

SUPPLEMENTARY INFORMATION

Surface Restructuring of a Perovskite-type Air Electrode for Reversible Protonic Ceramic Electrochemical Cells

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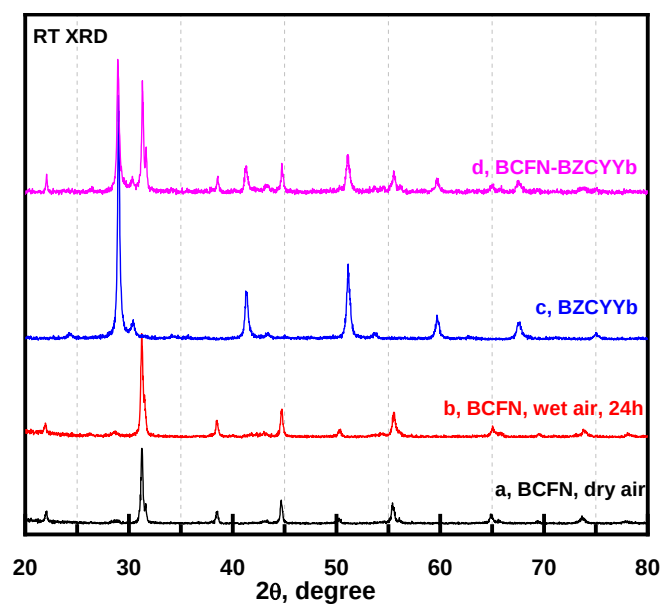
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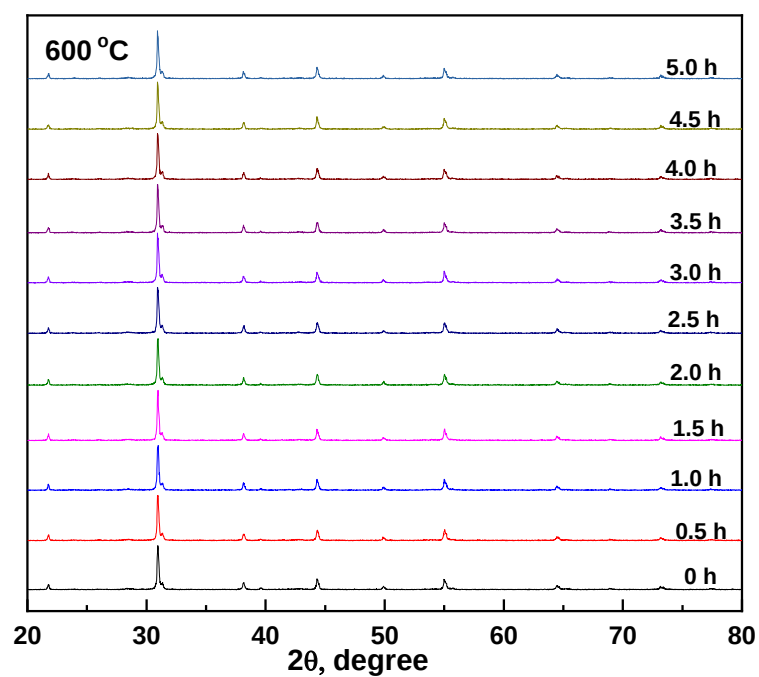
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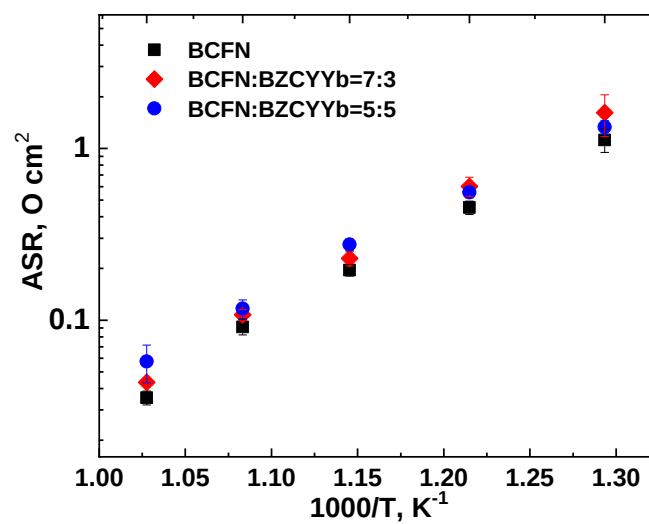
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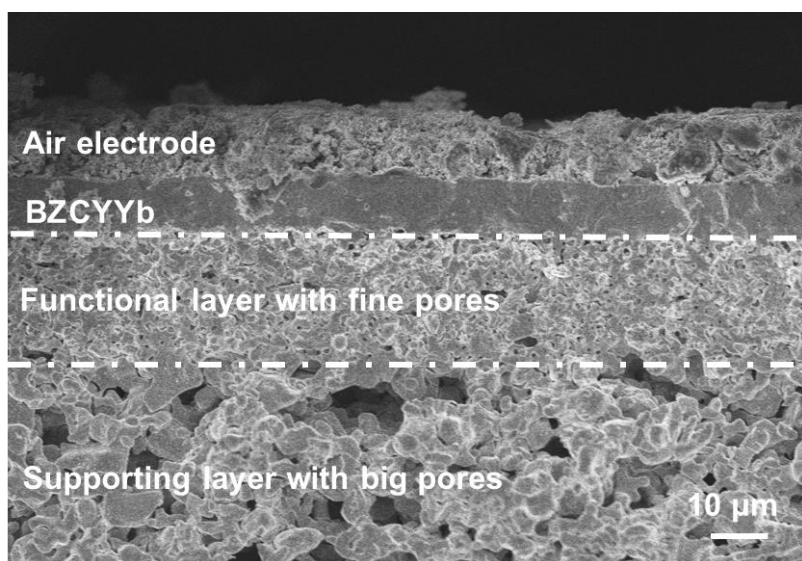
Supplementary Figure 1. XRD patterns of as-prepared BCFN powder **(a)**, BCFN powder treated in wet air (3 %) for 24 h at 700°C **(b)**, BZCYYb **(c)**, and mixed BZCYYb-BCFN (1:1 wt.%) **(d)** powders after calcining at 1000 °C for 2 h in air.



Supplementary Figure 2. In situ XRD patterns of BCFN powder in wet air (3% H₂O) at 600°C for 5 h. The data were collected every 30 min.

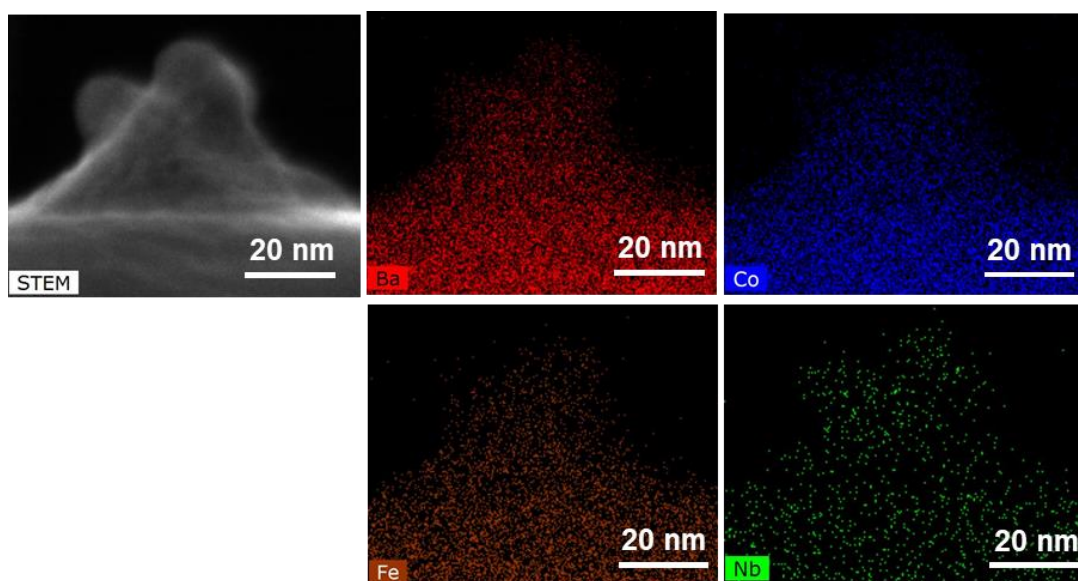


Supplementary Figure 3 Temperature dependence of the polarization resistance (R_p) of symmetrical cell with BCFN and composite electrodes

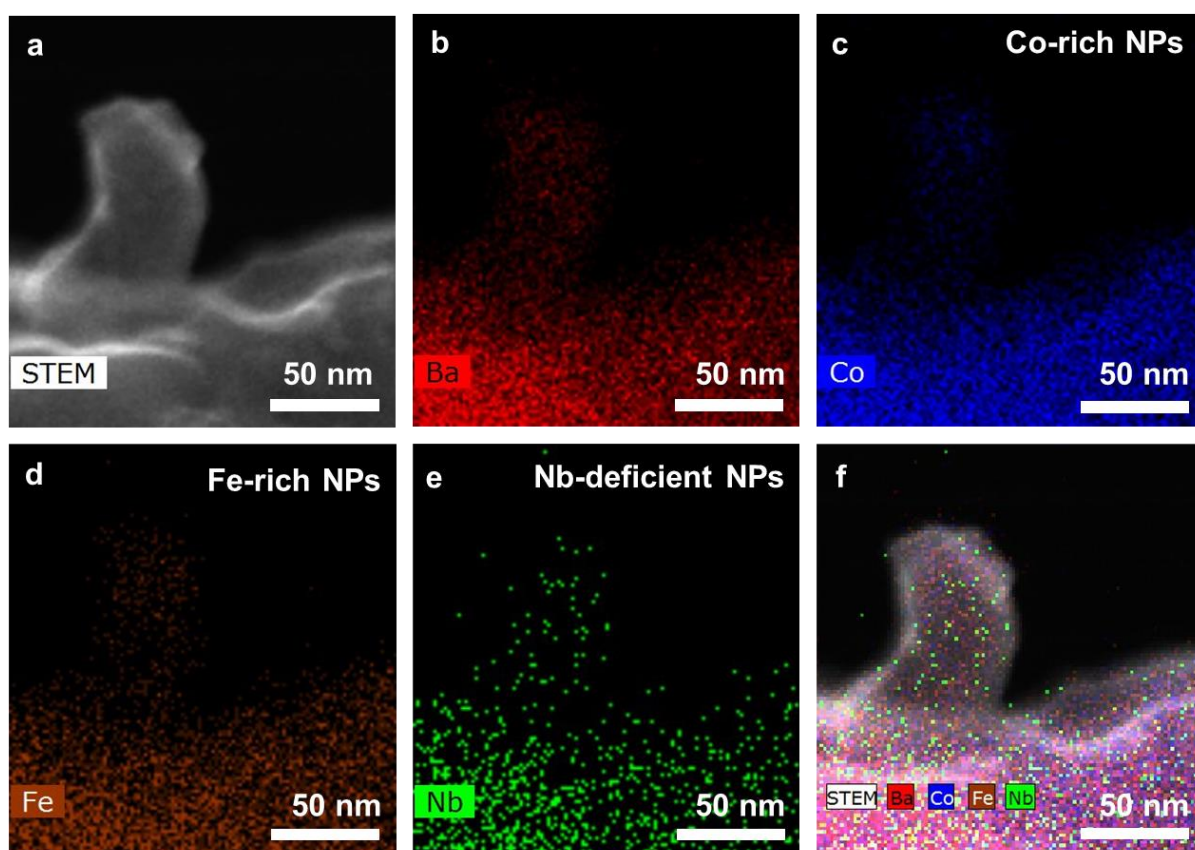


Supplementary Figure 4. Typical SEM image of a single cell with distinct four layers.

Supplementary Discussion: As shown, a multi-layered structure, including a porous Ni-BZCYYb anode supporting layer (ASL, $\sim 600\ \mu\text{m}$), a porous but fine Ni-BZCYYb anode functional layer (AFL, $\sim 25\ \mu\text{m}$), a dense BZCYYb electrolyte layer ($\sim 10\ \mu\text{m}$), and a porous BCFN layer ($\sim 15\ \mu\text{m}$), were adhered well with no cracks or delamination (**Supplementary Figure 4**). The functional layer has finer pores and a larger surface area (due mainly to the reduction of NiO), providing more triple-phase boundaries for electrochemical reactions. In contrast, the supporting layer has larger pores and continuous channels (due mainly to the removal of pore-former), providing facile paths for gas transport.

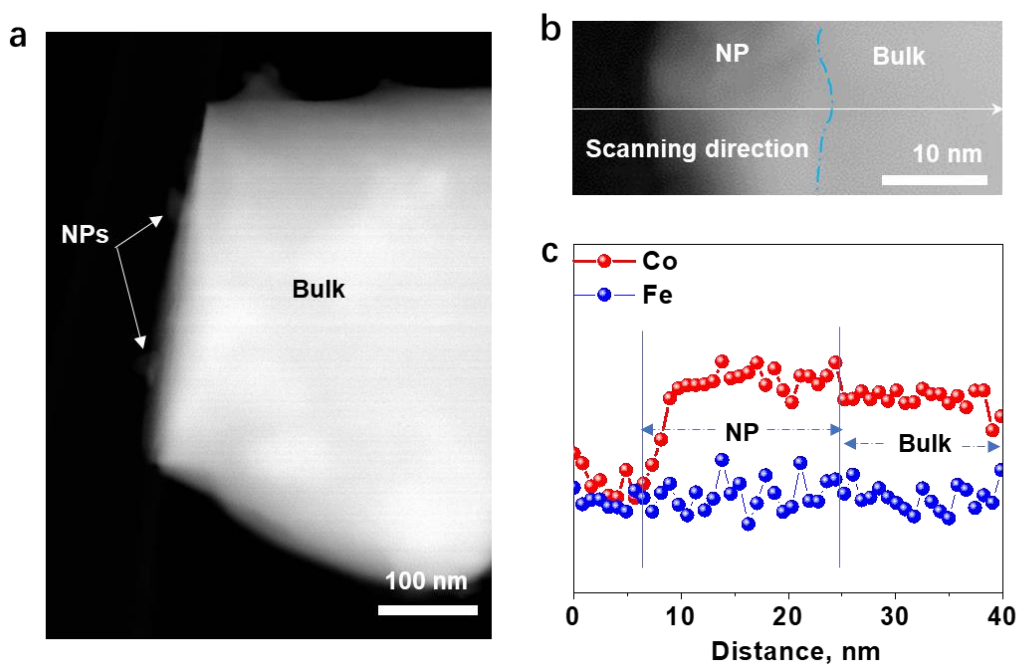


Supplementary Figure 5. STEM image of BCFN powder before the electrochemical test and the mapping of Ba, Co, Fe, Nb. The image shows a uniform element distribution.



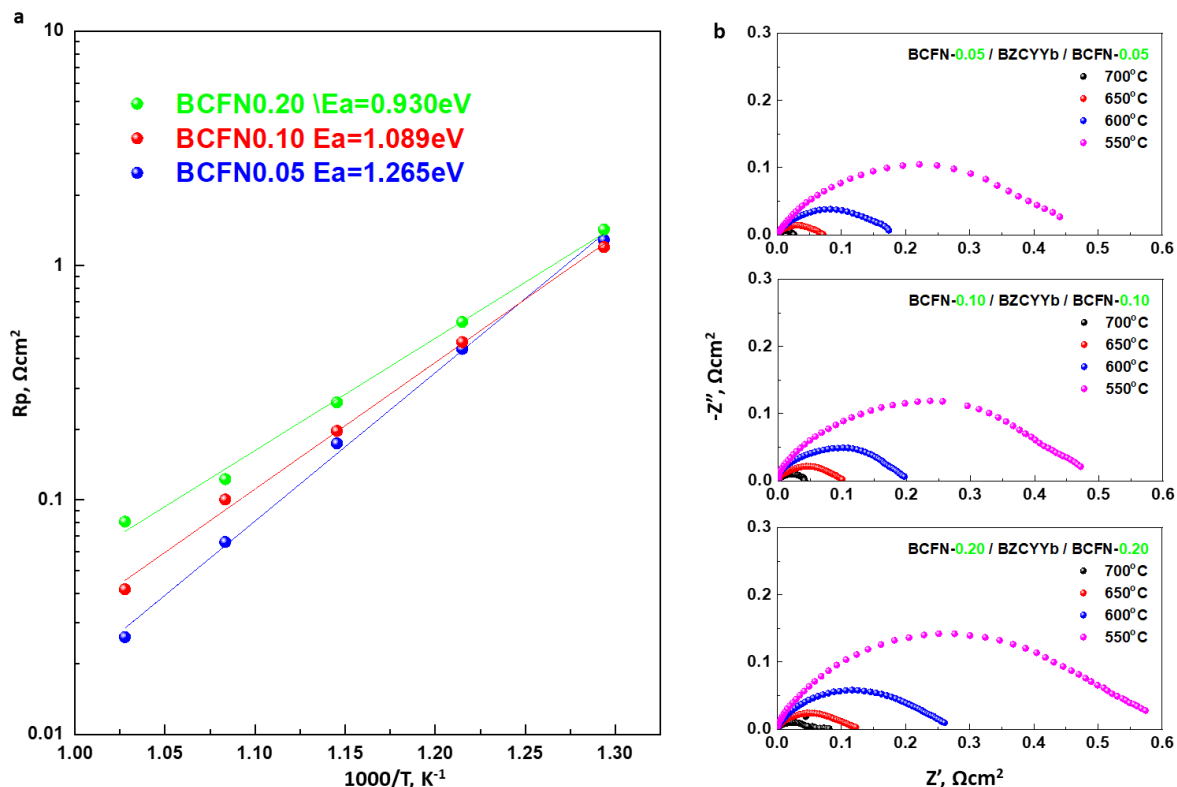
Supplementary Figure 6 An elemental mapping of BCFN grain covered with a nanoparticle (a), and the mapping of Ba (b), Co (c), Fe (d), Nb (e), and all (f).

Supplementary Discussion: We performed elemental mappings of Ba, Co, Fe, and Nb of a BCFN grain (after test) covered with a nanoparticle, as shown in **Supplementary Figure 6**. It is confirmed that there is likely a Co/Fe segregation within the nanoparticle.



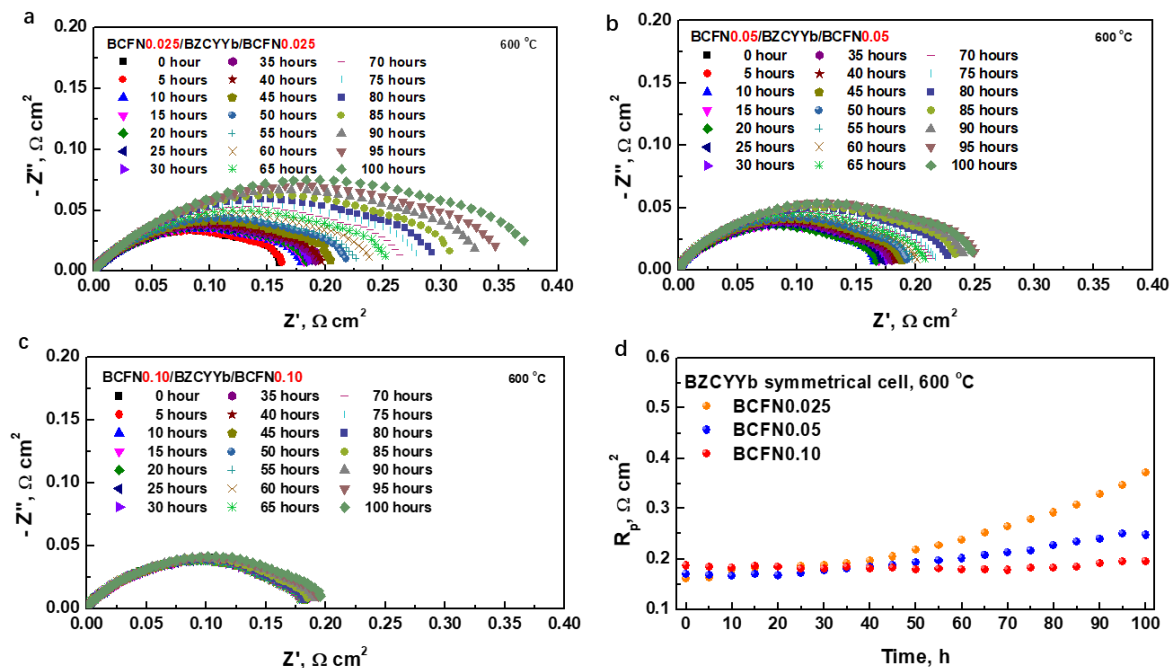
Supplementary Figure 7 (a) and (b) A STEM image of a BCFN grain covered with nanoparticles; and **(c)** an electron energy-loss spectroscopy (EELS) profile along the white line shown in (a).

Supplementary Discussion: Shown in **Supplementary Figures 7a** and **7b** are the STEM images of a BCFN grain covered with nanoparticles. Shown in **Supplementary Figure 7c** is the electron energy-loss spectroscopy (EELS) profile of Co and Fe along the scanning line shown in **Supplementary Figure 7b**. Slightly higher contents of Co or Fe are observed in the EELS profile (**Supplementary Figure 7c**), suggesting a possible Co/Fe segregation.



Supplementary Figure 8 (a) Arrhenius plots of the area-specific resistance (ASR, noted as R_p) for BCFN with different Nb content, measured from 700 to 500 °C, in flowing air (20 sccm) with 3% H₂O. (b) Detailed Temperature dependence of the polarization resistance (R_p) of symmetrical cell with BCFN (Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_xO_{3-δ}) with Nb content of 0.05, 0.10, 0.20, respectively. The electrode with 5% Nb doping at B-site showed the lowest R_p at 700-550°C, indicating that BCFN with less Nb shows a higher ORR activity.

Supplementary Discussion: A relatively higher E_a value for Nb deficient BCFN was observed, suggesting that there is a higher reaction barrier has to be overcome in the oxygen reaction process. It is shown that R_p values of BCFN0.05, BCFN0.1, and BCFN0.2 were similar at a low temperature of 550 °C. The difference became more pronounced as the operating temperature increased: Nb-deficient BCFN showed a lower R_p value, which is likely caused by the more oxygen vacancy formed at higher temperatures. Nb deficient BCFN is expected to have more oxygen vacancy at higher temperatures.

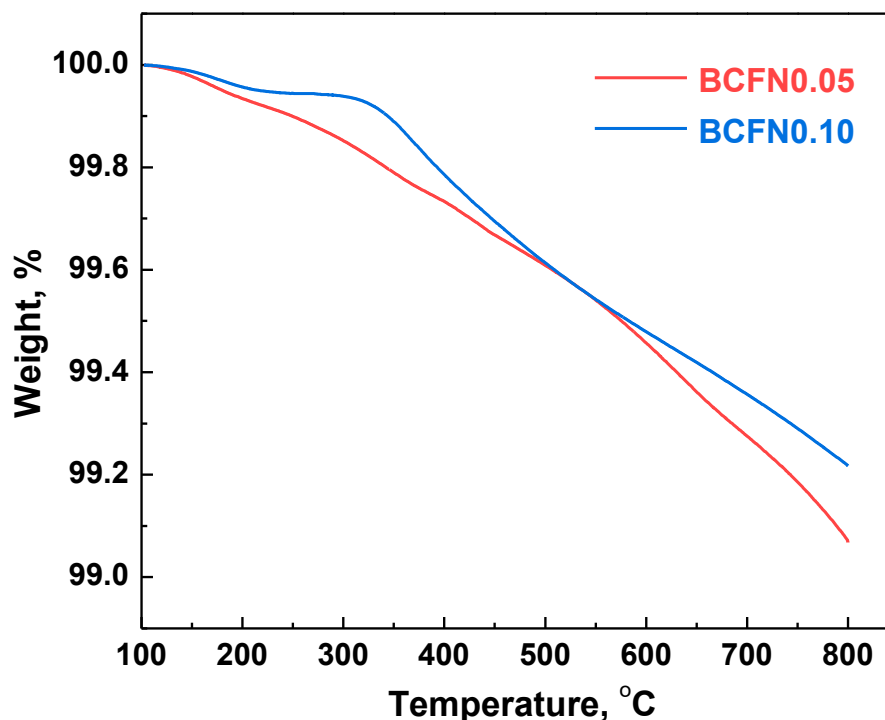


Supplementary Figure 9 Effect of Nb content in $\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_x\text{O}_3$ ($x=0.025$, 0.05, and 0.1, denoted as BCFN $_x$) on the electrode activity and durability. Electrochemical impedance spectra of BCFN $_x$ at different times and 600 °C: $x=0.025$ (a); $x=0.05$ (b); and $x=0.1$ (c); (d)

R_p changes as a function of testing time in a period of 100h.

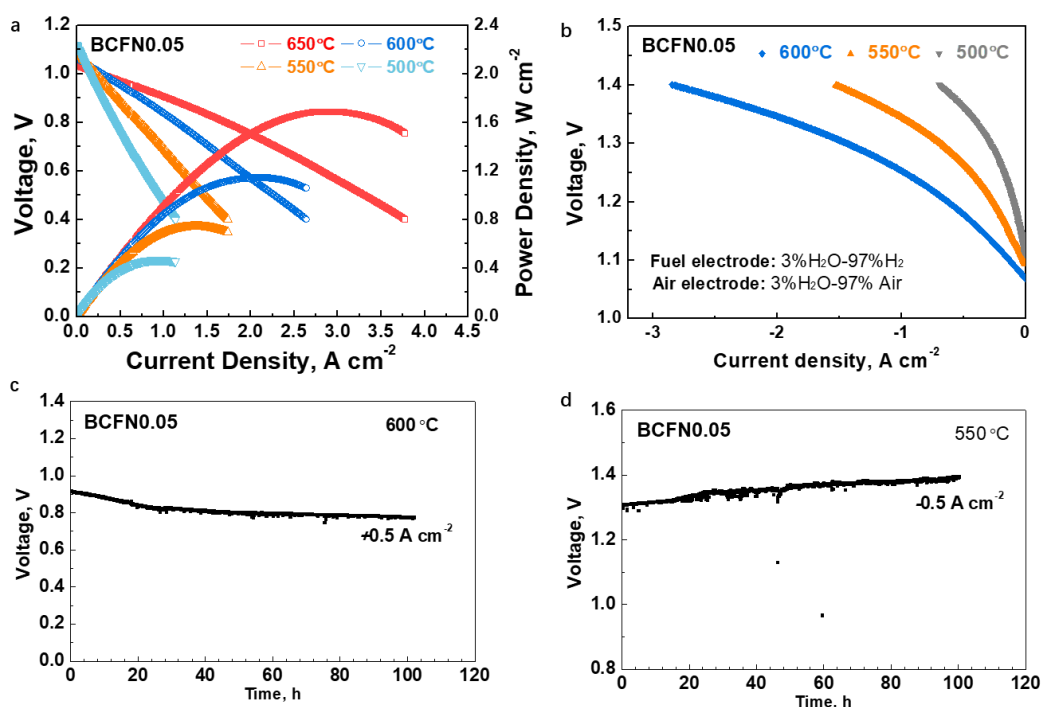
Supplementary Discussion: The electrode system (Nb-rich BCFN electrode covered by Nb-deficient BCFN NPs) showed a higher reaction activity compared to the single-phase Nb-deficient BCFN, as shown in the manuscript. In order to understand the effect of Nb content in the BCFN system on the activity and stability of $\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_x$ ($x=0.025$, 0.05, and 0.1, denoted as BCFN $_x$), we prepared BZCYYb electrolyte based symmetrical cells with BCFN $_x$ electrode. Shown in **Supplementary Figure 9** are the impedance spectra of BCFN $_x$ and the evolution of R_p value as a function of testing time. It is shown that BCFN $_x$ with less Nb showed a higher activity but worse durability, while BCFN with more Nb showed a lower activity but better durability. It has been reported that the *in-situ* formation of the Nb-deficient BCFN nanoparticles on BCFN electrodes is expected to have better structural stability since the risk of agglomeration is greatly reduced, thus enhancing the durability and thermal stability of the electrode. Such enhanced stability is also observed in other reports¹⁻⁴. In addition, the nanoparticles maintained a crystallographic coherence with the host perovskite lattice and consequently may experience lattice strain^{2,5,6}. Such confined and seemingly anchored particles

are expected to exhibit considerably different physical and chemical properties as compared with the unconstrained particles, introduced by the traditional solution infiltration process^{7,8}.

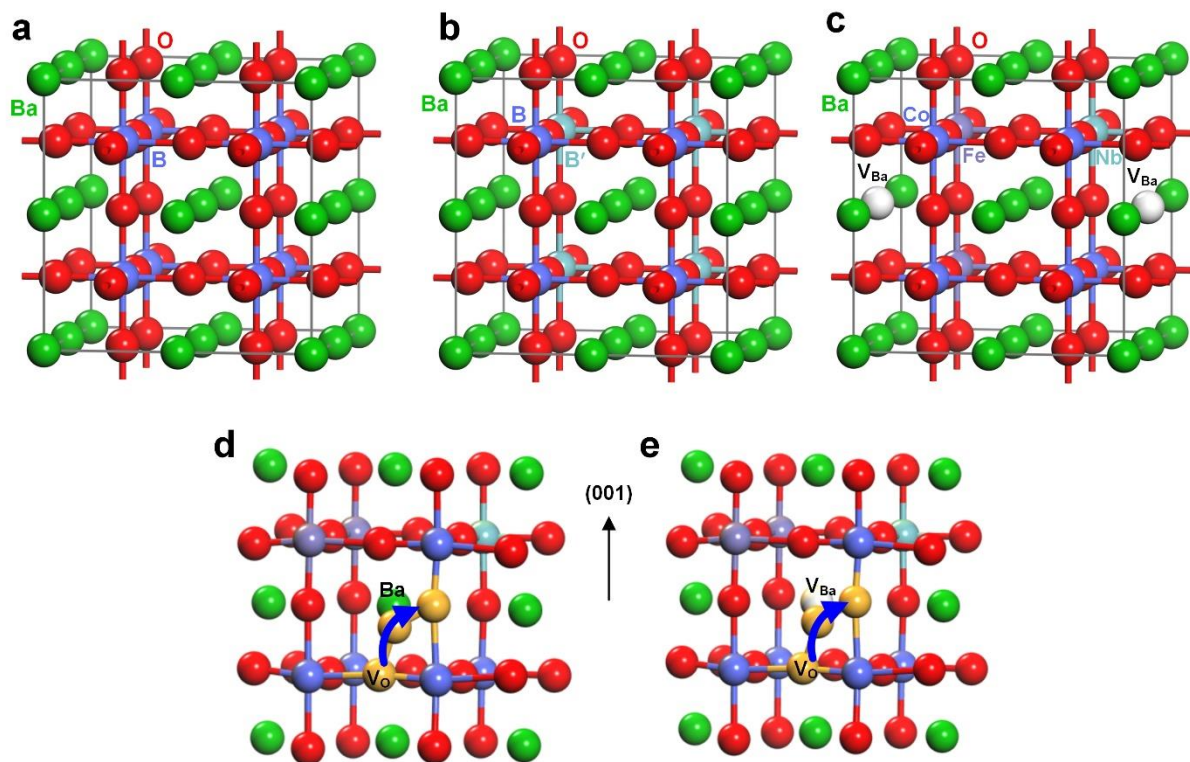


Supplementary Figure 10 Thermalgravimetric analyses of BCFN0.05 and BCFN0.1.

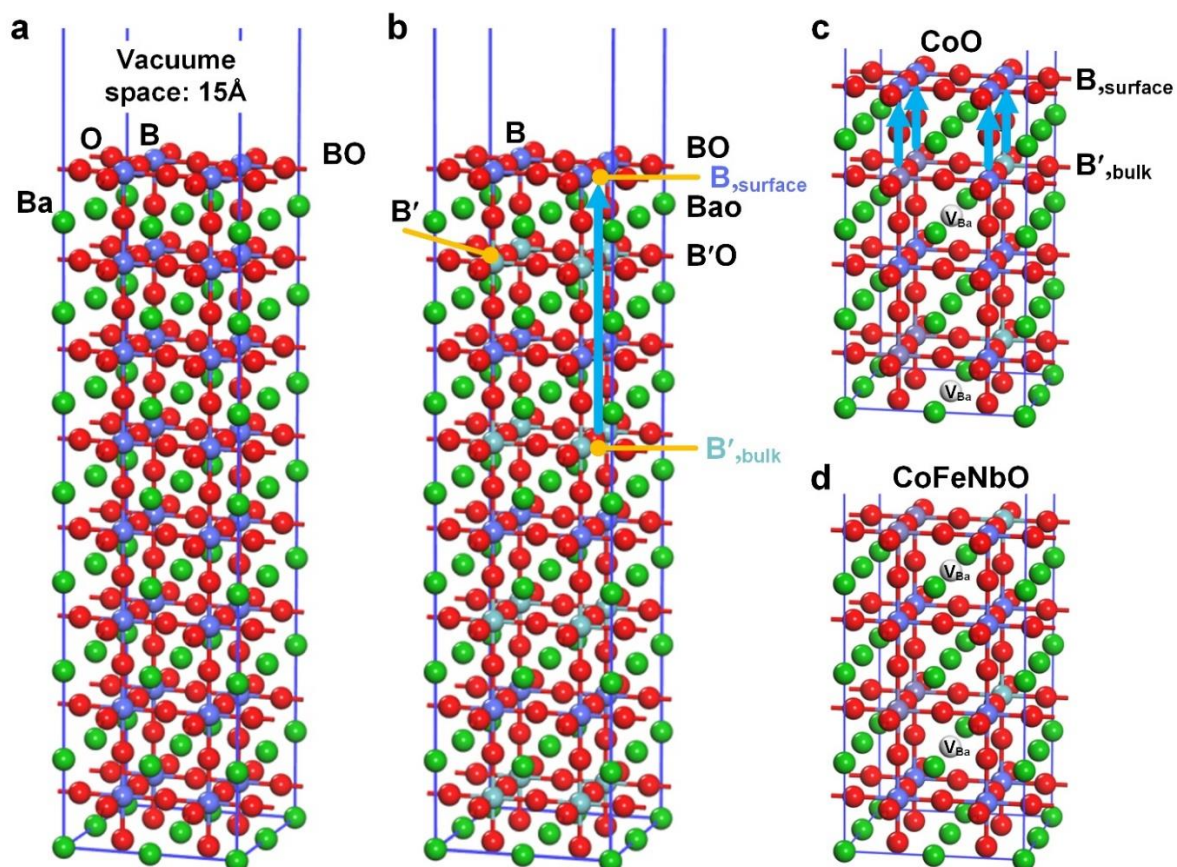
Supplementary Discussion: Nb-deficient BCFN (for example, $\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.05}\text{O}_3$) shows higher activity than BCFN with no deficiency ($\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_3$). It is reported that less reducible cations such as Zr, Ta, or Nb are expected to enhance the durability of perovskite materials^{9,10}. An Nb-deficient BCFN material on the surface is expected to have a higher concentration of oxygen vacancy than BCFN in the bulk (without an Nb deficiency), as confirmed by thermogravimetric analyses of BCFN0.1 and BCFN0.05 (**Supplementary Figure 10**). The valence changes of Co or Fe would provide more oxygen vacancies (more weight loss) at high temperatures in the oxygen reduction or evolution reactions, which is likely the reason for the higher activity of Nb-deficient BCFN nanoparticles.



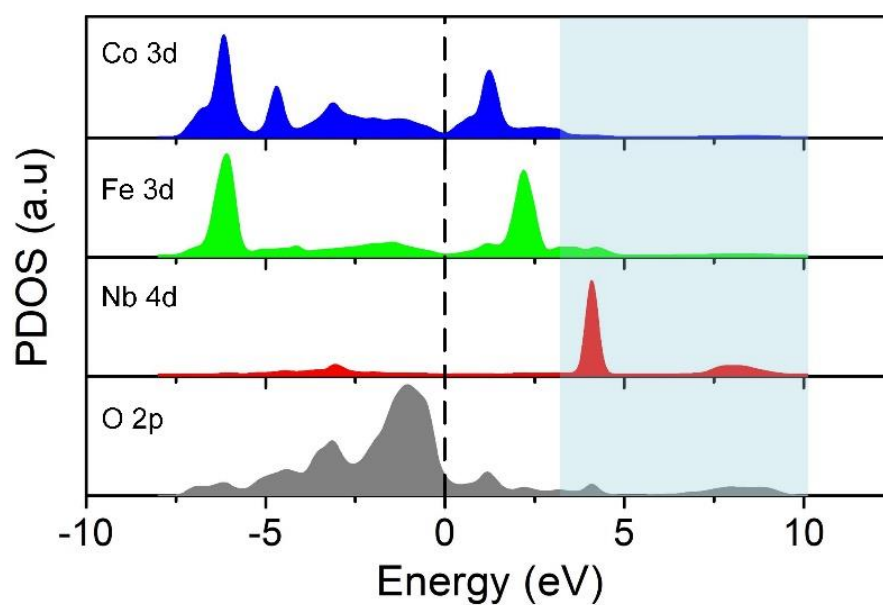
Supplementary Figure 11 Performance of a full cell with a BCFN0.05 air electrode. **(a)** Typical IVP curves in a fuel cell mode measured at 500-650 °C; **(b)** Typical IV curve in an electrolysis mode measured at 500-600 °C; **(c)** A short-term durability test of a fuel cell tested at 600 °C and a current density of +0.5 A cm^{-2} . and **(d)** A short-term durability test of an electrolysis cell tested at 550 °C and a current density of -0.5 A cm^{-2}



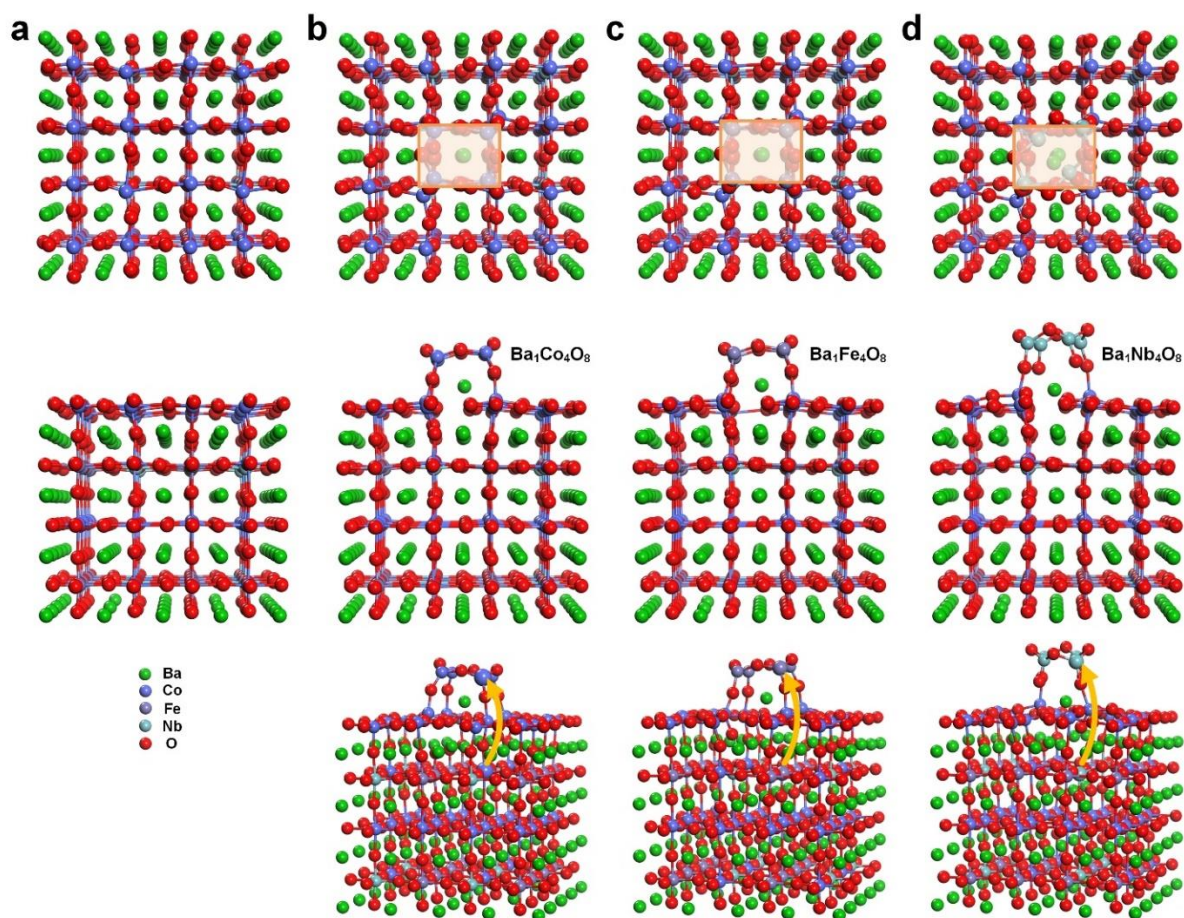
Supplementary Figure 12. Optimized bulk structures of **(a)** stoichiometric BaBO_3 perovskites with a cubic structure ($Pm\bar{3}m$) (8 Ba, 8 B, 24 O atoms) (B = Co, Fe, or Nb), **(b)** stoichiometric $\text{Ba}(\text{B}_{0.5}\text{B}'_{0.5})\text{O}_3$ perovskites with a cubic structure ($Pm\bar{3}m$) (B, B' = Co, Fe, or Nb; 8 Ba, 4 B, 4 B', and 24 O atoms), and **(c)** A-cation deficient $\text{Ba}_{0.9}(\text{Co}_{0.63}\text{Fe}_{0.25}\text{Nb}_{0.13})\text{O}_{3.0}$ with a cubic structure ($Pm\bar{3}m$) (7 Ba, 5 Co, 2 Fe, 1 Nb, 24 O atoms). V_{Ba} is a Ba vacancy. Schematic illustration of bulk diffusion of oxygen vacancies along the [001] direction of **(d)** $\text{Ba}(\text{Co}_{0.63}\text{Fe}_{0.25}\text{Nb}_{0.13})\text{O}_{3.0}$ with an migration energy of 0.58 eV and **(e)** A-cation deficient $\text{Ba}_{0.9}(\text{Co}_{0.63}\text{Fe}_{0.25}\text{Nb}_{0.13})\text{O}_{3.0}$ with that of 0.60 eV. V_{O} is an oxygen vacancy.



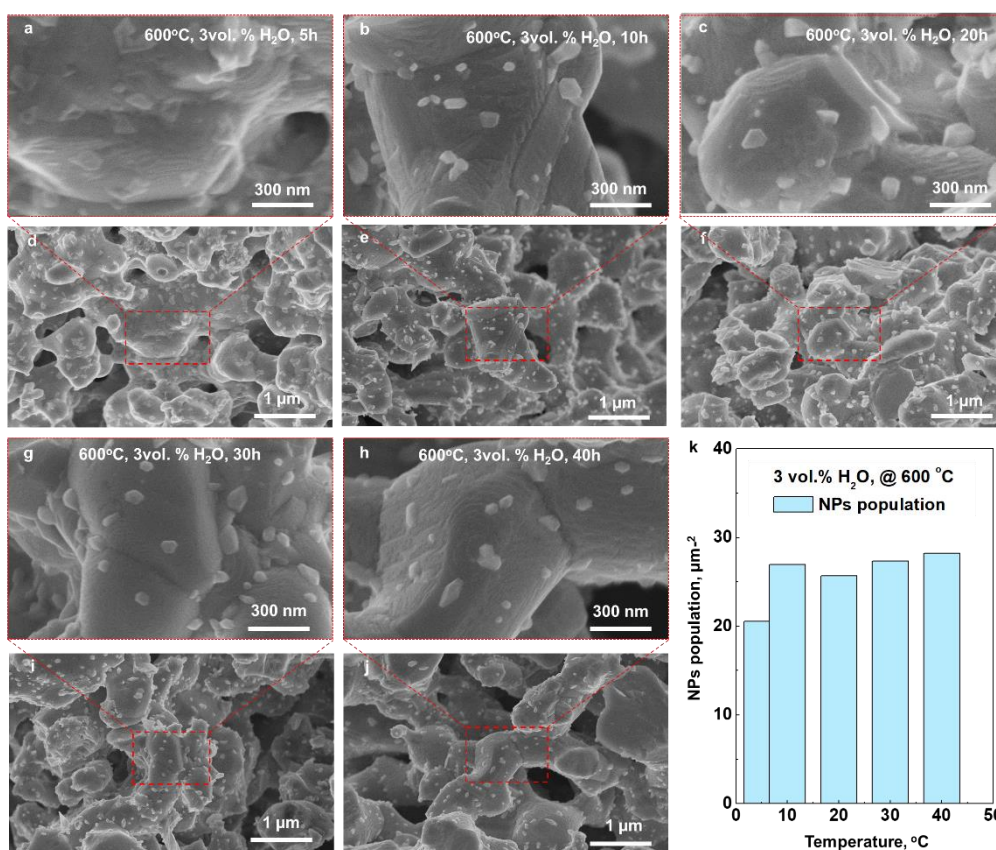
Supplementary Figure 13. 2-D slab models of (a) BaBO₃(001) (B = Co, Fe, or Nb) (32 Ba, 32 B, O 96 atoms) and (b) Ba(B_{0.5}B'_{0.5})O₃(001) (B, B' = Co, Fe, or Nb) (32 Ba, 16 B, 16 B', and 96 O atoms). (c) CoO-terminated and (d) CoFeNbO-terminated Ba_{0.9}(Co_{0.63}Fe_{0.25}Nb_{0.13})O_{3.0}(001) (14 Ba, 10 Co, 4 Fe, 2 Nb, 48 O atoms). V_{Ba} is a Ba vacancy. Note that the CoO-terminated BCFN(001) surface was used to examine the segregation energy from the bulk (B'_{bulk}) to the surface (B_{surface}) (*i.e.*, Co, Fe, or Nb to Co).



Supplementary Figure 14. Projected density of states (PDOSs) of the d-orbitals of Co, Fe, and Nb and the p-orbitals of O for $\text{Ba}_{0.9}(\text{Co}_{0.63}\text{Fe}_{0.25}\text{Nb}_{0.13})\text{O}_{3.0}$. The Fermi energy level (E_F) is set to zero.

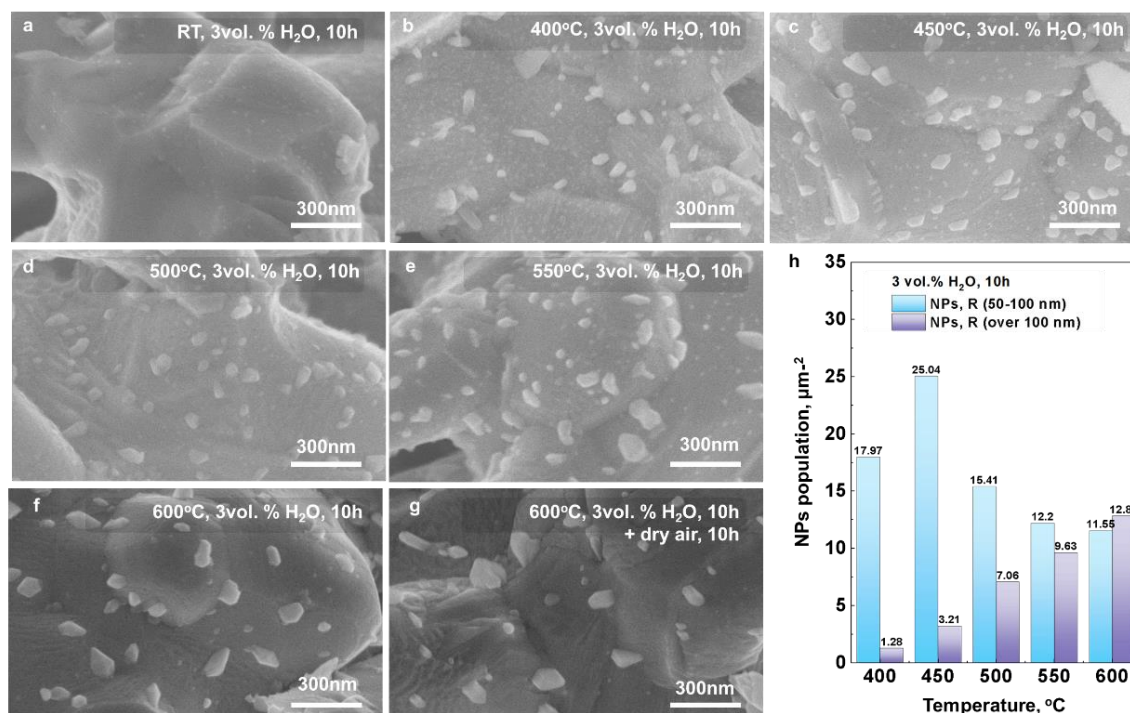


Supplementary Figure 15. 2-D slab models of (a) surface, (b) $\text{Ba}_1\text{Co}_4\text{O}_8$ NP, (c) $\text{Ba}_1\text{Fe}_4\text{O}_8$ NP, and (d) $\text{Ba}_1\text{Nb}_4\text{O}_8$ NP on BCFN(001) (56 Ba, 40 Co, 16 Fe, 8 Nb, 192 O atoms). The rectangular boxes are $\text{Ba}_1\text{B}_4\text{O}_8$ nanoparticles (B = Co, Fe, or Nb), while the arrows represent the segregation of a B cation from the bulk to the nanoparticle surface.



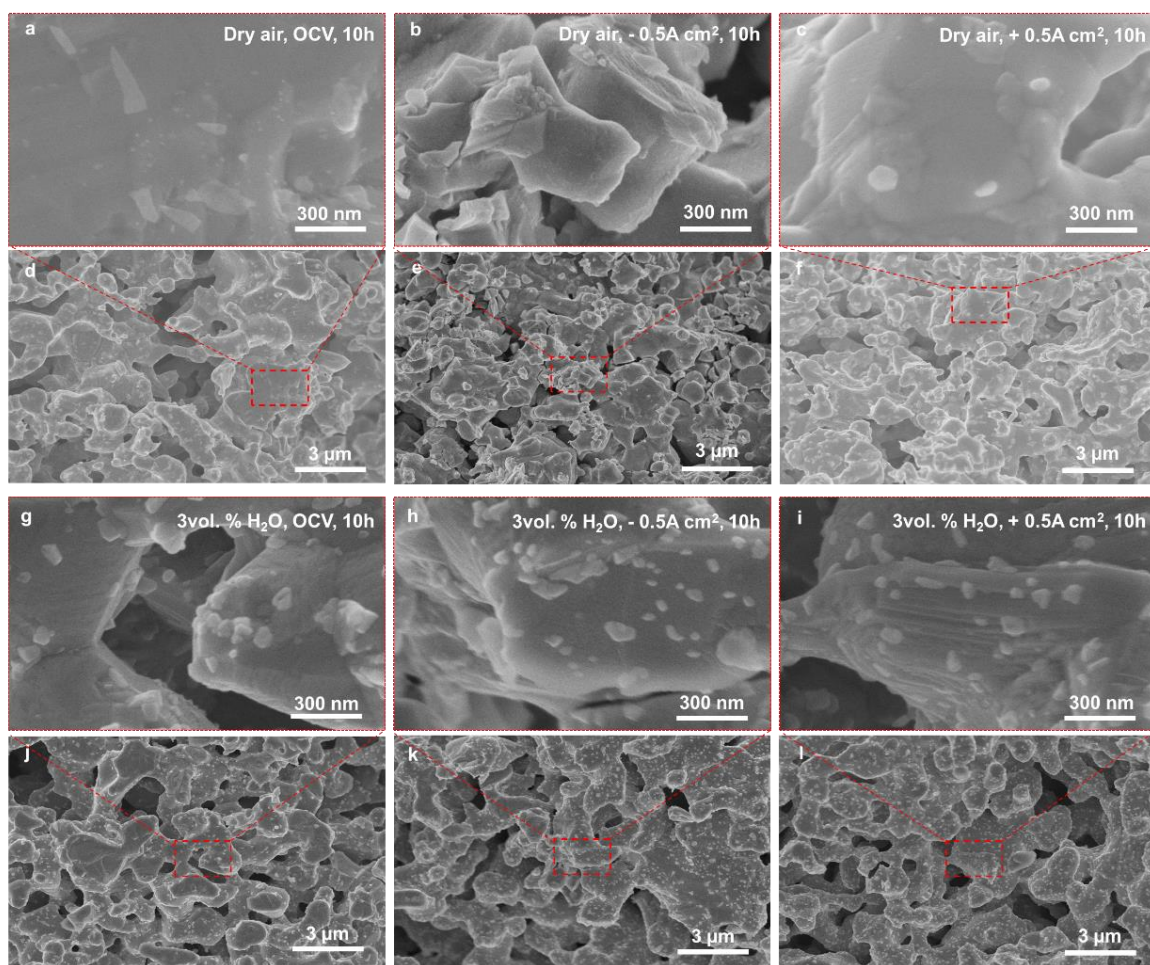
Supplementary Figure 16. Detailed SEM images of BCFN air electrode after operated under 3% humidified air at 600 °C for 5 hours (a) & (d), 10 hours (b) & (e), 20 hours (c) & (f), 30 hours (g) & (i), 40 hours (h) & (j), respectively. (k) Time dependence of exsolved nanoparticles populations of BCFN air electrode operated at 3% humidified H₂O at 600 °C.

Supplementary Discussion: First, we operated the BCFN air electrode at 600 °C in the air with 3% H₂O for different durations (5-40 hours) at OCV conditions to disclose the relationship between the amount of exsolved nanoparticles and operating time (**Supplementary Figure 16**). As shown, a considerable number of nanoparticles (with a population of ~20 μm⁻²) have been exsolved after 5 hours of treatment. The precipitated nanoparticles significantly increase as a function of treating time (in the following 35h). However, after 10h, the NP population tends to be stable.



Supplementary Figure 17 Detailed SEM images of BCFN air electrode after operated under 3% humidified air for 10 hours at (a) room temperature, (b) 400 °C, (c) 450 °C, (d) 500 °C , (e) 550 °C and (f) 600 °C, respectively. (g) Typical SEM images of BCFN air electrode after operated with 3% H₂O humidified air at 600 °C for 10 hours and followed operated with dry air at 600 °C for 10 hours. Temperature-dependent exsolved nanoparticles population of BCFN air electrode operated at 3% H₂O humidified air for 10 hours. (h) populations of the exsolved nanoparticles with a diameter of 50-100 nm (blue) and over 100 nm (purple) when BCFN electrode was operated at 3% humidified H₂O for 10 hours at 400-600 °C.

Supplementary Discussion: In order to investigate the specific temperature that nanoparticles start to exsolve from the skeleton, we operated the BCFN air electrode at different temperatures (400-600 °C) with 3% humidified air for 10 hours at OCV condition (**Supplementary Figure 17**). It is revealed that BCFN approximately started to exsolve at 400 °C. Similarly, we roughly estimated the population of the exsolved nanoparticles (NP) and found that the NP population (over 100nm) increased significantly as temperature increased.



Supplementary Figure 18. Typical SEM images of BCFN air electrode after operated at OCV condition with wet (3% H₂O) hydrogen as fuel and dry air as oxidant **(a) & (d)**, a current density of -0.5 A cm⁻² with wet (3% H₂O) hydrogen as fuel and dry air as oxidant **(b) & (e)**, and a current density of +0.5 A cm⁻² with wet (3% H₂O) hydrogen as fuel and dry air as oxidant **(c) & (f)** at 600 °C for 10 hours; Typical SEM images of BCFN air electrode after operated at OCV condition with wet (3% H₂O) hydrogen as fuel and wet (3% H₂O) air as oxidant **(g) & (j)**, a current density of -0.5 A cm⁻² with wet (3% H₂O) hydrogen as fuel and wet (3% H₂O) air as oxidant **(h) & (k)** and a current density of +0.5 A cm⁻² with wet (3% H₂O) hydrogen as fuel and wet (3% H₂O) air as oxidant **(i) & (l)** at 600 °C for 10 hours.

Supplementary Discussion: To evaluate if the voltage/current or the chemical potential of steam is the main reason for the exsolution, we treated the air electrode under the following conditions. First, we operated cells with BCFN air electrode at OCV condition when the air

electrode is exposed to dry air at 600 °C for 10 hours at current densities of 0, -0.5, and +0.5 Acm^{-2} . It is shown that very few nanoparticles are exsolved (**Supplementary Figure 18a-f**). In contrast, when the air electrode is exposed to wet air (3% H_2O) at current densities of 0, -0.5, and +0.5 Acm^{-2} , a great number of nanoparticles were observed on the skeleton (**Supplementary Figure 18g-l**), indicating that steam can lead to the exsolution. Therefore, it is reasonable to conclude that the current flowing may not be the factor required to induce the exsolution. The steam is most likely the main reason for the exsolution.

Supplementary Table 1. Temperature dependence of the polarization resistance (R_p) of BZCYYb symmetrical cell with BCFN and other high-performance electrodes reported recently.

Cathode	Temp. [°C]	R_p [Ω cm ⁻²]	Authors, Year
Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ} (BCFN)	700	0.04153	This work
	650	0.10028	
	600	0.19689	
	550	0.47147	
	500	1.19746	
Nd_{0.5}Ba_{0.5}Fe_{0.9}Co_{0.1}O_{3-δ} (NBFC)	750	0.126	Lyagaeva, J., <i>et al</i> , 2018 ¹¹
	700	0.178	
	650	0.390	
	600	1.000	
BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-δ} (BCFZ)	650	0.60	Shang, M., <i>et al</i> , 2013 ¹²
	600	1.00	
	550	1.80	
Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF)	700	0.794	Bi, L., <i>et al</i> , 2012 ¹³
	650	1.318	
	600	1.990	
	550	3.981	
Ba_{0.5}Sr_{0.5}Co_{0.72}Fe_{0.18}Ti_{0.10}O_{3-δ} (BSCFT)	700	0.891	Meng, Y., <i>et al</i> , 2021 ¹⁴
	650	1.580	
	600	3.160	
	550	4.460	
BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY)	700	0.10	Matsui, T., <i>et al</i> , 2021 ¹⁵
	650	0.40	
	600	0.85	
	550	1.15	
Ba₅SrSm₂Co₄O₁₅ (BSSC)	700	0.40	Huan, D., <i>et al</i> , 2020 ¹⁶
	650	0.68	
	600	1.20	

	550	2.20	
Sr₃EuFe_{2.5}Co_{0.5}O_{10-δ} (SEFC)	700	0.341	Huan, D., <i>et al.</i> , 2018 ¹⁷
	650	0.950	
	600	2.800	
Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}O_{3-δ} (BCFZY_{0.95})	650	0.2	He, F., <i>et al.</i> , 2020 ¹⁸
	600	0.3	
	550	0.8	
SrCo_{0.8}Fe_{0.15}Zr_{0.05}O_{3-δ} (SCFZ)	700	0.07	Lv, X., ., <i>et al.</i> , 2020 ¹⁹
	650	0.15	
	600	0.38	
	550	1.01	
	500	2.42	
BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY)	500	1.75	Liang, M., <i>et al.</i> , 2021 ²⁰
Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Ni_{0.05}O_{3-δ} (BCFZYN)	500	1.5	Liang, M., <i>et al.</i> , 2021 ²⁰
Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Zn_{0.05}O_{3-δ} (BCFZYZ)	500	1.83	Liang, M., <i>et al.</i> , 2021 ²⁰
Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Mn_{0.05}O_{3-δ} (BCFZYM)	500	2.38	Liang, M., <i>et al.</i> , 2021 ²⁰
Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Cu_{0.05}O_{3-δ} (BCFZYC)	500	1.70	Liang, M., <i>et al.</i> , 2021 ²⁰
Ba_{0.95}La_{0.05}Fe_{0.8}Zn_{0.2}O_{3-δ} - BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} (BLFZ-BZCYYb composite)	750	0.159	Wang, Z., <i>et al.</i> , 2020 ²¹
	700	0.297	
	650	0.683	
Ba_{0.95}Ca_{0.05}Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCCFZY)	750	0.290	Li, J., <i>et al.</i> , 2020 ²²
	700	0.631	
	650	1.488	
PrBa_{0.9}Co_{1.96}Nb_{0.04}O_{5+δ} (PBCN)	750	0.056	Zhang, W., <i>et al.</i> , 2021 ²³
	700	0.090	
	650	0.220	
	600	0.550	

Supplementary Table 2. Performance comparison of our cells and other high-performance cells reported recently.

Cathode	Electrolyte	Anode	Electrolyte thickness [μm]	Temp. [$^{\circ}\text{C}$]	P_{max} [W cm^{-2}]	Authors, Year
Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}	BaCe _{0.55} Zr _{0.3} Y _{0.15} O _{3-δ} (BCZY ₃)	NiO-BCZY ₃	5	650 600 550	1.610 1.302 0.920	An et al.,2018 ²⁴
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} (PBSCF)	BaZr _{0.4} Ce _{0.4} Y _{0.1} Yb _{0.1} O ₃ (BZCYYb4411)	NiO-BZCYYb4411	15	600	0.8	Choi et al.,2018 ²⁵
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} (PBSCF) PLD layer	BaZr _{0.4} Ce _{0.4} Y _{0.1} Yb _{0.1} O ₃ (BZCYYb4411)	NiO-BaZr _{0.4} Ce _{0.4} Y _{0.1} Yb _{0.1} O ₃ (BZCYYb4411)	15	650 600	1.4 1.1	Choi et al.,2018 ²⁵
BCZY631-BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY_{0.1})BCFZY	BCZYYb4411+1wt % NiO	NiO-BCZYYb4411	15 - 50	600 550	0.648 0.515	Duan et al.,2015 ²⁶
NdBa_{0.75}Ca_{0.25}Co₂O_{5+δ} (NBCaC)-BZCYYb1711	BaZr _{0.1} Ce _{0.7} Y _{0.1} Yb _{0.1} O ₃ (BZCYYb1711)	Ni ₄ Co-PrBaMn ₂ O _{5+δ} (PBM)-NiO-BZCYYb1711	15	700	1.48	Hua et al.,2016 ²⁷
NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}(NBSCF)	BCZYYb1711	NiO-BCZYYb1711	14.7	700 600	2.1 0.69	Kim et al.,2014 ²⁸
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} (PBSCF)	BCZYYb1711	NiO-BCZYYb1711	14.1	700 650 600	1.374 1.048 0.704	Seong et al.,2018 ²⁹
La_{0.6}Sr_{0.4}CoO_{3-δ}(LSC)	BaCe _{0.55} Zr _{0.3} Y _{0.15} O _{3-δ} (BCZY ₃)	NiO-BCZY, NiO-YSZ	1	650 600 550	1.3 1.1 0.8	Bae et al.,2018 ³⁰

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}(LS CF)	BCZYYb1711	NiO-BCZYYb1711	10	600	1.125	Yang et al.,2009 ³¹
BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-δ}	BCZYYb1711	NiO-BCZYYb1711	30	750 650	1.1 0.66	Shang et al.,2013 ³²
BCZY-LSCF	BCZYYb1711	NiO-BCZYYb1711	14.7	600	0.225	Kim et al.,2014 ²⁸
Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}	BaCe _{0.55} Zr _{0.3} Y _{0.15} O _{3-δ} (BCZY ₃)	NiO-BCZY ₃	1.5	600	0.508	Bae et al.,2016 ³³
La_{0.6}Sr_{0.4}CoO_{3-δ}(LSC)	BaCe _{0.55} Zr _{0.3} Y _{0.15} O _{3-δ} (BCZY ₃)	NiO-BCZY	5	600	0.74	Bae et al.,2017 ³⁴
BCZY	BCZYYb1711	NiO-BCZYYb1711	7	550	0.44	Braun et al.,2019 ³⁵
BaCo_{0.7}(Ce_{0.8}Y_{0.2})_{0.3}O_{3-δ}(B CCY)	BCZYYb1711	NiO-BCZYYb1711	16.1	650 600	0.993 0.73	Song et al.,2019 ³⁶
PrCo_{0.5}Ni_{0.5}O_{3-δ} nano-fiber	BCZYYb4411	NiO-BCZYYb4411	10	600 550	0.607 0.444	Ding et al.,2020 ³⁷
PrNi_{0.5}Mn_{0.5}O_{3-δ} (PNM)	BCZYYb1711	NiO-BCZYYb1711	30	700 650	0.8 0.441	Chen et al.,2018 ³⁸
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} (PBSCF)	BCZYYb4411	NiO-BCZYYb4411	10	650 600 550	1.9 1.45 1.01	Choi et al.,2021 ³⁹
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} (PBSCF)	BCZYYb1711	NiO-BCZYYb1711	10	700 650 600 550	1.609 1.257 0.723 0.360	Hua et al.,2021 ⁴⁰
Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ}	BCZYYb1711	NiO-BCZYYb1711	10	650 600 550 500	1.707 1.207 0.820 0.550	This work

Supplementary Table 3. Performance comparison of our cell and other cells reported by others.

Cathode	Electrolyte	Anode	Electrolyte thickness [μm]	Temp. [°C]	Current Density@1.3 V [A cm ⁻²]	Authors, Year
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}(PBSCF)	BaZr _{0.4} Ce _{0.4} Y _{0.1} Yb _{0.1} O ₃ (BZCYYb4411)	NiO-BZCYYb4411	15	650	-2.208	Choi et al.,2019 ⁴¹
				600	-1.926	
NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}(NBSCF)-BZCYYb	BCZYYb1711	NiO-BCZYYb1711	14.7	650	-1.705	Kim et al.,2018 ⁴²
				600	-0.805	
				550	-0.399	
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}(PBSCF)	BaHfCeYYbO (BHCYYb3511)	Ni-BHCYYb (3511)	15	650	-0.695	Murphy et al.,2020 ⁴³
				600	-0.285	
Pr₂NiO₄-BZCY	BaZr _{0.2} Ce _{0.6} Y _{0.2} O ₃ (BZCY)	Ni-BZCY	20	650	-0.604	Li et al.,2018 ⁴⁴
				600	-0.349	
				550	-0.221	
PrCo_{0.5}Ni_{0.5}O_{3-δ} nano-fiber	BCZYYb4411	NiO-BCZYYb4411	PrCo _{0.5} Ni _{0.5} O _{3-δ} nano-fiber	600	-1.000	Ding et al.,2020 ³⁷
				550	-0.698	
PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}(PBSCF)	BaZr _{0.8} Y _{0.2} Yb _{0.1} O ₃ (BZY20)	NiO-BZY20	15	600	-0.903	Duan et al.,2019 ⁴⁵
				550	-0.708	
				500	-0.500	
BaGd_{0.8}La_{0.2}Co₂O_{6-δ}	BaZr _{0.2} Ce _{0.7} Y _{0.1} O ₃ (BZCY)	Ni-BZCY	25	600	-0.131	Vøllestad et al.,2019 ⁴⁶
				500	-0.074	
Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ}	BCZYYb1711	NiO-BCZYYb1711	10	650	-2.735	This work
				600	-1.511	
				550	-0.718	
				500	-0.265	

Supplementary Table 4. Optimized lattice parameters (a_0) of BaBO_3 (B = Co, Fe, or Nb) and the surface energies of BaO- and BO-terminated $\text{BaBO}_3(001)$.

	bulk	slab	
	a ₀ (Å)	surface energy (J/m ²)	termination
BaCoO ₃	3.9562	0.45	BaO
		0.51	CoO
BaFeO ₃	3.9761	0.81	BaO
		0.82	FeO
BaNbO ₃	4.1208	0.94	BaO
		0.93	NbO
Surface stability of BO termination			CoO > FeO > NbO

Note: In this comparison, all layers were fully relaxed without any restriction. As shown in the summary of BaO-terminated surfaces, the stability may be dependent on B cation types.

Supplementary Table 5. Optimized lattice constants (a_0) of $\text{Ba}(\text{B}_{0.5}\text{B}'_{0.5})\text{O}_3$ (B, B' = Co, Fe, or Nb) and the segregation energy of $\text{Ba}(\text{B}_{0.5}\text{B}'_{0.5})\text{O}_3(001)$.

	bulk	slab			
	a ₀ (Å)	segregation atom	segregation energy (J/m ²)	termination	segregation tendency
Ba(Co _{0.5} Fe _{0.5})O ₃	3.9725	Co	−0.14	CoO	Co > Fe
		Fe	+0.33	FeO	
Ba(Co _{0.5} Nb _{0.5})O ₃	4.0581	Co	−0.54	CoO	Co > Nb
		Nb	+0.38	NbO	
Ba(Fe _{0.5} Nb _{0.5})O ₃	4.0693	Fe	−0.57	FeO	Fe > Nb
		Nb	+1.13	NbO	
Total segregation order					Co > Fe > Nb

Supplementary Table 6. Optimized lattice constant (a_0) and oxygen vacancy formation energies (E_{OV}) of $Ba_{0.9}(Co_{0.63}Fe_{0.25}Nb_{0.13})O_{3.0}$ (BCFN) and surface energies of $Ba_{0.9}(Co_{0.63}Fe_{0.25}Nb_{0.13})O_{3.0}(001)$ (BCFN(001)).

	bulk		slab	
	a_0 (Å)	E_{OV} (eV) ¹	termination	surface energy (J/m ²) ²
$Ba_{0.9}(Co_{0.63}Fe_{0.25}Nb_{0.13})O_{3.0}$ (7 Ba, 5 Co, 2 Fe, 1 Nb, 24 O)	3.9768	2.95	CoO	0.78
			CoFeNbO	1.03
			BaO	0.93

Note 1: The oxygen vacancy formation energy was averaged after calculating at 24 oxygen vacancy positions.

An oxygen vacancy formation energy of $Ba(Co_{0.63}Fe_{0.25}Nb_{0.13})O_{3.0}$ with a cubic structure (8 Ba, 5 Co, 2 Fe, 1 Nb, 24 O atoms) calculated is 1.87 eV, indicating ~37% more difficult to generate oxygen vacancies.

Note 2: It is an averaged surface energy of two BaO-terminated models (1. BaO-CoFeNbO-BaO-CoO- (0.91 J/m²) and 2. BaO-CoO-BaO-CoFeNbO- (0.95 J/m²)). The surface models were prepared with 16 layers, and the bottom eight layers were fixed at the bulk parameters.

Supplementary Table 7. Segregation energies of $\text{Ba}_{0.9}(\text{Co}_{0.63}\text{Fe}_{0.25}\text{Nb}_{0.13})\text{O}_{3.0}(001)$.

surface configuration ¹	segregation energy (eV) ²				remark
	Co	Fe ₁	Fe ₂	Nb	
CoO	0.39	0.71	2.33	1.18	before swapping Co (surface) and Nb (bulk)
CoNbO	-	0.09	-0.04	-	before swapping Co (surface) and Nb (bulk)

1. The energy difference of CoNbO (after swapping Nb and Co atoms) and CoO (before switching Nb and Co atoms) is 0.17 J/m^2 , indicating that Nb makes the surface less stable than the CoO-terminated surface.
2. The segregation energy of Fe becomes smaller after an Nb atom segregates to the surface. It explains that Nb that locally segregates to the surface augments the segregation of Fe.

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