

Supporting information for

Tuning the Co/Fe ratio in $\text{BaCo}_x\text{Fe}_{0.8-x}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$, a promising triple ionic and electronic conducting oxide, to boost electrolysis and fuel cell performance

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Sample preparation for isotope exchange

The pre-calcined BCFZY powders were mixed with 5wt.% polyvinyl alcohol (PVA) aqueous solution as a binder and pressed into 3/4" diameter (2 mm thick) pellets, Next, the pellets were dried in air at 100 °C for an hour to evaporate the water, then at 500 °C for 5 h to burn out PVA, and finally at 1250 °C for 10 h to obtain well-sintered final pellets with 95 – 96% theoretical density. The dense sintered pellets were then mounted with crystal bond and polished with successive grades of diamond spray down to a final polish of 0.05 µm.

Fabrication of symmetric cell

Electrolyte-supported symmetric cells based on a $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb7111) + NiO 1 wt.% electrolyte were prepared by the solid-state reactive sintering (SSRS) method. A precursor powder was prepared from appropriate stoichiometric amounts of BaCO_3 (Alfa Aesar, 99.8 %), CeO_2 (Alfa Aesar, 99.9 %), ZrO_2 (Alfa Aesar, 99 %), Y_2O_3 (Alfa Aesar, 99.999%), Yb_2O_3 (Alfa Aesar, 99.9%) and NiO (Alfa Aesar, 45094) with IPA and YSZ 3 mm spherical grinding media. The precursors were ball-milled for 120 h, and then planetary ball-milled for 24 h to form a homogeneous powder mixture. The precursor powder was mixed with 5% polyvinyl alcohol (PVA) solution, then pressed in a circular stainless-steel die set with a diameter of 19 mm under 375 MPa for 2 min to form white electrolyte pellets. The electrolyte pellets were then fired at 1450 °C for 18 h. Pre-calcined electrode powders (BCFZY1711, BCFZY4411, and BCFZY7111) were calcined at 900 °C for 5 h to ensure single phase material. After that, the BCFZY powders were ball milled with IPA and YSZ 3 mm spherical grinding media for 24 h. The powders were then dried at 90 °C for 12 h to remove the solvent and then prepared into pastes with 5 wt.% V-006A in alpha terpineol, and 20 wt.% Solsperse 28,000 in alpha terpineol as dispersant. The pastes were manually mixed using mortar and pestle. After that, the cathode pastes were manually applied to both sides of the electrolyte pellets by brush painting. The assembled symmetric cells were fired at 900 °C for 5 h.

Preparation of anode substrate

Anode cermet of 40 wt.% $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb4411) + 60 wt.% NiO was prepared by mixed appropriate stoichiometric quantities of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 ,

Yb_2O_3 , and NiO 20 wt.% corn starch was then added to the anode precursor mixture as pore former. This mixture was ball-milled in IPA with 3 mm YSZ balls for 120 h and then ball-milled with the planetary mill for 24 h. The solvent was subsequently evaporated at 90 °C in a drying oven. The anode green bodies were prepared by die pressing under 375 MPa for 2 min in a circular carbon aided steel die set with a diameter of 19 mm. The anode cermet powder and 5% PVA solution were mixed and dry pressed for 2 min.

Preparation of half-cell by SSRS method

The half-cell was fabricated to deposit electrolyte on the anode substrate using an ultrasonic sprayer as described by Feng et al.²³ The electrolyte suspension solution for ultrasonic spray coating was prepared by mixing stoichiometric ratios of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 , Yb_2O_3 , NiO 1 wt.%, V-006 (Heraeus), PEG 400 (Alfa Aesar), and PVP 40000 (Alfa Aesar) were used as a binder, plasticizer, and dispersant, respectively. The mass ratios amount to 13 wt.% electrolyte powder mixture, 1 wt.% PEG 400, 1 wt.% PVP 40000, 2.5 wt.% V-006A, 2.5 wt.% α -terpineol (Alfa Aesar), and 80 wt.% IPA. To ensure adequate dispersion, the solution was placed in a sonicator for 2 h and then further mixed using a high-speed vortexer for 5 min. The mixed solution was supplied to an ultrasonic spray atomizer (Sonotek ALIGN). The solution was sprayed 5 times on the anode support on both sides to compensate for stress. The spray deposition process was performed with a nozzle power of 5 W, a frequency of 20 kHz, and a liquid dispenser rate of $0.3 \text{ mL} \cdot \text{min}^{-1}$. After spray deposition, the electrolyte/anode half-cell was dried under ambient temperature for 24 h to evaporate the solvent. A BCZYYb7111 pellet was placed on the top of the half-cell to reduce Ba evaporation, and the cell was fired at 1475 °C for 5 h. After that, the bottom-side electrolyte layer was removed with sandpaper and the thickness of the anode support was ground down to a thickness of 0.55 mm.

Preparation of full assembly cell with $\text{BaCo}_{1-x}\text{Fe}_x\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ ($x=0.1, 0.4, \text{ and } 0.7$)

The same BCFZY 1711, 4411, and 7111 pastes used for the symmetric cells were also used for the full cells. The pastes were brushed onto the sintered half-cells, which were then fired at 900 °C for 5 h. After firing, Pt paste (FuelCell Energy) was painted on top of the electrodes, and silver paste (DAD-87) was brushed as grid. Silver wires (Alfa

Aesar, 0.5 mm) were attached on both sides of the cell and then baked at 200 °C for an hour on a hotplate to ensure adhesion.

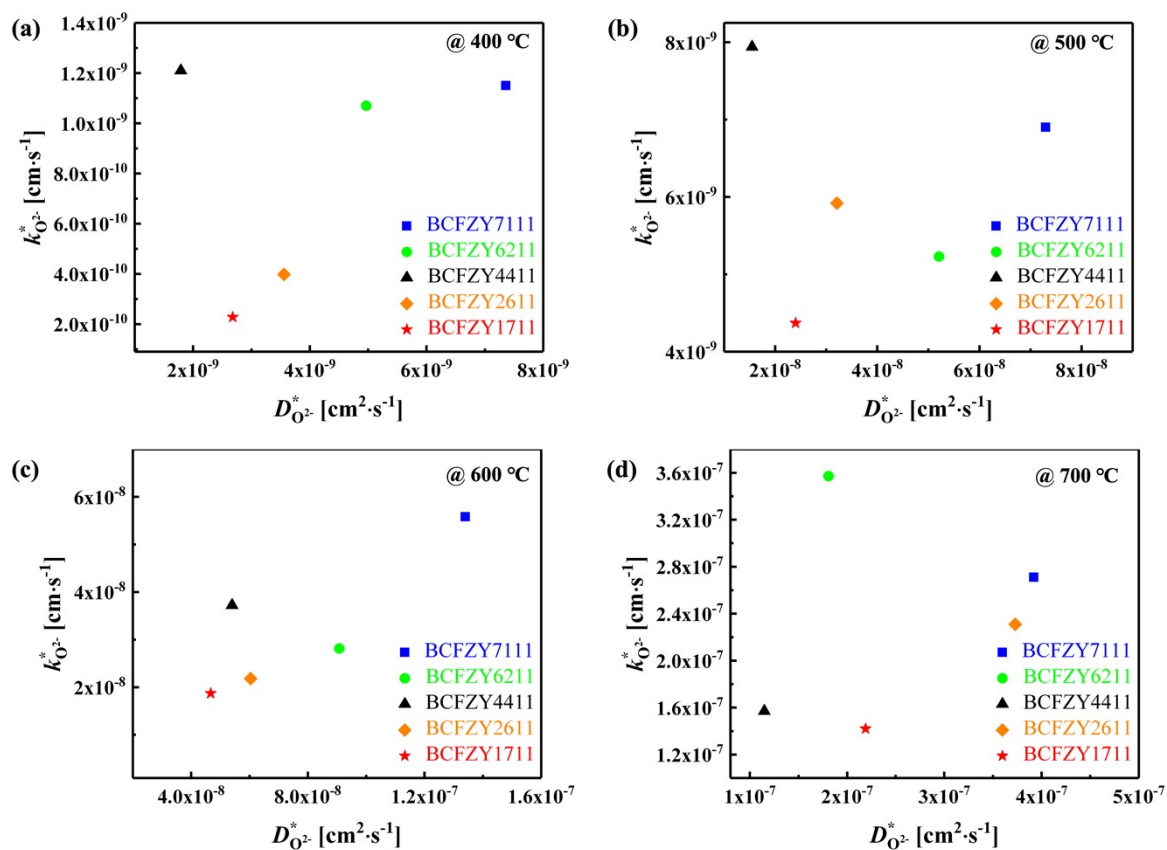


Fig S1. Comparison plots of oxygen ion tracer diffusivity and surface exchange rate for various BCFZY compositions at a) 400 °C, b) 500 °C, c) 600 °C, and d) 700 °C.

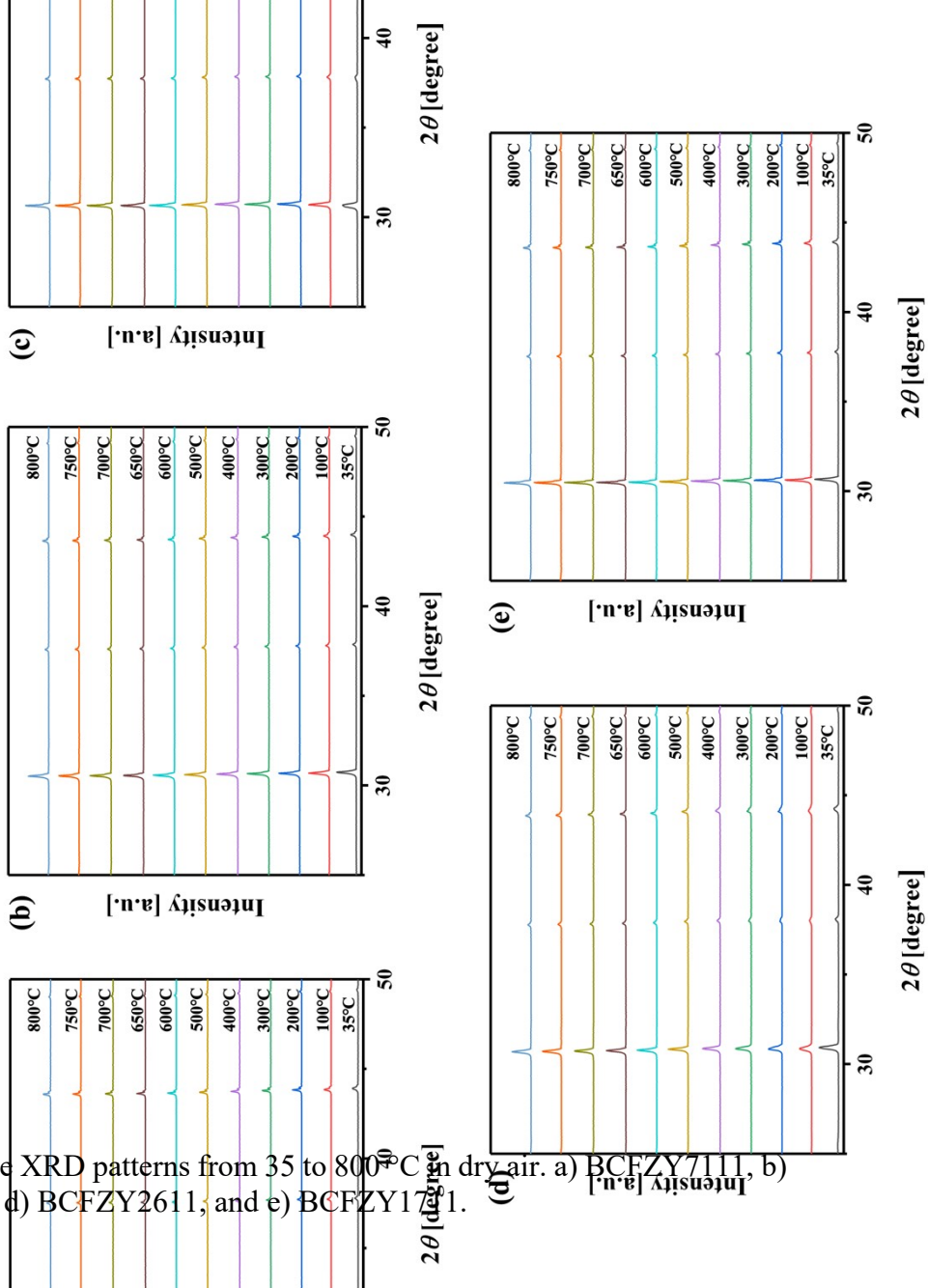


Fig S2. In-situ high temperature XRD patterns from 35 to 800 °C in dry air. a) BCFZY7111, b) BCFZY6211, c) BCFZY4411, d) BCFZY2611, and e) BCFZY1711.

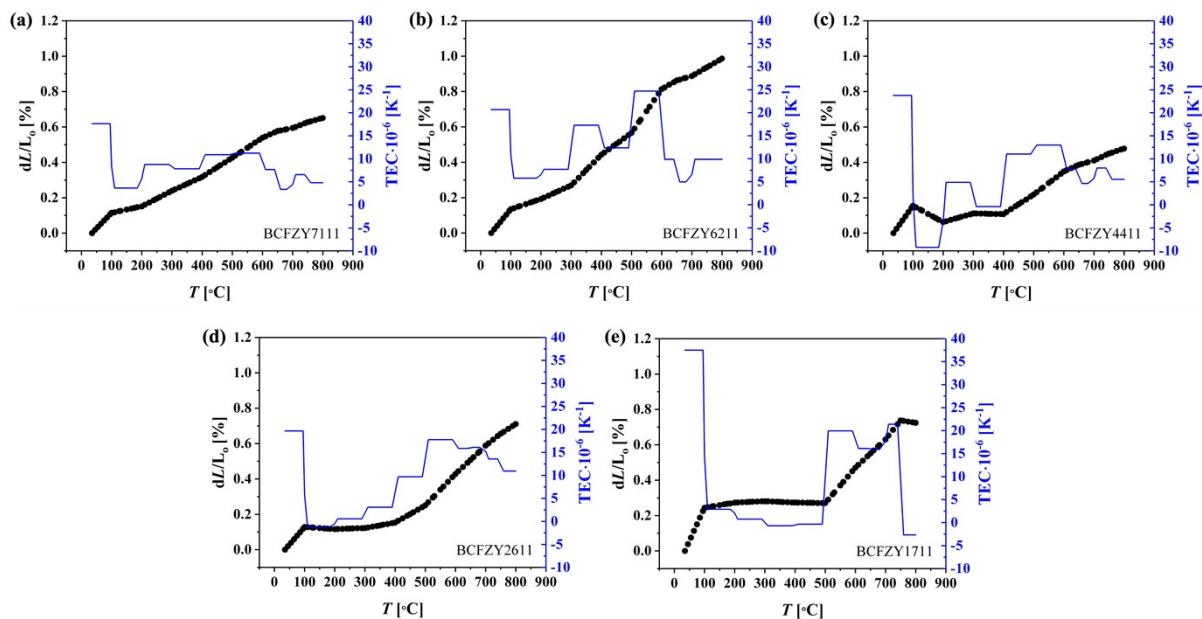


Fig S3. Total expansion and thermal expansion coefficient curves for various BCFZY compositions in the temperature range 35 – 800 °C: a) BCFZY7111, b) BCFZY6211, c) BCFZY4411, d) BCFZY2611, and e) BCFZY1711.

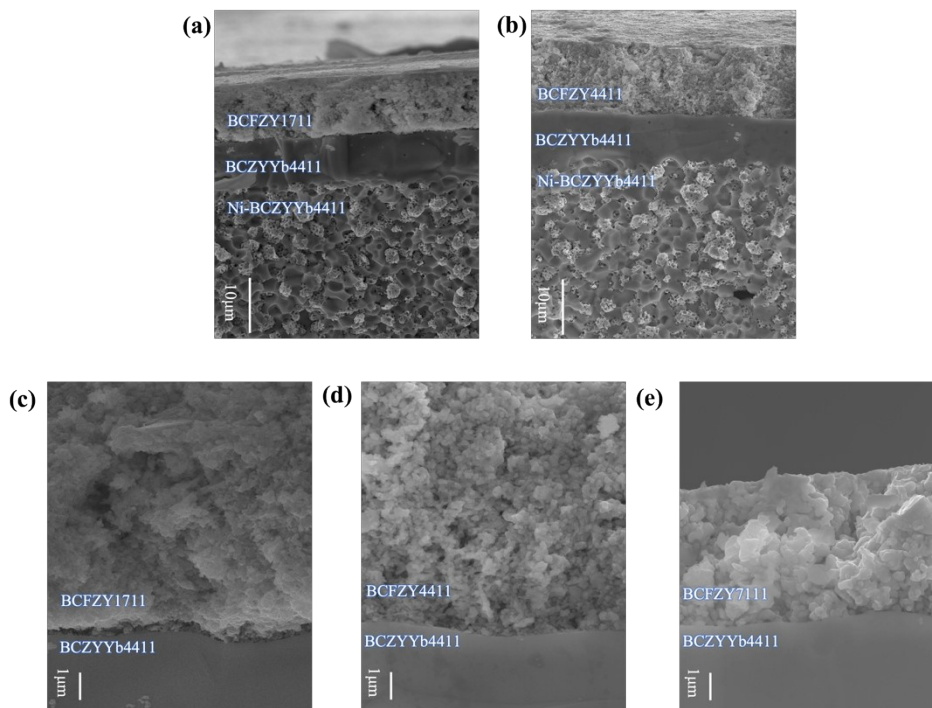


Fig S4. FE-SEM cross-sectional image of BCFZY1711, 4411, and 7111 (a-b) low magnification image of BCFZY1711 and 4411 (c-e) high magnification image of BCFZY 1711, 4411, and 7111 with cathode morphology.

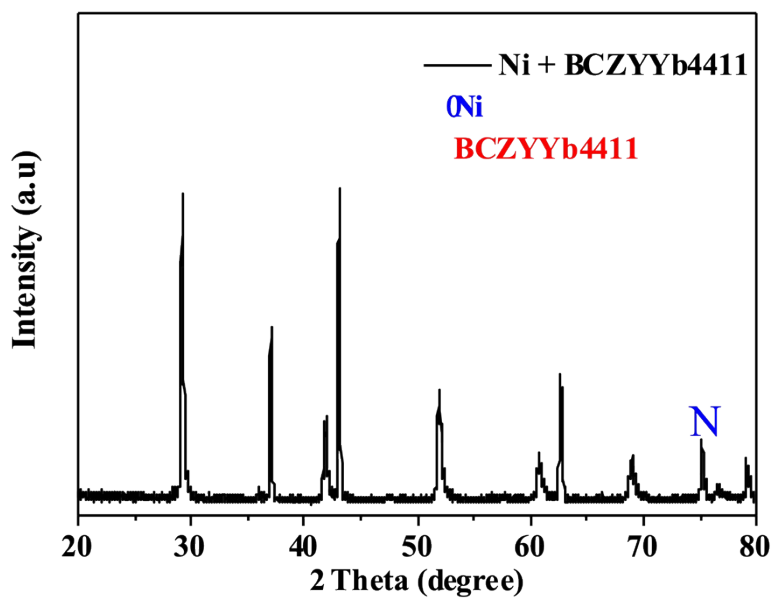


Fig S5. XRD pattern of Ni +BCZYYb4411 with solid-state reactive sintering after 1475 °C for 5 h sintering.

Table S1. Oxygen ion tracer diffusivities and surface exchange coefficients of various BCFZY compositions obtained at 400 – 700 °C.

Composition	Temperature [°C]	$D_{O^{2-}}^*$ [cm ² ·s ⁻¹]	$k_{O^{2-}}^*$ [cm·s ⁻¹]
BCFZY4411	700	1.35E-07	1.41E-06
	600	5.4E-08	3.72E-08
	500	2.55E-08	7.50E-09
	400	1.79E-09	1.21E-09
BCFZY7111	700	3.92E-07	2.71E-07
	600	1.34E-07	5.58E-08
	500	7.3E-08	6.9E-09
	400	7.36E-09	1.15E-09
BCFZY6211	700	3.57E-07	1.81E-07
	600	9.08E-08	2.81E-08
	500	5.21E-08	5.23E-09
	400	4.97E-09	1.07E-09
BCFZY2611	700	3.73E-07	2.31E-07
	600	6.04E-08	2.18E-08
	500	3.21E-08	5.92E-09
	400	3.56E-09	3.98E-10
BCFZY1711	700	2.19E-07	1.42E-07

600	4.67E-08	1.87E-08
500	2.4E-08	4.37E-09
400	2.68E-09	2.28E-10

Table S2. Unit cell parameters of BCFZY compositions obtained by in-situ HT-XRD at 35 – 800 °C in dry air.

Temperature [°C]	BCFZY1711 [Å]	BCFZY2611 [Å]	BCFZY4411 [Å]	BCFZY6211 [Å]	BCFZY7111 [Å]
35	4.019	4.028	4.053	4.046	4.054
100	4.029	4.033	4.06	4.052	4.058
200	4.03	4.032	4.056	4.054	4.06
300	4.031	4.032	4.058	4.057	4.063
400	4.03	4.034	4.058	4.064	4.067
500	4.03	4.038	4.062	4.069	4.071
600	4.038	4.045	4.067	4.079	4.076
650	4.041	4.048	4.069	4.081	4.077
700	4.045	4.051	4.07	4.082	4.078
750	4.049	4.054	4.072	4.084	4.079
800	4.048	4.056	4.073	4.086	4.08
35 after cooling	3.997	4.023	4.035	4.043	4.047