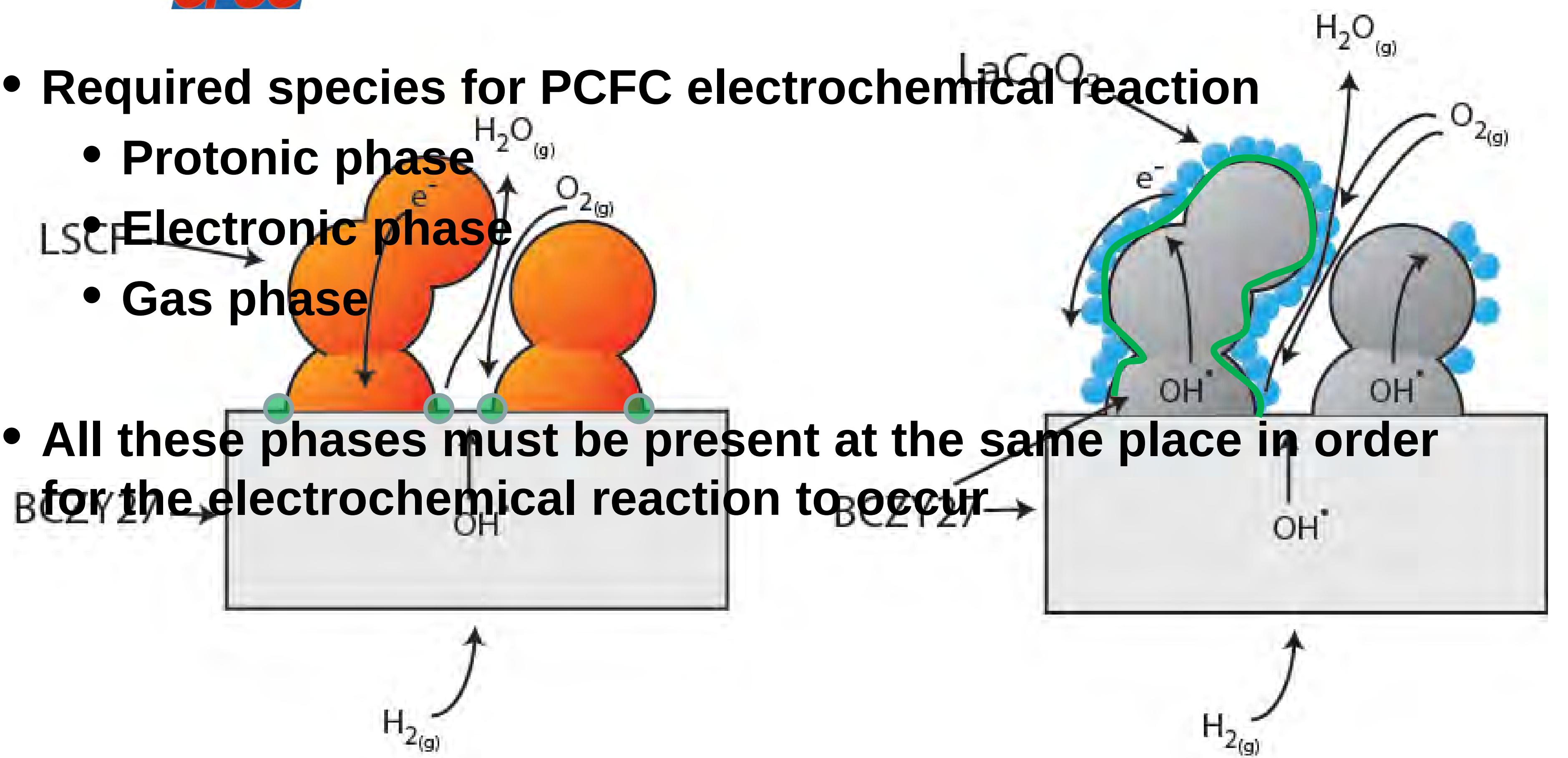


LSCF cathode delaminations reduce three-phase boundary density and reduce cell performance



Traditional SOFC cathodes lack necessary species transport for high three-phase boundary densities

- Required species for PCFC electrochemical reaction
  - Protonic phase
  - Electronic phase
  - Gas phase



- All these phases must be present at the same place in order for the electrochemical reaction to occur

- Increased three-phase boundary densities will likely lower polarization resistance significantly

Previous literature supports infiltrated cathodes

- **Infiltration into a porous BCZY backbone connected to the electrolyte allows protonic transfer past the electrolyte**
  - **Extends three-phase region into the cathode**
- **S. Ricote et. al report that infiltrated $LaCoO_3$ greatly reduces polarization resistance of the cathode**

Cathode material	Electrolyte	Cathode fabrication method	$p(H_2O)$ (atm)	R_p (Ω cm^2)
$LaCoO_3$	BCZY27	Infiltration into porous backbone	0.01 0.03	0.11 0.14
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	$BaCe_{0.9}Y_{0.1}O_{3-\delta}$	Screen printing	0.03	~1.5
		Spray deposition	–	~0.5
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	$BaCe_{0.9}Y_{0.1}O_{3-\delta}$	Screen printing	0.03	~6
	$BaCe_{0.9}Y_{0.1}O_{3-\delta}$	Painting of slurry	0.03	~7.9

Ricote et. al ~ *JPS* 218 (2012) 313-319

- **Infiltrated $LaCoO_3$ a good choice for PCFC cathode**

Fabrication and synthesis of infiltrated $LaCoO_3$ cathode

- **BCZY porous “backbone” roll-coated on electrolyte**
  - **Sintered at 1300°C**

- **La and Co nitrates dissolved in water at stoichiometric amounts**
  - **Cation solution beneficial for small-particle synthesis**

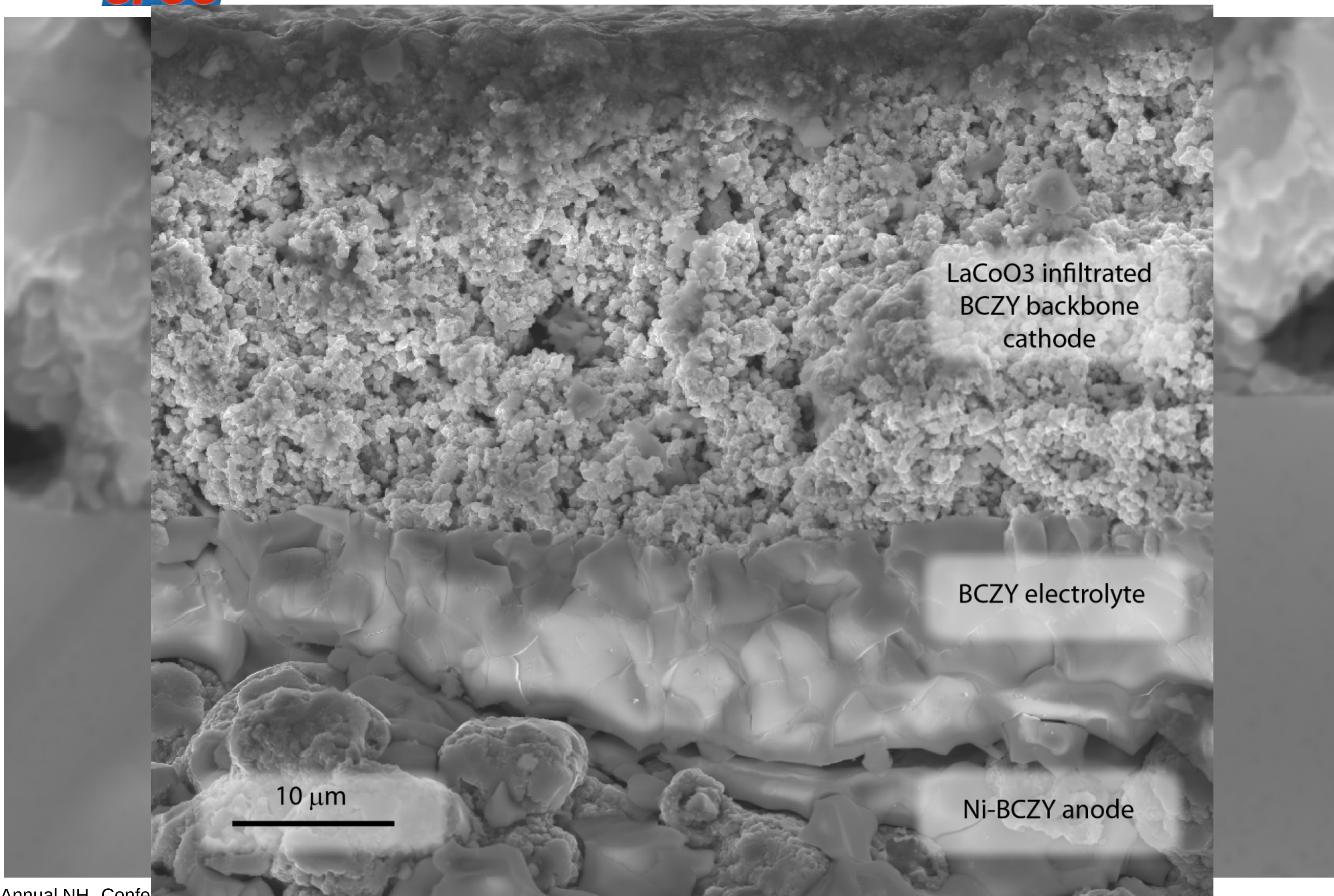
- **Solution infiltrated into BCZY cathode**
  - **Dried at 300°C, repeated 6 times to get adequate loading**

- **Final calcination occurs at 700°C**
  - **Performed in-situ for 2 hours**

Test failed: Calcination of $LaCoO_3$ in electrolyte pinholes shorted anode and cathode

- **Cell initially had electrical isolation between anode and cathode**
- **After 2 hour calcination of $LaCoO_3$, no cell potential present**
  - **Multi-meter test indicates short between anode and cathode**
  - **Resistance of ~26 Ohms**
- **Short remains present even when temperature reduced to 400°C**
- **Short disappears when cell is at room temperature**
  - **$LaCoO_3$ not adequately conductive at room temperature**

Most-mortem SEM images show good microstructure and well-dispersed $LaCoO_3$ nano-particles



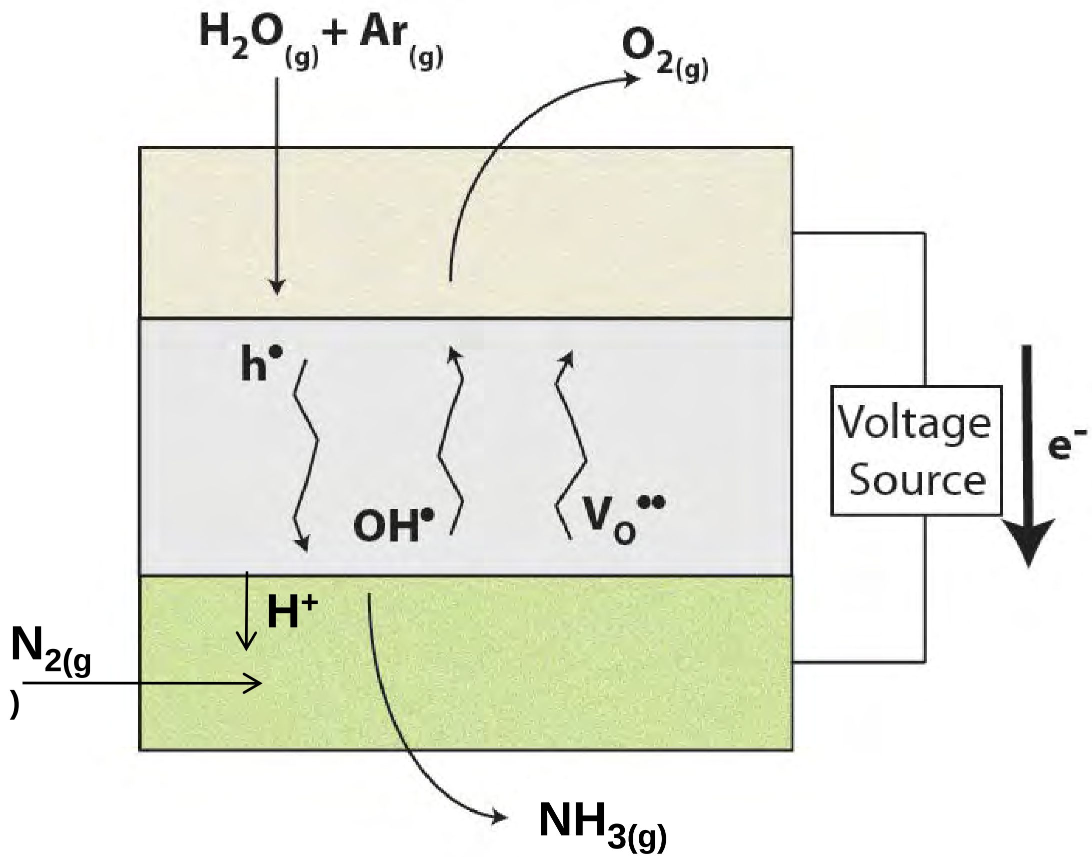
Where to go from here?

- **Resolve macroscopic pinhole issue**
  - **Plug with glass**
  - **Sinter pinholes with small particle BCZY**

- **Finish performance testing as fuel cells**

- **Begin using protonic ceramic cells as electyrolyzers**

Protonic membranes allow a product stream free of diluants



PCFC allows synthesis of anhydrous ammonia!

Acknowledgements and Questions

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Questions?