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Low-Cost Intermediate-Temperature Fuel-Flexible Protonic Ceramic Fuel Cell and Stack

Jianhua TONG

Ryan O'Hayre (lead PI), Neal Sullivan, Robert Braun, Sandrine Ricote

Colorado School of Mines

Golden, CO 80401, USA

jiantong@mines.edu

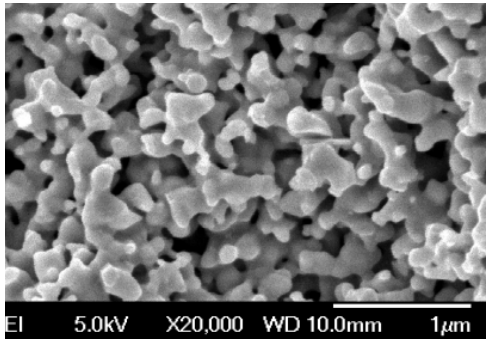
COLORADO CENTER FOR ADVANCED CERAMICS

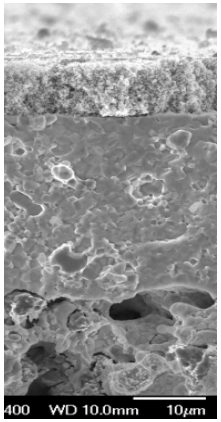
Colorado Fuel Cell Center

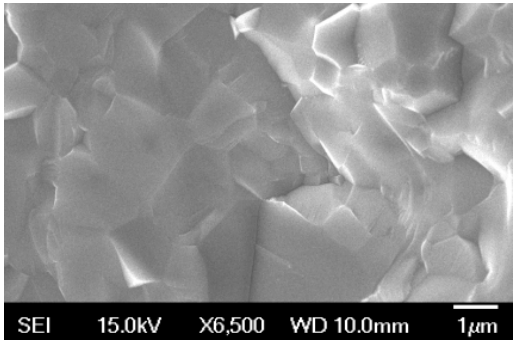
Conclusions

New Triple Conducting Cathode

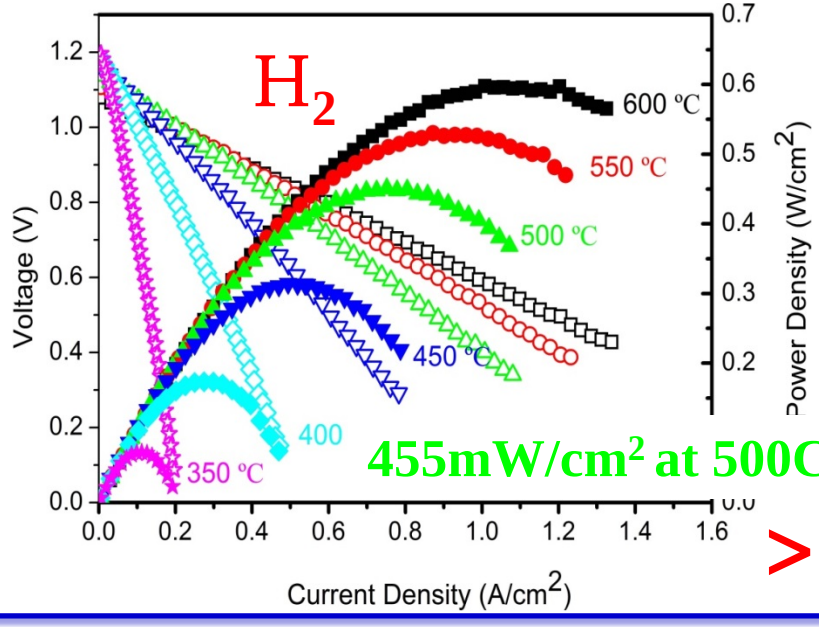
Simplified Fabrication Process



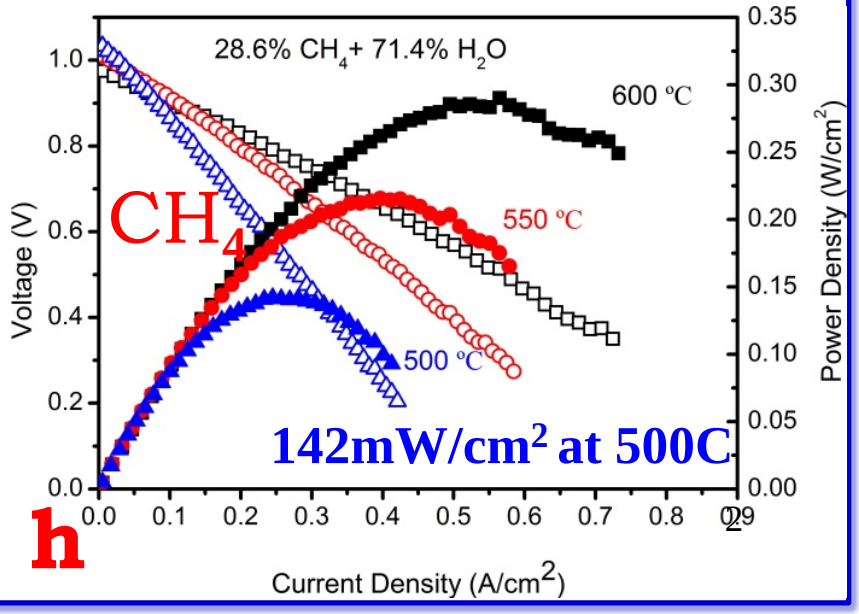




Low Cost Fuel-Flexible Protonic Ceramic Fuel Cells with Excellent Low-T Performance and Durability



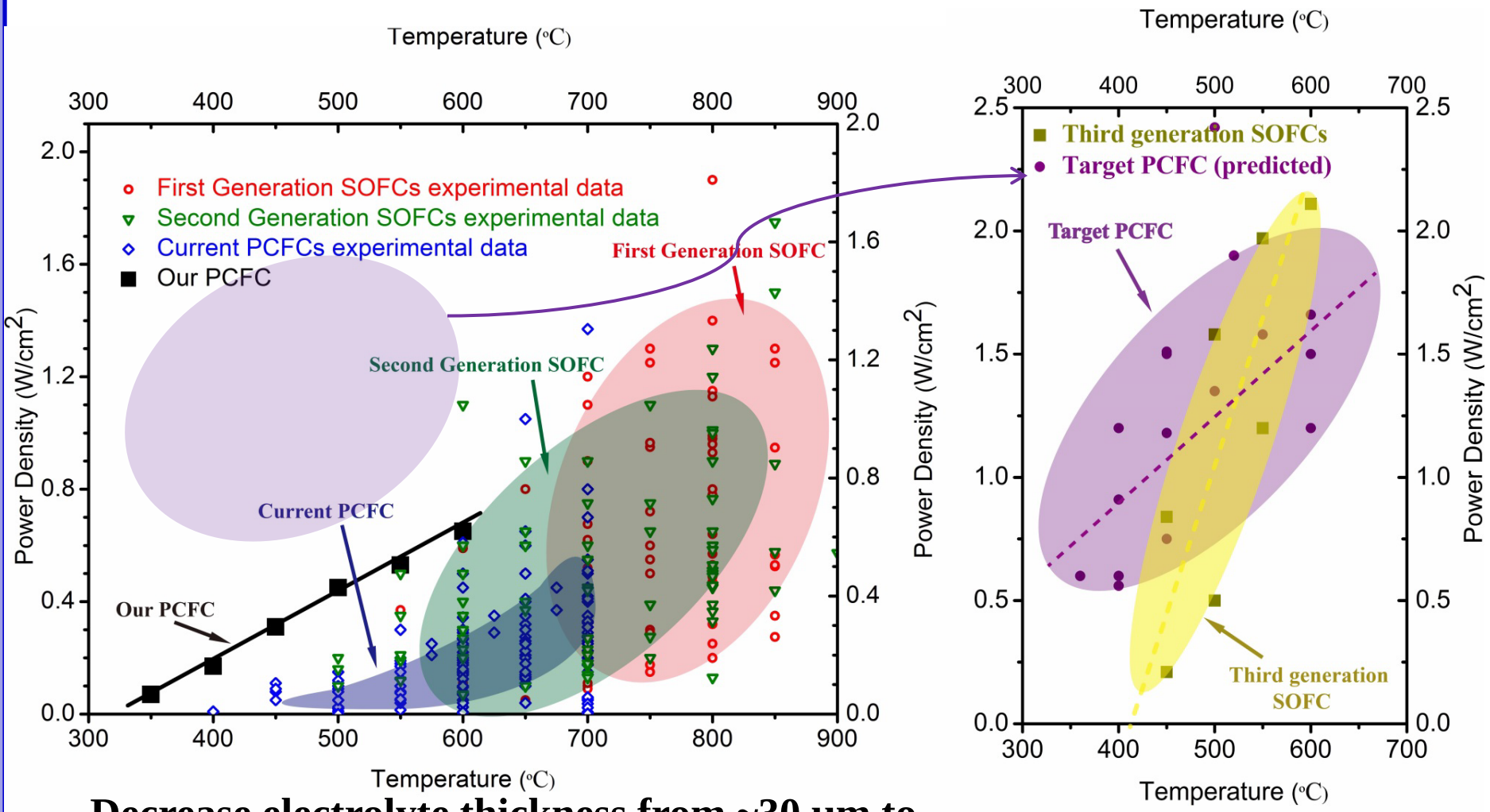
455mW/cm^2 at 500C



142mW/cm^2 at 500C

>1100 h

The Position of Our PCFC Button Cells

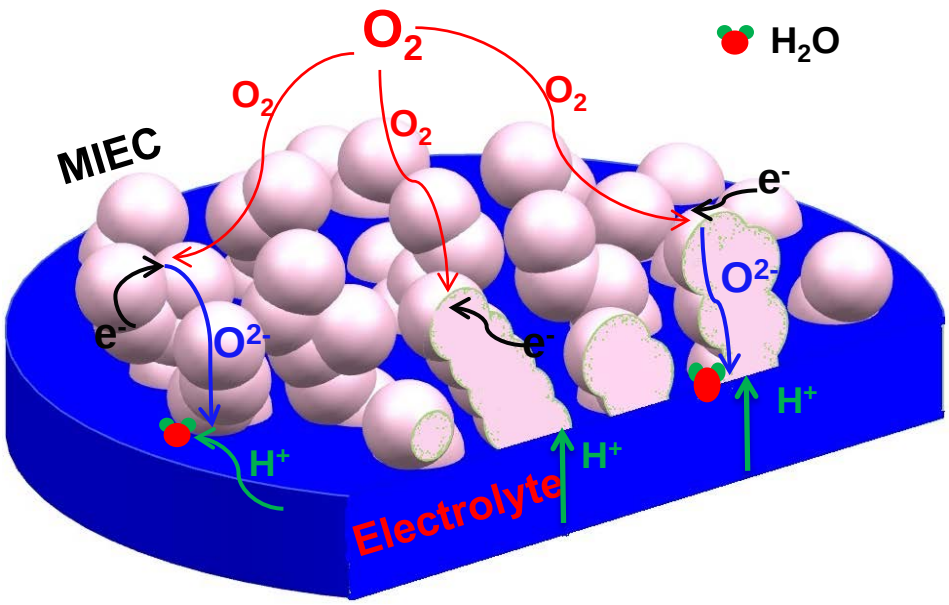


Decrease electrolyte thickness from ~30 μm to 10 μm and keep the same electrode ASR

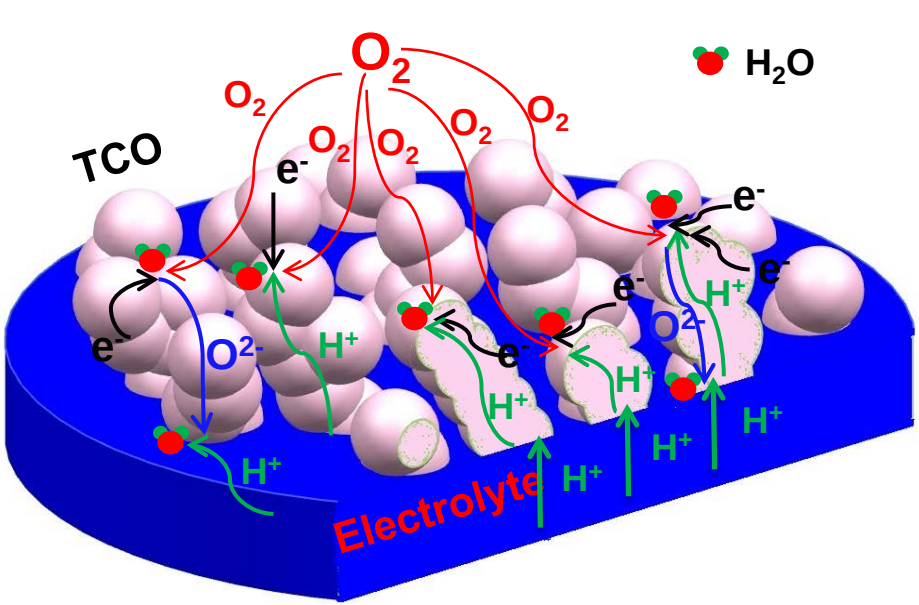
Outline

- Triple Conducting Oxide (TCO) Cathode
- Solid State Reactive Sintering Fabrication
- Performance of Our PCFC Button Cells

ORR Mechanisms on PCFC Cathodes



Traditional MIEC cathode

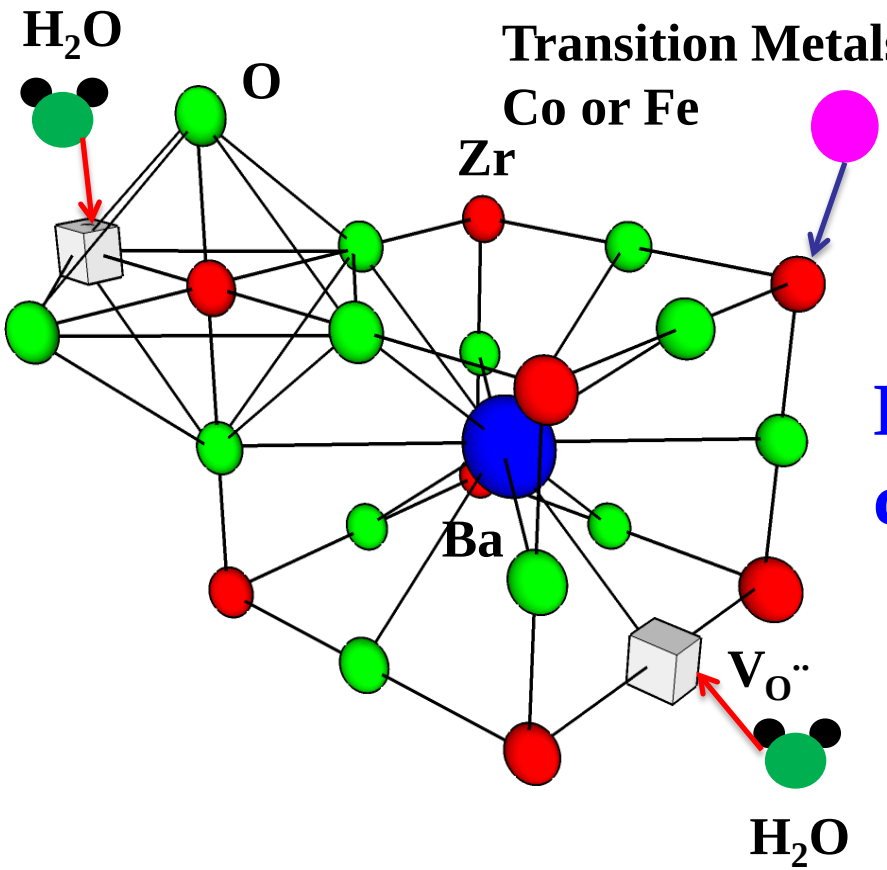


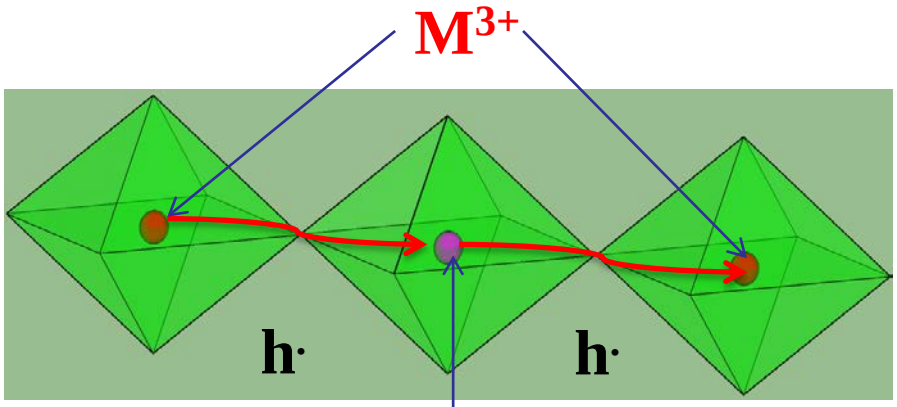
Novel TCO cathode

[1] A. Grimaud et al, *Journal of the Electrochemical Society*, **2012**, 159 (6), B683.
[2] J. Kim et al, *ChemSusChem*, **2014**, 7, 2811.

Design New TCO Cathode Materials

Highly doped barium zirconate protonic ceramic materials with transition metals





Electronic conductivity M^{4+} **Proton conductivity**

$BaCo_{0.4}Fe_{0.4}Zr_{0.2}Y_{0.0}O_{3-\delta}$

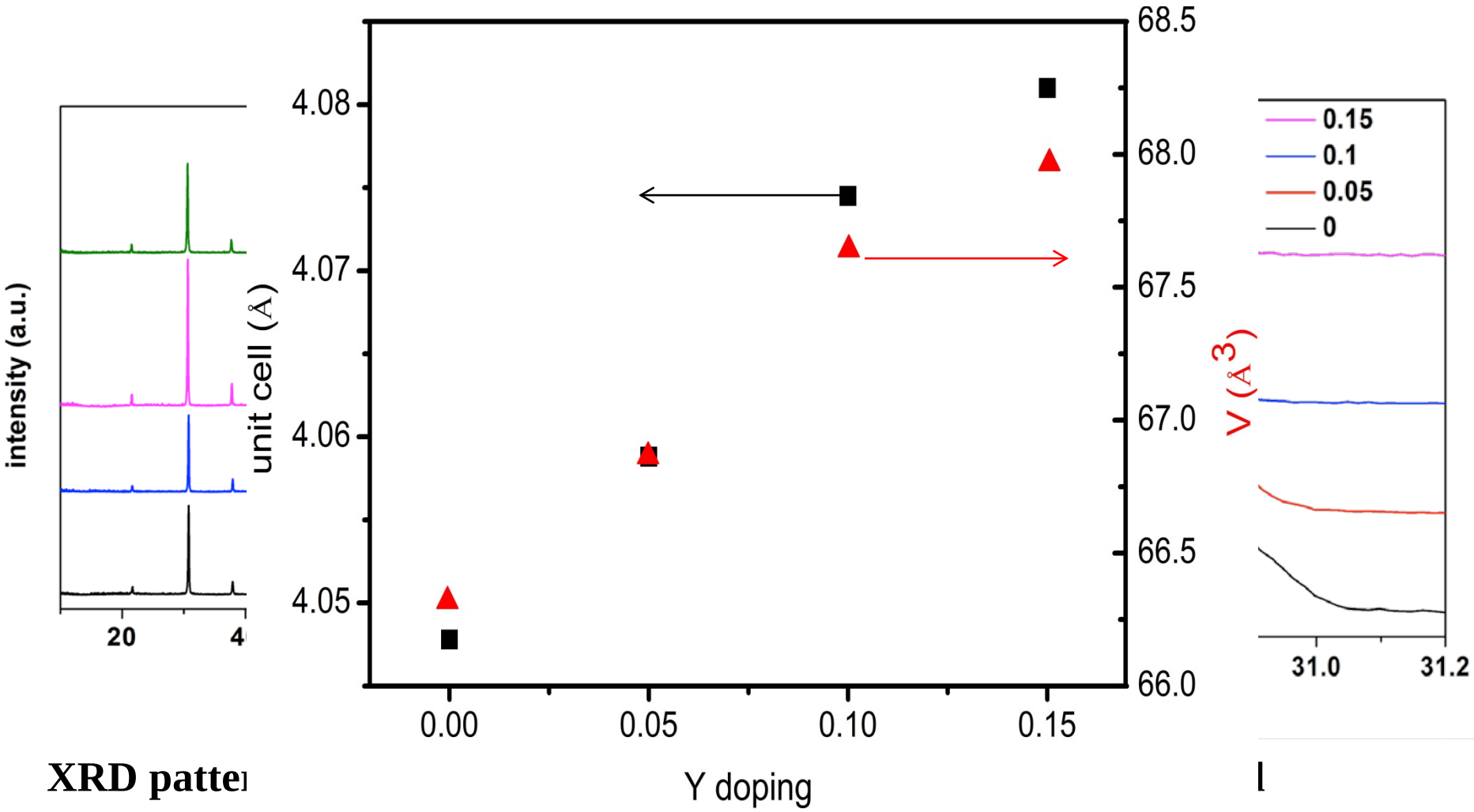
$BaCo_{0.4}Fe_{0.4}Zr_{0.15}Y_{0.05}O_{3-\delta}$

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

$BaCo_{0.4}Fe_{0.4}Zr_{0.05}Y_{0.15}O_{3-\delta}$

[1] J. Tong et al, *US Provisional Patent*, 62101285, *Jan. 08,* **2015**.

Crystal Structures of Cathode Materials

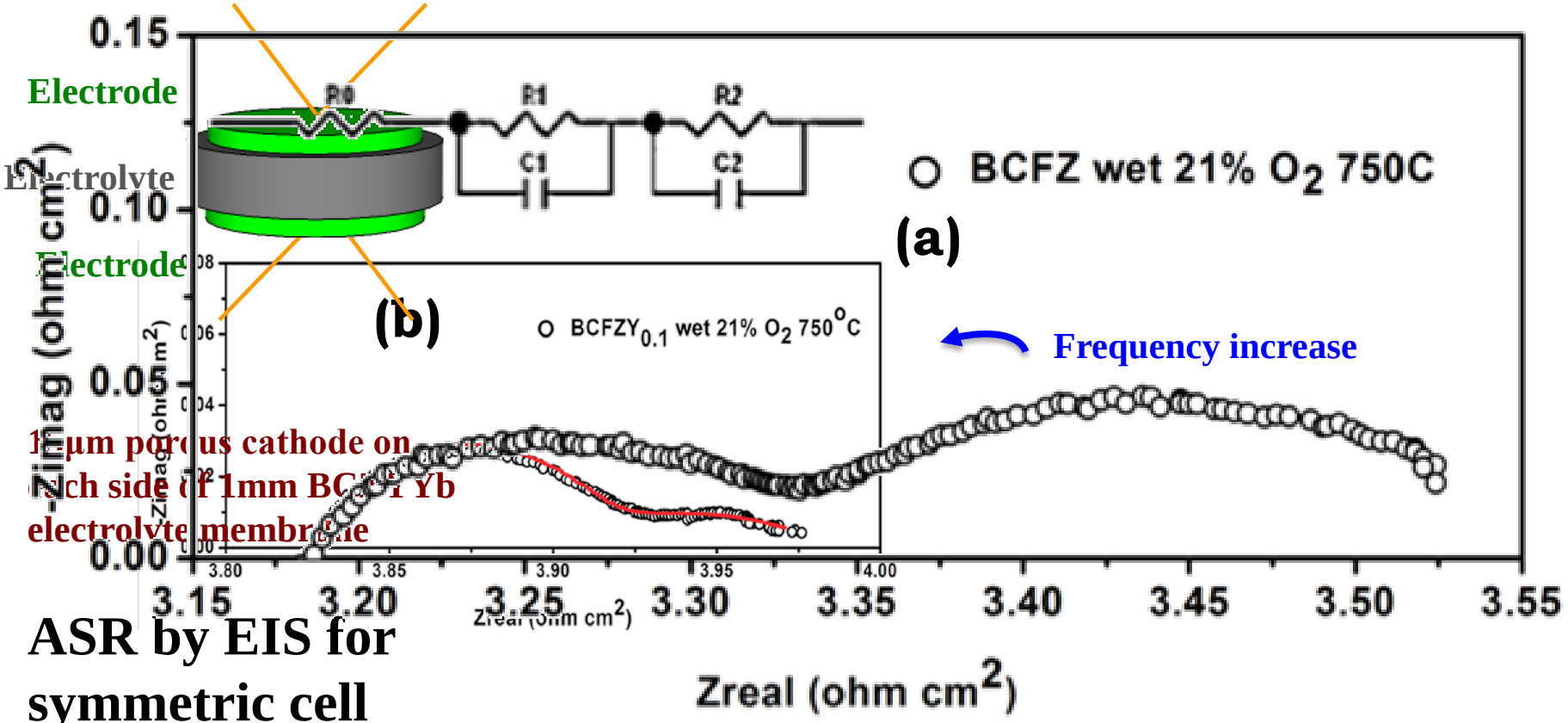


XRD patte l

enlarged peaks around 30 degree (b).

Increase in cell volume with Y benefits proton conductivity

EIS Spectra of BCFZY TCO Cathodes

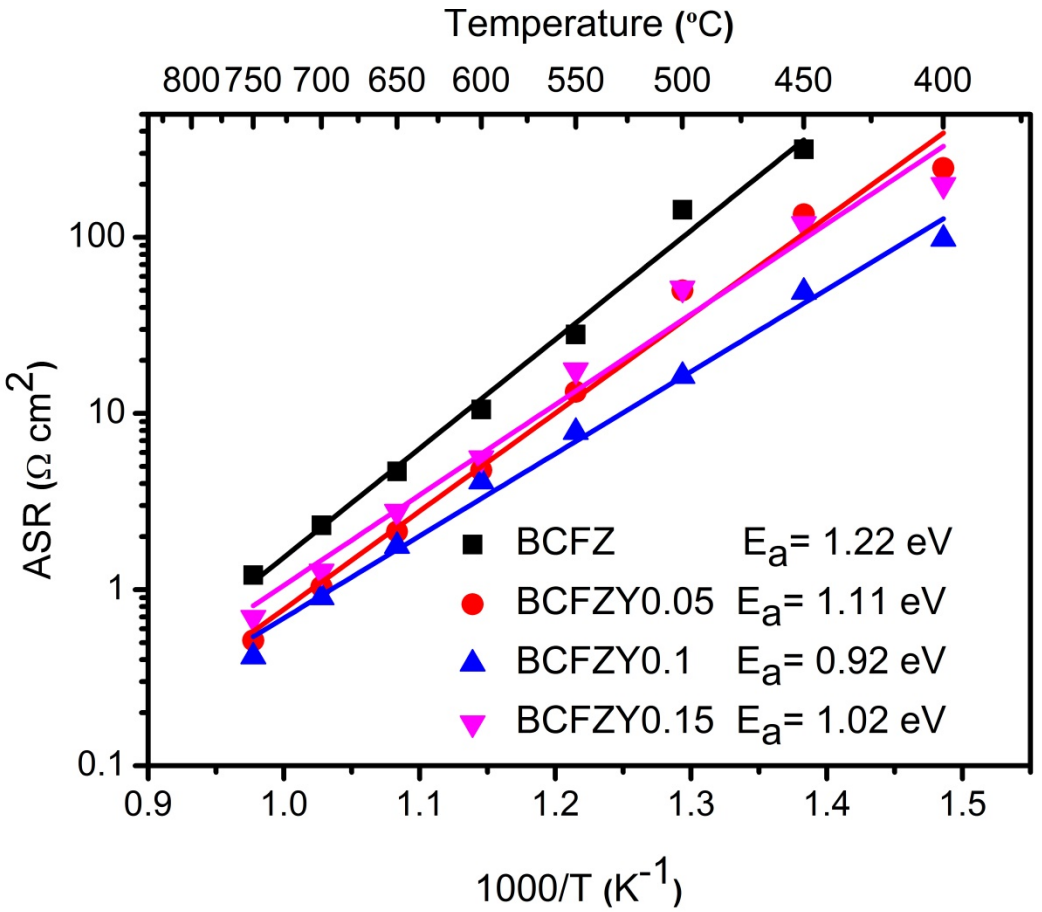


1-µm porous cathode on each side of 1mm BCZY Yb electrolyte membrane

ASR by EIS for symmetric cell

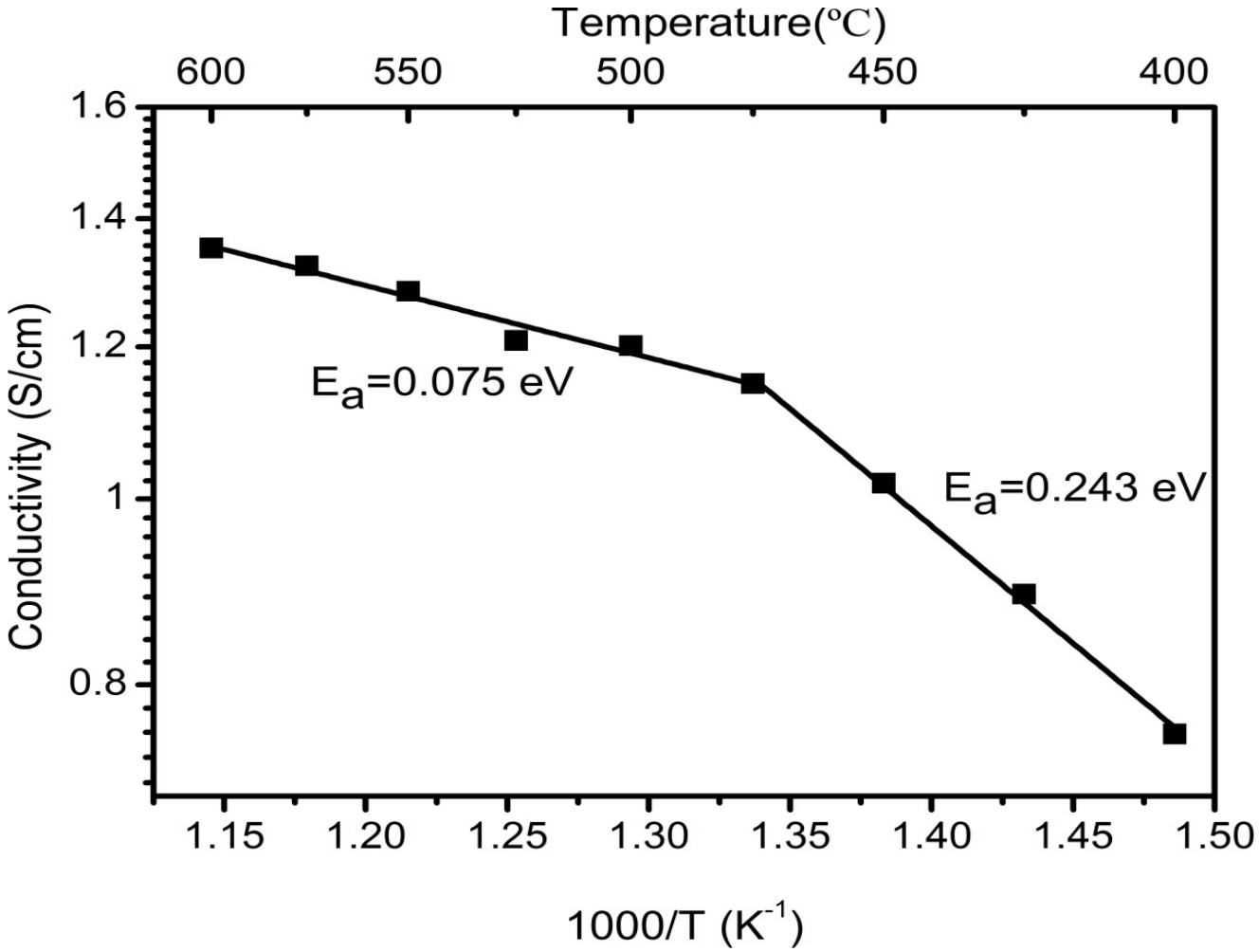
Typical impedance spectrum (T = 750°C) of a symmetrical cell with (a) BCFZ; (b) optimized $BCFZY_{0.1}$ cathode.

Cathode ASR for from Symmetric Cells



Cathode ASR values for the BCFZY symmetric cell in an Arrhenius diagram in air as a function of temperature.

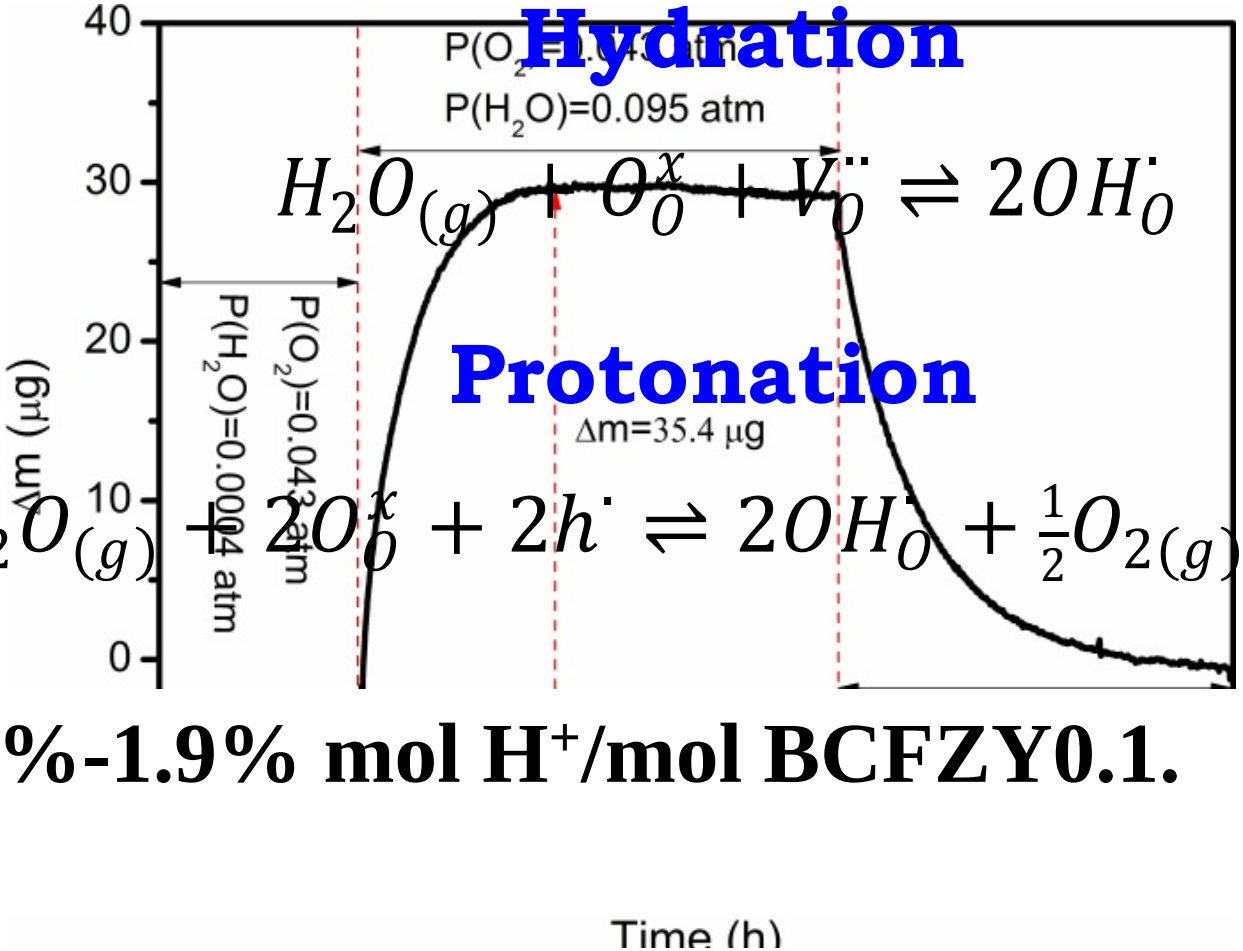
Total Conductivity of BCFZY0.1



DC conductivity of BCFZY0.1 in air measured by the 4 probe method.

BCFZY0.1 exhibits electronic conduction above 475C with low activation energy

Proton Concentration



$$H_2O_{(g)} + O_O^x + V_O^{\cdot\cdot} \rightleftharpoons 2OH_O^{\cdot}$$

$$H_2O_{(g)} + 2O_O^x + 2h^{\cdot} \rightleftharpoons 2OH_O^{\cdot} + \frac{1}{2}O_{2(g)}$$

0.21%-1.9% mol H^+/mol BCFZY0.1.

Confirmed triple conductivities (electron, oxygen ion, and proton.

Outline

- Triple Conducting Oxide (TCO) Cathode
- **Solid State Reactive Sintering Fabrication**
- Performance of Our PCFC Button Cells

Definition of Solid State Reactive Sintering

BZY20 As An Example

→ Ball Milling – 24h

SSRS

- Cost-effective raw materials such as carbonates and oxides
- Small amount of effective sintering additive (e.g., NiO, CuO)
- Single high-temperature processing step
- Combination of phase formation, ceramic densification, and grain growth

P / Methods					nt
Sol-gel	$1608/kg	1600C	6-9 days	Good	Bad
SSRS	$178/kg	1350C	3-4 days	Good	Good

The SSRS route is faster, cheaper, and better!

PCFC Fabrication Approaches

Traditional approach

A Completed PCFC sandwich structure can be fabricated in one or two moderate temperature steps

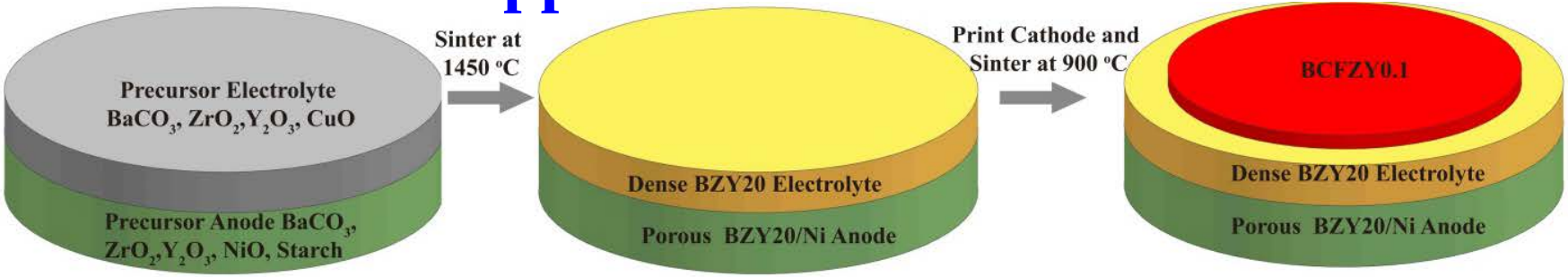
Nanopowder

Full SSRS approach

B

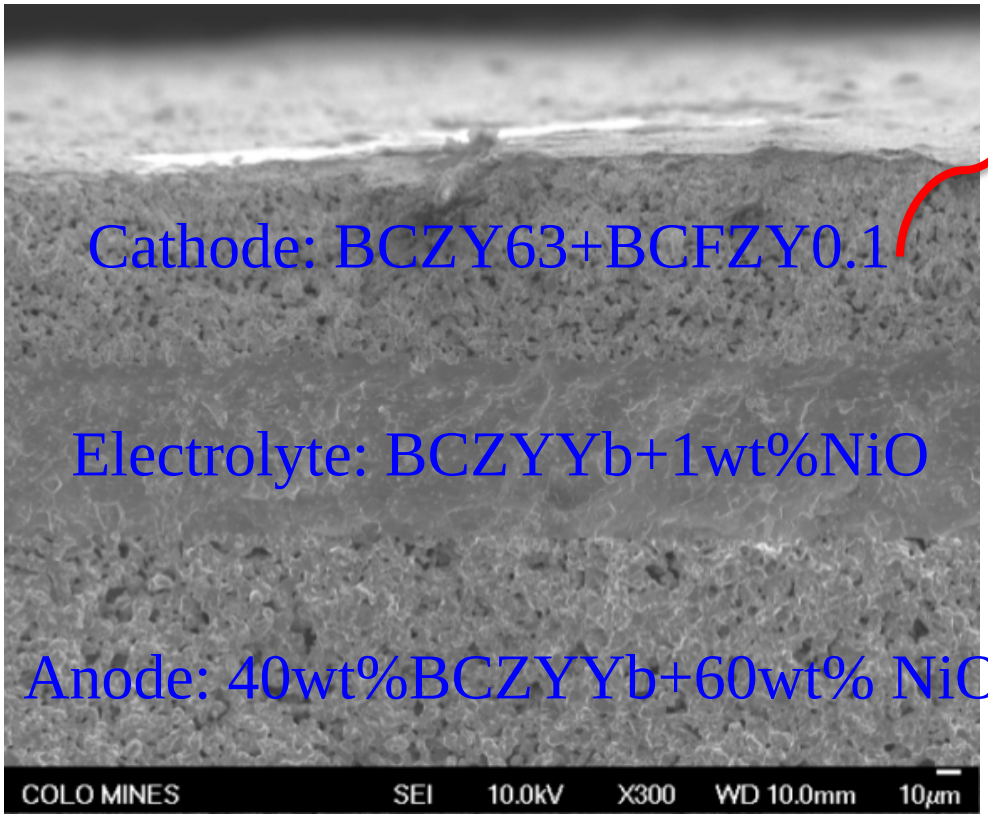
Half SSRS approach

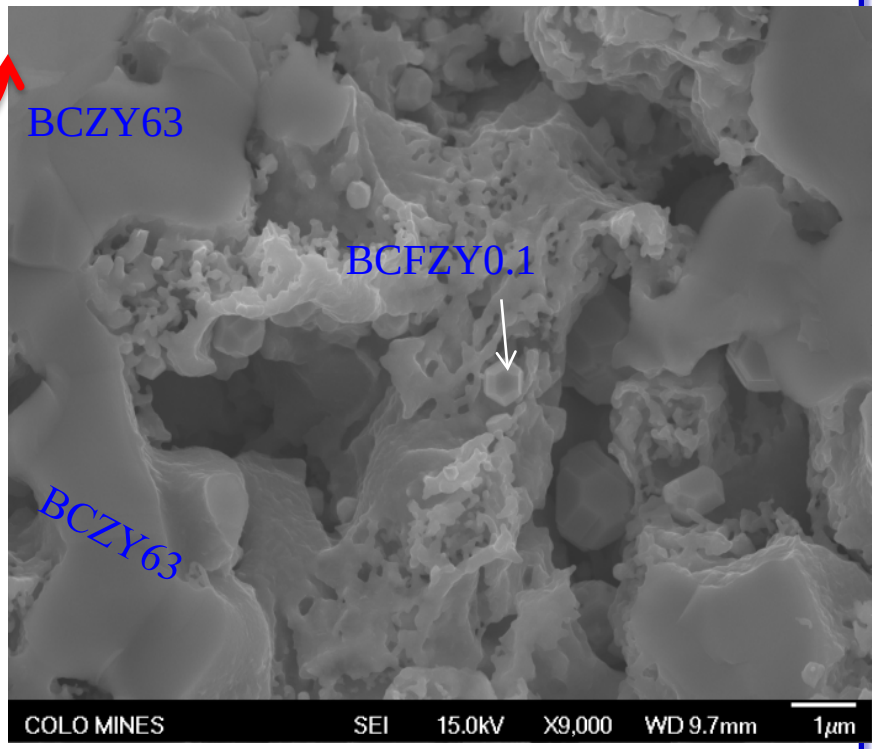
C



[1] J. Tong et al, US Patent application 14/621,091, 2015 .

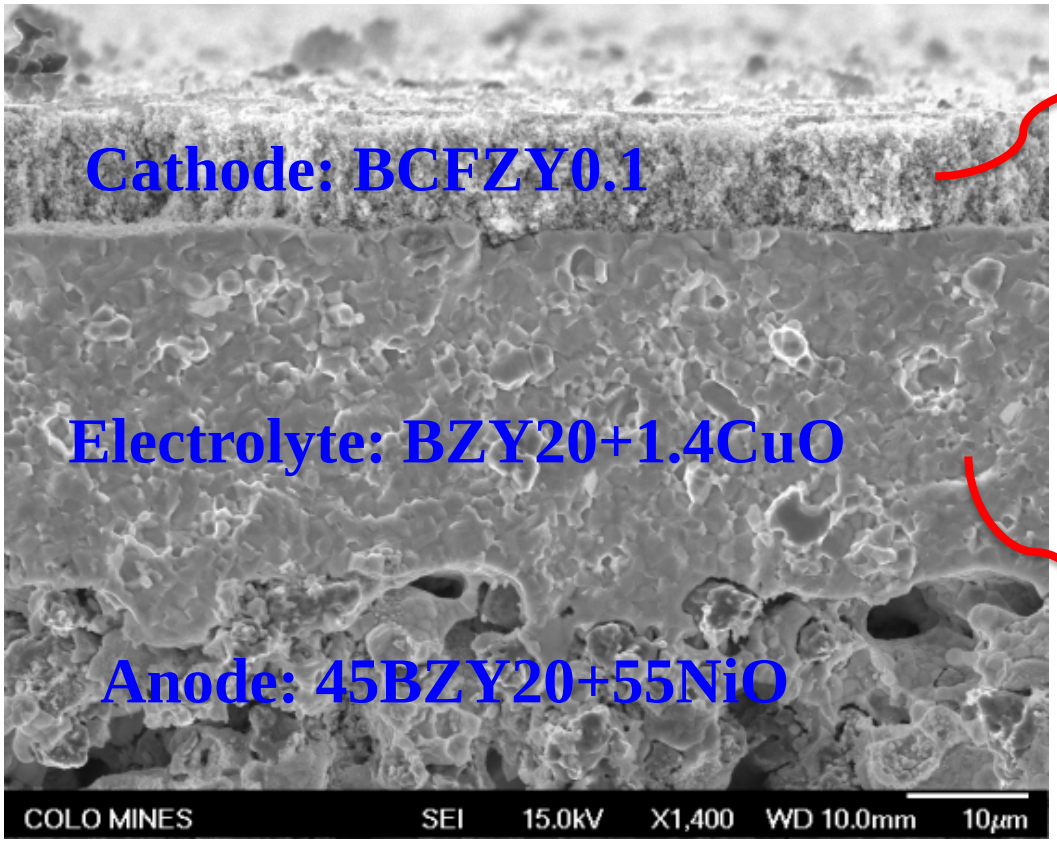
SEM Images of Full SSRS Approach (B)

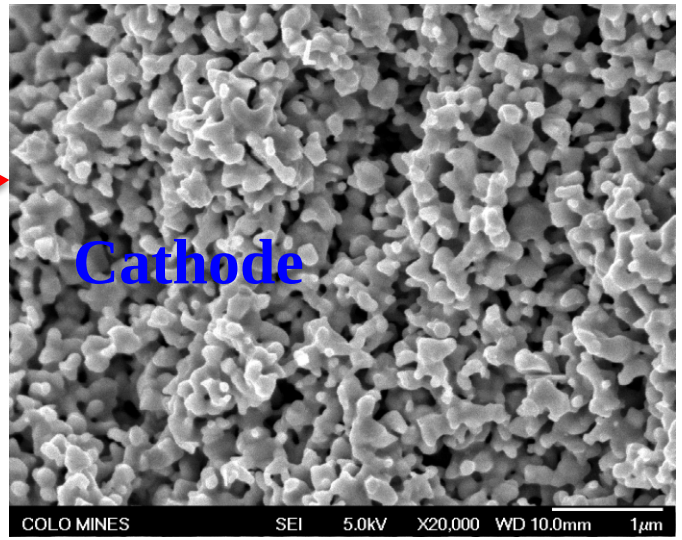


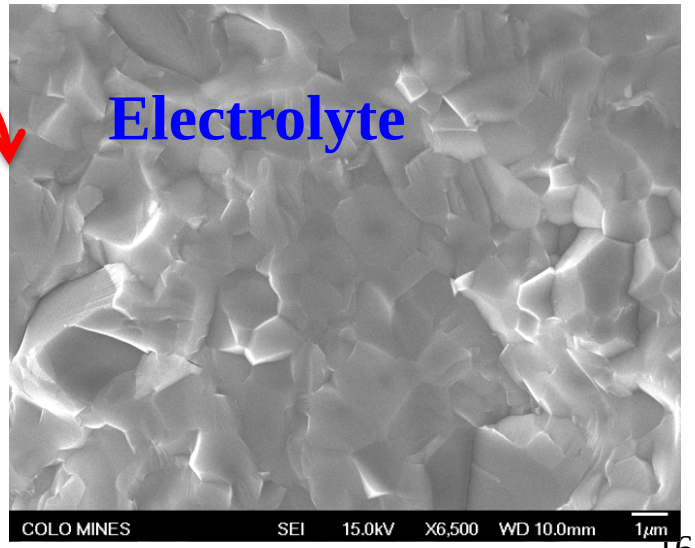


The full SSRS approach can even be used for fabrication for very complicated component systems.

SEM Images of Half SSRS Approach (C)





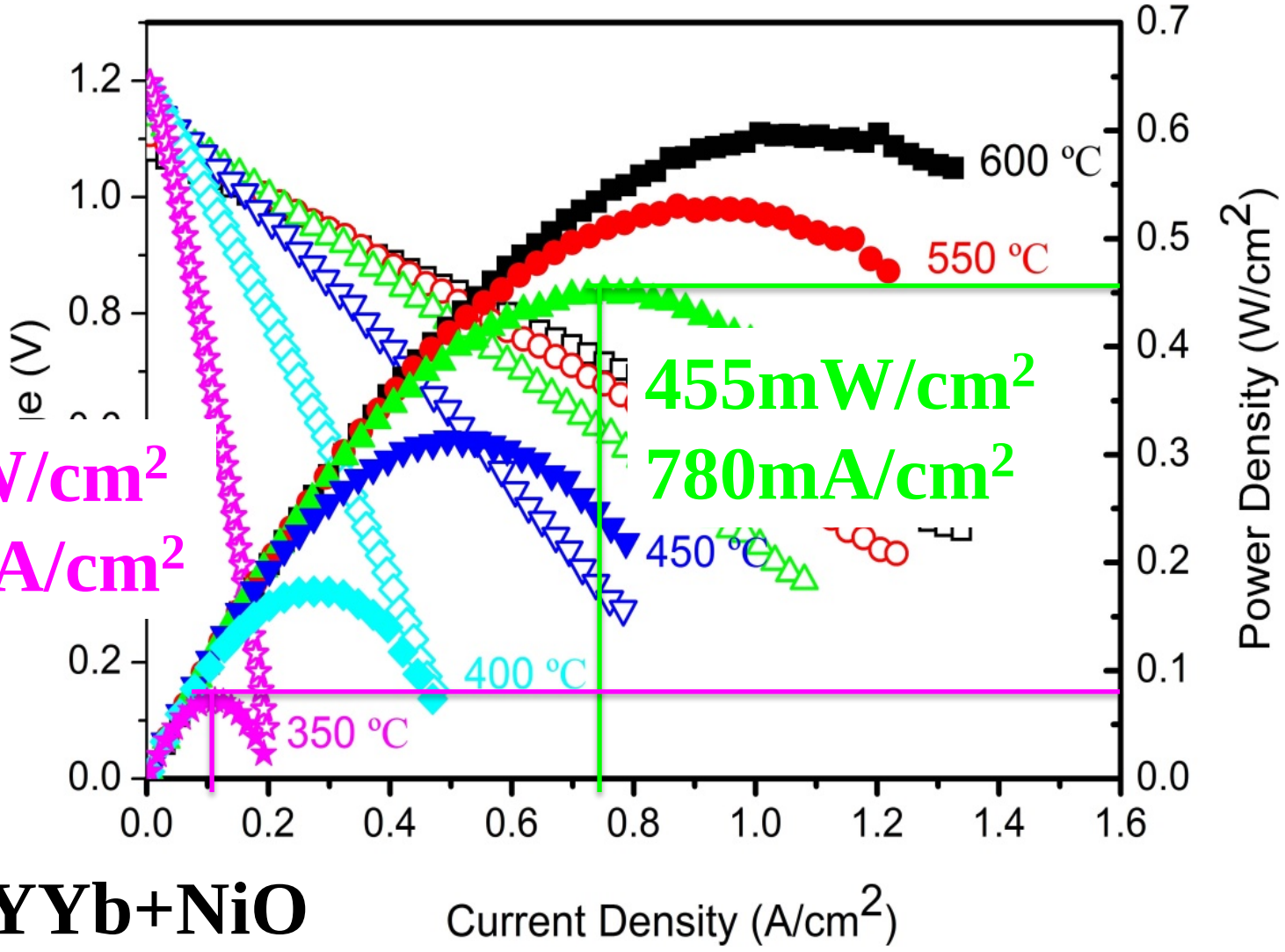


PCFC cell based refractory BZY20 electrolyte can be fabricated at moderate temperature.

Outline

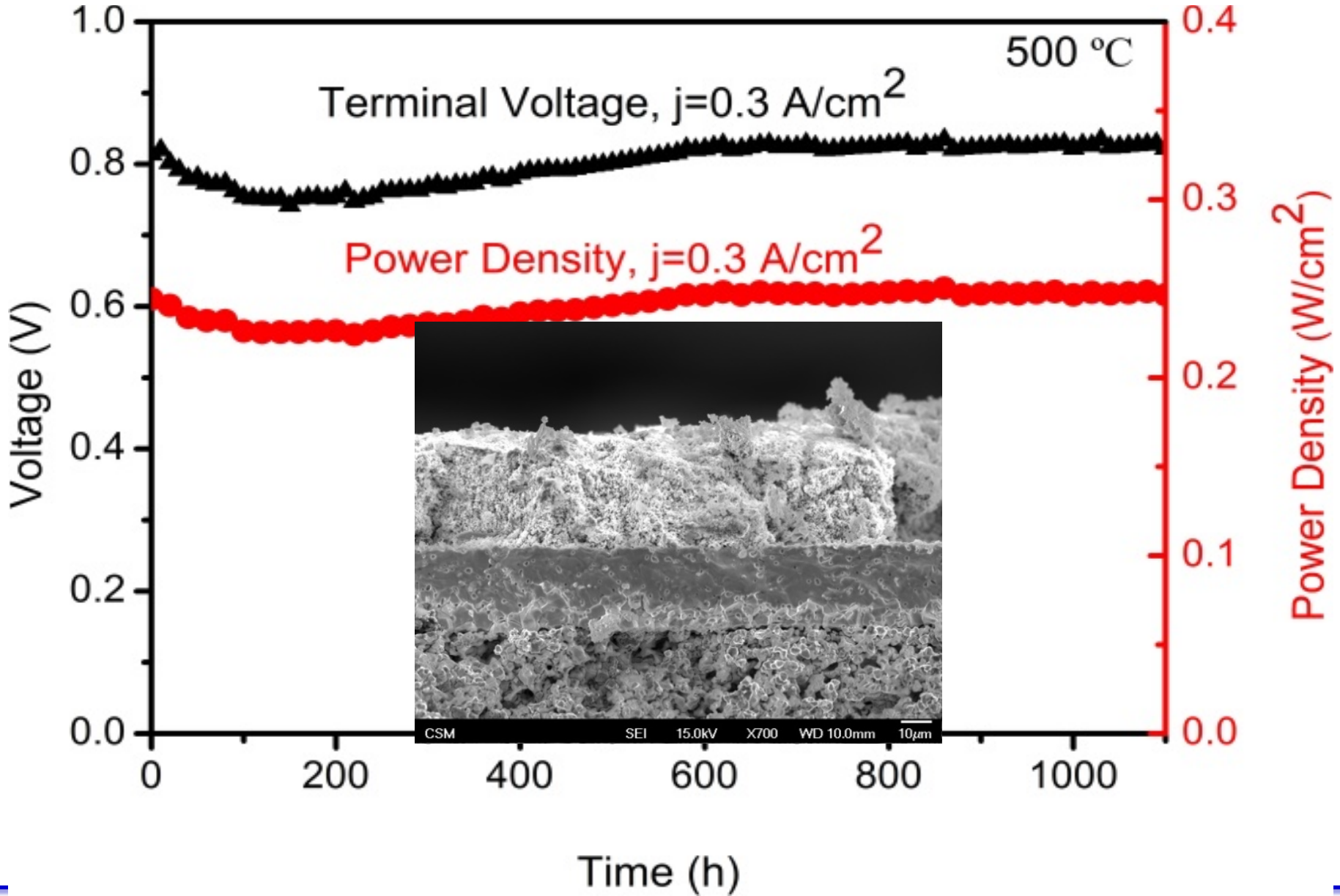
- Triple Conducting Oxide (TCO) Cathode
- Solid State Reactive Sintering Fabrication
- **Performance of Our PCFC Button Cells**

Representative I-V Curve for Button Cells under H_2/Air

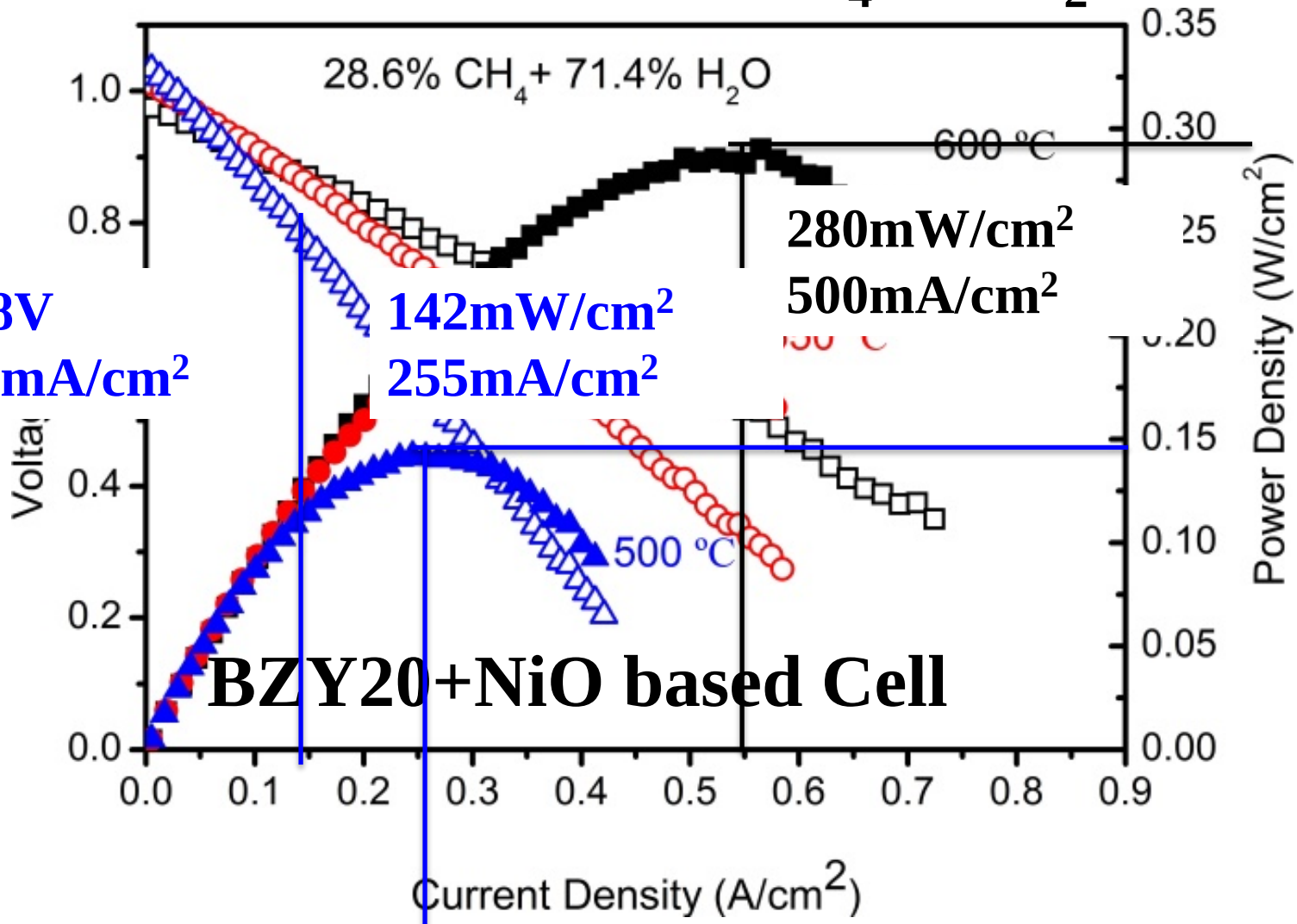


BCZYYb+NiO

Long-term Stability under H_2/Air at 500C



I-V Curve vs. T under CH_4+2.5H_2O/Air



0.78V
140mA/cm²

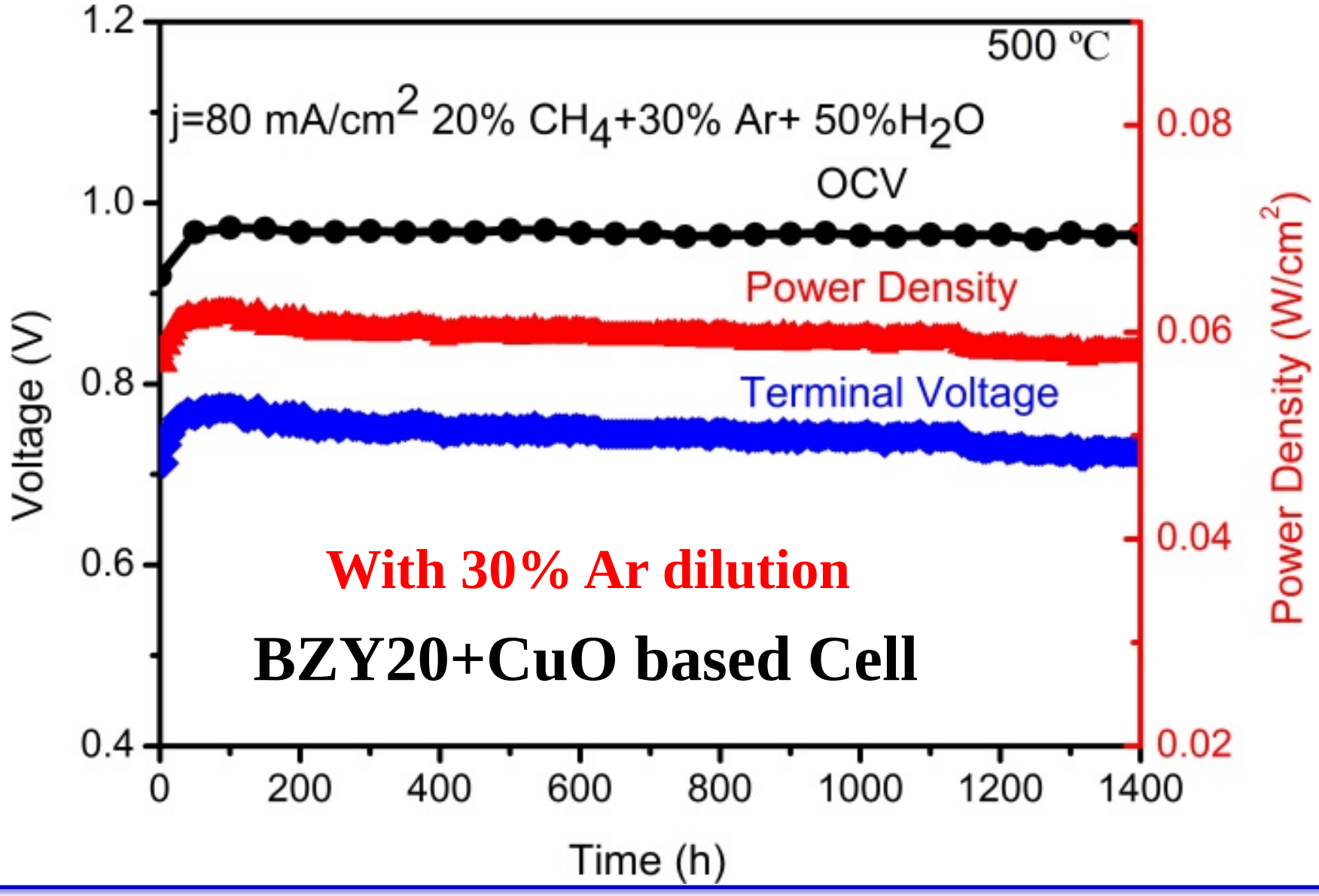
142mW/cm²
255mA/cm²

280mW/cm²
500mA/cm²

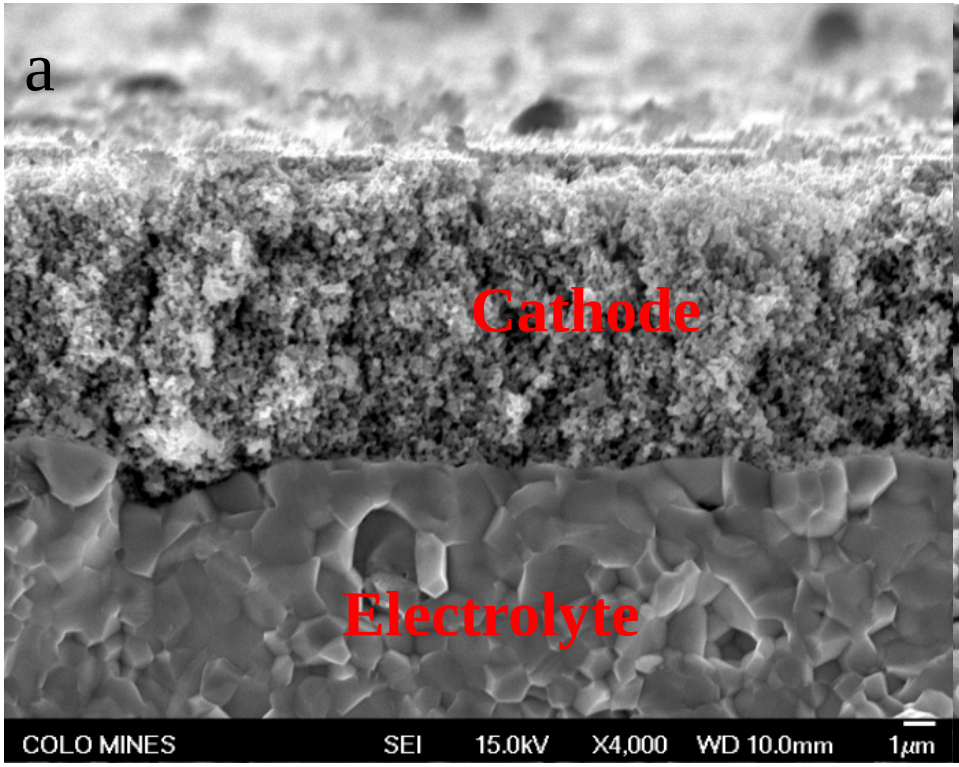
BZY20+NiO based Cell

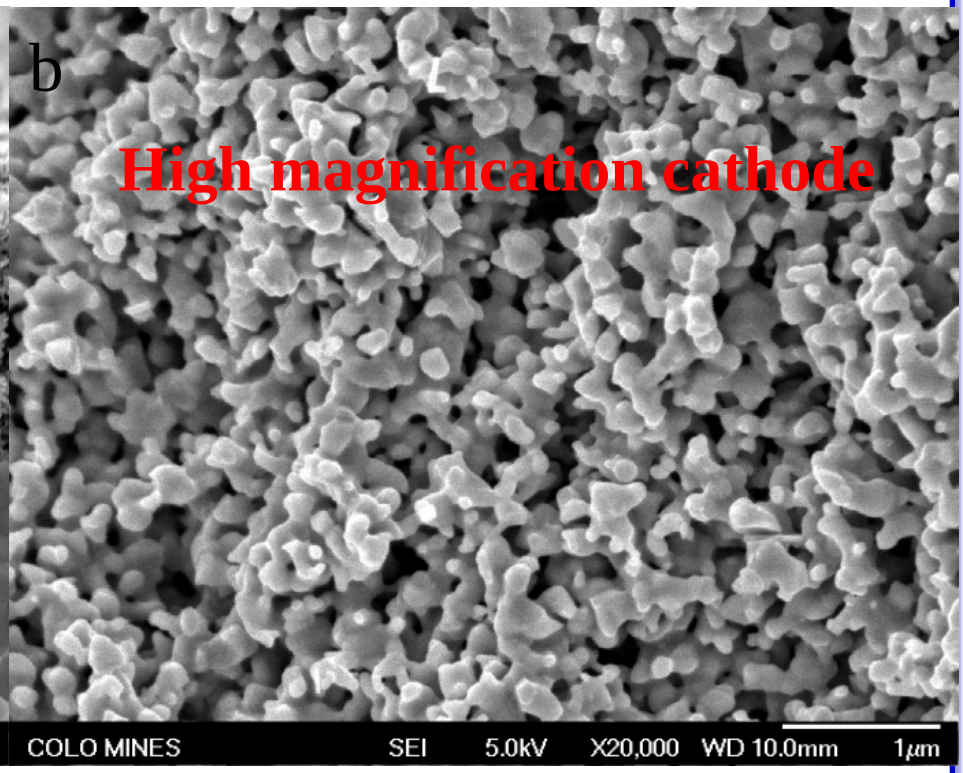
Without Ar dilution

Long-term Stability under CH_4+2.5H_2O+Ar/Air at 500C



SEM Images of Cathode after 1400 h

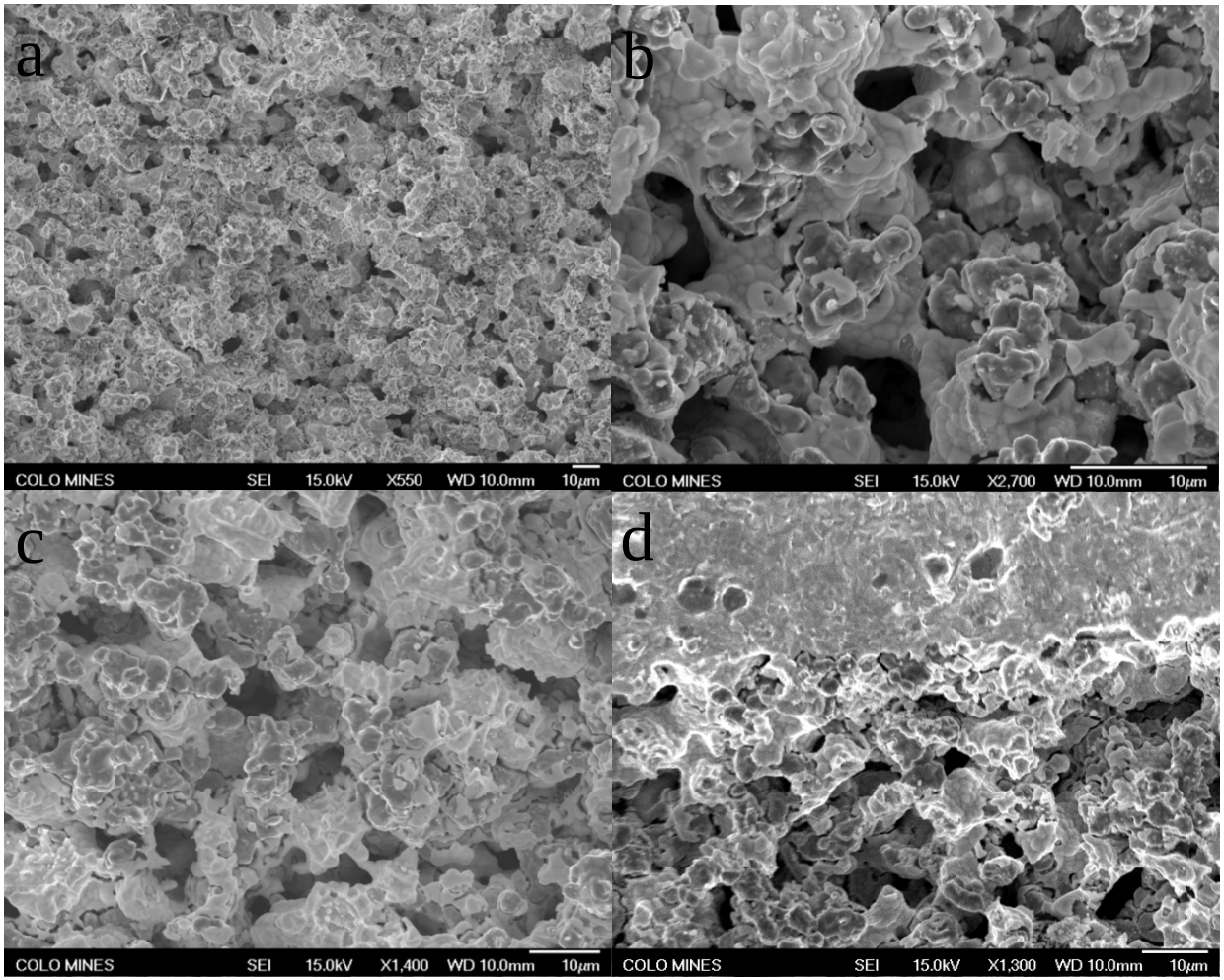




BZY20+CuO based Cell

No change in cathode nanostructure after 1400 h operation

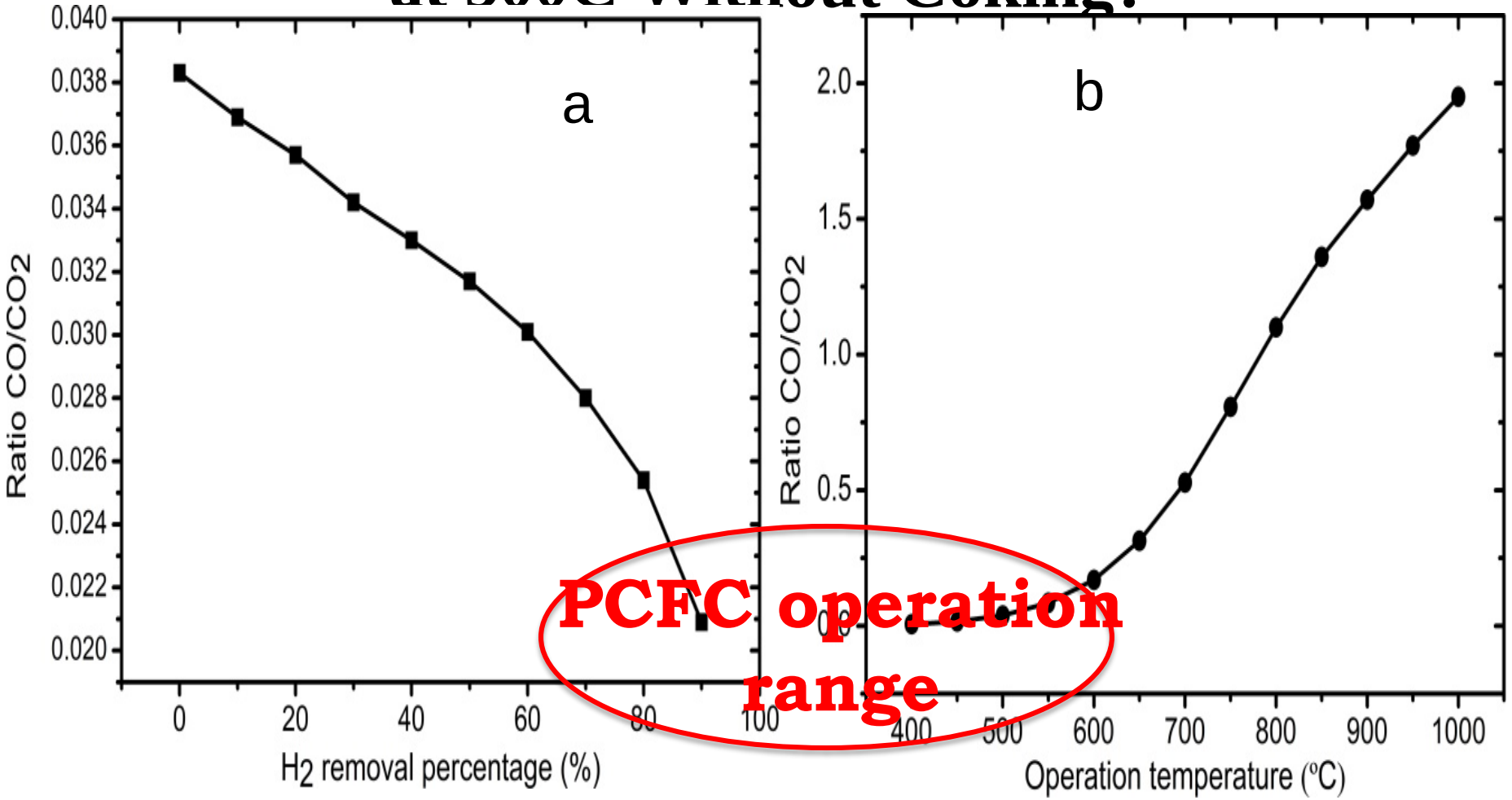
SEM Images of Anode after 1400 h



BZY20+CuO based Cell

No evidence of carbon deposition on anode

How Can PCFC Directly Run on Methane at 500C Without Coking?

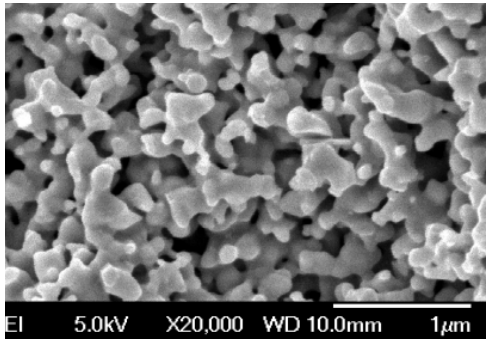


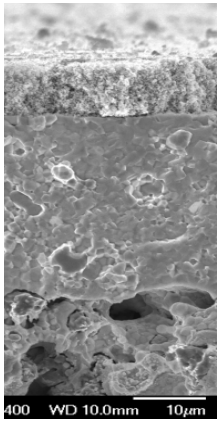
The ratio of CO/CO_2 versus hydrogen removal percentage at 500C (a) and versus operation temperature without hydrogen removal (b). Pressure, 10bars; H_2O/CH_4, 3.[24]

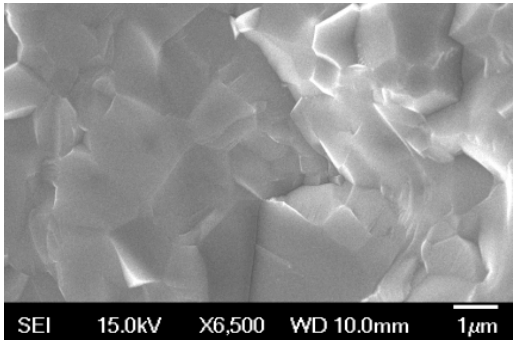
Conclusions

New Triple Conducting Cathode

Simplified Fabrication Process







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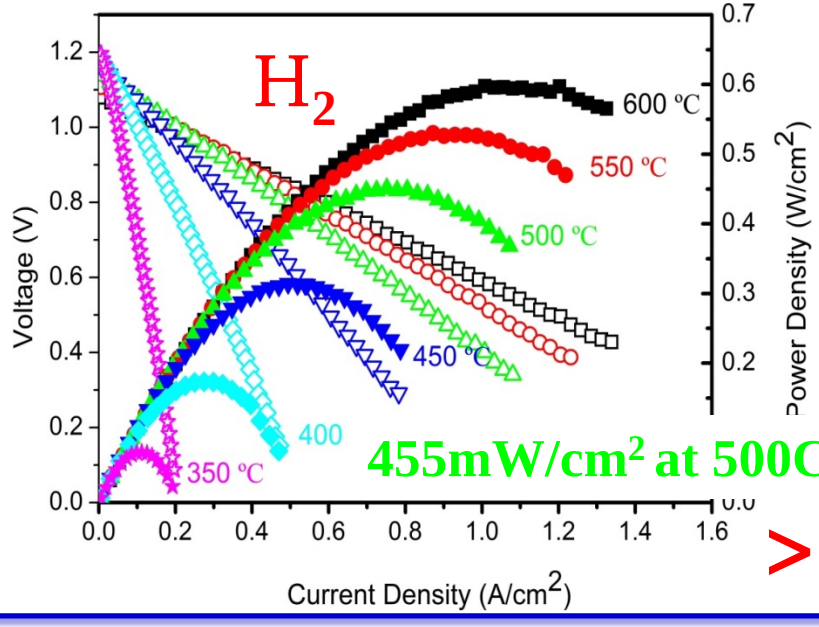
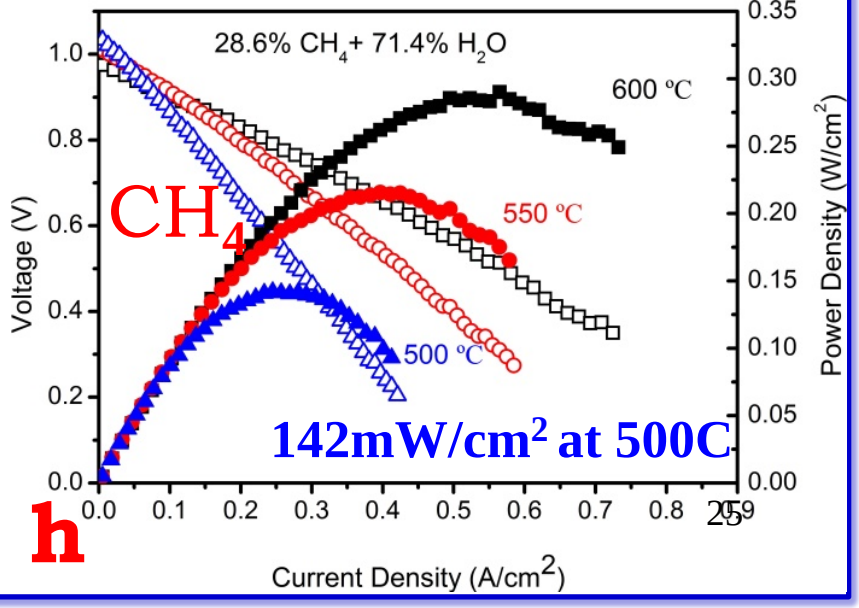


455mW/cm^2 at 500C



142mW/cm^2 at 500C

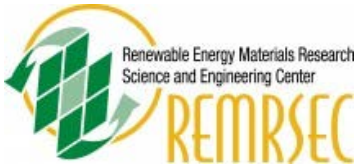
>1100 h

Current Funding Support

REBELs Program: Dr. John Lemmon
Dr. John Tuttle
Dr. Scott Litzelman

Research group members at CSM

Facility Supports



This work is related to two patents and an accepted Science paper. For details please check the following sources.

1) J. Tong et al, *US Provisional Patent*, 62101285, *Jan. 08*, 2015 (cathode).

2) J. Tong et al, US Patent application, 14/621,091, 2015 (fabrication).

3) C. Duan, J. Tong et al, Readily Processed Protonic Ceramic Fuel Cells with High Performance at Low Temperatures, *Science* (aab3987), accepted, July 13, 2015.