International Institute for Carbon-Neutral Energy Research

Processing yttrium-doped barium zirconate cerate for energy-efficient electrochemical devices

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PPCC 2022

6th International Workshop
PROSPECTS ON PROTONIC CERAMIC CELLS
June 8 -10, 2022 - Dijon, France

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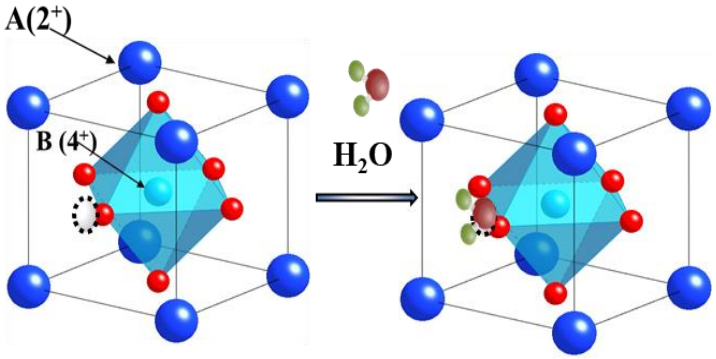
General Introduction



$$V_O^{\cdot\cdot} + \frac{1}{2}O_2 \rightleftarrows O_O^{\times} + 2h^{\cdot}$$

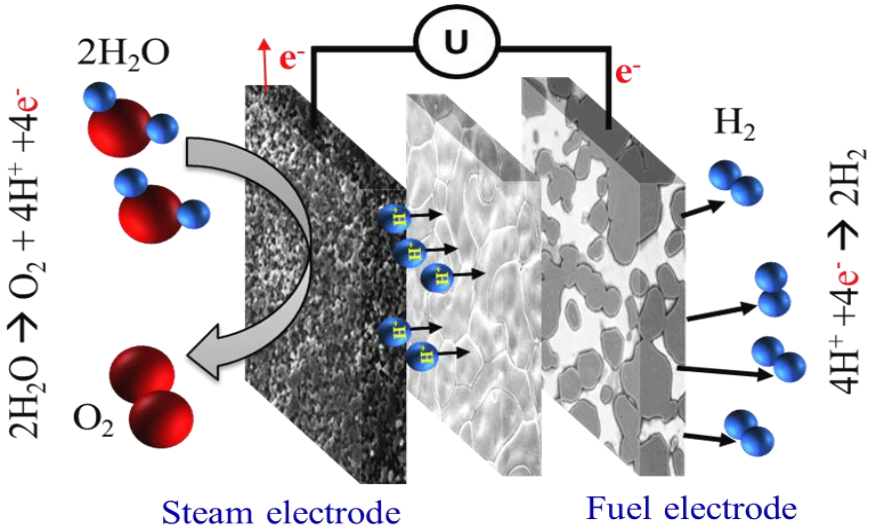
$$H_2O + 2h^{\cdot} \rightleftarrows 2H_i^{\cdot} + \frac{1}{2}O_2$$

$$V_O^{\cdot\cdot} + H_2O \rightleftarrows O_O^{\times} + 2H_i^{\cdot}$$

Ceramic material that exhibits proton conductivity in the temperature range 400 ~ 800 °C

Useful for energy conversion and storage.

- ✓ Efficient production of electric power (PCFC)
- ✓ Efficient production of valuable fuels, (PCEC)



Key indicators for electrolysis performance evaluation

Operating voltage

- ✓ defines the electrolysis (electrical) efficiency.

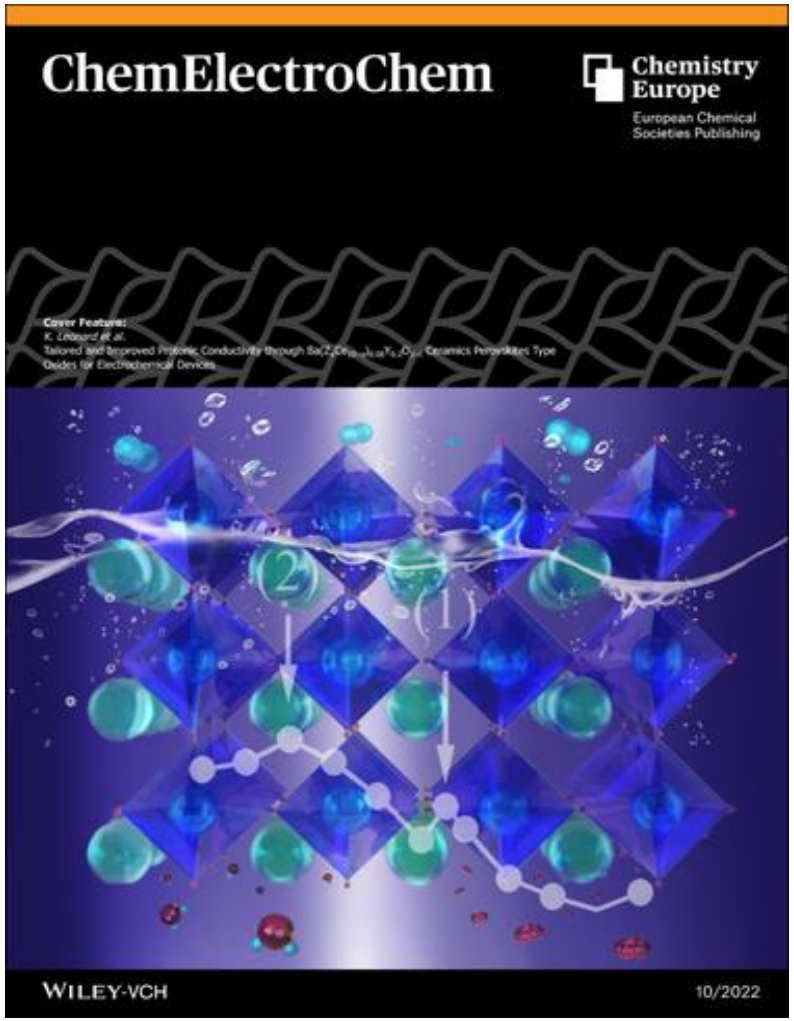
Current density

- ✓ determines hydrogen production per cell area

Operating voltage ⇩ **Low**

Current density ⇧ **High**

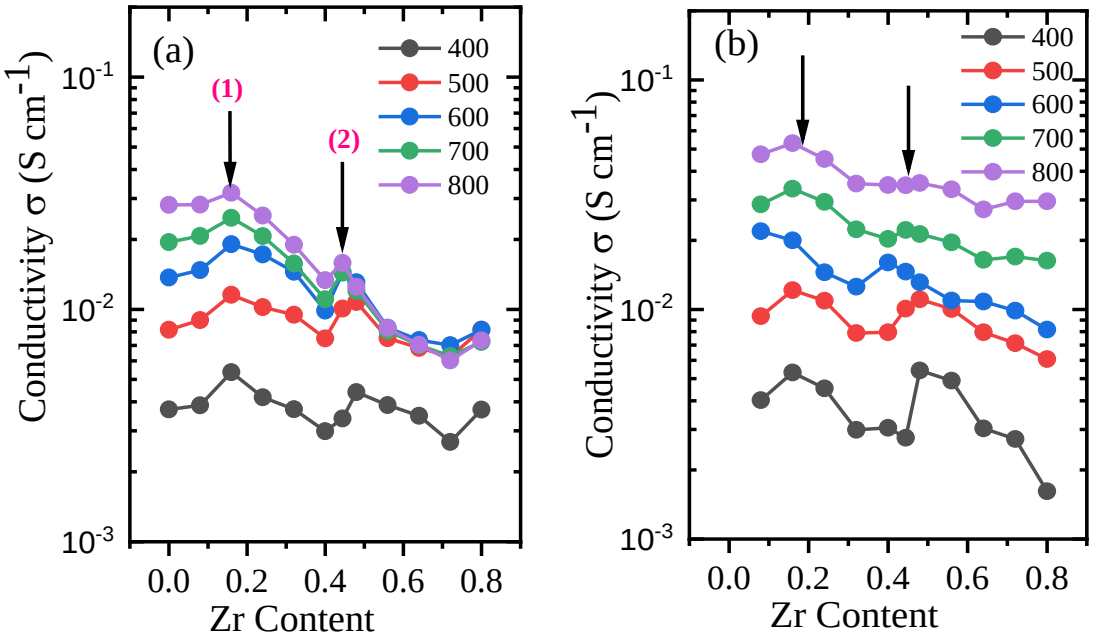
Conductivity/ Stability of electrolyte Materials

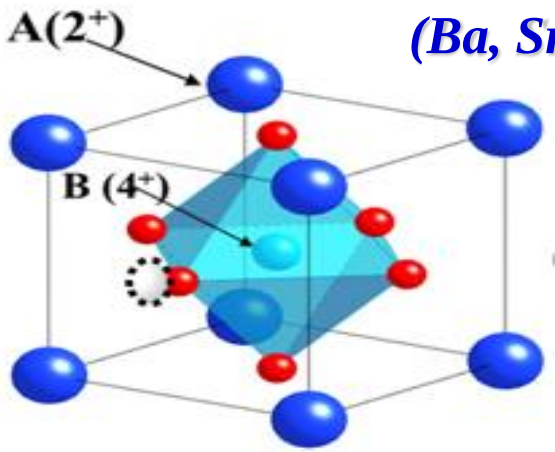


K. Leonard et al. ChemElectroChem (2022) ,9

$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$ (1) *demonstrates a superior ionic conductivity to stability trade-off (10.1mS/cm @ 500°C)* $BaZr_{0.16}Ce_{0.64}Y_{0.2}O_{3-\delta}$ (2) *superior σ_H 11.5mS/cm*

State-of-the-art electrolytes-(Ba,)(Ce,Zr,Y)$O_{3-\delta}$



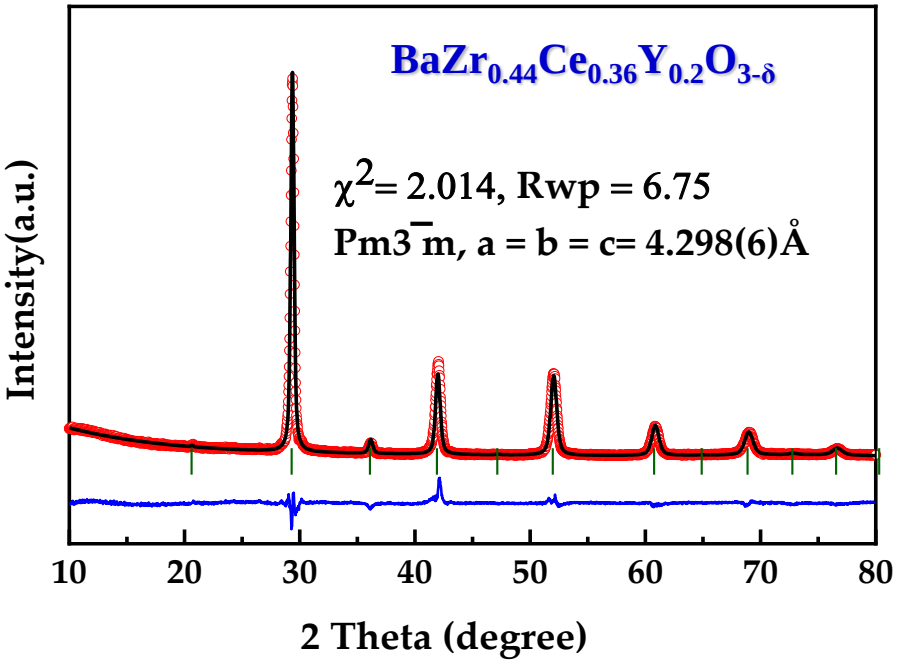


(Ba, Sr)(Ce,Zr,Y)$O_{3-\delta}$

perovskite B-site.
Zr:Ce=5/4

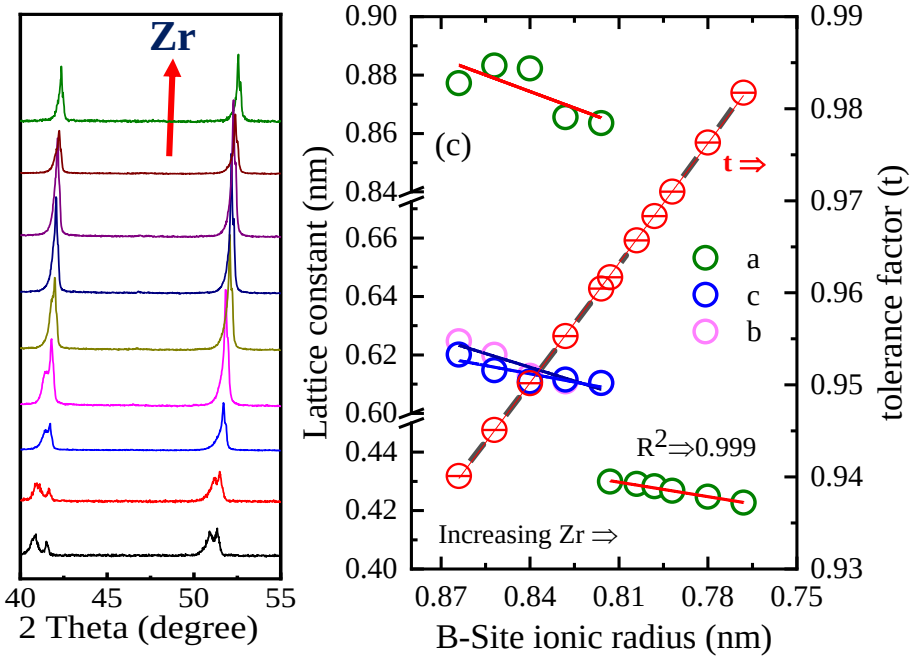
Two new composition variants

Phase and structural characterization



900 ºC perovskite dominant phase, however with some secondary phases ($BaCO_3$, CeO_2, Y_2O_3)
1300 ºC single-phase perovskite structures

$Ba(Zr_xCe_{10-x})_{0.08}Y_{0.2}O_{3-\delta}$ $(1 \leq x \leq 9)$



The range $5.5 \leq x \leq 9$ =cubic perovskites

The range $1 \leq x \leq 5$ =orthorhombic

$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$ (1)		$BaZr_{0.16}Ce_{0.64}Y_{0.2}O_{3-\delta}$ (2)
Space group	*Pm3̄m*	*Pnma*
Lattice parameter	**a= 4.2986**	**a= 8.8328, b= 6.2678 c= 6.1475**

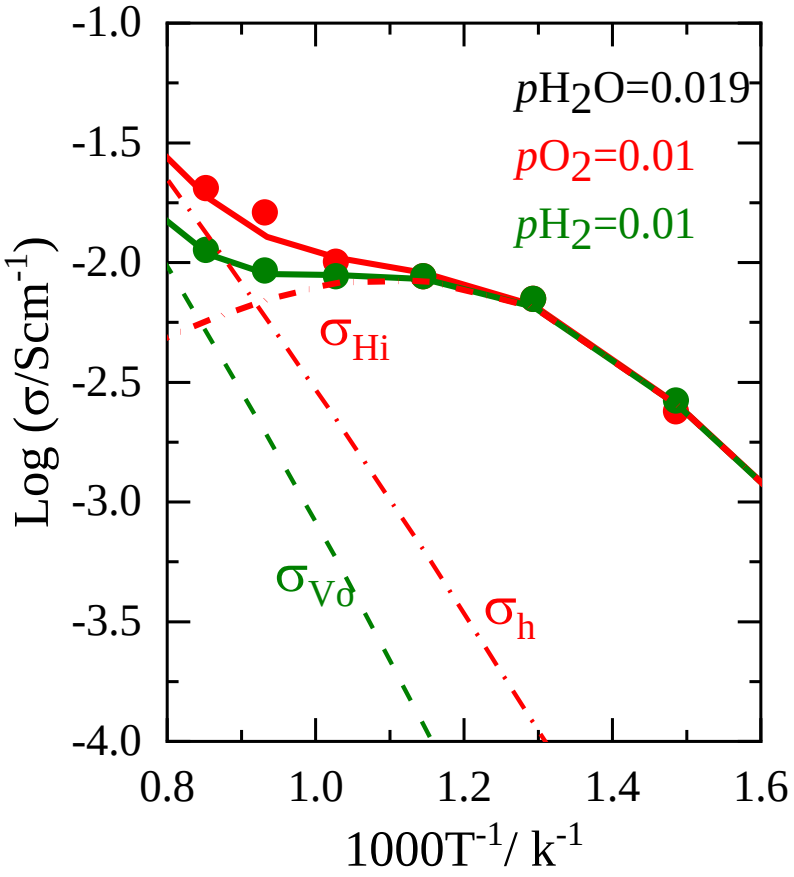
- ✓ ***An angular shift of the XRD pattern towards higher angles reflecting the substitution of Ce^{4+} for the Zr^{4+} in the lattice***
- ✓ ***Linear dependence of the calculated lattice constants against the B-site ionic radius***

Protonic electrolyte development

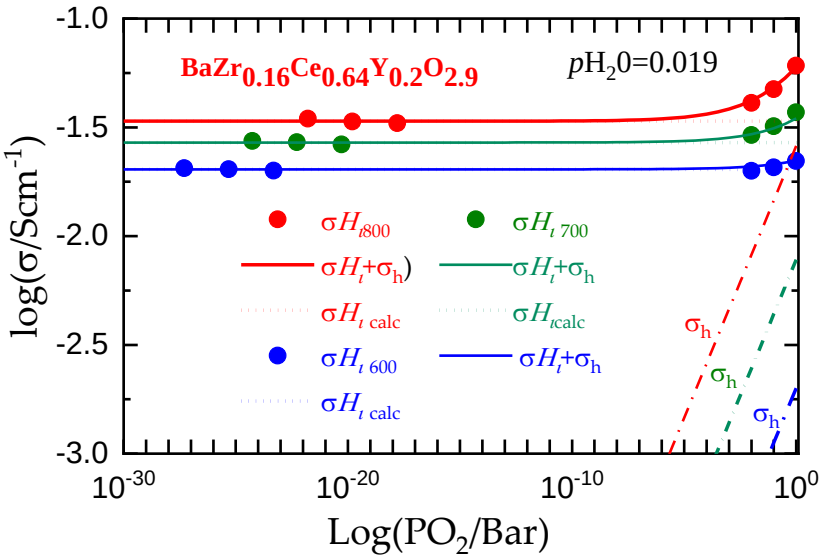
$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$ (BZCY(54)$_{8/9}$2)

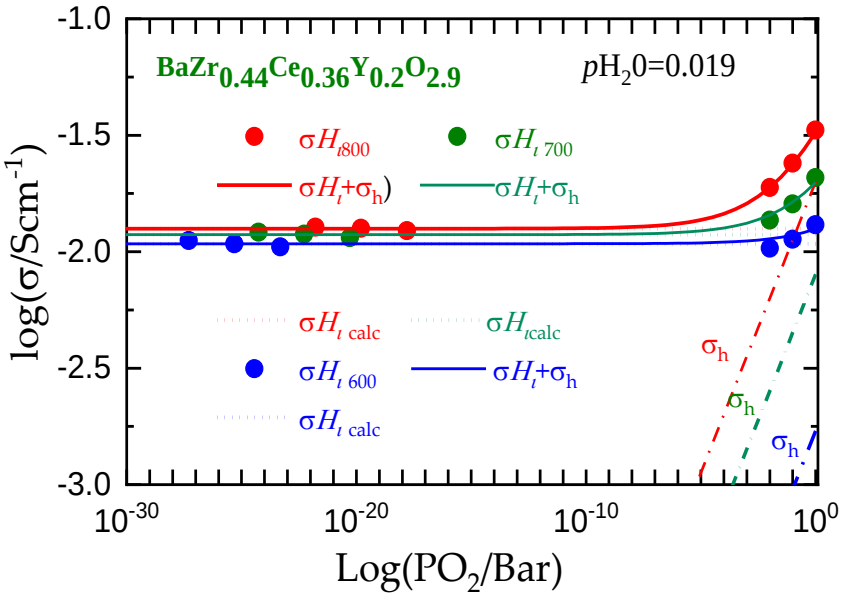
Many charge carriers existing simultaneously

$[V_o^{\cdot\cdot}]$, $[h^{\cdot}]$, and $[H^{\cdot}]$



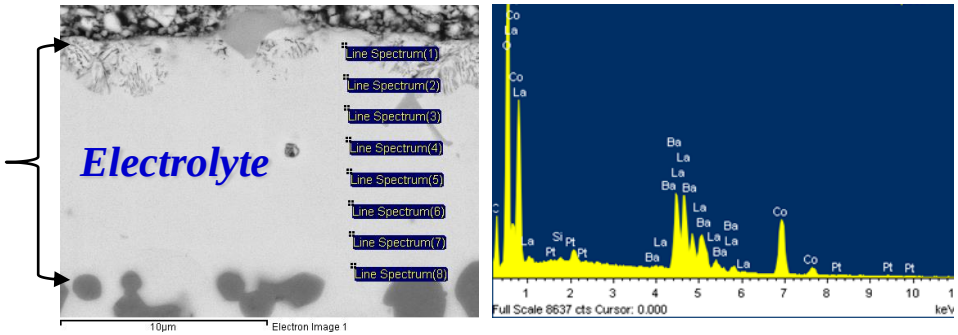
$P(O_2)$ dependence of conductivity

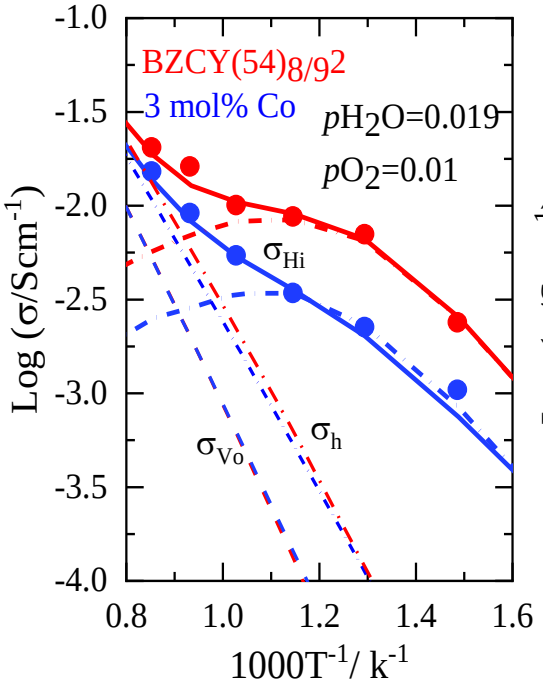


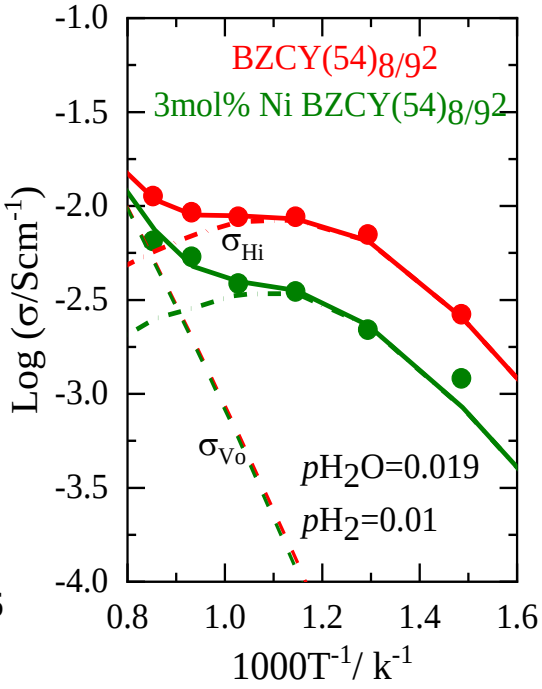


- ***The hole conductivity is minimal at 600 °C***
- ***The hole conductivity increases at 800 °C in oxidizing atmosphere***

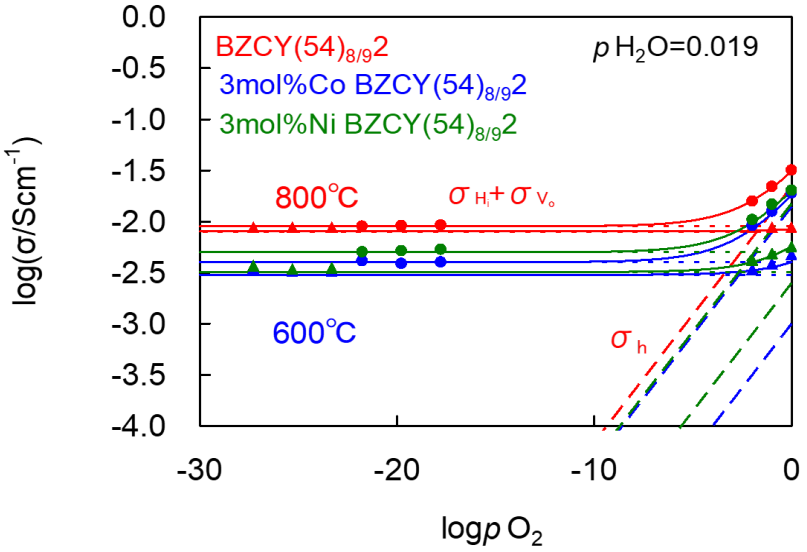
Effect of Co and Ni addition to $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$

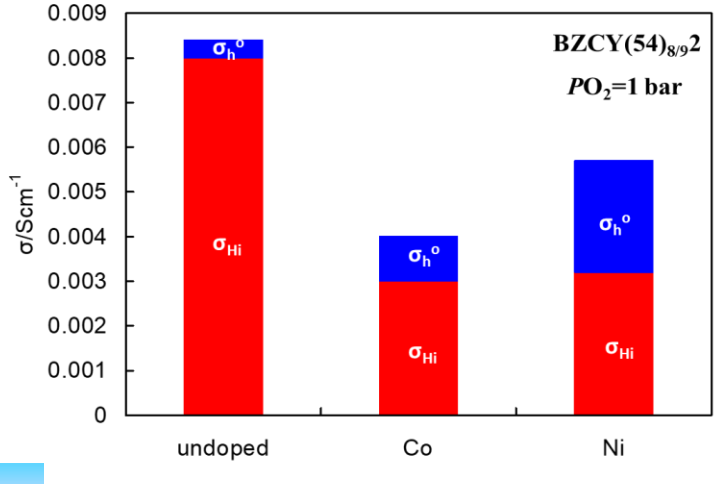






$P(O_2)$ dependence of conductivity





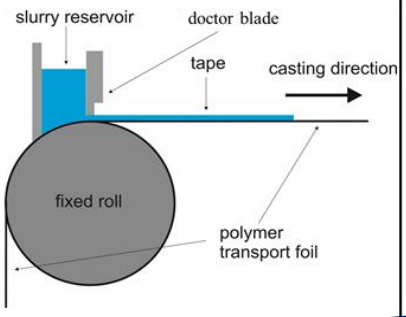
An ~1/3 drop in Conductivity by either Ni and Co addition

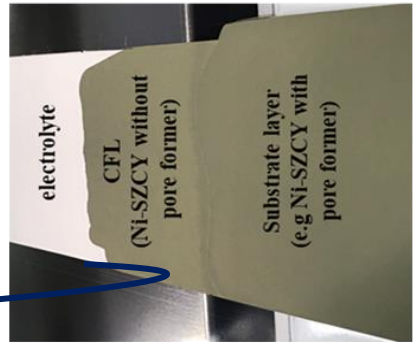
K. Leonard et al., J. Matter Chem. A (2018)

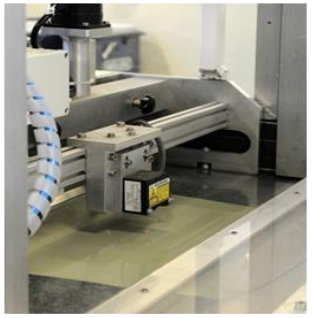
Achievements and progress

Improved Processing and fabrication by Sequential tape casting

Electrolyte	*Cathode (functional layer)*	*Cathode (substrate)*	*Anode*
(12~20µm) $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$	(8~15µm) NiO-$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$	(~ 0.4 mm) NiO-$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$	(~25µm) $Ba_{0.5}La_{0.5}CoO_{3-\delta}$
Tape casting			*Screen printing*

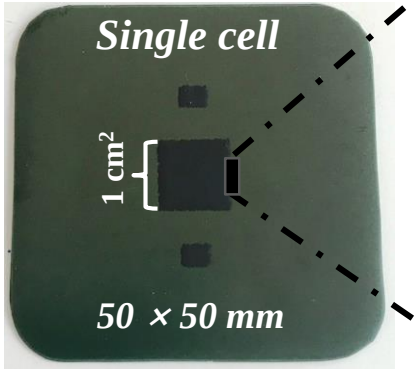




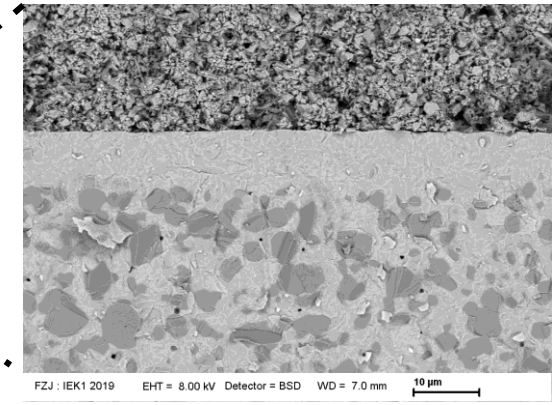


Punching, cutting and Lamination

De-binding and Sintering

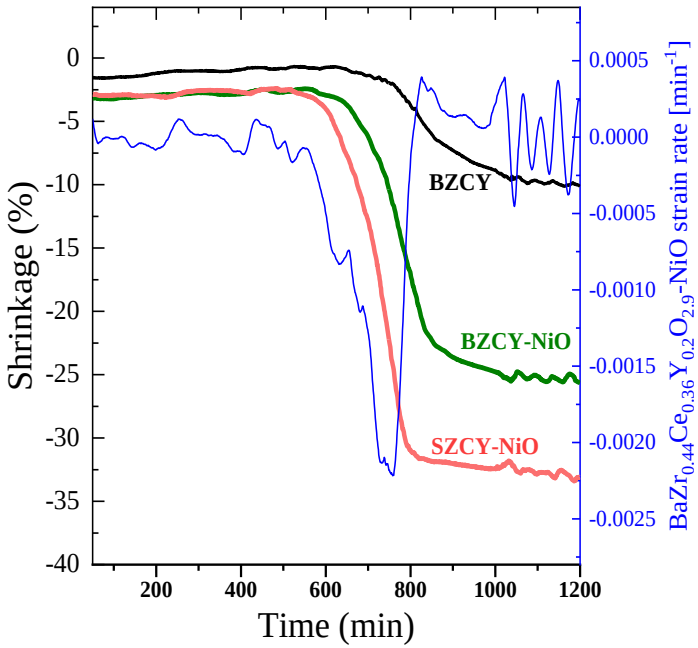


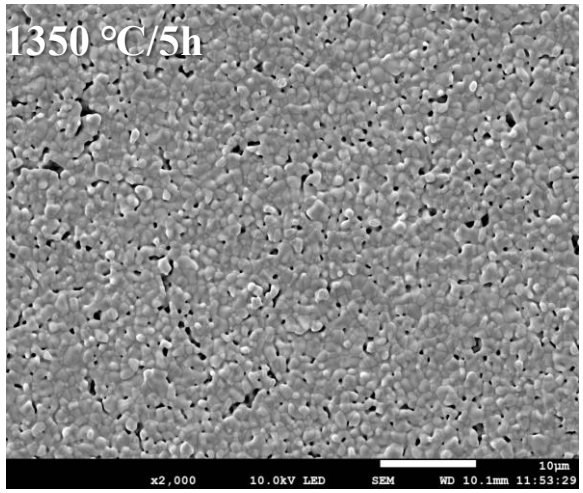
Cell Microstructure



Enhanced sinter-ability with $NiO\text{-}SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$

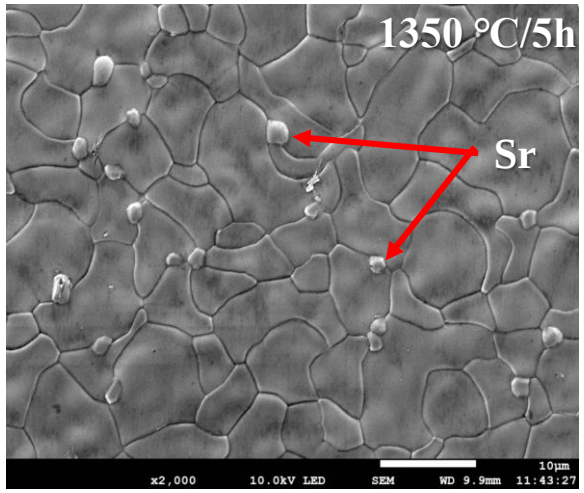
Lowering the sintering temperature of the $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$ (BZCY) based half-cell below 1300°C is our utmost desire.





$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$

$NiO\text{-}BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$



$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$

$NiO\text{-}SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{2.95}$

Liquid phase sintering

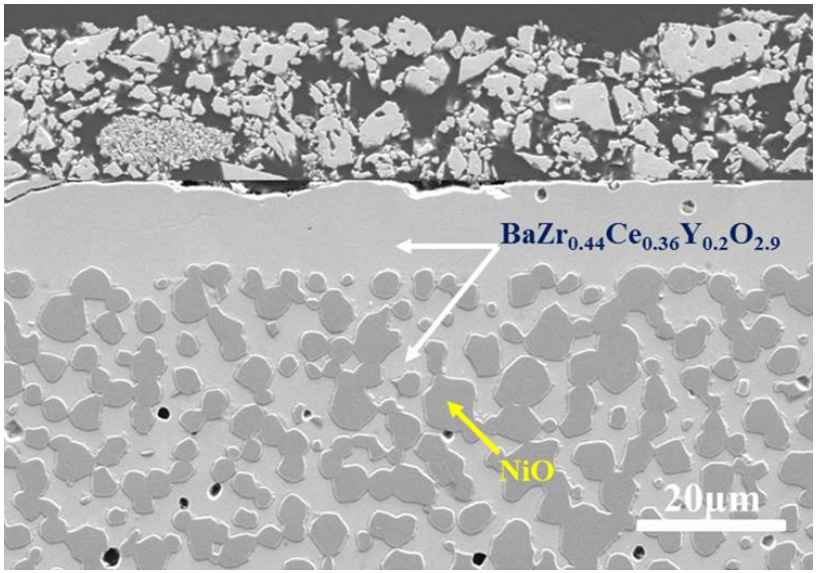
BaO-NiO ↑ Higher temp.

SrO-NiO ↓ Lower Temp.

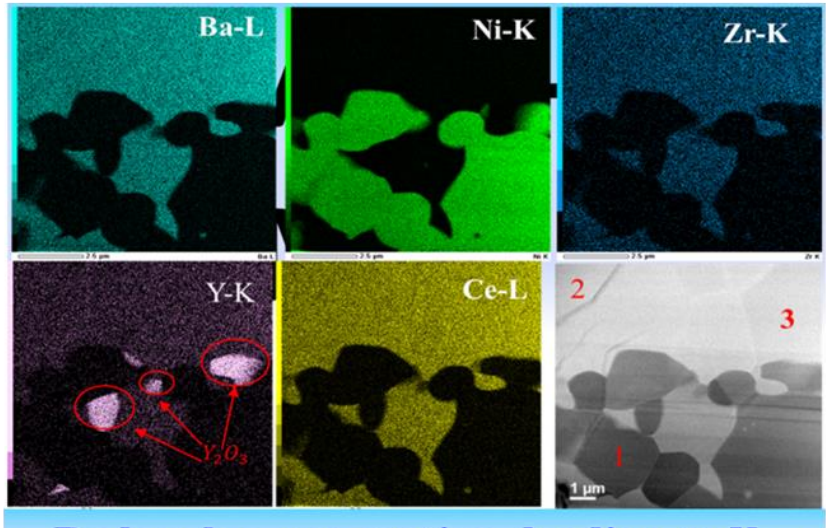
✓ ***$NiO\text{-}SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ substrate positively influenced the densification of $BZCY(54)_{8/9}2$***

✓ ***Lowering operating temperature reduces nickel mobility and nucleation, reducing the driving force of this degradation***

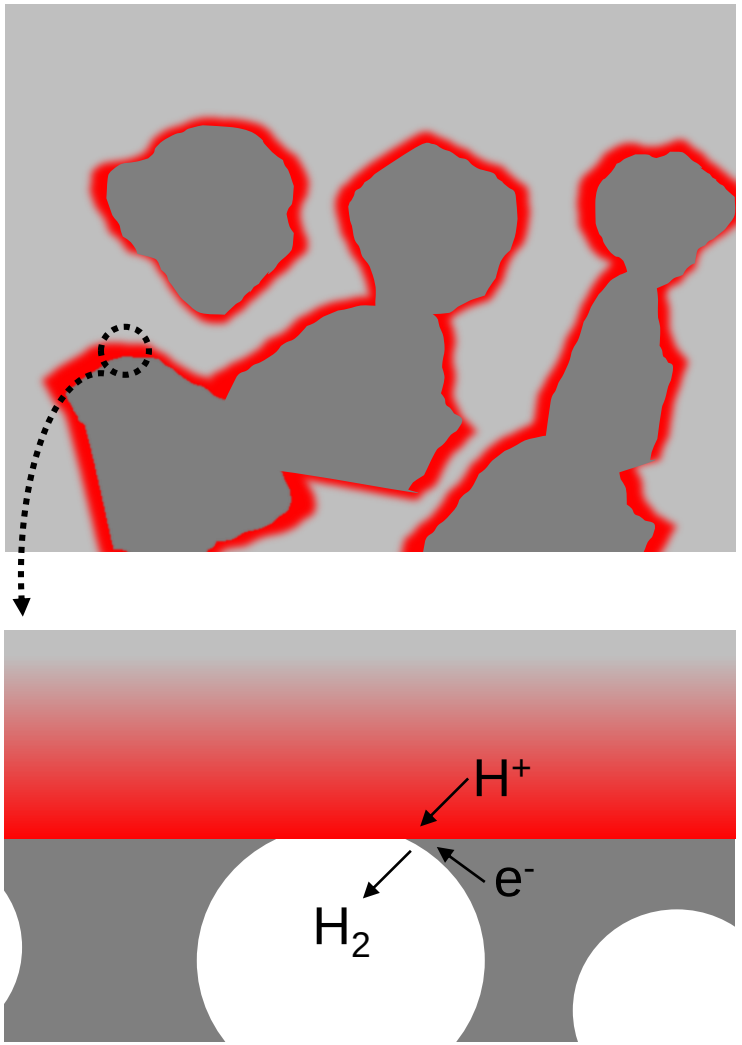
Schematic of Ni diffusion



BZCY / Ni-BZCY sintered at 1500 °C



- **Ba loss by evaporation, leading to Y_{Ba}^{*}**

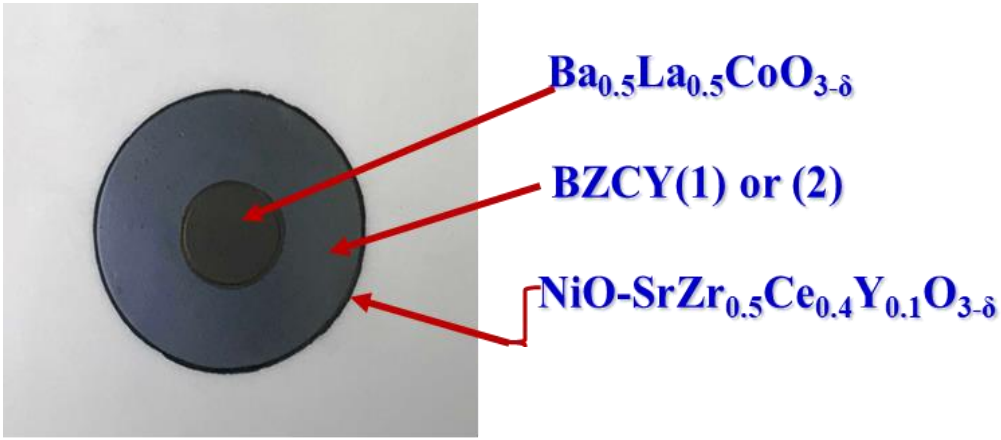


➢Ni diffuse to the electrolyte in the vicinity of NiO grain, resulting in an increase of resistance. High resistance part is in series with the electrode reaction

Progress on bottom size cell configuration (PCEC mode)

BLC| BZCY| Ni-SZCY541

Cell size: φ22 mm, Anode Size: φ 8 mm
Electrolyte thickness: ~12 μm
Anode gas: 1% O_2-Ar, 20 % H_2O
Cathode gas: 1% H_2-Ar, 2 % H_2O



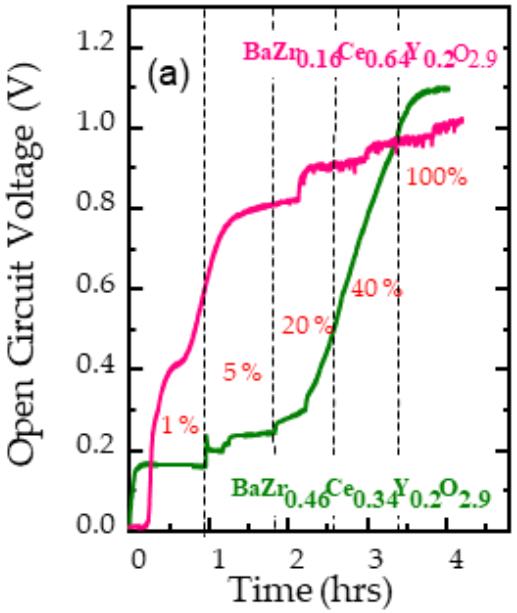
Glass seal:

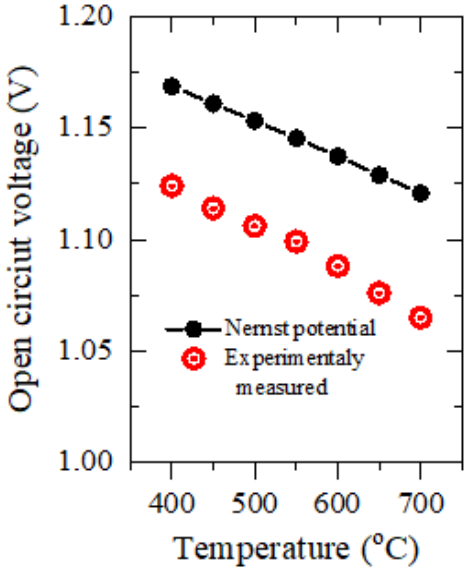
- ✓ Pirex glass
- ✓ 800°C for 1h
- ✓ Reduction @ 600 °C
- ✓ Current collectors
- ✓ ○ Ag-Pd @ Positrode
- ✓ ○ Ni mesh @ hydrogen side
- ✓ ○ Pt #80 mesh at both

Almost no cross leak is observed

- ➢ *Inlet and outlet flow where very similar (within experimental error)*
- ➢ *No significant leakage through the glass sealant*

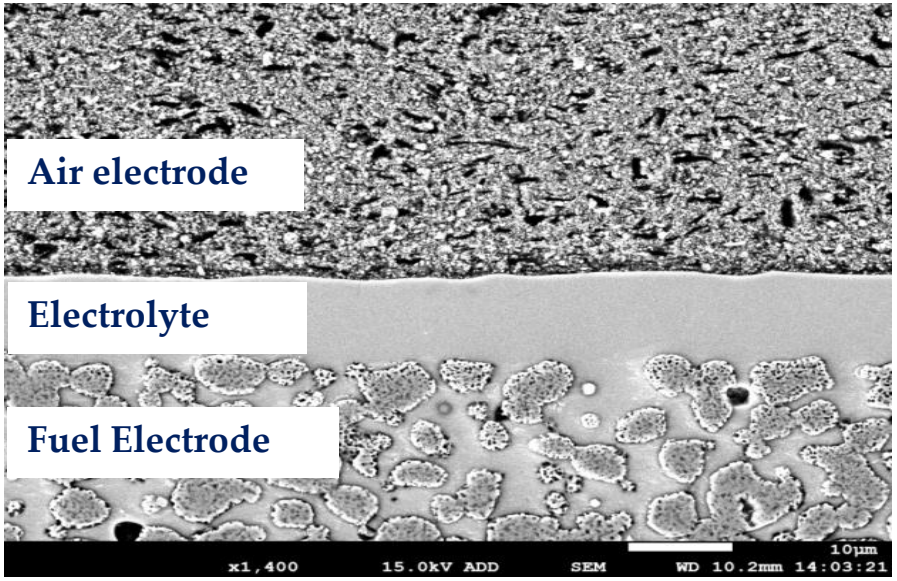
Cell reduction OCV Vs Time and temperature

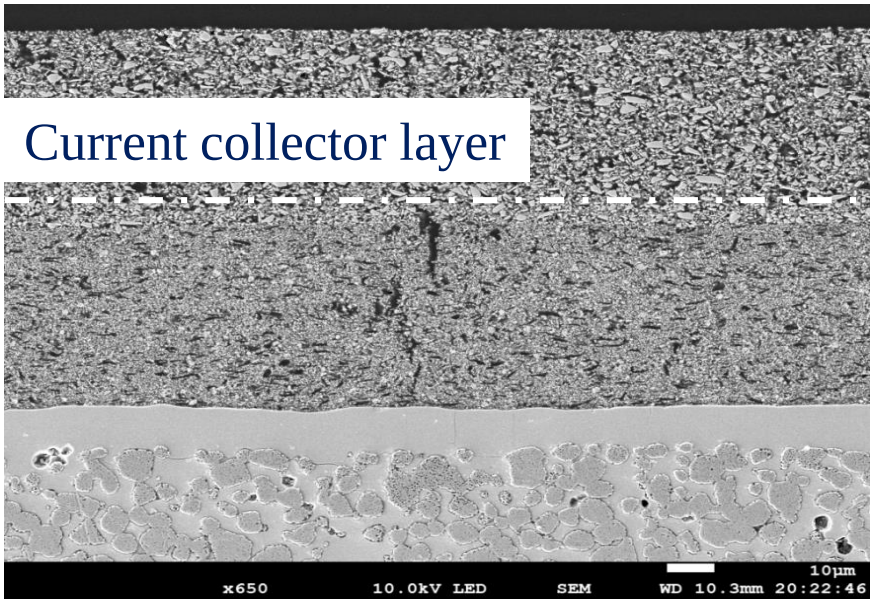


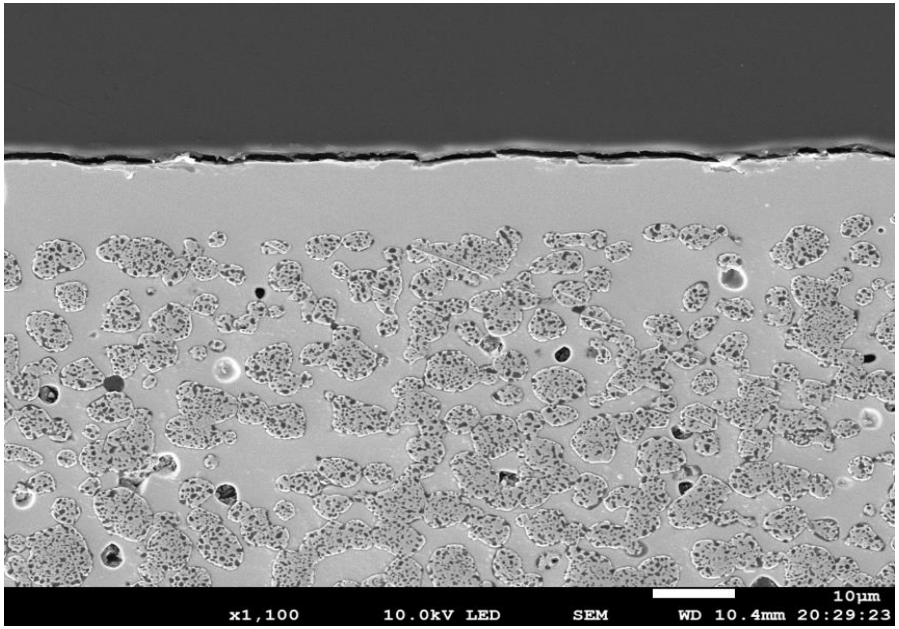


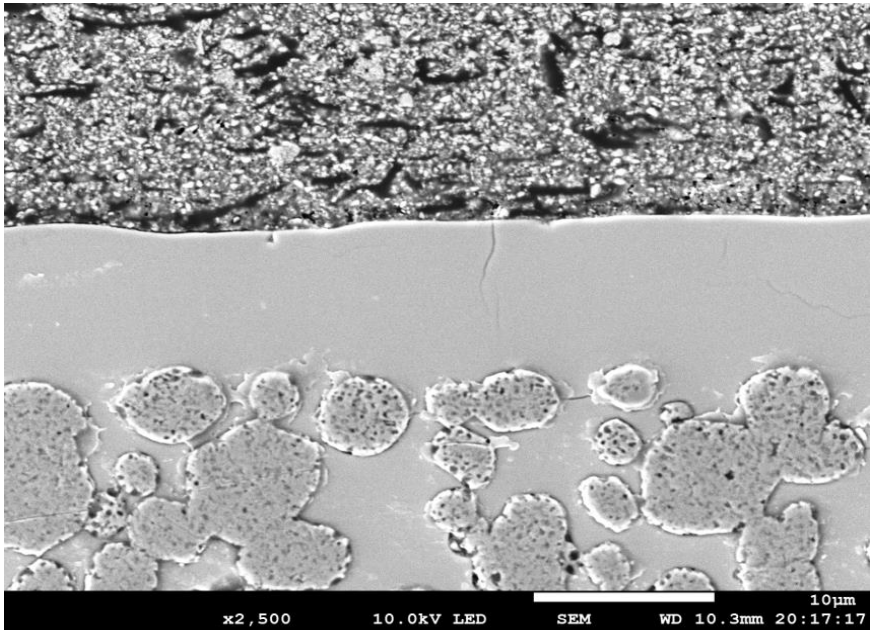
Typical cell microstructure

Microstructure post measurement



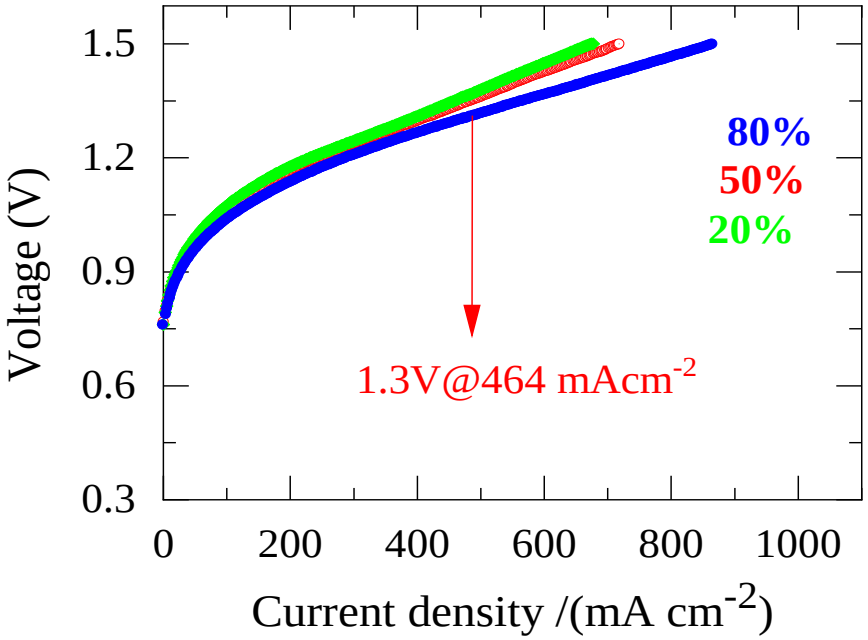




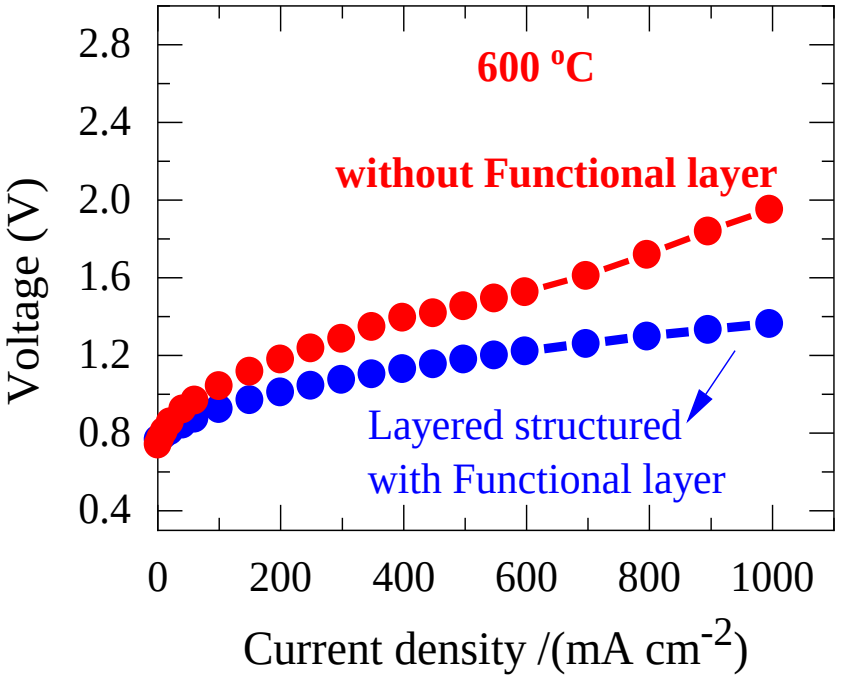


Progress on bottom size cell configuration (PCEC mode)

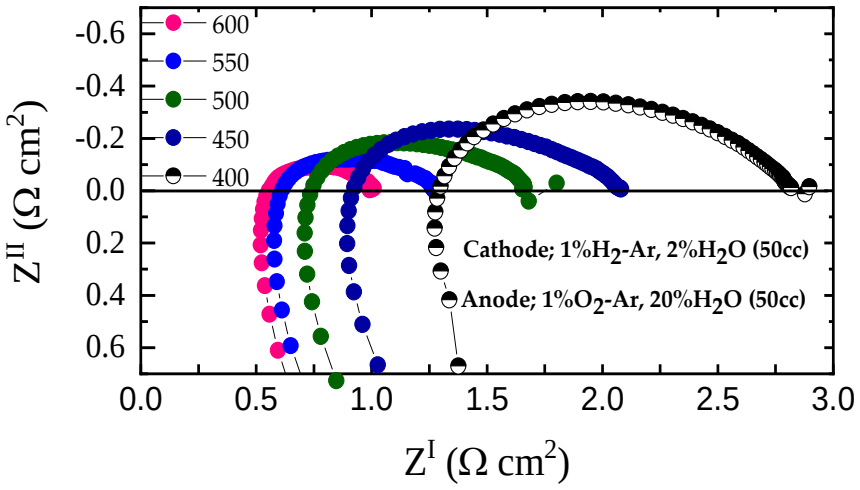
$Ba_{0.5}La_{0.5}CoO_{3-\delta}$| $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$

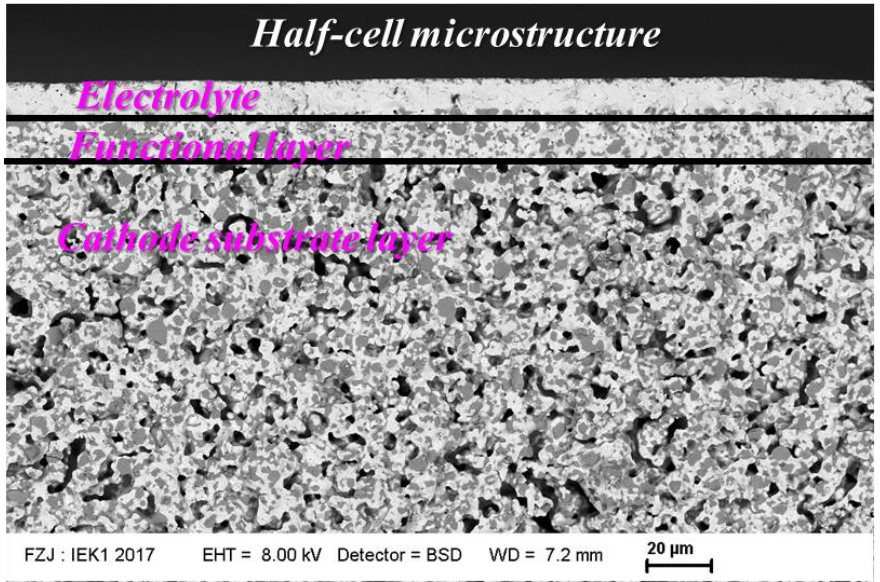


BLC| BZCY| Ni-SZCY541|Ni-$BZCY(54)_{8/9}2$



$Ba_{0.5}La_{0.5}CoO_{3-\delta}$| $BaZr_{0.16}Ce_{0.64}Y_{0.2}O_{3-\delta}$



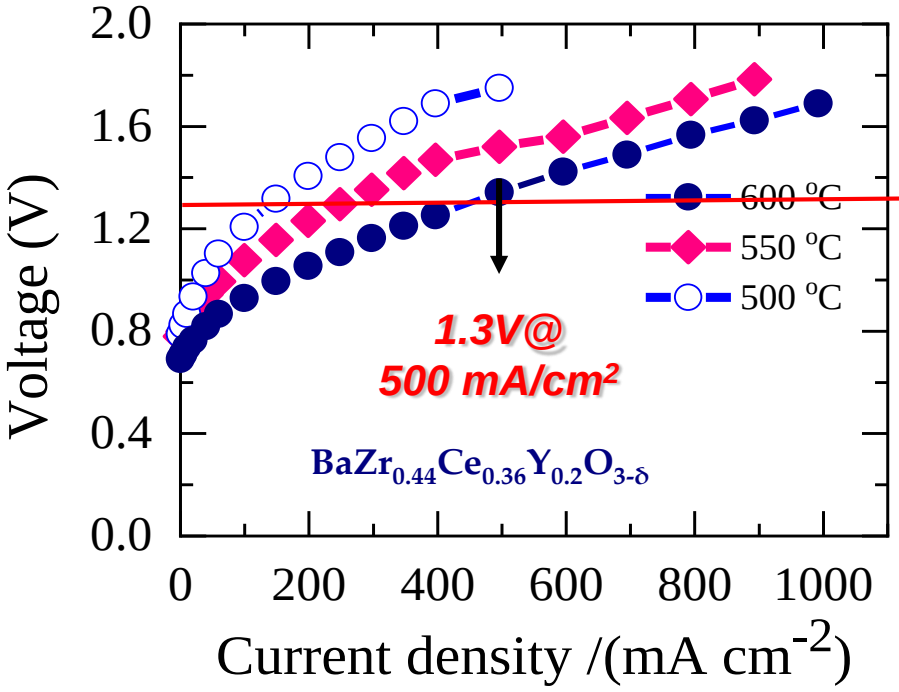


Steam electrolysis performance (PCEC)

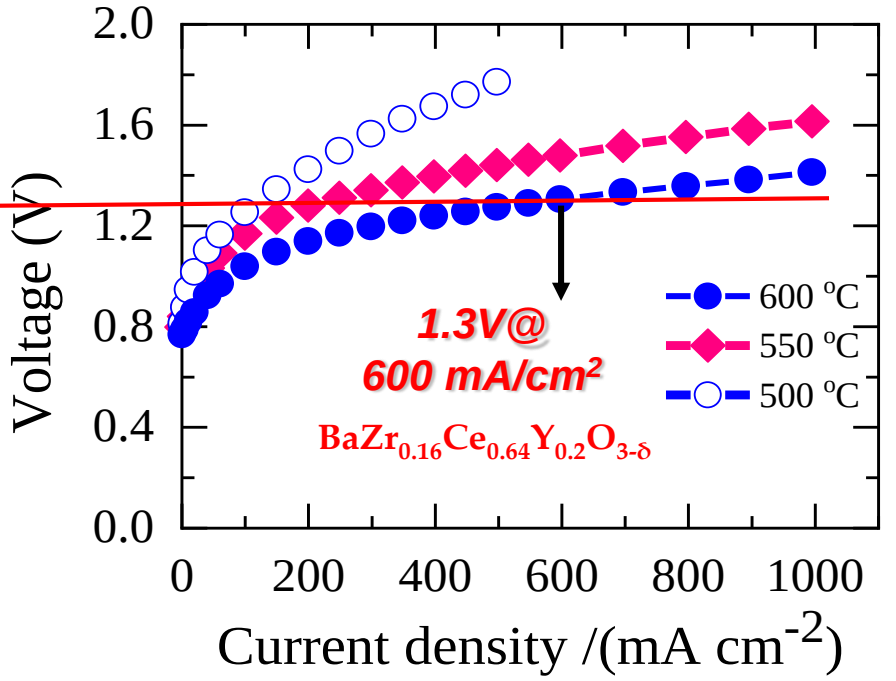
Cell configuration; BLC| BZCY| Ni-SZCY541

I-V characteristics:

$Ba_{0.5}La_{0.5}CoO_{3-\delta}$| $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$

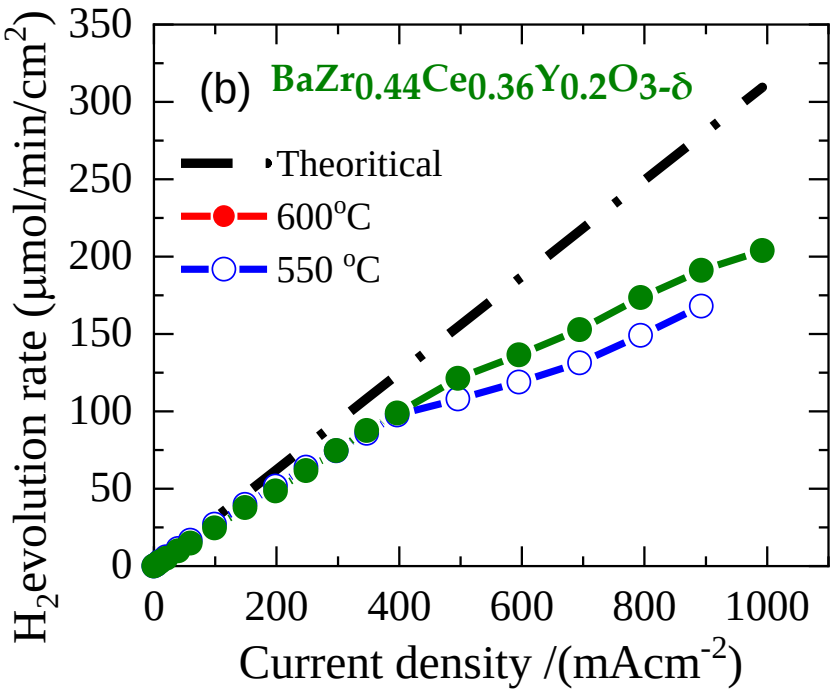


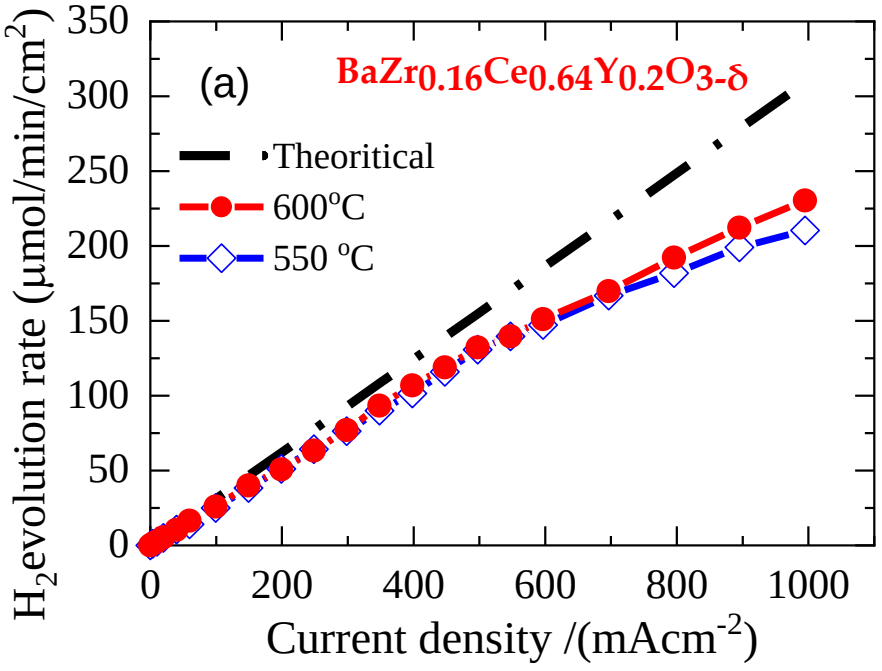
$Ba_{0.5}La_{0.5}CoO_{3-\delta}$| $BaZr_{0.16}Ce_{0.64}Y_{0.2}O_{3-\delta}$



Hydrogen evolution rate at 600 and 550 °C

- *Hydrogen evolution determined from the increase in hydrogen concentration at the cathode outlet using gas chromatography*



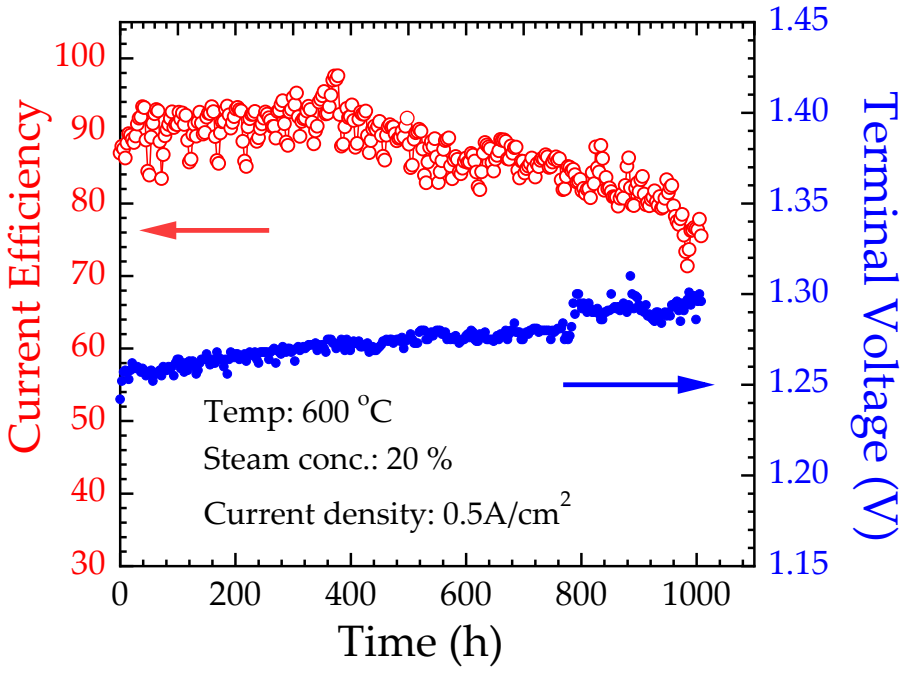


Hydrogen production mirrors Faraday's law
Deviation at high current density due to Electronic leakage
Current efficiency
78.5 and 82.7 % at 600 °C and 250 m Acm^{-2}

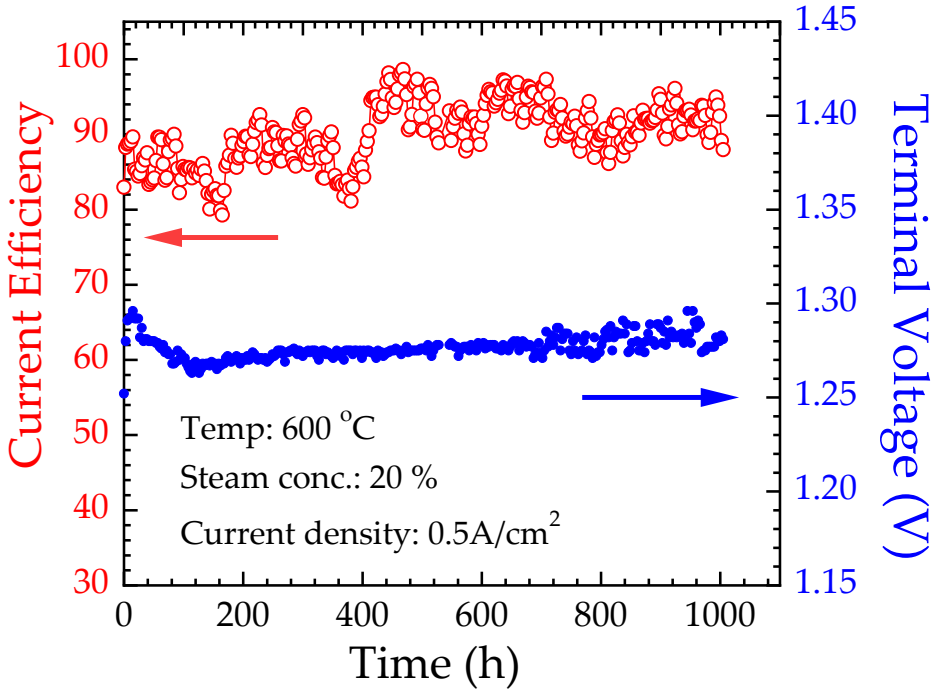
Stable performance
Current efficiency
81.5 and 83.1 % at 600 °C and 250 m Acm^{-2}
Impact; The calculated amount of electricity to produce 1 Nm^3 of H_2 is 3.8 kWh

Hydrogen Evolution and durability testing

Sample 1 Positrode ($Ba_{0.5}La_{0.5}CoO_3$)



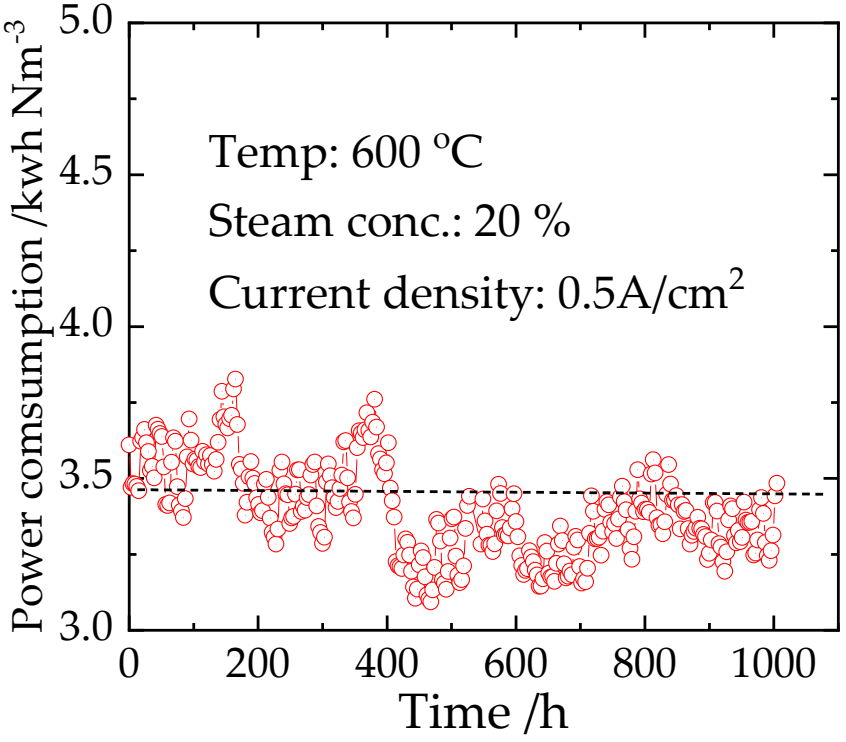
Sample 2 Positrode ($Ba_{0.5}La_{0.5}CoO_3$) For reproducibility

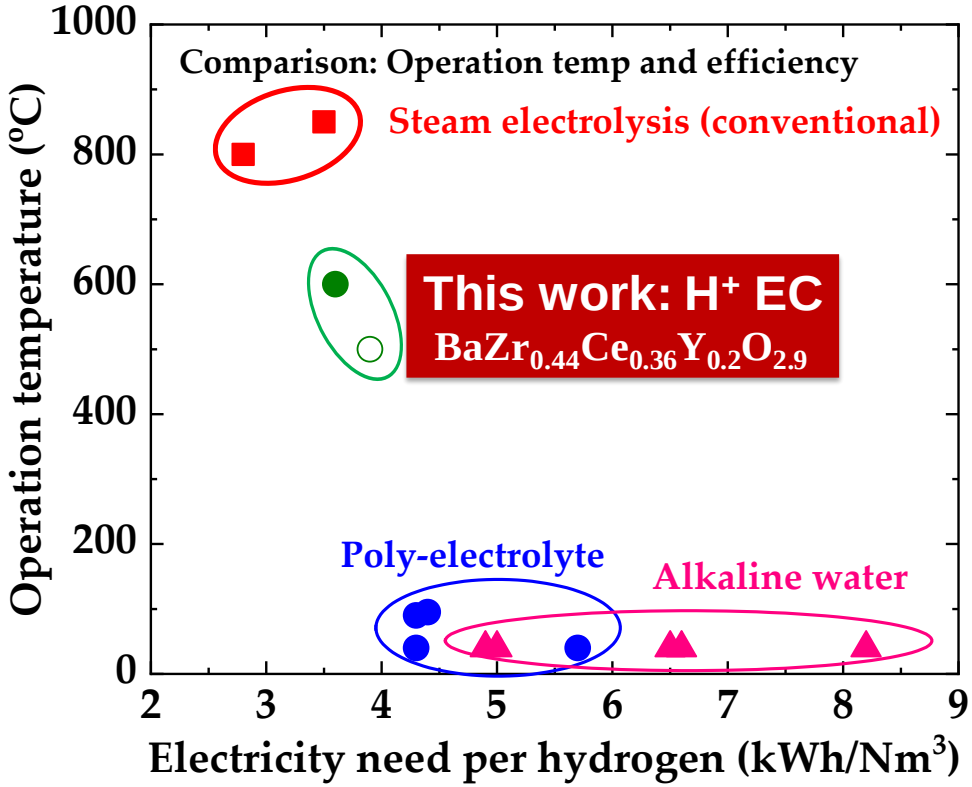


1.25 V@0.5 A/cm^2, η_{eff}= 80~92%(~10 μm)

Stable operation, degradation rate < 30mV over 1000 h

Summary and Comparison

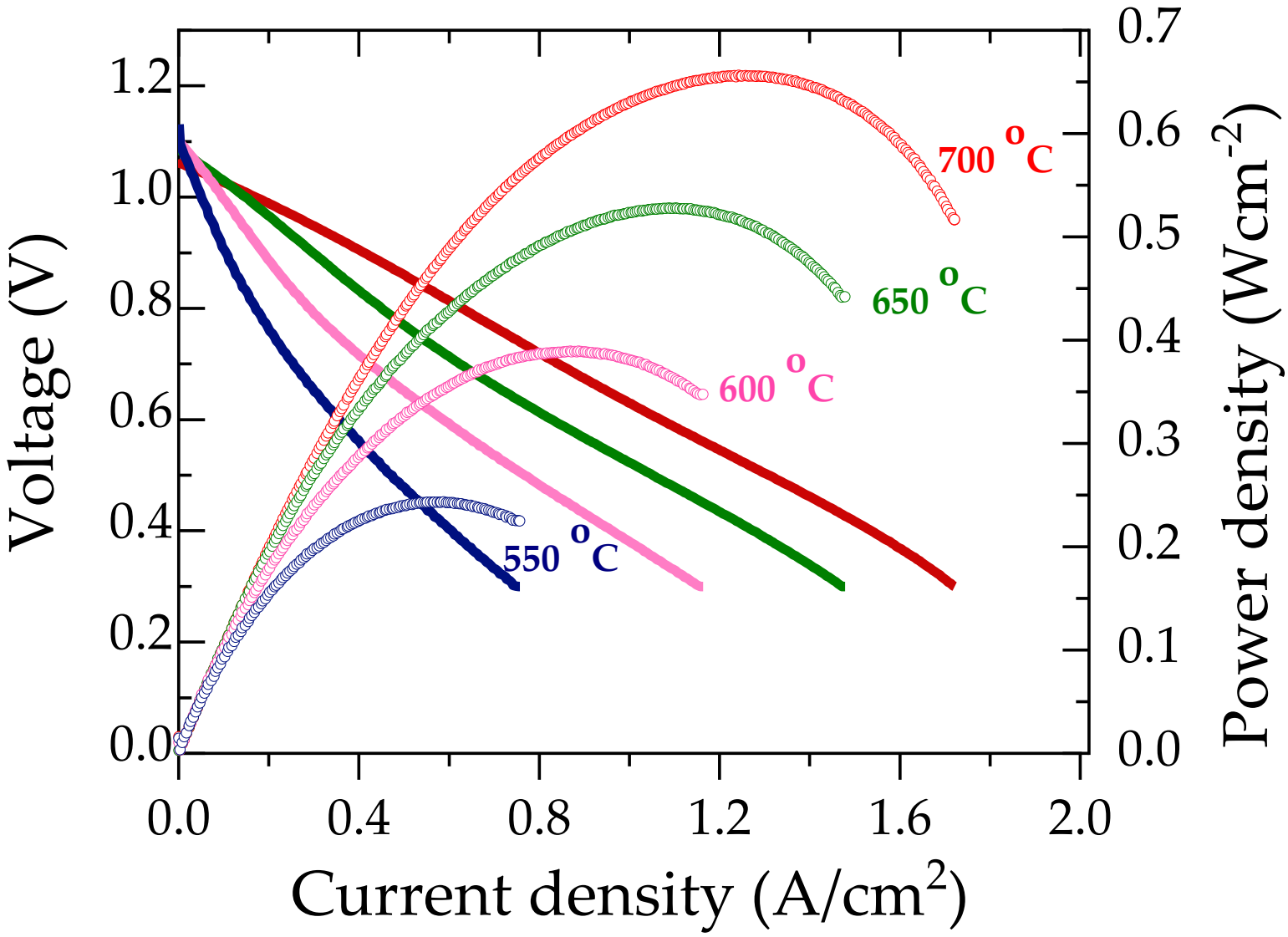




Stable power consumption. Impact; The calculated amount of electricity to produce 1 Nm^3 of H_2 is ~3.5 kWh at 600°C

PCFC performance

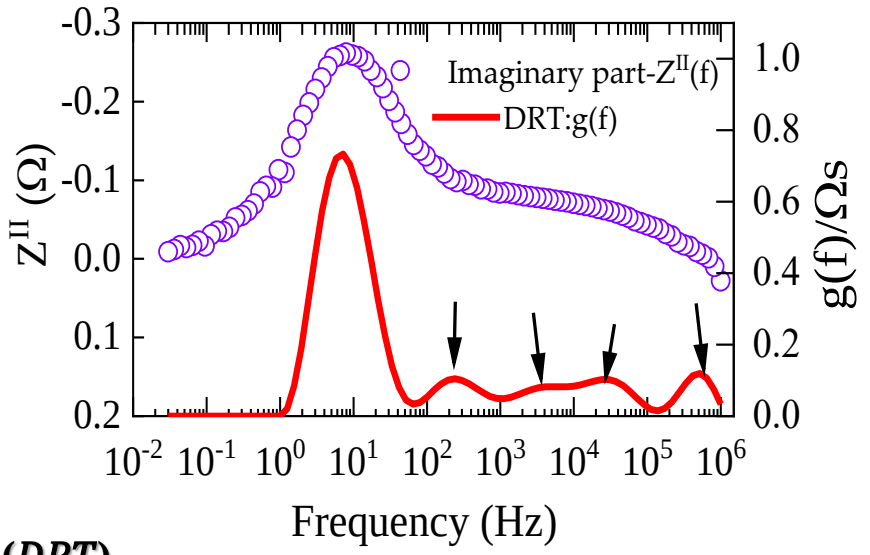
$Ba_{0.5}La_{0.5}CoO_3$ (BLC55)



Distribution Function of relaxation Times (DRT)

- Deconvolution of physicochemical processes in PCFC, to identify all performance-related polarization processes.

Due to inhomogeneity (Microstructure, gas composition etc.) Electrode processes show different behavior



Distribution function obtained by;

$$Z(\omega) = R_o + Z_{pol}(\omega) = R_o + \int_o^{\infty} \frac{g_{(t)}}{1+j\omega\tau} d\tau$$

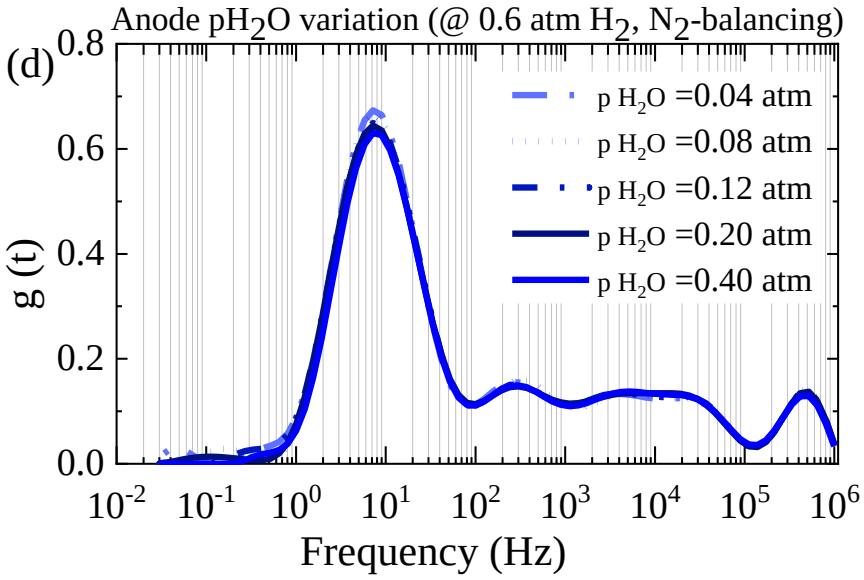
g(f) is the obtained (DRT)

Approach :

- Stepwise variation of operating Parameters e g. Temperature

Steam partial pressure (pH_2O an)

Oxygen partial pressure (pO_2,cat)



Results :

- All DRT-peaks are temperature dependent
- Strong impact of the oxidant composition
- The steam content in the fuel shows nearly no effect

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Summary

- ***NiO-$SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ cathode uniformly promotes densification of $Ba(Zr_{0.5}Ce_{0.4})_{8/9}Y_{0.2}O_{2.9}$ at 1350 ºC/5h.***

BLC| BZCY| Ni-SZCY541|Ni-$BZCY(54)_{8/9}2$

- ***The introduction of a NiO-$SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ Functional layer is effective in increasing the triple-phase boundaries and, therefore the cathode activity***

$$BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}/NiO\text{-}BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$$

- ***Ni diffuse to the electrolyte in the vicinity of NiO grain, resulting in an increase of resistance. High resistance part is in series with the electrode reaction***

Acknowledgements

Prof. Hiroshige Matsumoto
I²CNER Kyushu University

Prof. Tatsumi Ishihara
I²CNER Kyushu University

The financial support for this work from the Cross-ministerial Strategic Innovation Promotion Program (SIP), "energy carrier"(Funding agency: JST), JSPS Core-to-Core Program of Advanced Research Networks (Solid Oxide Interfaces for Faster Ion Transport), the Ministry of Economy, Trade and Industry (METI), and by the International Institute for Carbon Neutral Energy Research (I²CNER) sponsored by the World Premier International Research Center Initiative (WPI), MEXT Japan is gratefully acknowledged .

JÜLICH FORSCHUNGSZENTRUM

Prof. Wilhelm Albert Meulenberg

Dr. Mariya E. Ivanova

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Thank you for listening