Modularization of Ceramic Hollow Fiber Membrane Technology for Air Separation

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Projection Objective and Tasks

Objective:

Develop membrane stack and module for air separation and oxygen production using ceramic hollow fiber membrane technology

Strategic alignment of project to Fossil Energy objectives

- **Cost of Energy and Carbon Dioxide (CO2) Capture**
  - Using pure oxygen instead of air for combustion of power plant produces CO2, no need to separate nitrogen from down stream;
  - Can reduce the cost and simplify the system for CO2 capture.
- **Power Plant Efficiency Improvements**
  - Pure oxygen instead of air increases efficiency of power plant;
  - Cost-effective, reliable technologies to improve the efficiency of coal-fired power plants.

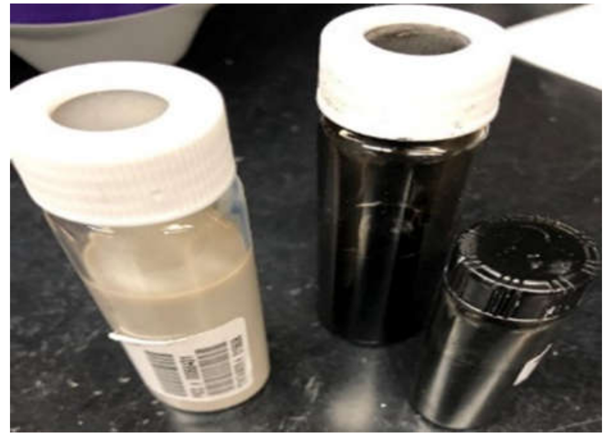
Current Status

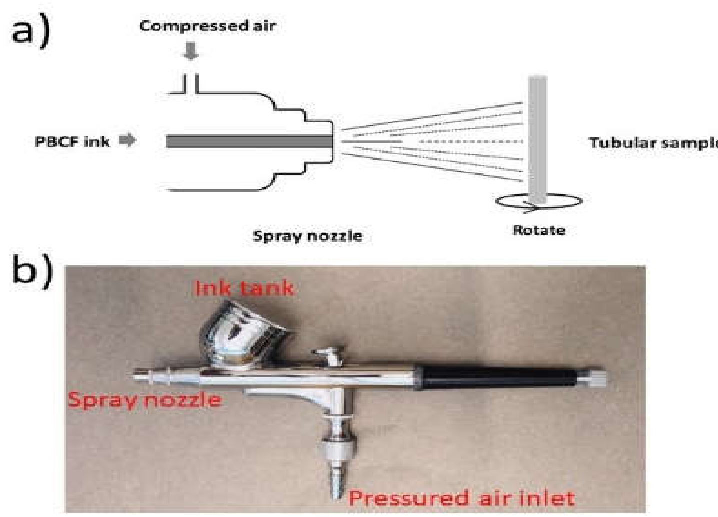
material *preparation*

Materials processing

materials processing

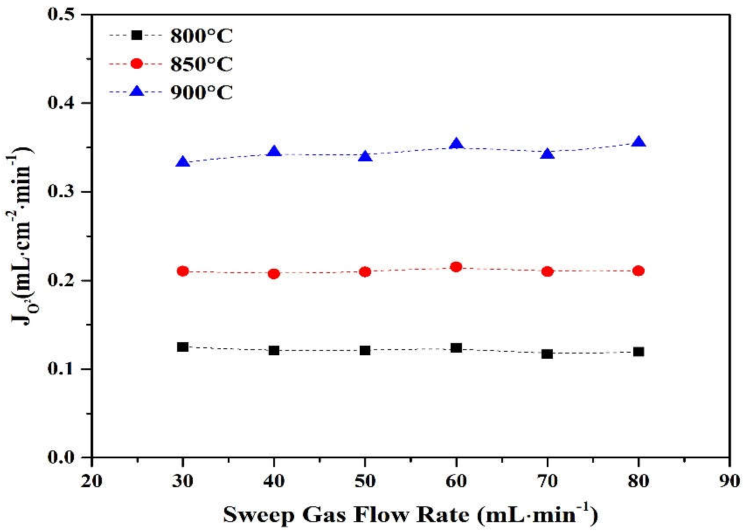
Current Status



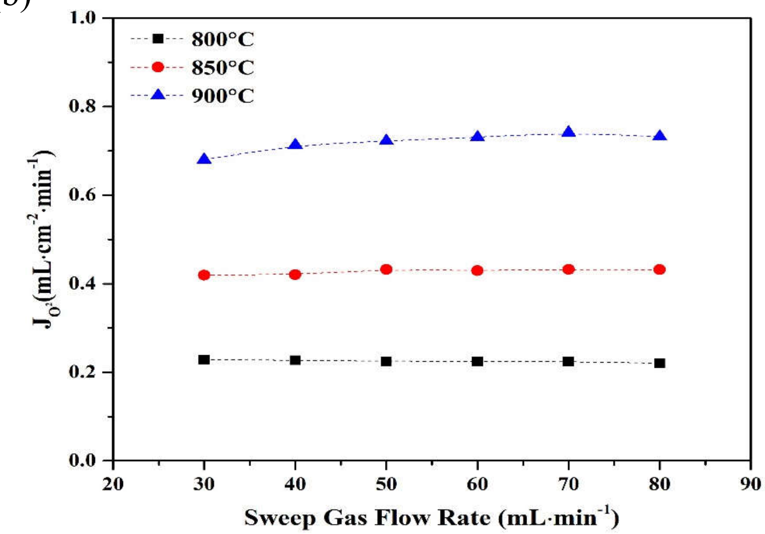


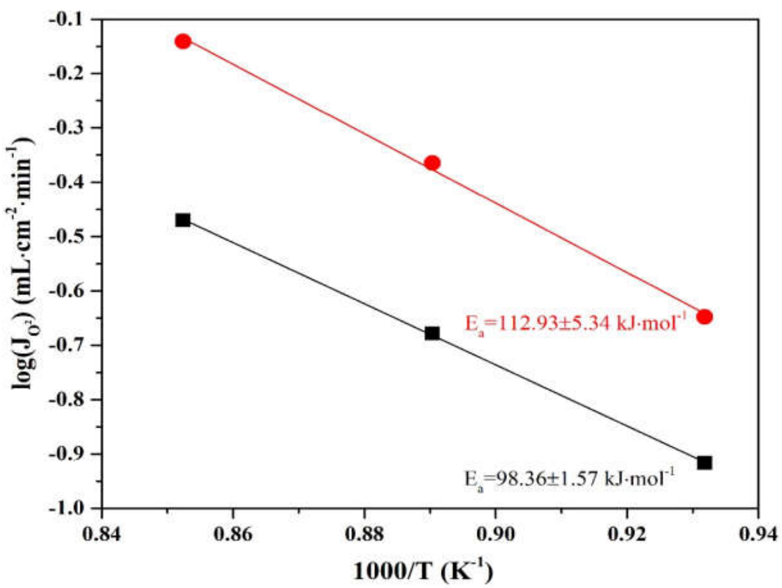
Performance test

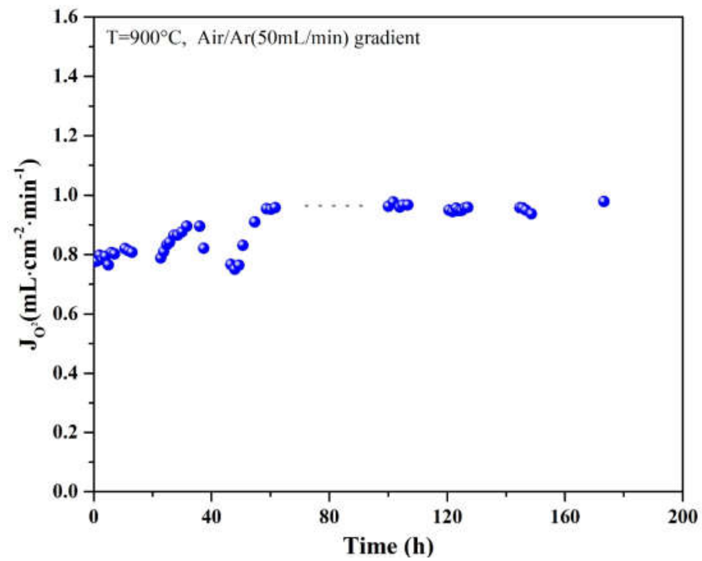
(a)



(b)







Characterization

$BaCoO_{3-\delta}$ family

Tradeoff of activity-stability $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$

Increase T →

Room Temperature

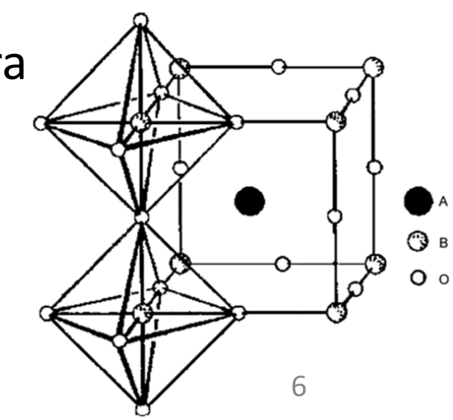
Hexagonal ➔ Tetragonal ➔ Cubic

← Decrease T

10% volume change ➔ delamination and component fractures

<u>Early Research:</u>

- High valance elements doped into B-site Nb^{5+}, Zr^{4+}, Ti^{4+} ,etc.
- Reason: Increase electrostatic repulsion between BO_6 octahedra
- Problems: 20 mol% of Ti is needed to substitute Co/Fe



P. Shen, et al, *The Journal of Physical Chemistry C*, **114**, 22338 (2010).
J. Tong, et al, *J. Membr. Sci.*, **203**, 175 (2002).
J. Tong, et al, *Sep. Purif. Technol.*, **32**, 289 (2003).

Characterization

Ytterbium (Yb)

$BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ → $BaCo_{0.7}Fe_{0.3-x}Yb_xO_{3-\delta}$

1. Tolerance Factor $t = 1 \rightarrow$ Cubic

Structure

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

✓ Yb^{3+}(VI) = 0.868 Å > Fe^{4+}(VI) = 0.585 Å

2. Electronic Structure

Kinetic property

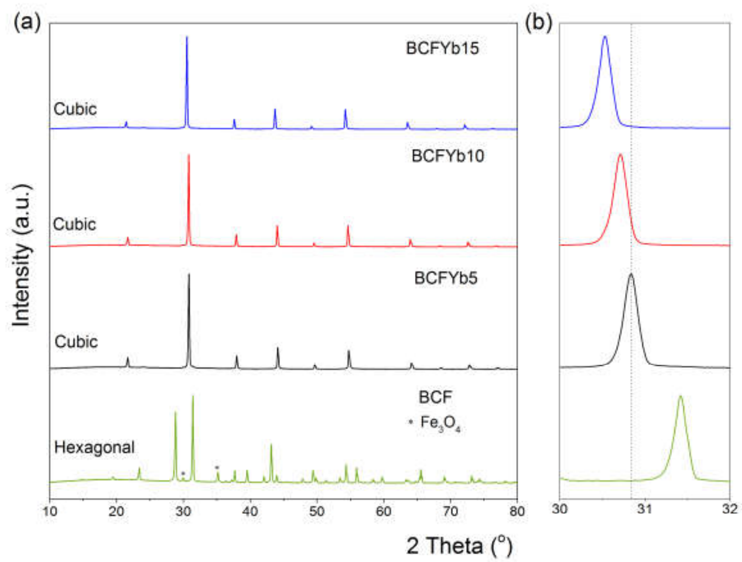
✓ Electronegativity Yb (1.1) < Co(1.7), Fe(1.8)

- Induce a slightly lower valance of B-site cations
- Facilitate formation of $V_O^{\cdot\cdot}$, bulk diffusion and surface exchange process

Characterization

1. Crystal Structure: x = 0, 0.05, 0.10 and 0.15

$BaCo_{0.7}Fe_{0.3-x}Yb_xO_{3-\delta}$

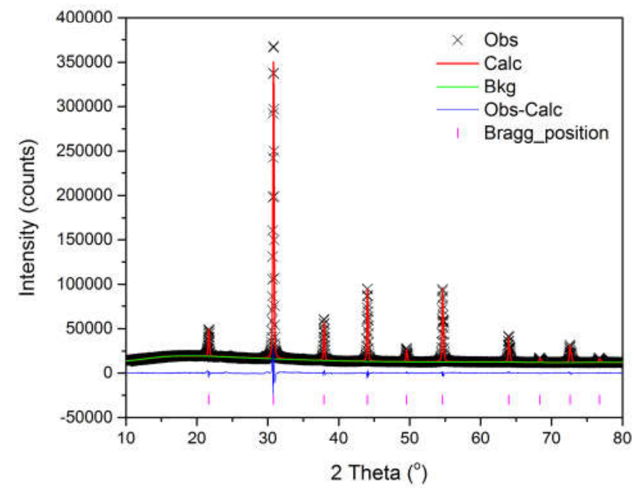


XRD patterns of BCF, BCFYb5, BCFYb10 and BCFYb15

Lattice Expansion

$Yb^{3+}(VI) = 0.868$ Å

$Fe^{4+}(VI) = 0.585$ Å



Rietveld refinement result of sample BCFYb10

Increase T

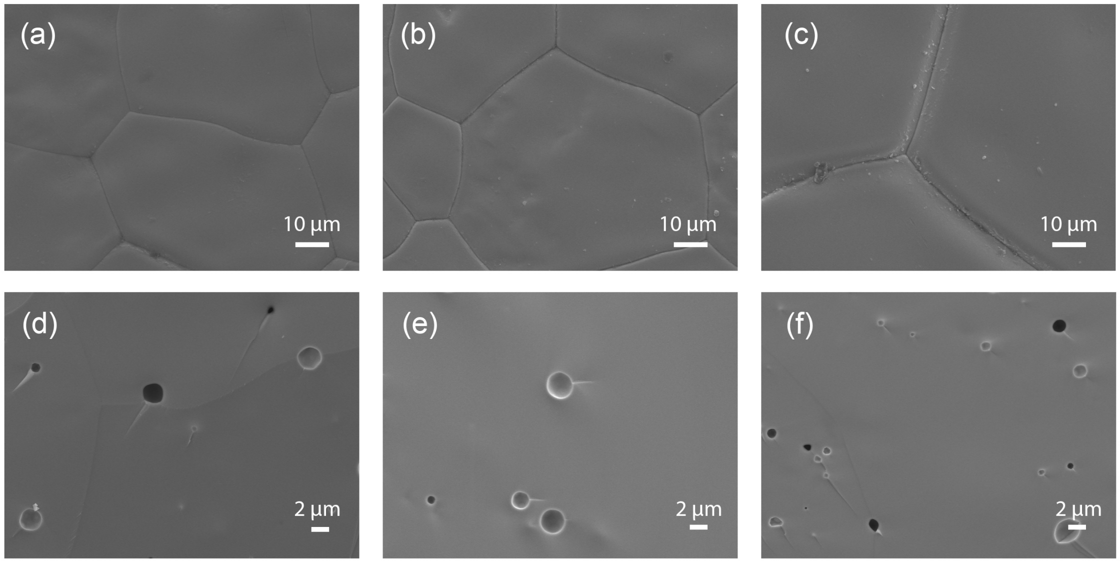
Problem: Hexagonal➔Tetragonal➔Cubic

Decrease T

	x=0.05	x=0.10	x=0.15
a (Å)	4.1042(7)	4.1153(5)	4.1367(7)
V(Å^3)	69.136(56)	69.698(00)	70.791(99)
GOF (χ^2)	4.59	4.93	4.92
R_F (%)	3.15	2.57	2.56
R_{wp} (%)	3.59	3.77	3.82

Characterization

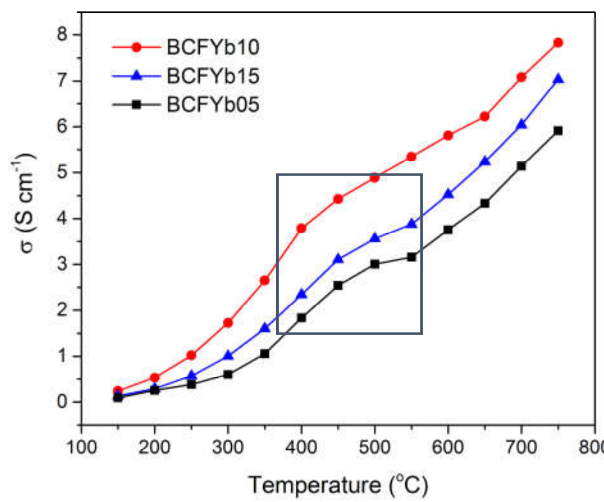
2. Sintering ability and Electrical conductivity

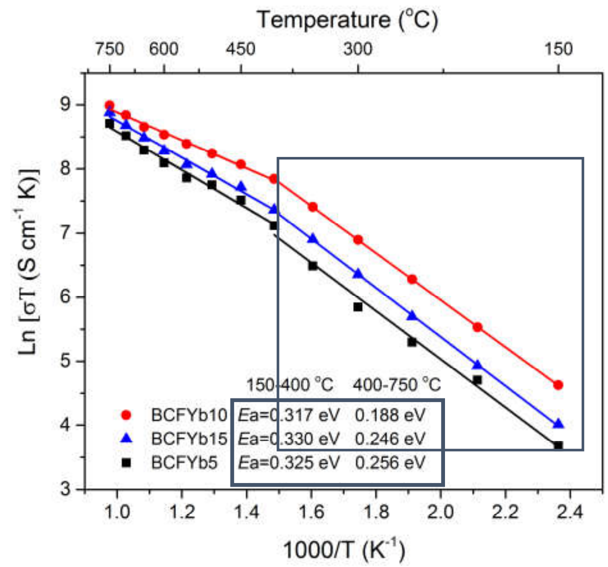


Yb05 1190 ^{o}C | Yb10 1220 ^{o}C | Yb15 1260 ^{o}C

Yb doping inhibits densification of the bulk

2. Sintering ability and Electrical conductivity





$$-B-O-B-$$

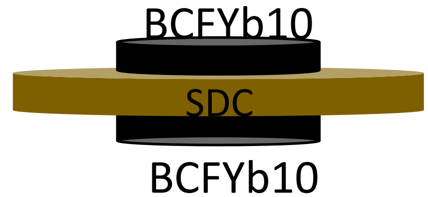
Fluctuation at 450 °C $\quad O_O^{\times} + 2h^{\cdot} \rightarrow V_O^{\cdot\cdot} + \frac{1}{2}O_2$

Yb05 → Yb10 → Yb15

↑ Electronegativity Yb (1.1) < Co(1.7), Fe(1.8)

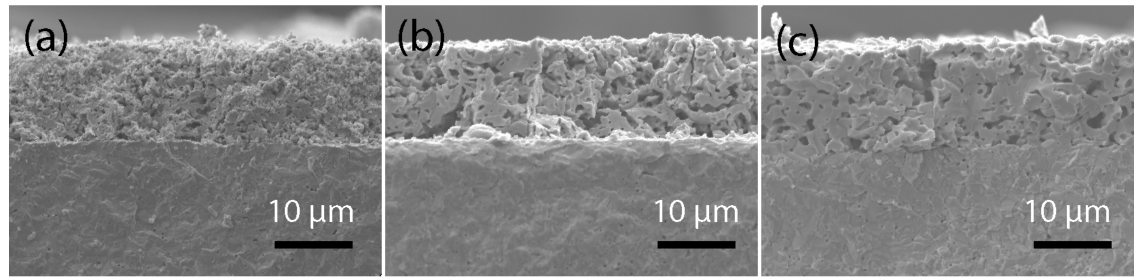
↓ More oxygen vacancies $\quad -B \times V_O^{\cdot\cdot} \times B-$

3. Compatibility and Best sintering temperature

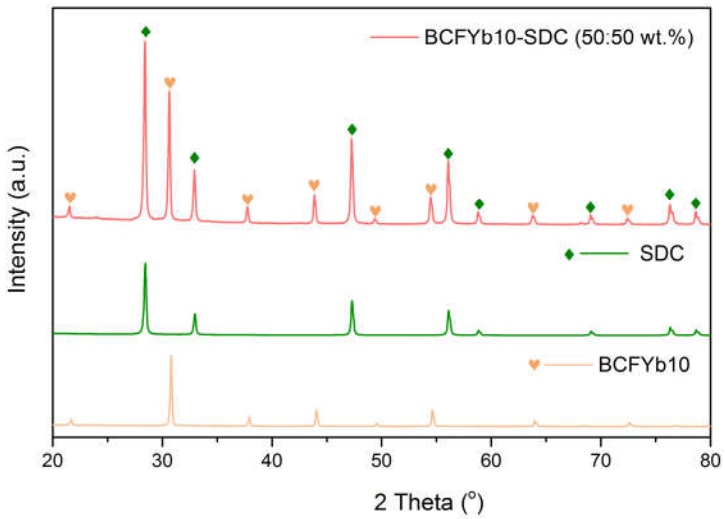


Electrolyte: $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)

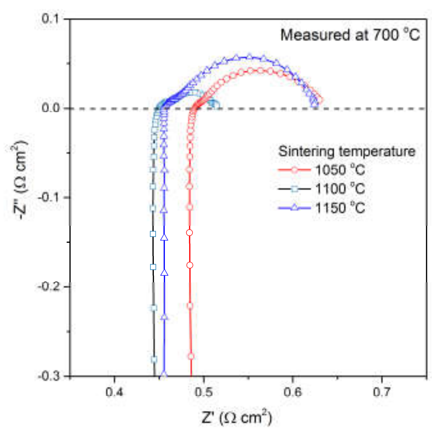
Cathode: BCFYb10

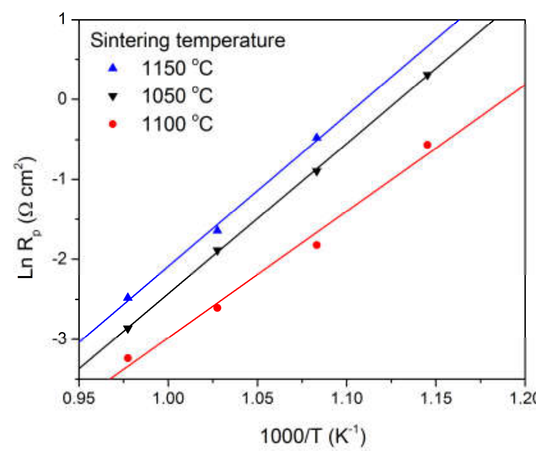


1050 °C   1100 °C   1150 °C



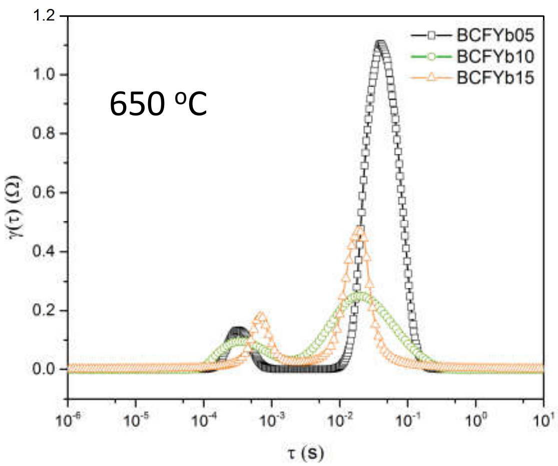
Yb10-SDC mixtures sinter at 1150 °C in air for 5 h.



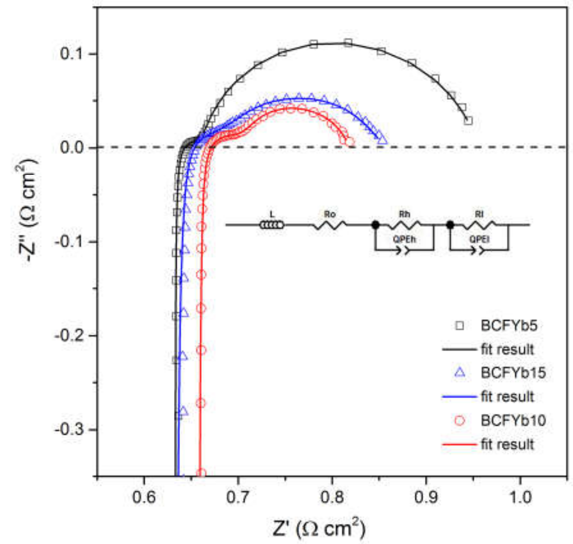


Characterization

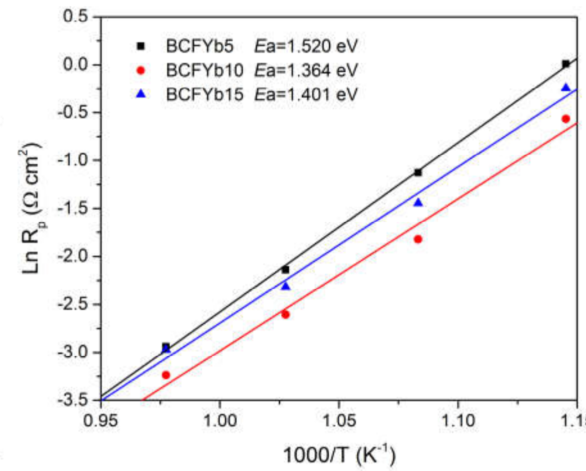
4. Electrochemical Performance



Distribution of relaxation times (DRTs)



EIS profiles of Yb5, Yb10 and Yb15



Polarization resistance of BCFYb

Yb05 → Yb10 → Yb15

Lower electronegativity of Yb

More oxygen vacancies

Characterization

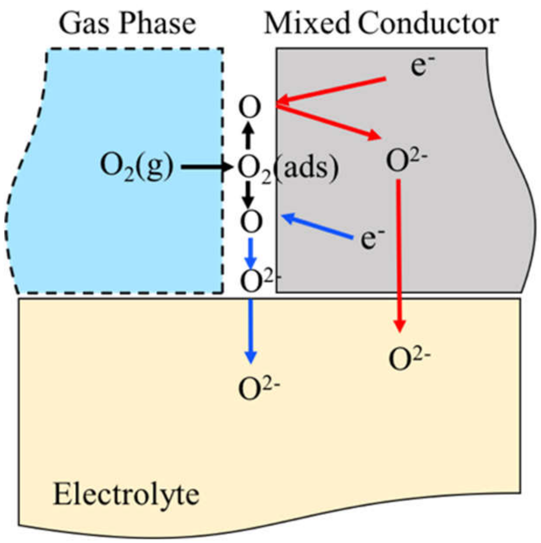
5. Oxygen Reduction Reaction activity

Cathode: $\frac{1}{2}O_2 + 2e^- = O^{2-}$

Indicator

link to specific rate-limiting step

$R_i \in P_{O_2}^{-m}$



Pathway of cathode reaction in a porous mixed conducting cathode.

(1) O_2 diffusion from gas phase to the cathode;

(2) O_2-adsorption on the cathode and triple phase boundary (TPB): ← $m = 1$

$$O_{2(g)} \rightarrow O_{2,ad}$$

(3) O-dissociation on the cathode and TPB:

$$O_{2,ad} \rightarrow 2O_{ad}$$ ← $m = 0.5$

(4) Charge transfer: ← $m = 0.25$

$$O_{ad} + 2e^- + V_O^{\cdot\cdot} \rightarrow O_o^{\times}$$

Characterization

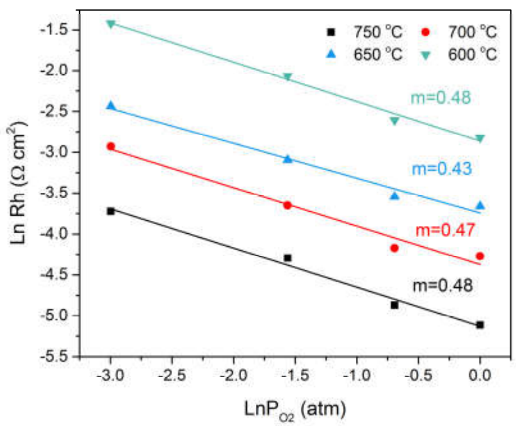
Polarization resistance vs. Oxygen partial pressure

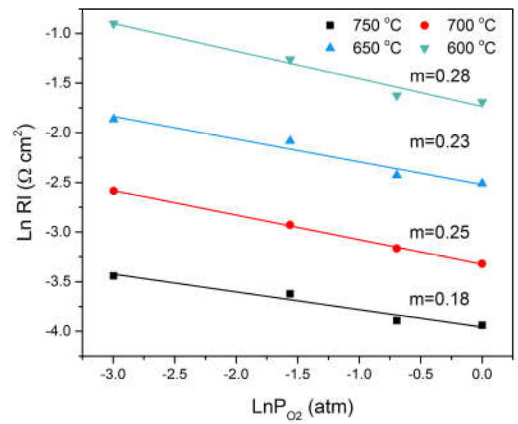
High frequency

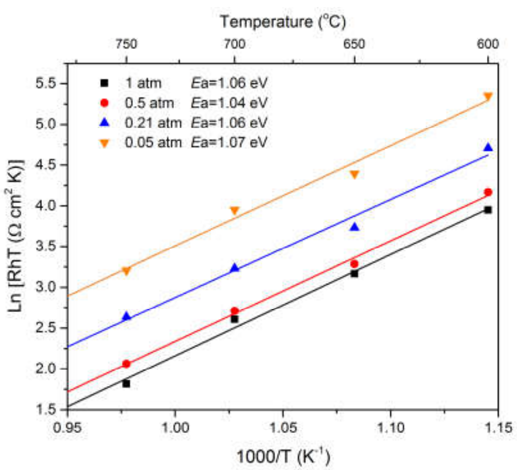
m = 0.5

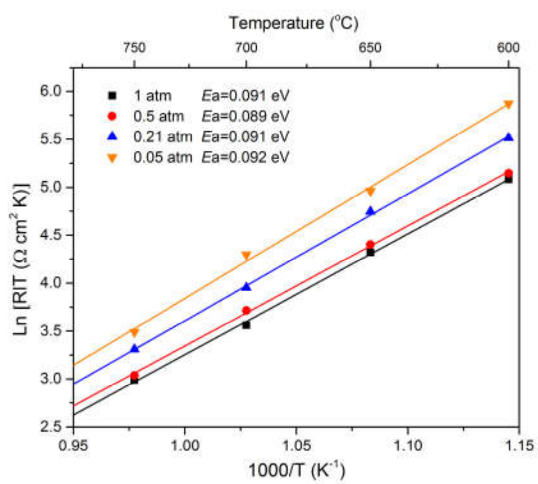
$$O_{2,ad} \rightarrow 2O_{ad}$$

Ea = ~ 1.0 eV









Low frequency

m = 0.25

$$O_{ad} + 2e' + V_O^{\cdot\cdot} \rightarrow O_O^{\times}$$

Ea = ~ 0.09 eV

Acknowledgment

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