

# Proton conducting ceramic cells with $\text{Ba}_{1-x}\text{Gd}_{0.8}\text{La}_{0.2+x}\text{Co}_2\text{O}_{6-\delta}$ oxygen electrode for steam electrolysis application

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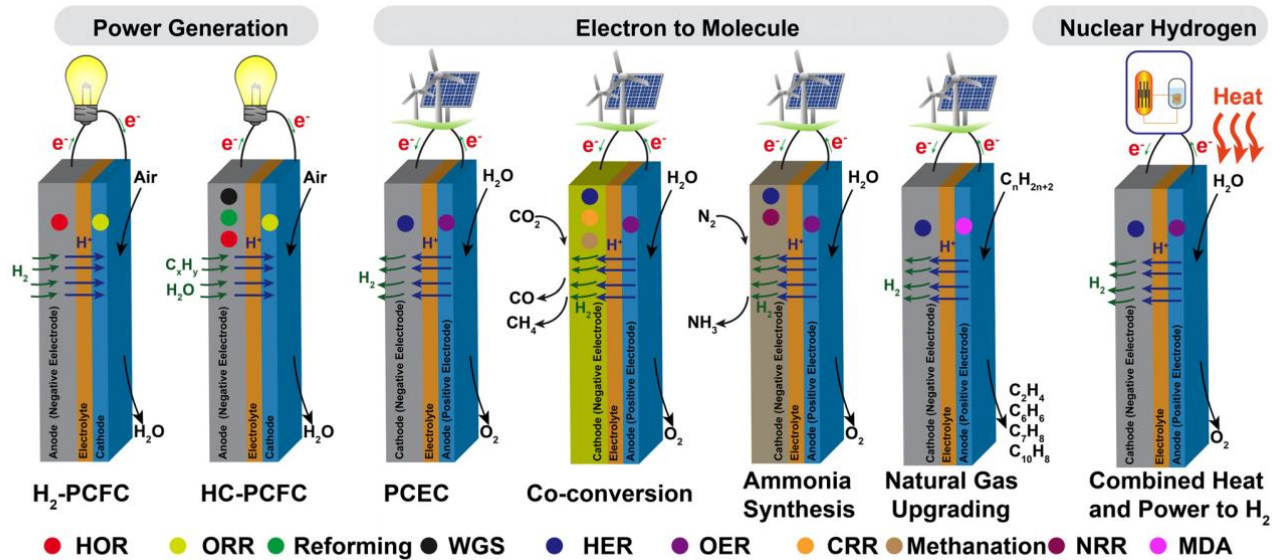
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Knowledge for Tomorrow



# Proton Conducting Ceramic (PCC) Cells



Ref. Duan, C. et al. Appl. Phys. Rev. 7, 011314 (2020)

❖ Operating temperature typically > 400 – 600 °C

Fuel cells	Lower Operating T / Higher P(fuel) at fuel electrode / Higher fuel utilization
Steam electrolysis	Produce pure hydrogen
Potential application of PCC	Electro-synthesis of ammonia, hydrocarbon products
Energy sources Coupling	Industrial waste steam, nuclear energy

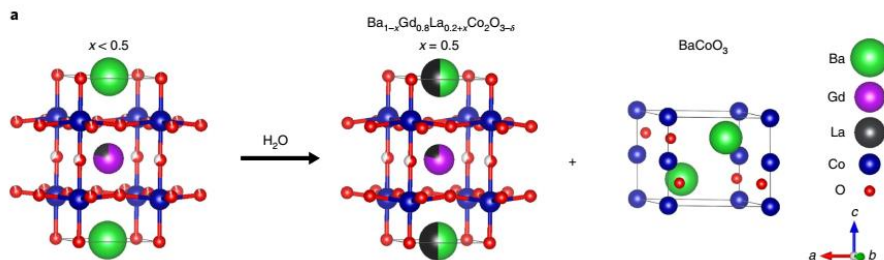


# Oxygen electrode materials

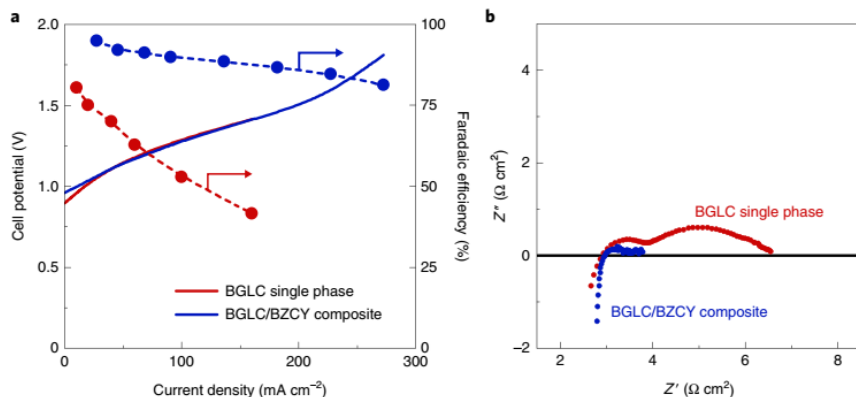
➤ **Double perovskite**  $\text{Ba}_{1-x}\text{Gd}_{0.8}\text{La}_{0.2+x}\text{Co}_2\text{O}_{6-\delta}$

➤ **Previous research on BGLC**

Ref. Einar Vøllestad et al. Nat Mater, 18 7 752-759.



- $X=0.5$ ,  $\text{Ba}_{0.5}\text{Gd}_{0.8}\text{La}_{0.7}\text{Co}_2\text{O}_{6-\delta}$  (BGLC587)
- Chemical stability with 1.5 bar steam for 72h



- Faradaic efficiency: 80-90% (3 bar)
- Current density is higher than  $100 \text{ mA cm}^{-2}$
- High  $R_\Omega$  ( $\sim 2.8 \Omega \text{ cm}^2$ ) and  $R_p$  ( $\sim 0.8 \Omega \text{ cm}^2$ ) tubular cell

**Goal:** Evaluation of the performance (FC and EC) of BGLC587 oxygen electrode on planar cells architecture (fuel electrode supported cells and **metal-supported cells**)

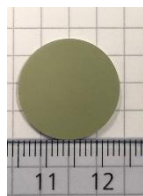


# Methodology

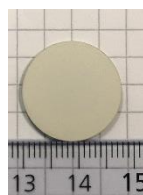
## Fuel electrode supported proton conducting cells manufacture



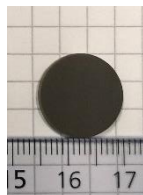
Mixing ceramic powders



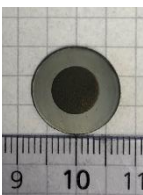
NiO-BZCY  
Dry-pressing mixed powder  
Pre-sintering at 1200 °C  
Anode substrate



Drop-coating BZCY electrolyte

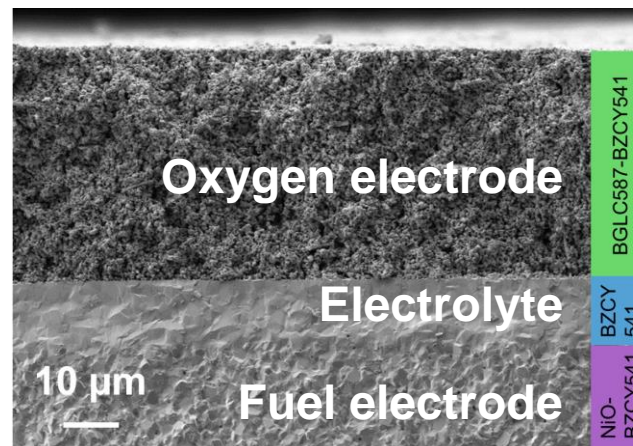


Sintering at 1450 °C  
Ni-BZCY/BZCY Half cell

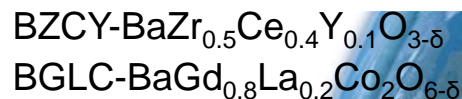
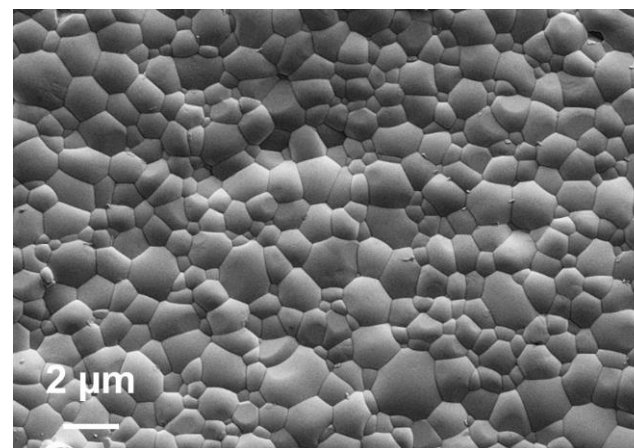


Screen-printing air electrode  
BGLC-BZCY  
Sintering at 900 °C  
AS-PCC full cell

### ➤ Cross-section

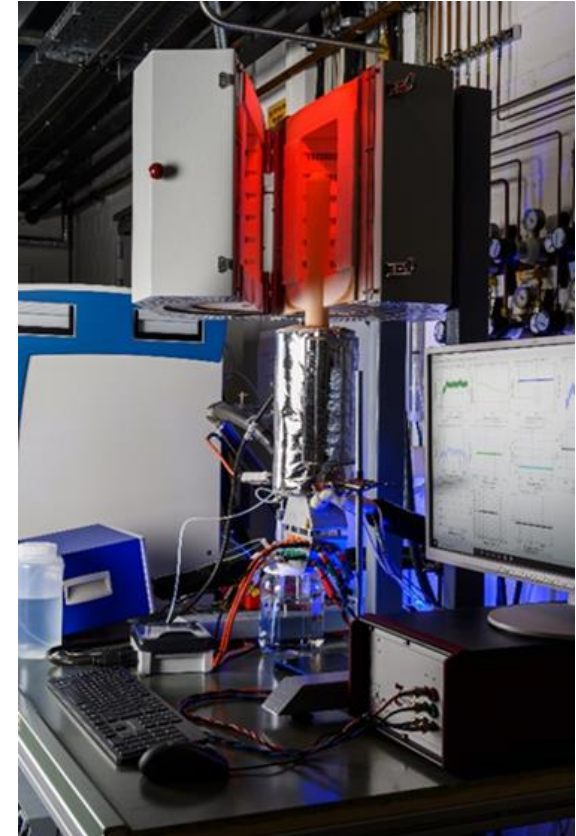


### ➤ Surface image of BZCY electrolyte



# Methodology cell test

- Operating mode
  - Fuel cell
  - Steam electrolysis
- Parameter variations
  - temperature,  $P(\text{O}_2)$ ,  $P(\text{H}_2\text{O})$ , electronic loading (V, I)
- Electrochemical analysis
- Outlet gas composition analysis (electrolysis mode)

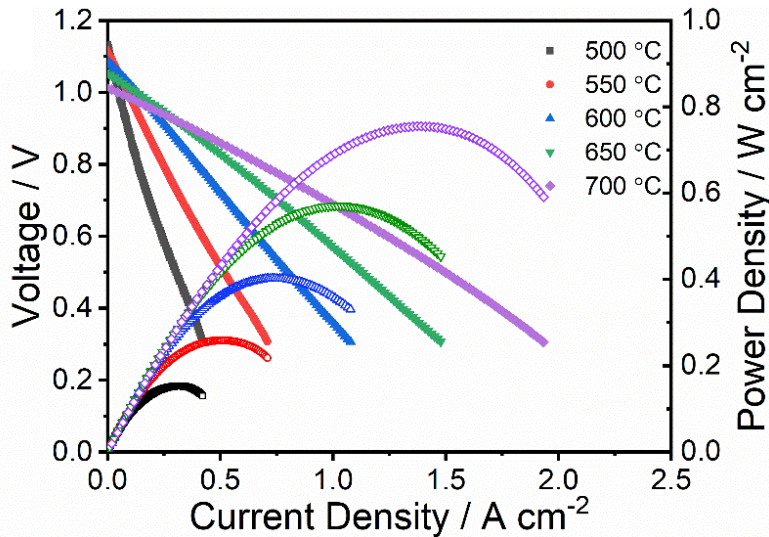


BGLC-BZCY

BZCY

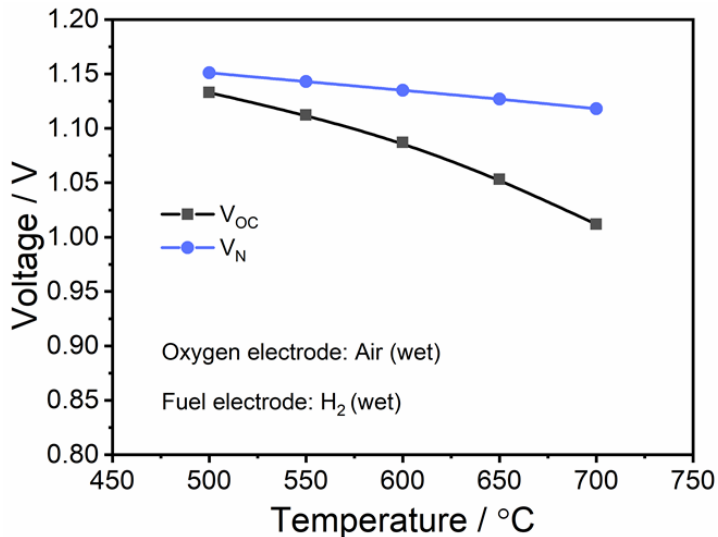
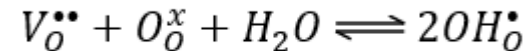
NiO-BZCY

# BGLC587-BZCY541: Fuel cell operation (PCFC)



## ➤ Polarization curves

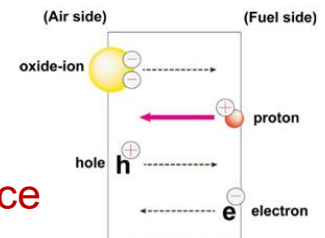
- 50 sccm H<sub>2</sub> (3% H<sub>2</sub>O)/ 50 sccm Air (3% H<sub>2</sub>O)  
Fuel electrode/ oxygen electrode
- P<sub>max</sub>: 755 mW cm<sup>-2</sup> at 700 °C  
403 mW cm<sup>-2</sup> at 600 °C
- Protonic charge carrier by hydration process



## ➤ Comparison of OCV and theoretical potential

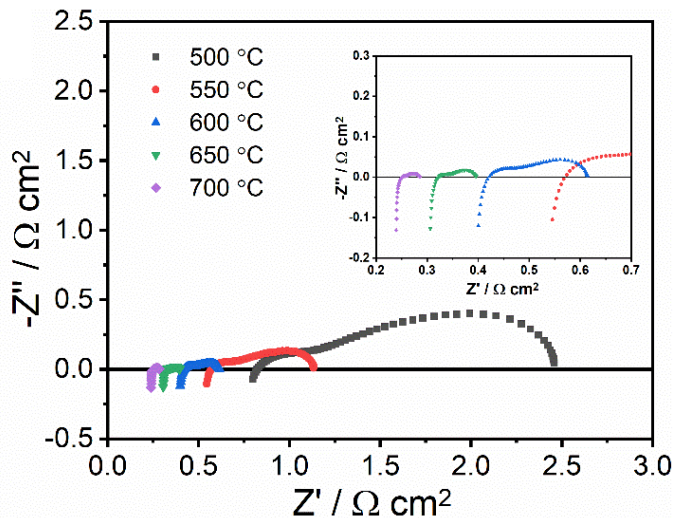
- Low OCV, p-type electronic conduction in electrolyte
- Oxygen incorporation :  $\frac{1}{2}O_2 + V_O^{**} \rightleftharpoons O_O^x + 2h^*$
- $h^* + e^- \rightarrow 0$

Current leakage ? → PCCs performance

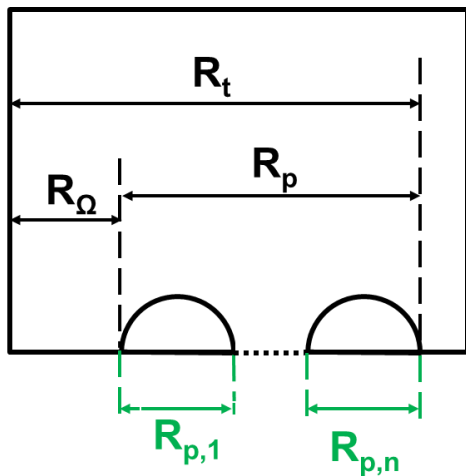
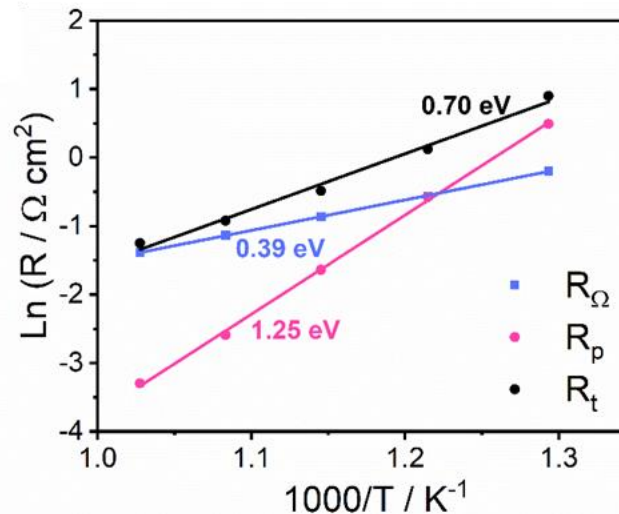
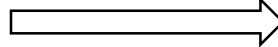


# Fuel cell operation

## ➤ EIS at different temperatures under OCV



Arrhenius plot

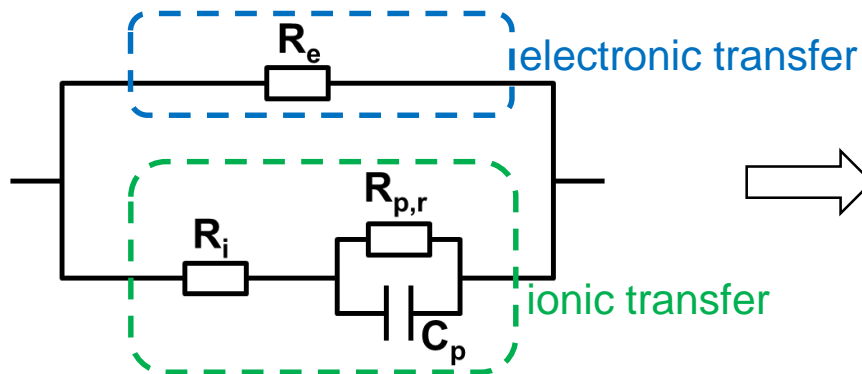


- 600 °C,  $R_{\Omega}=0.421\Omega\text{ cm}^2$ ,  $R_p=0.194\Omega\text{ cm}^2$
- Performance was limited by Zr-rich BZCY541 electrolyte
- Activation energy of ohmic resistance is 0.39 eV (proton conduction 0.3-0.5 eV)
- If electronic conduction take into account

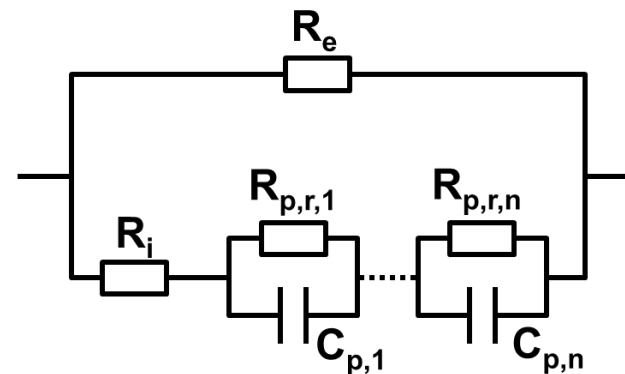
Apparent resistance  $\stackrel{?}{=}$  Real resistance



# EIS model



## ➤ multi-electrode process



### ➤ At high frequencies

Ohmic resistance:  $R_{\Omega} = \frac{R_e R_i}{R_e + R_i}$

### ➤ At low frequencies

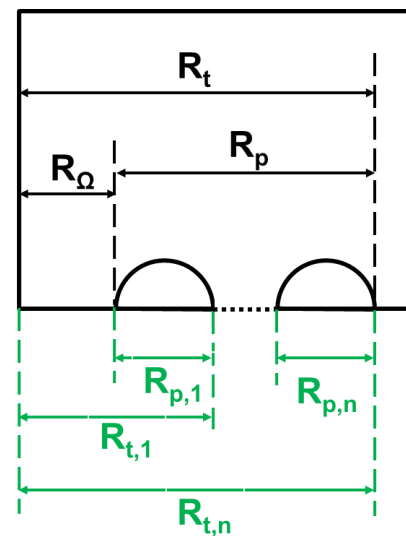
Total resistance:  $R_t = \frac{R_e (R_i + R_{p,r})}{R_e + (R_i + R_{p,r})}$

Electronic resistance<sup>1</sup>:  $R_e = \frac{R_t}{1 - \frac{V_{OC}}{V_N}}$

Ionic transfer number:  $t_i = \frac{R_e}{R_e + R_i}$

$t_i = 1$ , ionic conductor

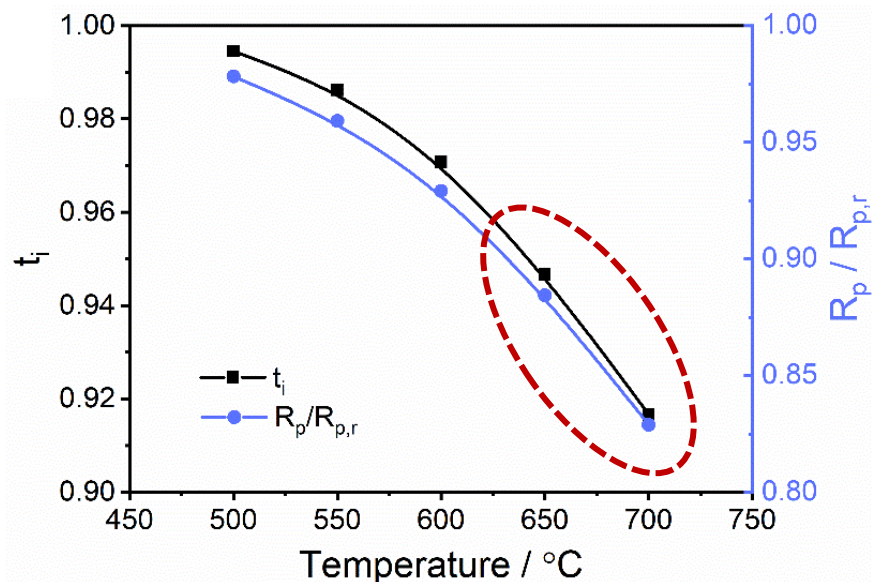
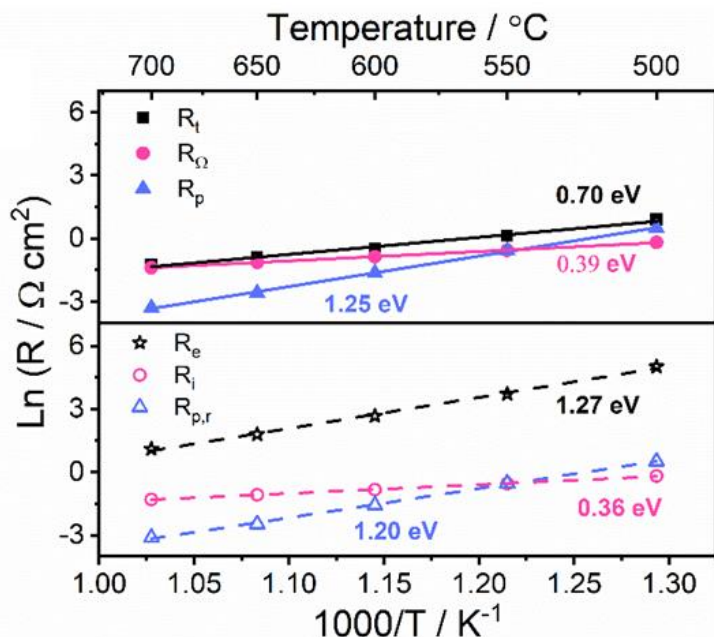
$t_i < 1$ , ionic-electronic conductor



$R_{p,r,1}, R_{p,r,2}, \dots, R_{p,r,n}$

# Fuel cell operation

## ➤ Comparison of Arrhenius plot

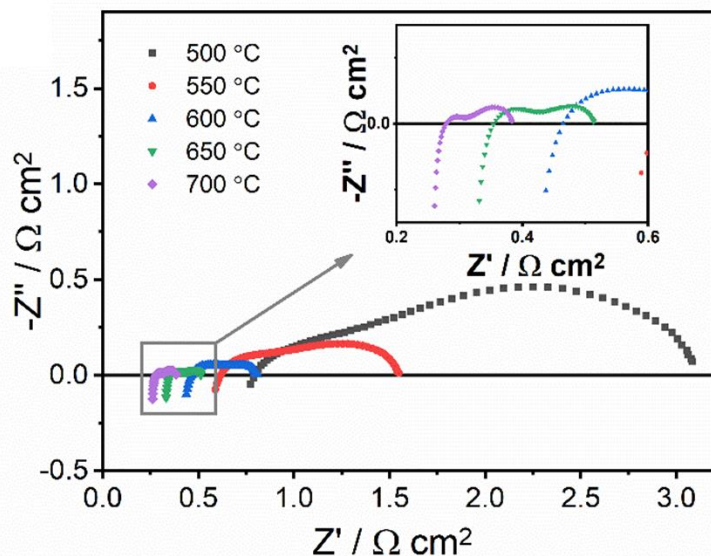


- Activation energy ( $E_a$ ) decreased, when the electronic conduction was taken into account
- The real resistance values were larger than the apparent resistance values  
 $R_{\Omega}: 0.421 \Omega \text{ cm}^2 \rightarrow R_i: 0.434 \Omega \text{ cm}^2$       $R_p: 0.194 \Omega \text{ cm}^2 \rightarrow R_{p,r}: 0.209 \Omega \text{ cm}^2$
- PCCs is better to operate at low temperatures ( $< 600 \text{ }^\circ\text{C}$ )

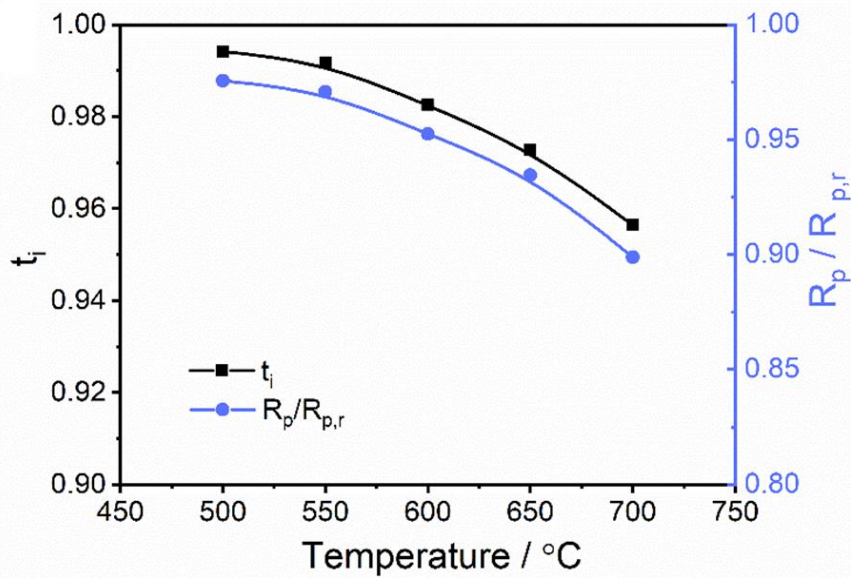
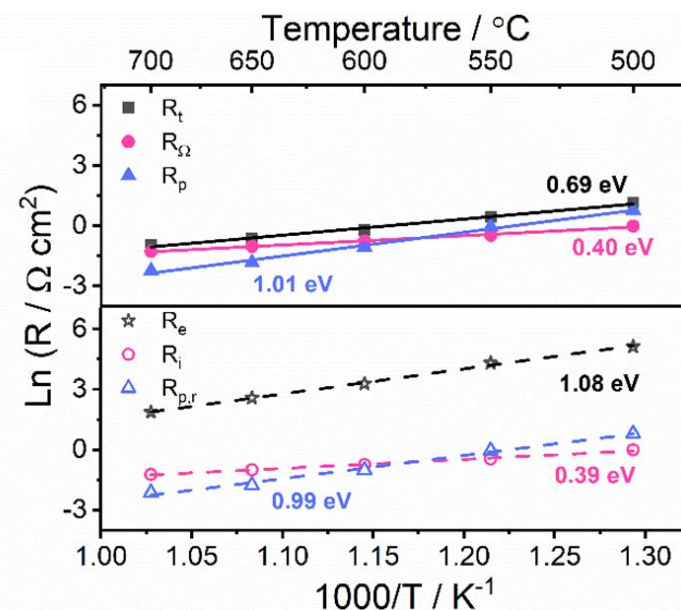
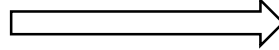


# Steam electrolysis operation (PCEC)

## ➤ EIS at different temperatures under OCV



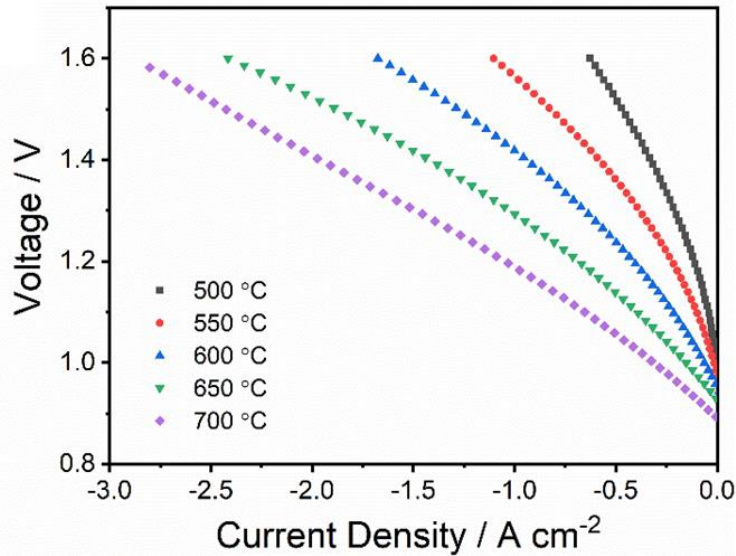
Arrhenius plot



- Deviation of  $E_a$  is smaller in PCEC than PCFC mode
- $E_a(R_{p,r})$ : 0.99 eV (PCEC), 1.20 eV (PCFC)
- Ionic transfer number and  $R_p/R_{p,r}$  in PCEC higher than PCFC mode



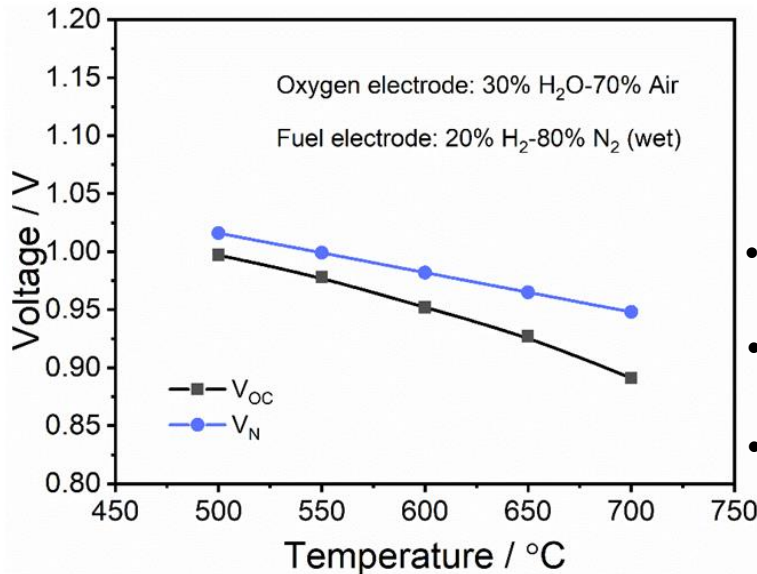
# Steam electrolysis operation (PCEC)



## ➤ Polarization curves

	500 °C	550 °C	600 °C	650 °C	700 °C
I / A cm <sup>-2</sup> (at 1.3 V)	-0.22	-0.40	-0.67	-1.05	-1.48

Influence from electronic conduction



## ➤ Comparison of OCV and theoretical potential

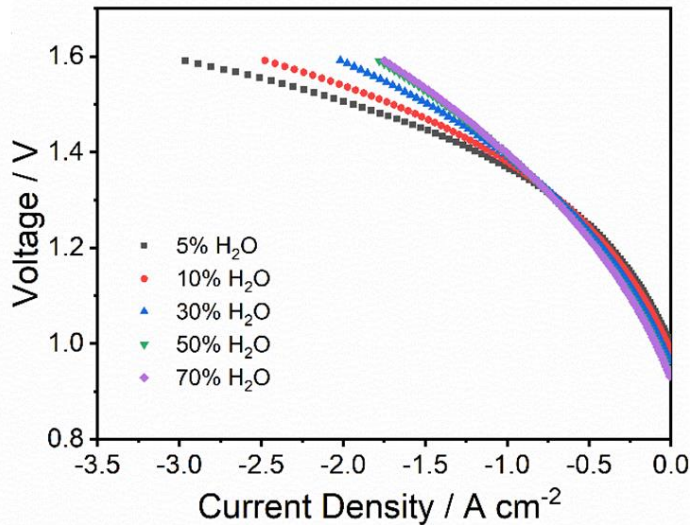
$$[h^\bullet] = K_H^{-\frac{1}{2}} K_O^{\frac{1}{2}} [OH_O^\bullet] [O_O^x]^{-1} P_{H_2O}^{-\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$$

- Oxygen electrode:  $P(H_2O) \uparrow$  and  $P(O_2) \downarrow \Rightarrow [h^\bullet] \downarrow$
- I-V curves, "high" current  $\neq$  high performance
- Faradaic efficiency:  $\eta_{FE} = \frac{n_{measured, H_2}}{n_{theoretical, H_2}} = \frac{n_{measured}}{I \times (n \times F)^{-1}}$



# Gas variation- $P(\text{H}_2\text{O})$ and Faradaic efficiency- $\eta_{FE}$

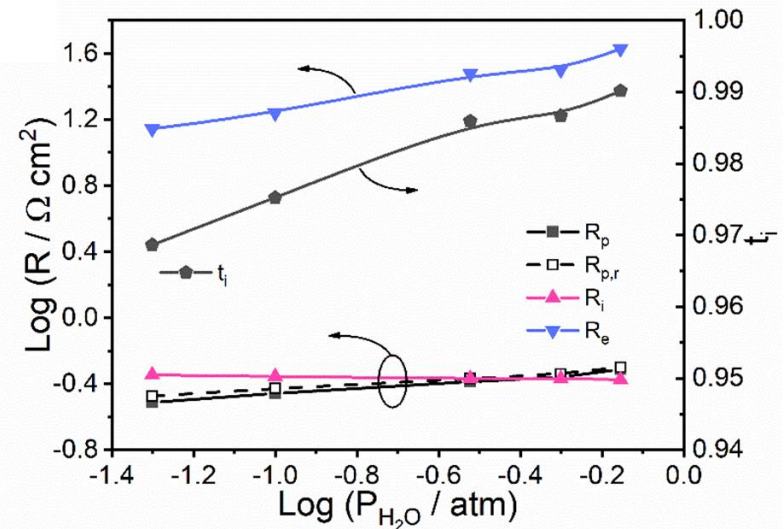
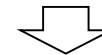
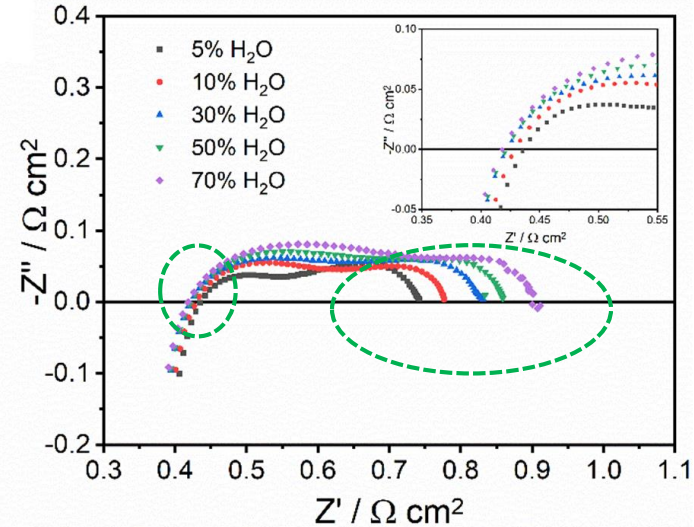
## ➤ I-V curves with different $P(\text{H}_2\text{O})$



600 °C  
 Oxygen electrode: P(H<sub>2</sub>O)/Air  
 Fuel electrode: 20% H<sub>2</sub>/80% N<sub>2</sub> (wet)

- $[h^\bullet] = K_H^{-\frac{1}{2}} K_O^{\frac{1}{2}} [\text{OH}_O^\bullet] [\text{O}_O^x]^{-1} P_{\text{H}_2\text{O}}^{\frac{1}{2}} P_{\text{O}_2}^{\frac{1}{4}}$
- In PCCs, the conflicting trends higher  $P(\text{H}_2\text{O})$ ,  $R_i \downarrow$ , but  $R_p \uparrow$

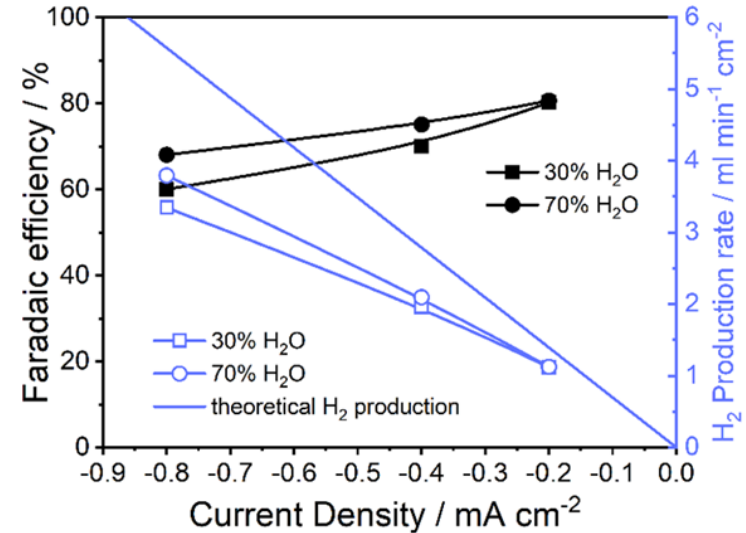
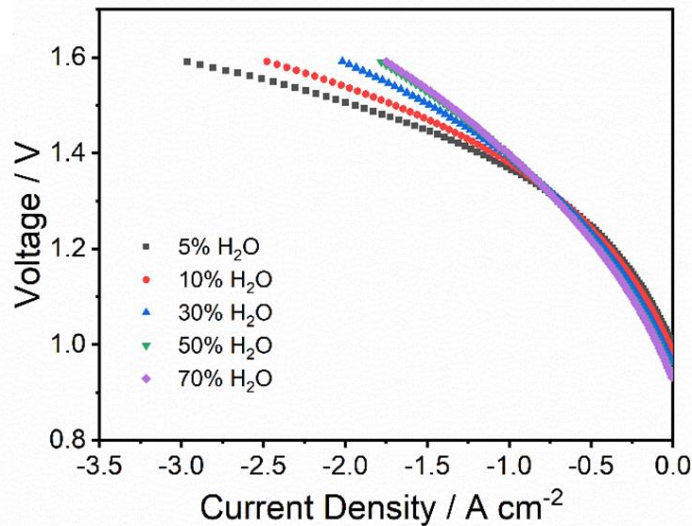
## ➤ EIS under OCV



# Gas variation- $P(\text{H}_2\text{O})$ and Faradaic efficiency- $\eta_{FE}$

## ➤ I-V curves with different $P(\text{H}_2\text{O})$

## ➤ Faradaic efficiency



600 °C  
 Oxygen electrode: P(H<sub>2</sub>O)/Air  
 Fuel electrode: 20% H<sub>2</sub>/80% N<sub>2</sub> (wet)

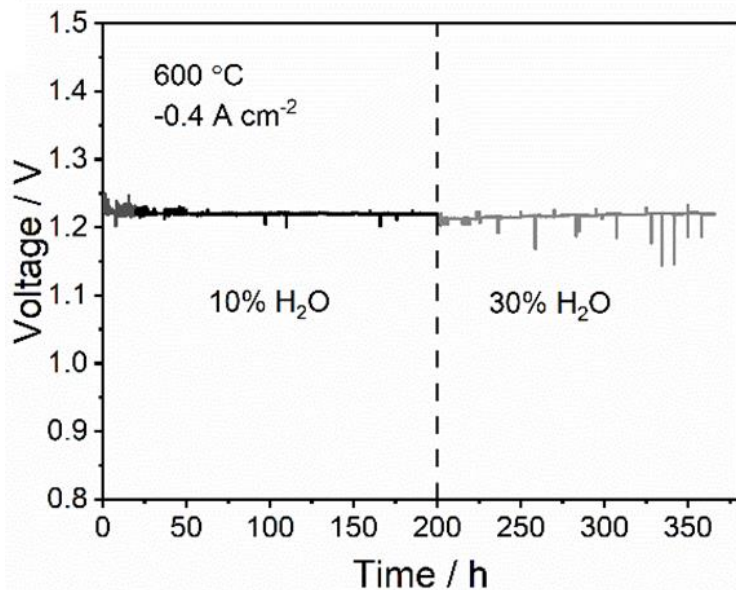
$$[h^\bullet] = K_H^{-\frac{1}{2}} K_O^{\frac{1}{2}} [\text{OH}_O^\bullet] [\text{O}_O^x]^{-1} P_{\text{H}_2\text{O}}^{-\frac{1}{2}} P_{\text{O}_2}^{\frac{1}{4}}$$

$$[h] = K_{\text{ox}} [\text{OH}_O^\bullet] p_{\text{H}_2\text{O}}^{-\frac{1}{2}} p_{\text{O}_2}^{\frac{1}{4}} = K_{\text{ox}} \exp\left(\frac{F(E-E^0)}{RT}\right)$$



# Steam electrolysis: long-term durability

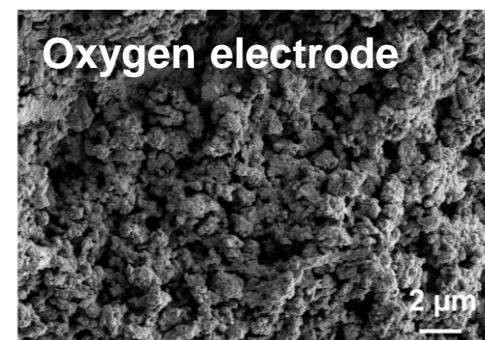
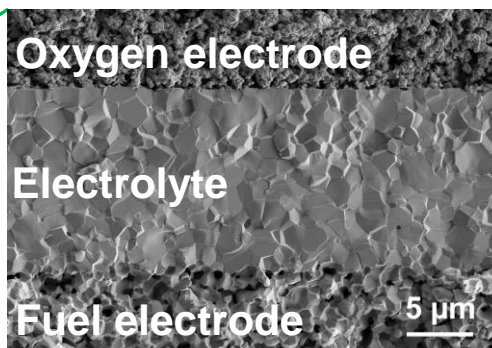
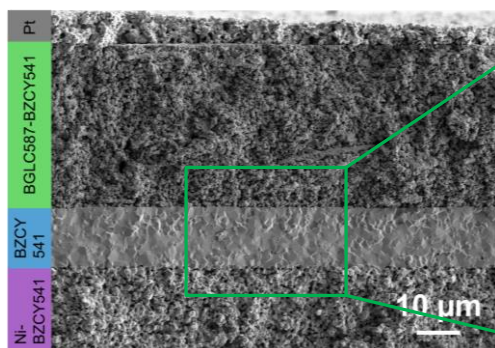
## ➤ Voltage VS time



Test time	Voltage change
0h -> 200h	1.223V -> 1.219V ( $\Delta=4\text{mV}$ )
200h ->366h	1.215V -> 1.217V ( $\Delta=2\text{mV}$ )

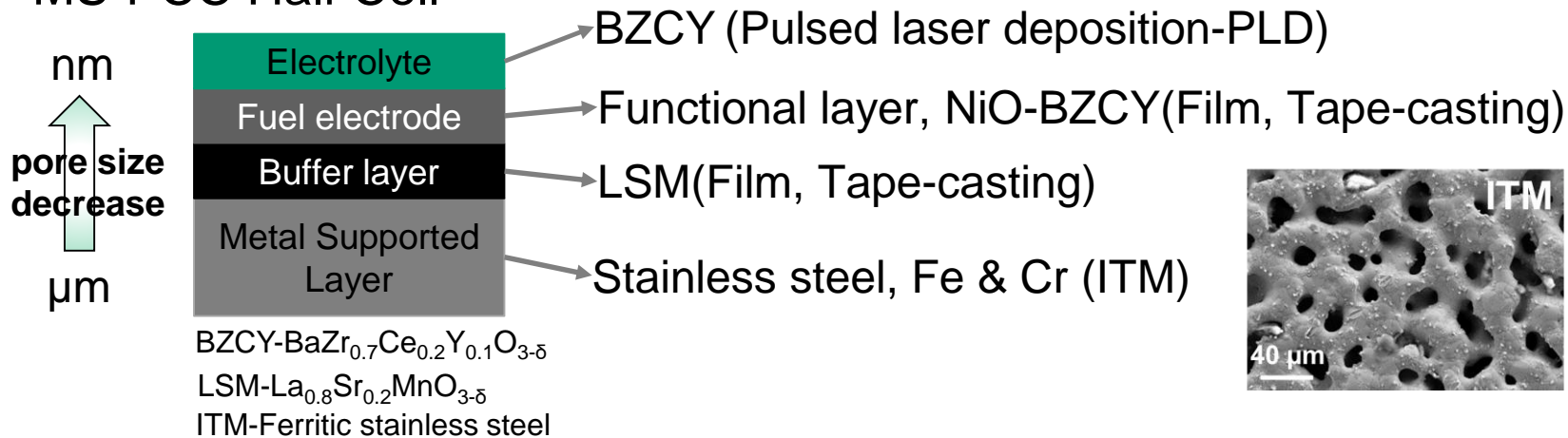
- Voltage is stable over 366h test

## ➤ SEM of the cell after measurement

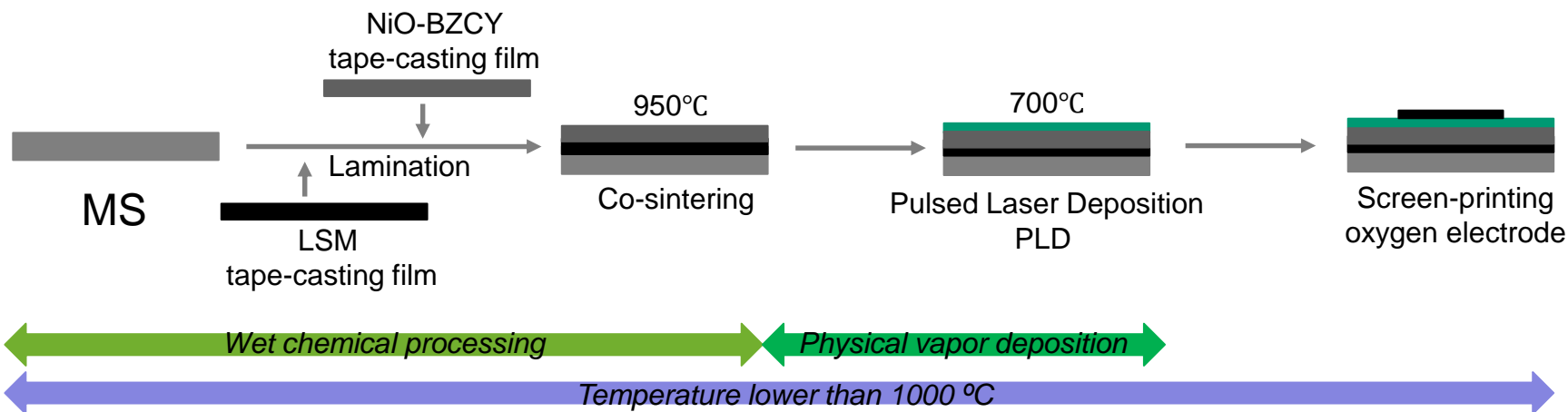


# Development of metal-supported PCCs

## ➤ MS-PCC Half Cell



## ➤ Flow chart for fabrication of the MS-PCC half cells

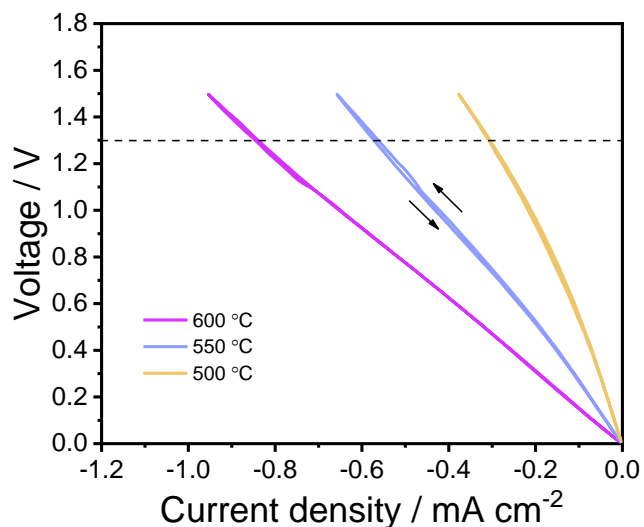


Ref. F. Han, X. Zhou, A. M. Dayaghi, T. Norby, M. Stange, N. Sata, R. Costa, ECS Transactions, 91(1), 1035 (2019)



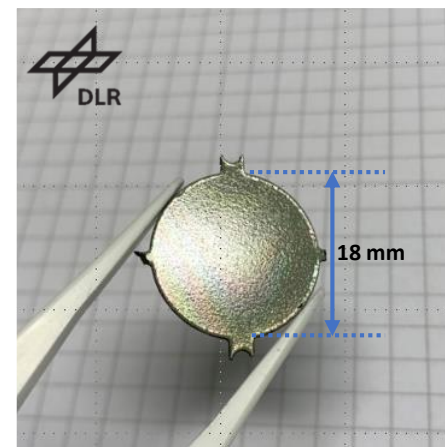
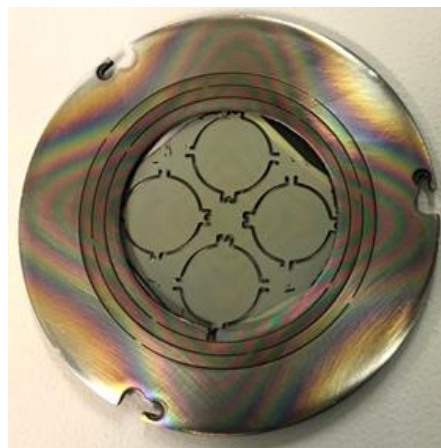
# Results: MS-PCC with BGLC oxygen electrode

## ➤ BGLC-BZCY oxygen electrode



Temperature / °C	500	550	600
Current density at 1.3 V / mA cm <sup>-2</sup>	306	567	842

## ➤ MS-PCC samples



## ➤ More details in MS-PCC development at DLR

(A1204)

Rémi Costa, Progress in the development of metal-supported-cell architecture with proton conducting ceramics



# Conclusions

- $X=0.5$ ,  $\text{Ba}_{0.5}\text{Gd}_{0.8}\text{La}_{0.7}\text{Co}_2\text{O}_{6-\delta}$  (BGLC587), BGLC587-BZCY541 composite oxygen electrode shows good initial performance in both fuel cell and steam electrolysis operation, and also good durability
- The electronic conduction through BZCY electrolyte was determined by a equivalent circuit mode
- In order to have a high faradaic efficiency, the optimized operation conditions are low testing temperature, high  $P(\text{H}_2\text{O})$  and low  $P(\text{O}_2)$  in oxygen electrode
- The new concept of metal-supported proton conducting ceramic cells for steam electrolysis was successfully clarified



# Acknowledgments



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- China Scholarship Council, Haoyu Zheng (201806160173).

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