

Supplementary Information

Highly ionic-dispersion oxygen electrode for proton ceramic electrochemical cells

*Xiaoyu Wang^{1,2}, Zhaohui Cai², Zeping Chen^{1,2}, Donliang Liu^{1,2}, Wanqing Chen^{1,2}, Jianqiu Zhu³,
Wenhui Li¹, Xixi Wang⁴, Linjuan Zhan³, Wei Wang^{1,2}, Chuan Zhou^{1,2*}, Wei Zhou^{1,2*}, Zongping Shao^{5*}*

¹State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China.

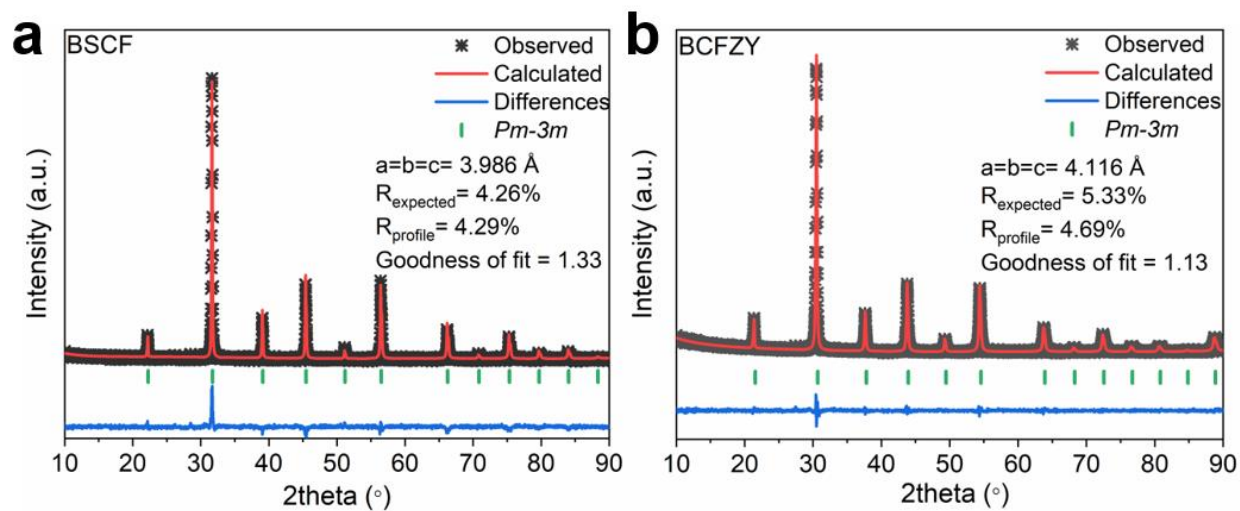
²Suzhou Laboratory, Suzhou 215000, China

³Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

⁴School of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, China

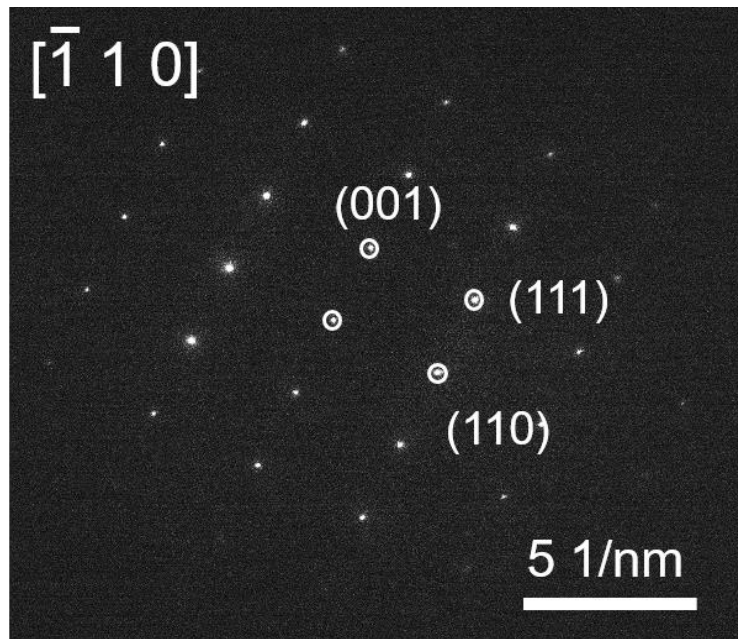
⁵Curtin Centre for Advanced Energy Materials and Technologies (CAEMT), Western Australian School of Mines (WASM), Curtin University, Perth, Western Australia 6102, Australia

*Corresponding author E-mail: zhouc@szlab.ac.cn (C. Zhou), zhouwei1982@njtech.edu.cn (W. Zhou), Zongping.Shao@curtin.edu.au (Z. Shao).



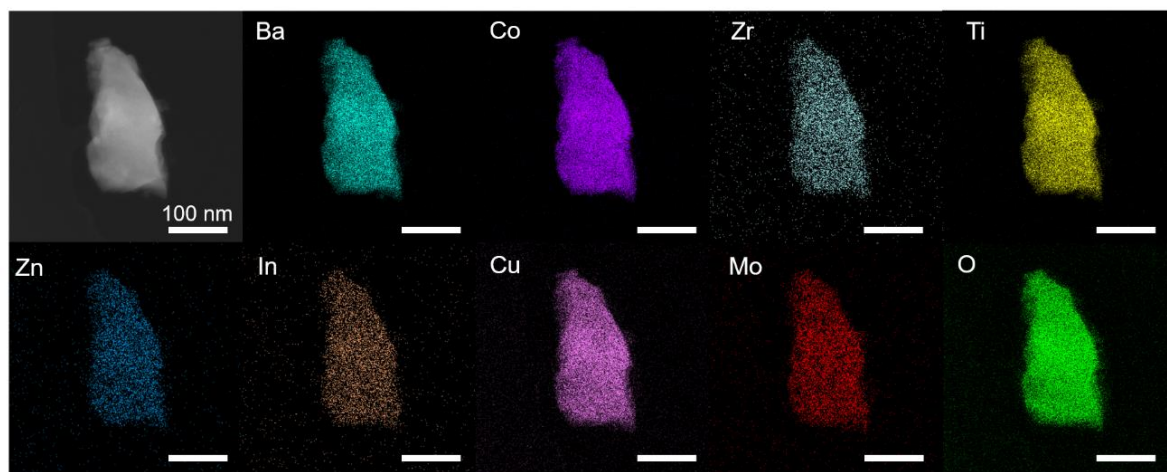
Supplementary Fig. 1.

Rietveld Refinement XRD profiles of the prepared (a) BSCF and (b) BCFZY.



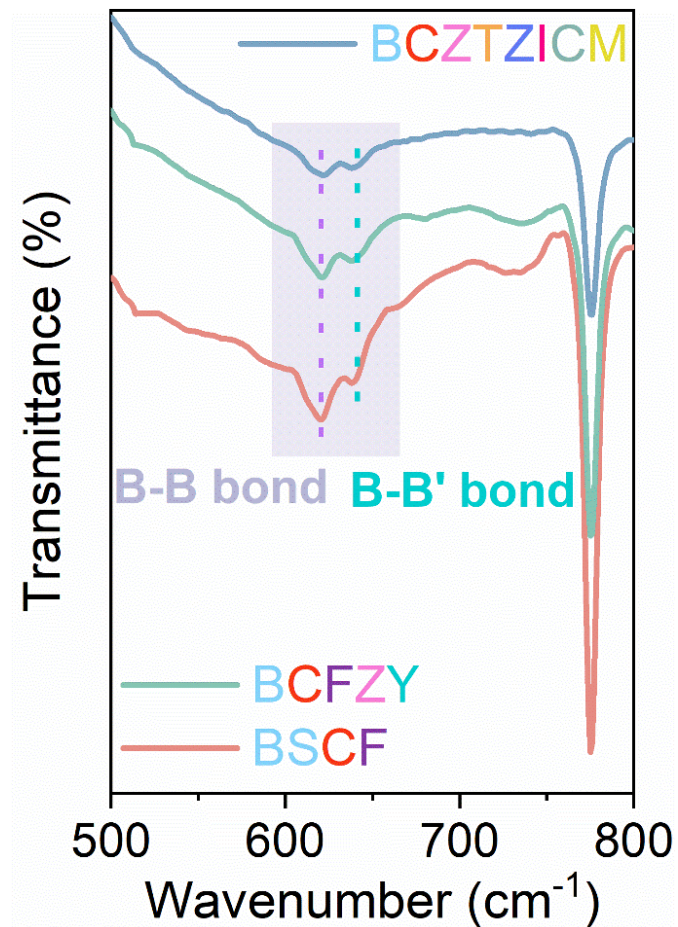
Supplementary Fig. 2.

SEAD pattern of the $[\bar{1}10]$ zone axis of the BCZTZICM.



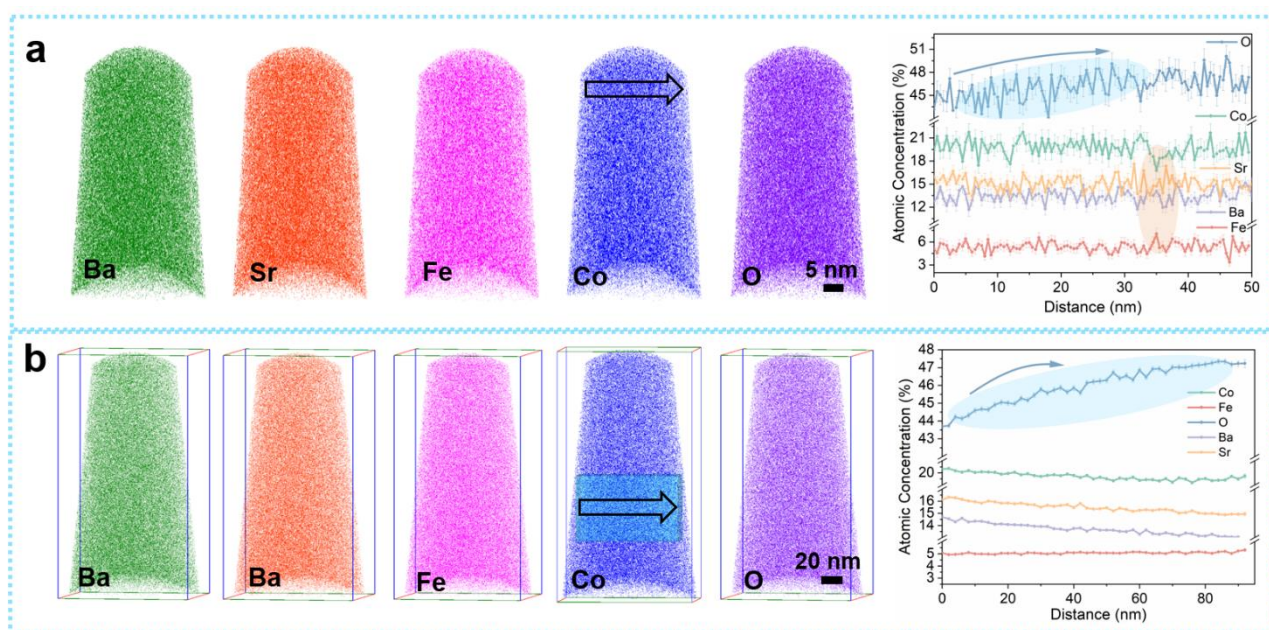
Supplementary Fig. 3.

EDS-mapping result of BCZTZICM.



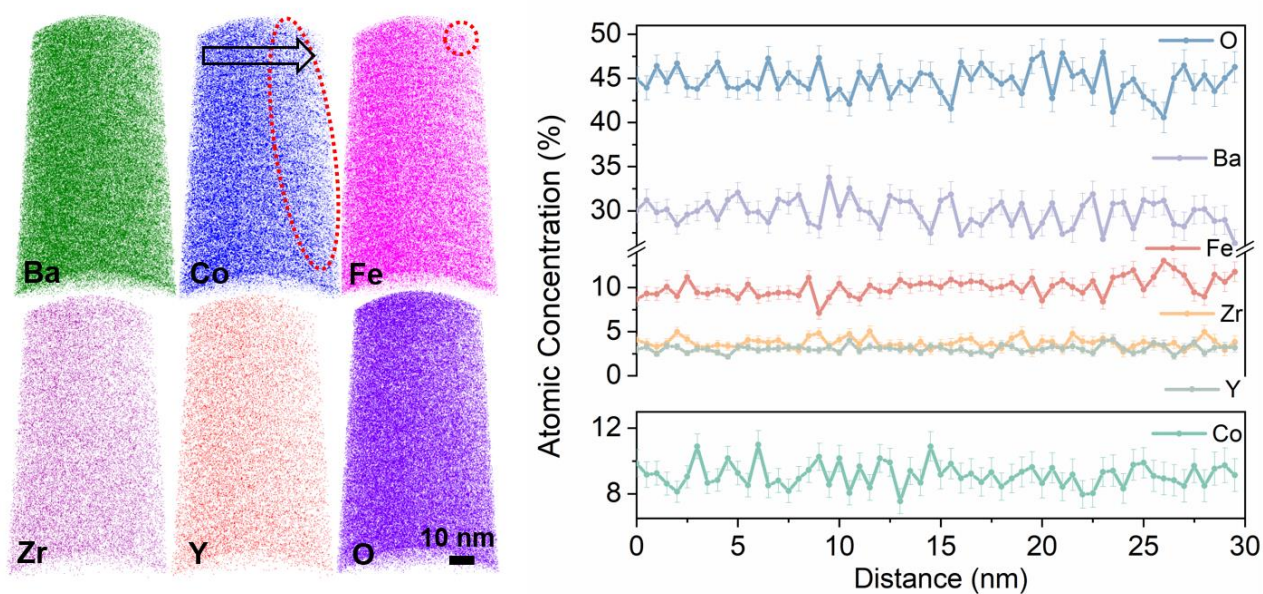
Supplementary Fig. 4.

FT-IR spectra of BCZTZICM, BSCF and BCFZY samples.



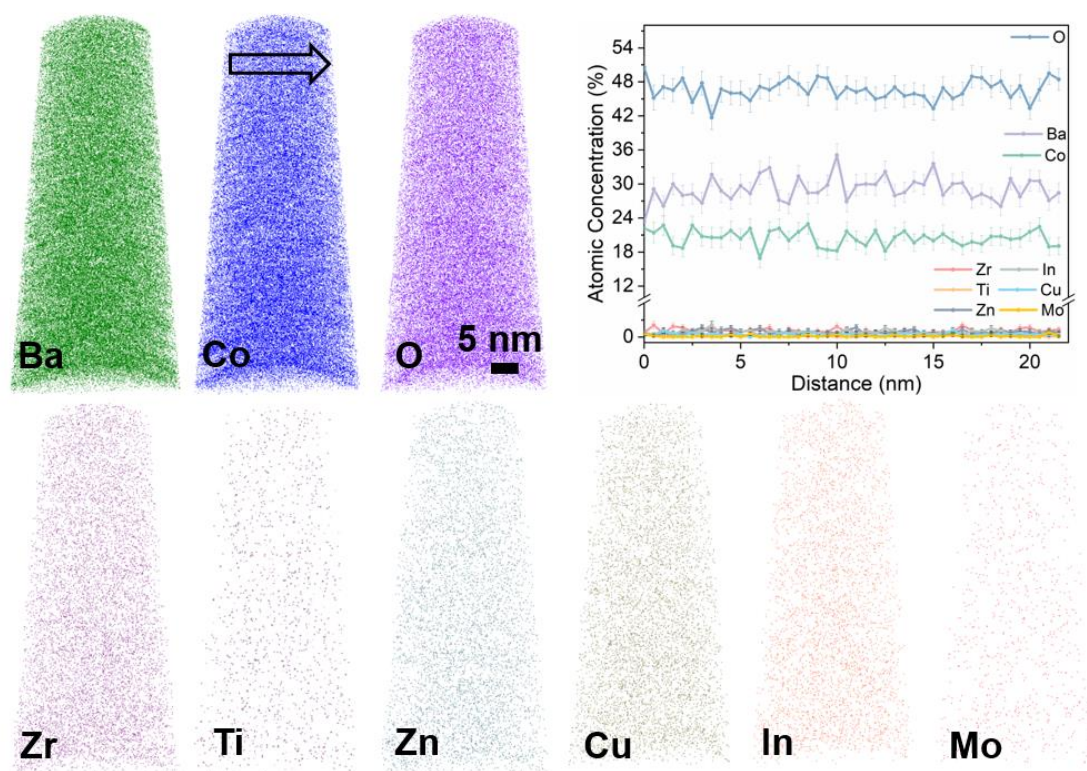
Supplementary Fig. 5.

3D reconstruction of the APT data showing mapping of the BSCF sample with Ba, Sr, Co, Fe, and O ionic distributions. Integrated line profiles show chemical composition at the (a) apex and (b) midsection regions of the analyzed needle.



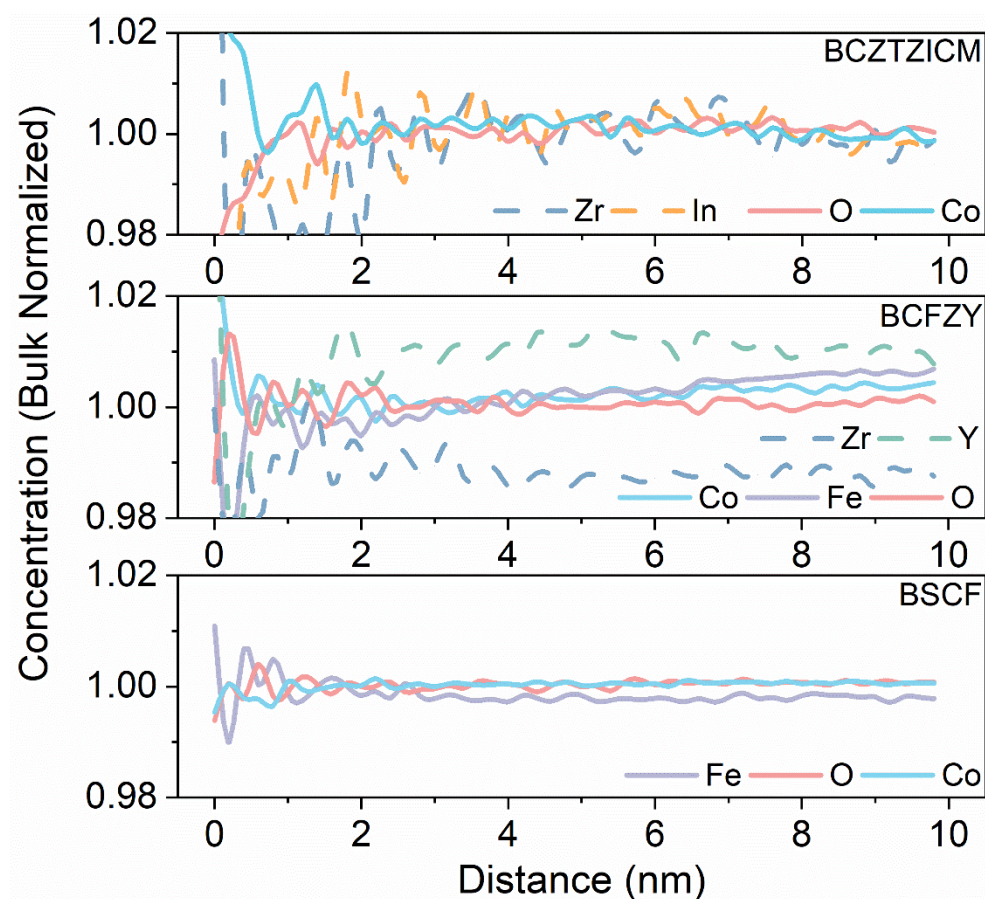
Supplementary Fig. 6.

3D reconstruction of the APT data showing mapping of the BCFZY sample with Ba, Co, Fe, Zr, Y, and O ionic distributions. Integrated line profiles show chemical composition at the apex regions of the analyzed needle.



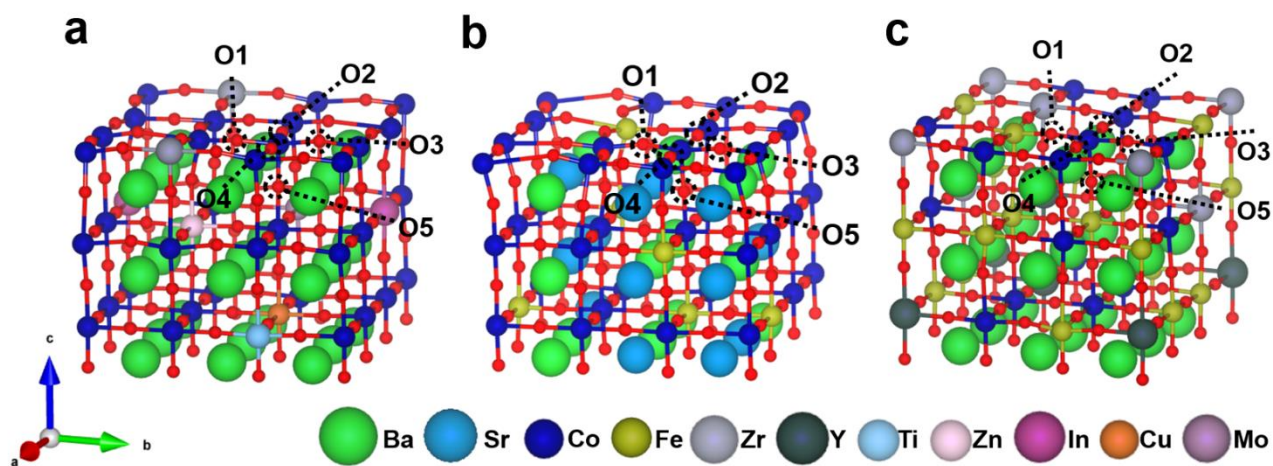
Supplementary Fig. 7.

3D reconstruction of the APT data showing mapping of the BCZTZICM sample with elements distributions. Integrated line profiles show chemical composition alongside the y-axis of the analyzed needle.



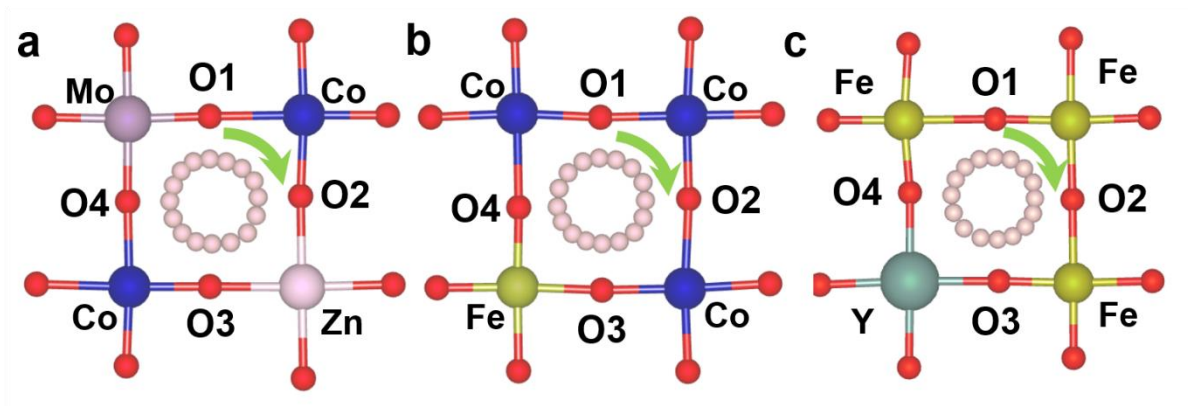
Supplementary Fig. 8.

Radial distribution function (RDF) analysis of neighboring ions around Co centers within a 10 nm range, derived from APT data.



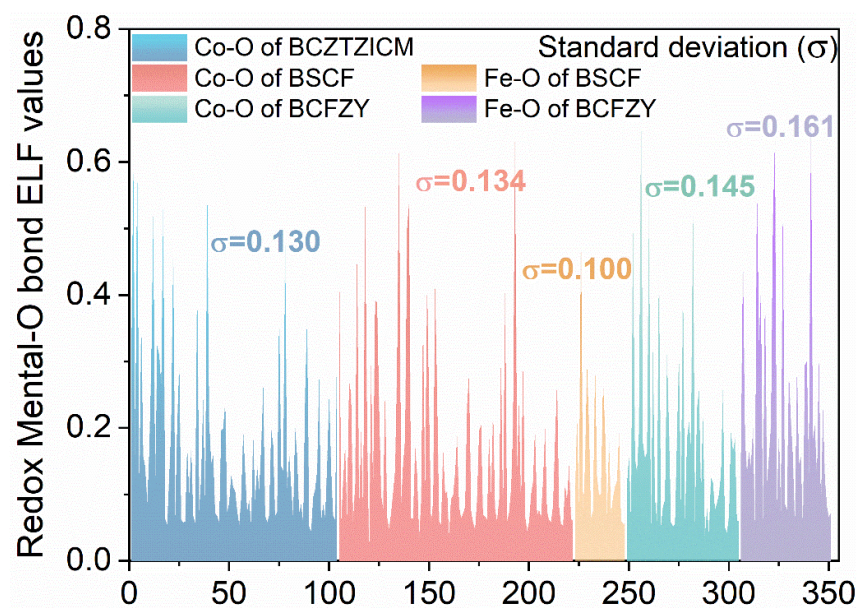
Supplementary Fig. 9.

Optimized structure of stoichiometric pristine of (a) BCZTZICM, (b) BSCF, and (c) BCFZY, and unit cell oxygen sites in perovskite are labeled as calculated sites.



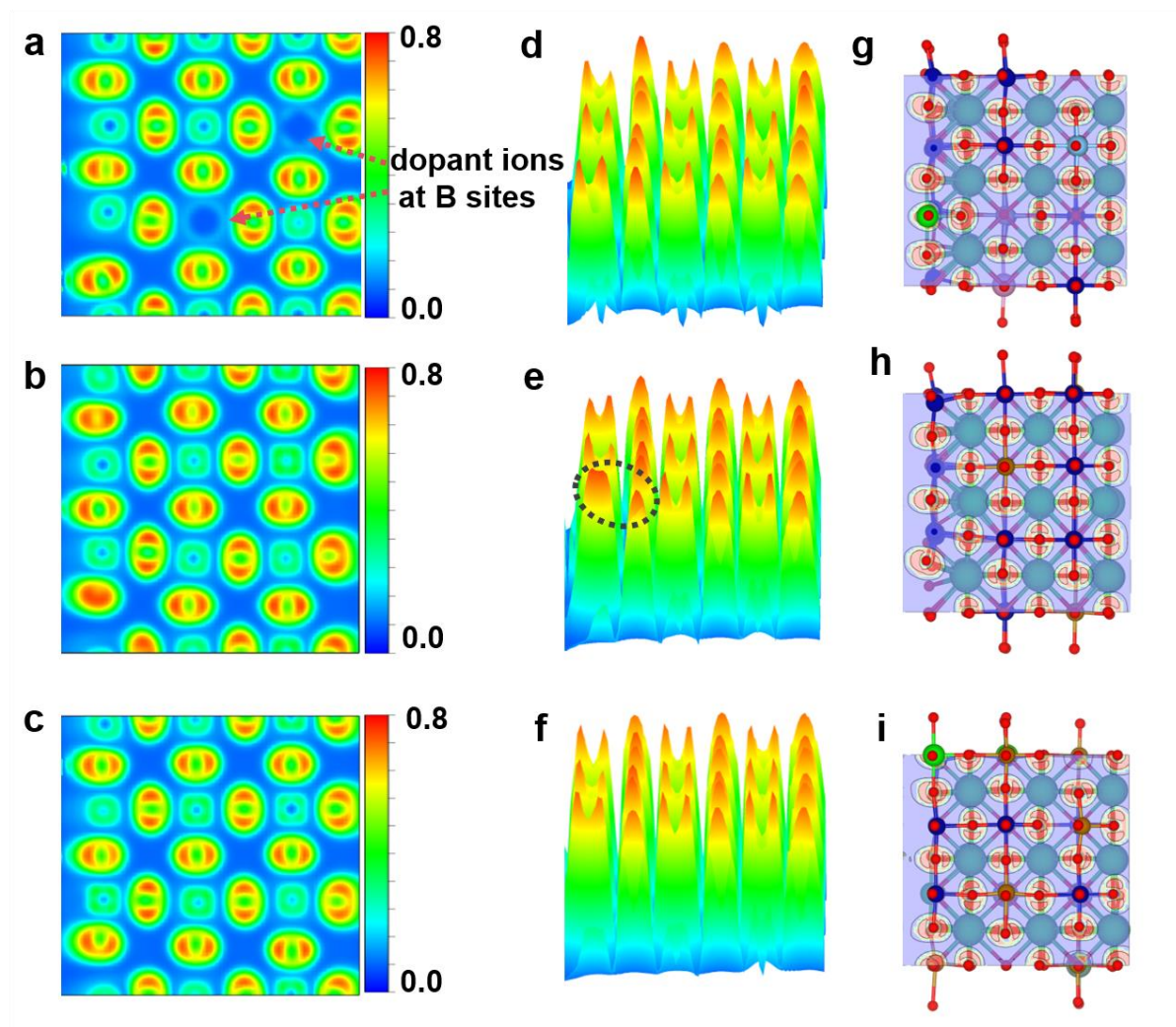
Supplementary Fig. 10.

Proton diffusion paths of the perovskites (a) BCZTZICM, (b) BSCF, and (c) BCFZY, with the direction of the proton migration indicated on the inside.



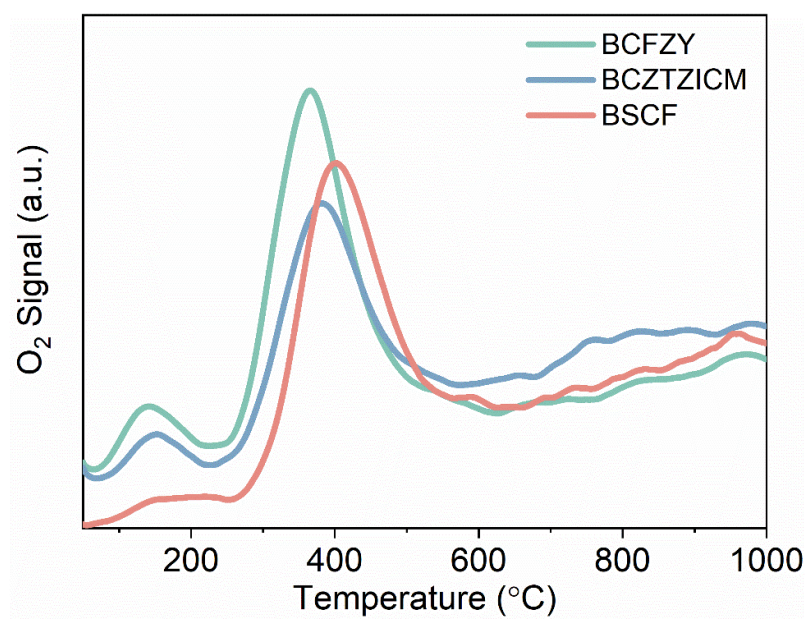
Supplementary Fig. 11.

ELF values of redox metal-oxygen bonds of BSCF, BCFZY, and multi-element micro-doping BCZTZICM sample.



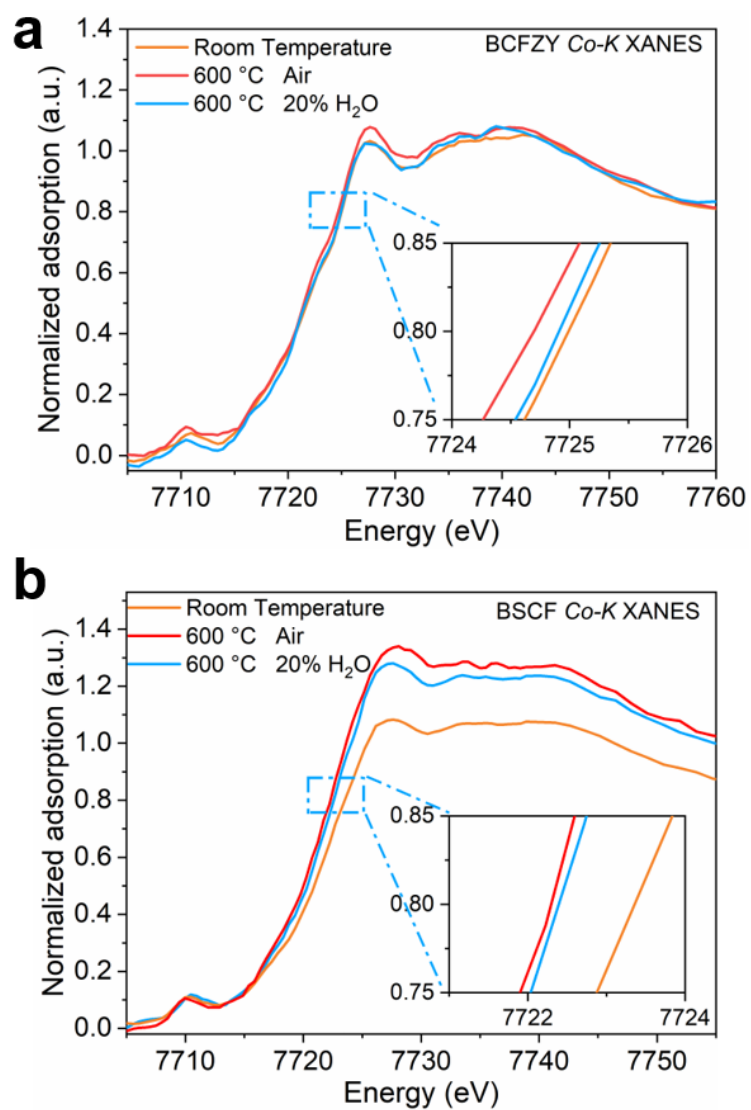
Supplementary Fig. 12.

ELF visualizations diagram along the (100) plane of (a) BCZTZICM, (b) BSCF, and (c) BCFZY, where the color bars indicate ELF values. Bird's-eye view of ELF distributions for (d) BCZTZICM, (e) BSCF, and (f) BCFZY. Electron density isosurfaces for (g) BCZTZICM, (h) BSCF, and (i) BCFZY, respectively.



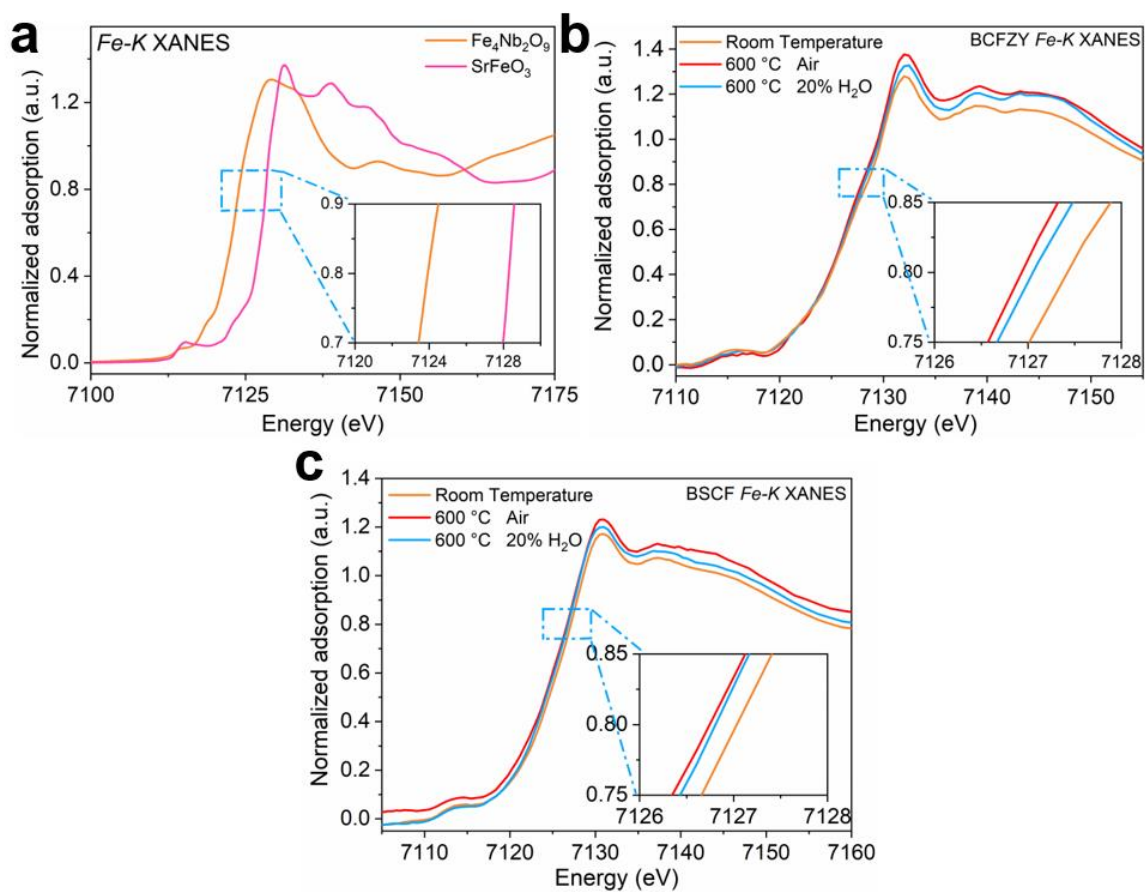
Supplementary Fig. 13.

O₂-TPD profiles from 25 °C to 1000 °C.



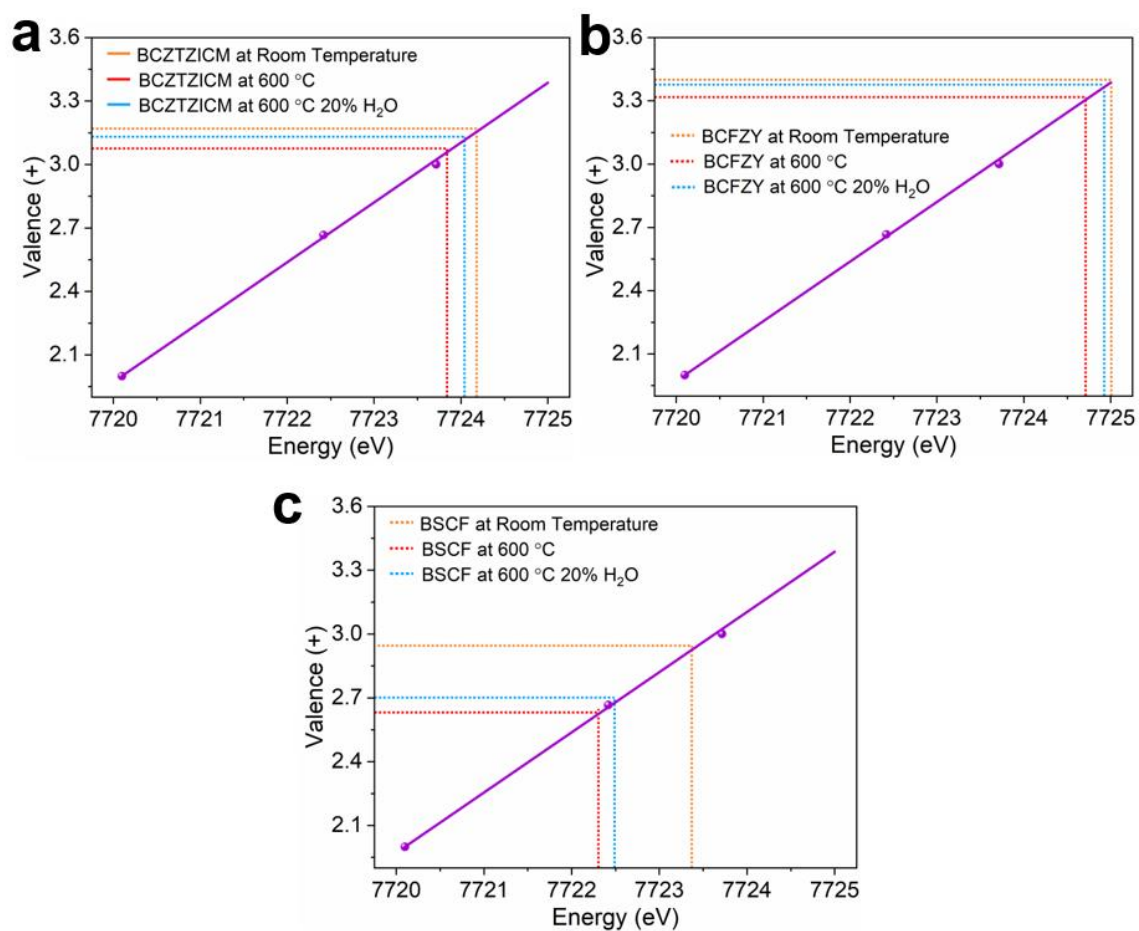
Supplementary Fig. 14.

Co K-edge XANES data of (a) BCFZY and (b) BSCF at different temperatures and treatments.



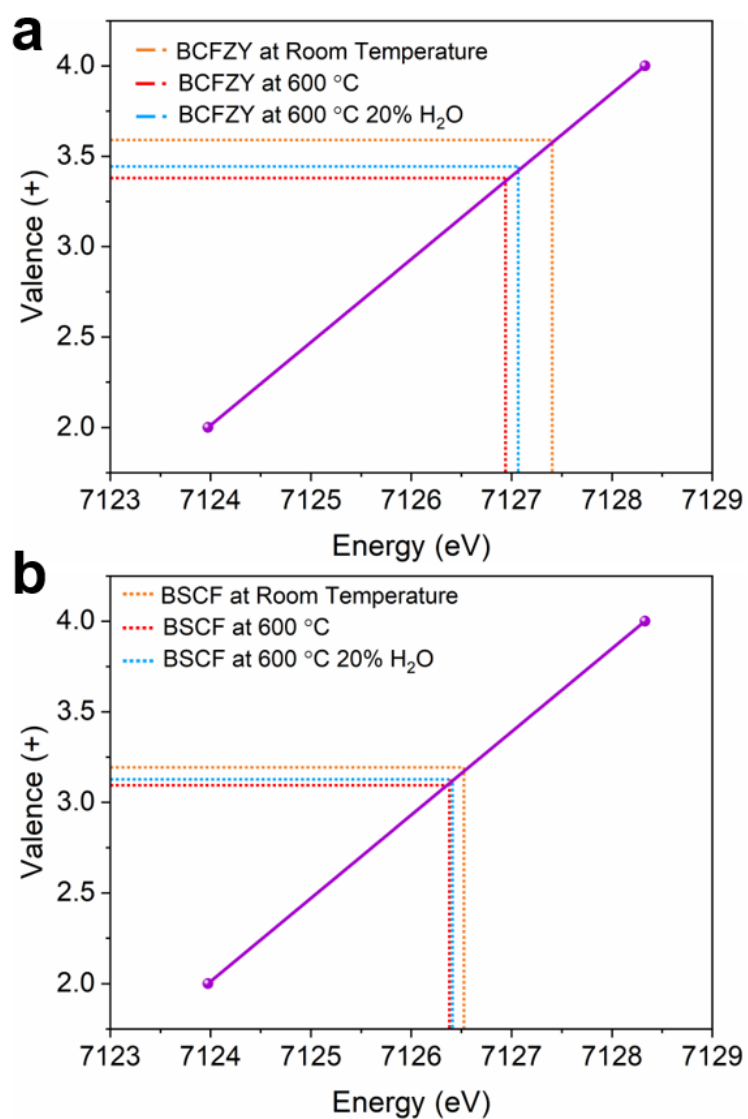
Supplementary Fig. 15.

(a) XANES data for Fe standard samples. Fe K-edge XANES data of (b) BCFZY and (c) BSCF at different temperatures and treatments.



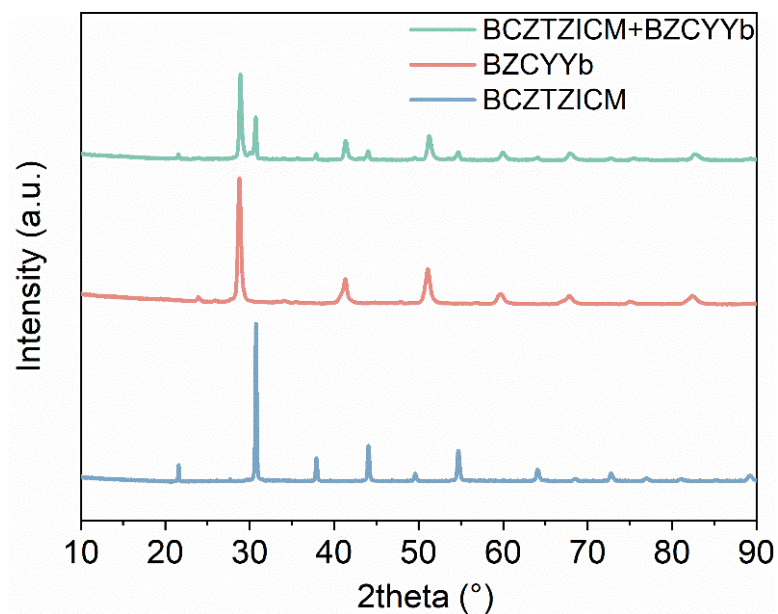
Supplementary Fig. 16.

Co ions average valence calculated from the absorption edge shift in XANES data of (a) BCZTZICM, (b) BCFZY, and (c) BSCF at different temperatures and treatments.



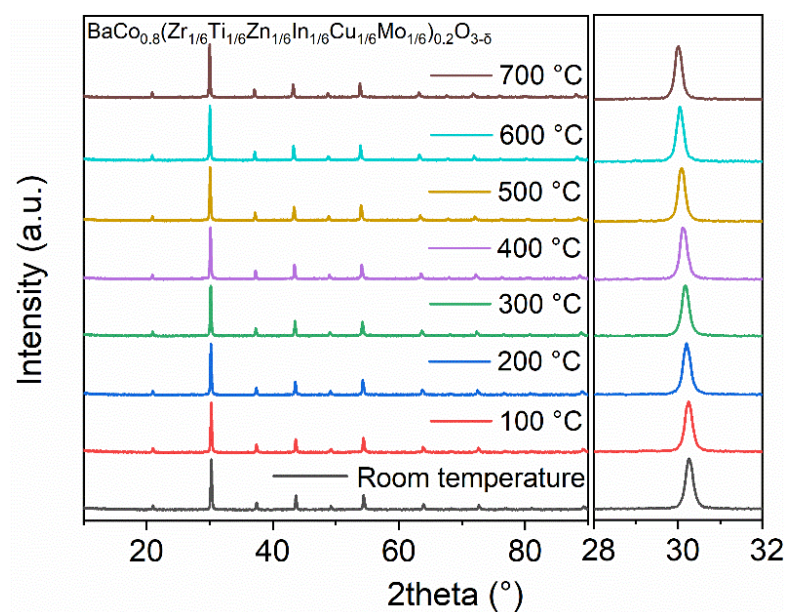
Supplementary Fig. 17.

Fe average valence calculated from the absorption edge shift in XANES data of (a) BCFZY and (b) BSCF at different temperatures and treatments.



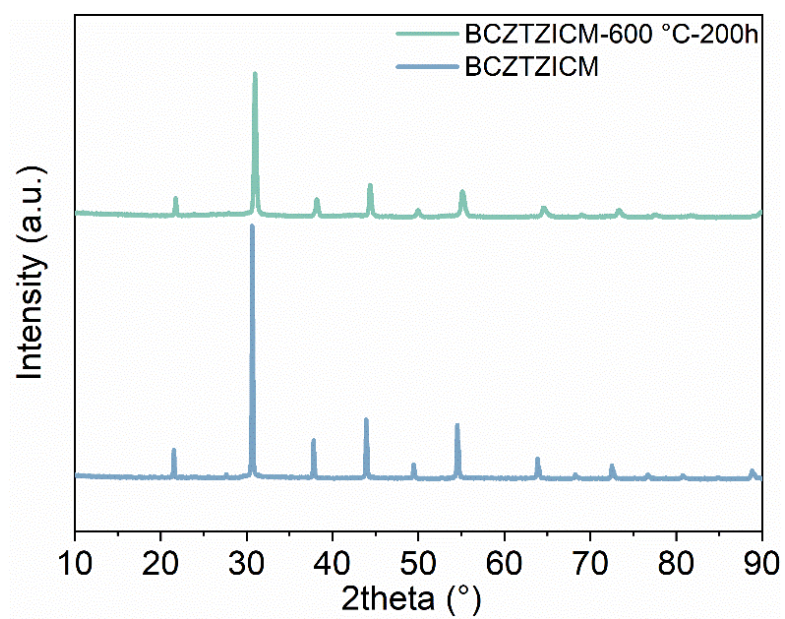
Supplementary Fig. 18.

XRD patterns of BCZTZICM electrode, BZCYYb electrolyte, and their composites with a mass ratio of 1:1 after calcination at 1000 °C for 2 h in air.



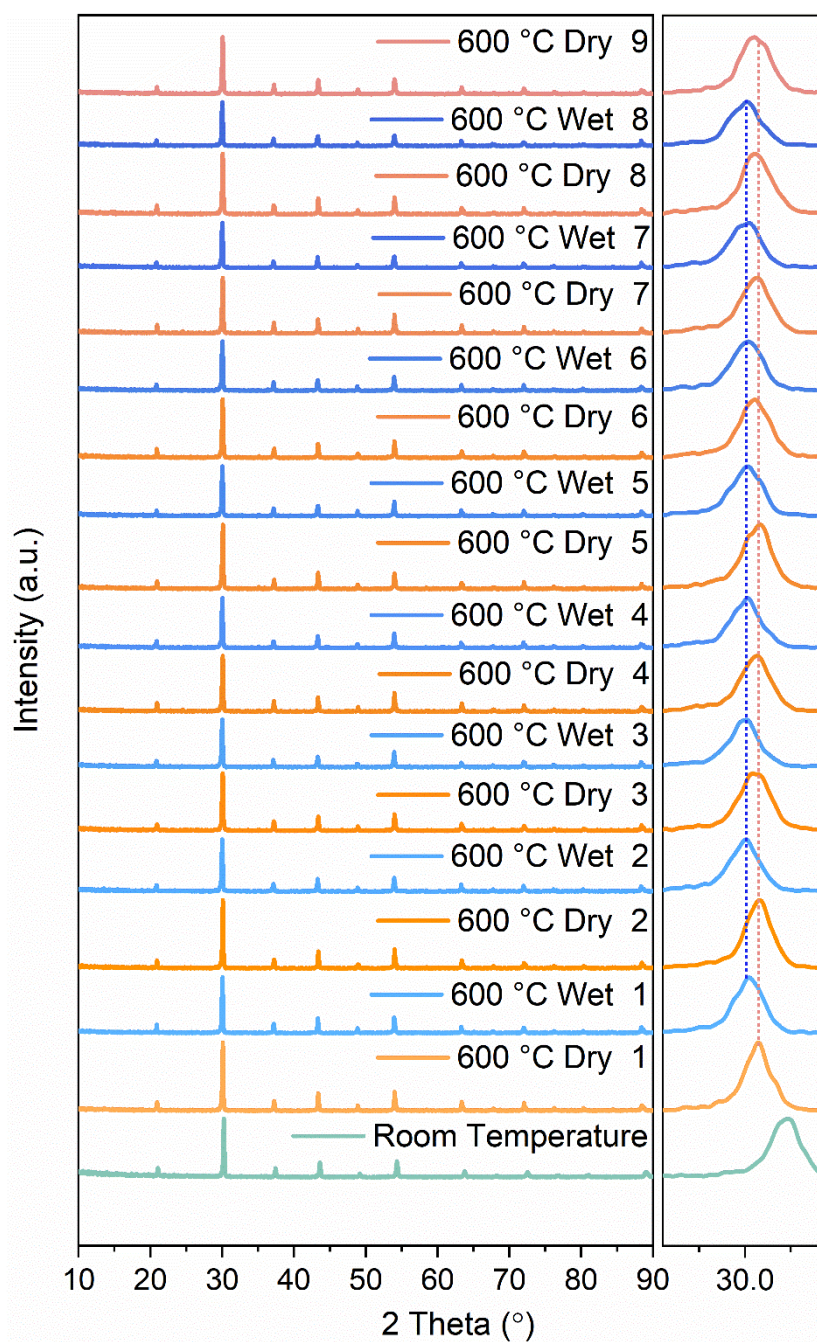
Supplementary Fig. 19.

High temperature XRD patterns of BCZTZICM powder, and magnified XRD patterns of the selected 2θ range of 28-32°.



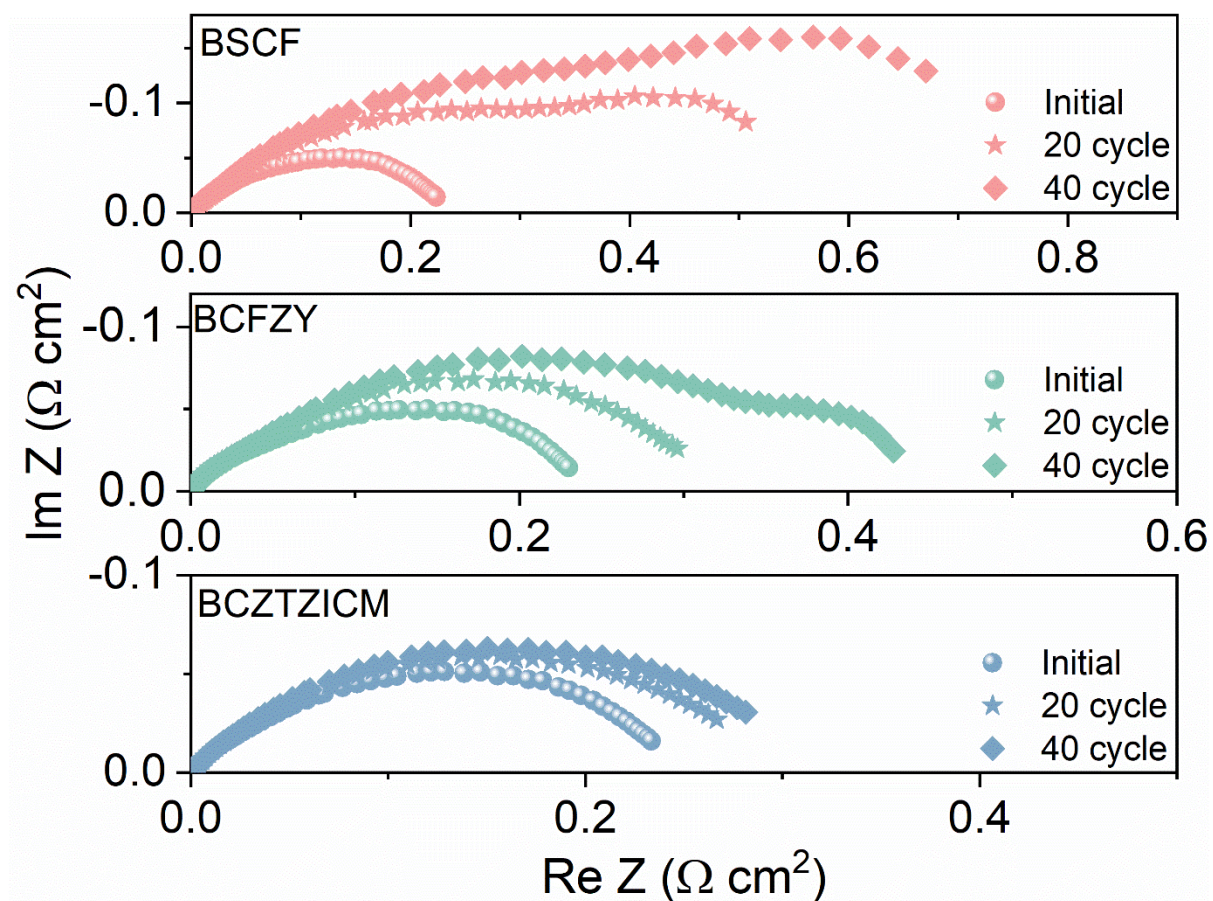
Supplementary Fig. 20.

XRD patterns of the BCZTZICM material after calcination at 600 °C for 200 h in air.



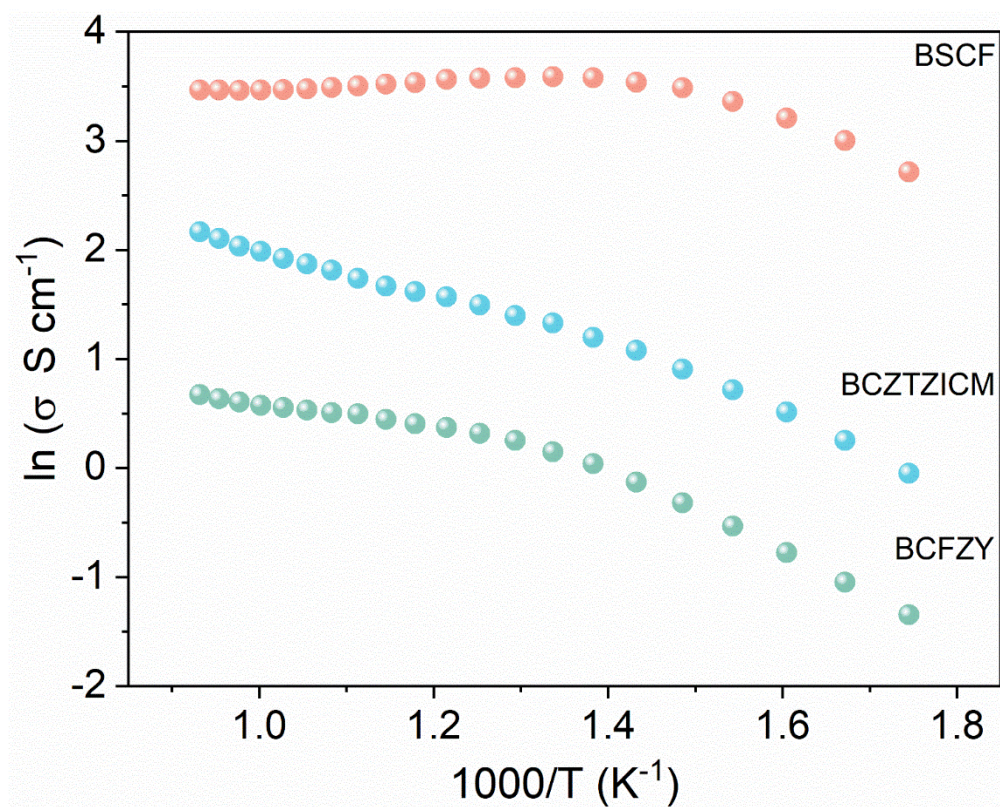
Supplementary Fig. 21.

High temperature XRD patterns of BCZTZICM at 600 °C during switching between dry and humid air atmospheres, and magnified XRD patterns of the selected 2 theta range of 29.55-30.45°.



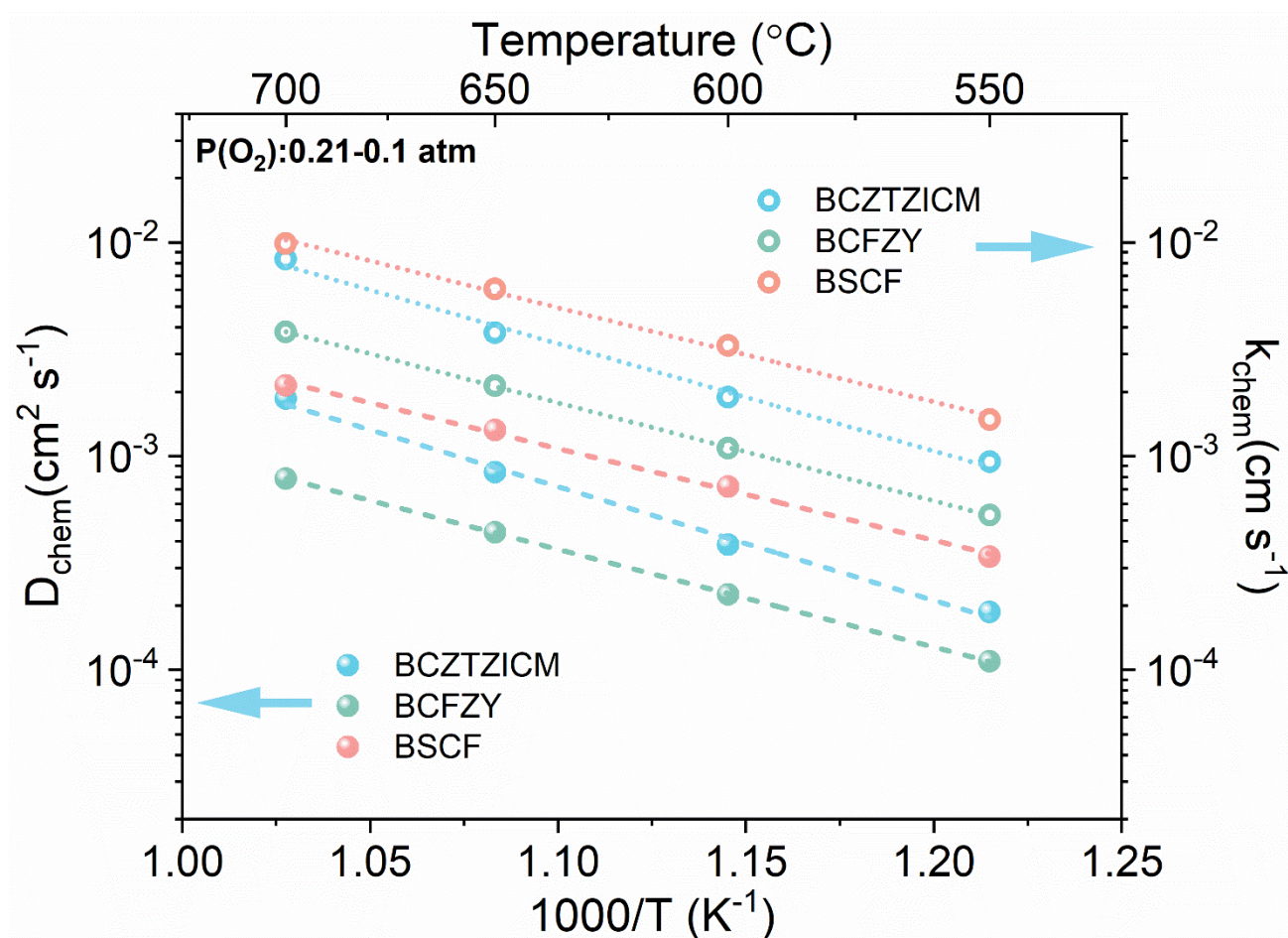
Supplementary Fig. 22.

Polarization resistance of BSCF, BCFZY, and BCZTZICM electrodes initially, after 20 and 40 thermal cycles, respectively.



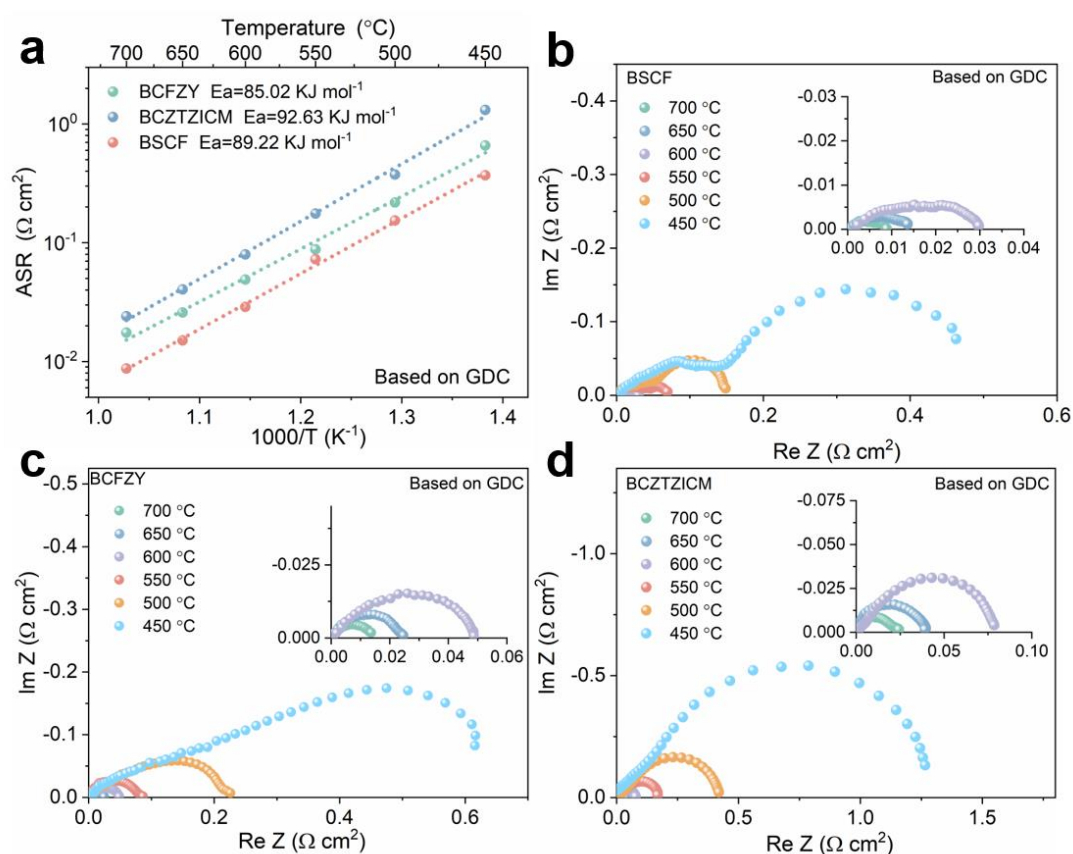
Supplementary Fig. 23.

Electronic conductivities of the BCZTZICM, BSCF, and BCFZY samples at 300-800 °C in air, as measured by the 4-probe DC conductivity technique.



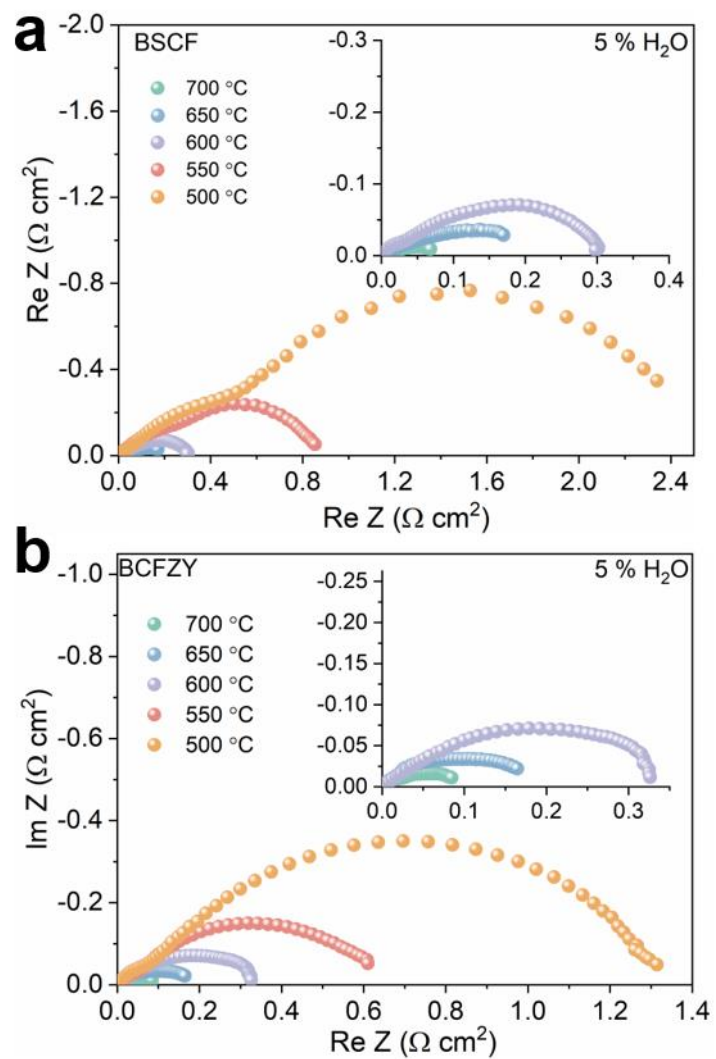
Supplementary Fig. 24.

The fitted values of D_{chem} and k_{chem} of BCZTZICM, BSCF, and BCFZY samples at temperature range of 550-700 °C from electronic conductivity relaxation curves.



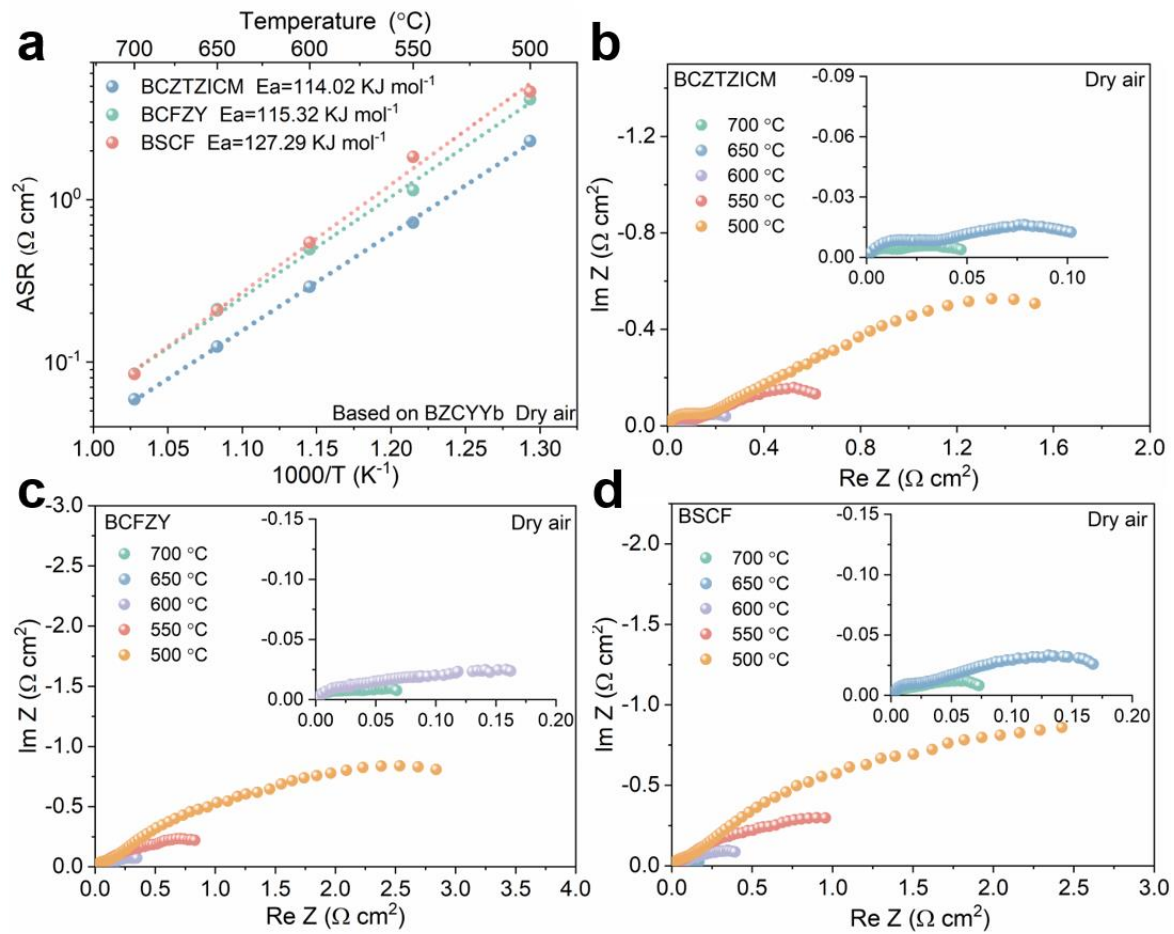
Supplementary Fig. 25.

(a) Arrhenius plots of different electrodes in dry air based on GDC symmetric cells. EIS curves of GDC based-supported symmetrical cells with (b) BSCF, (c) BCFZY and (d) BCZTZICM measured at 500, 550, 600, 650, and 700 $^{\circ}\text{C}$.



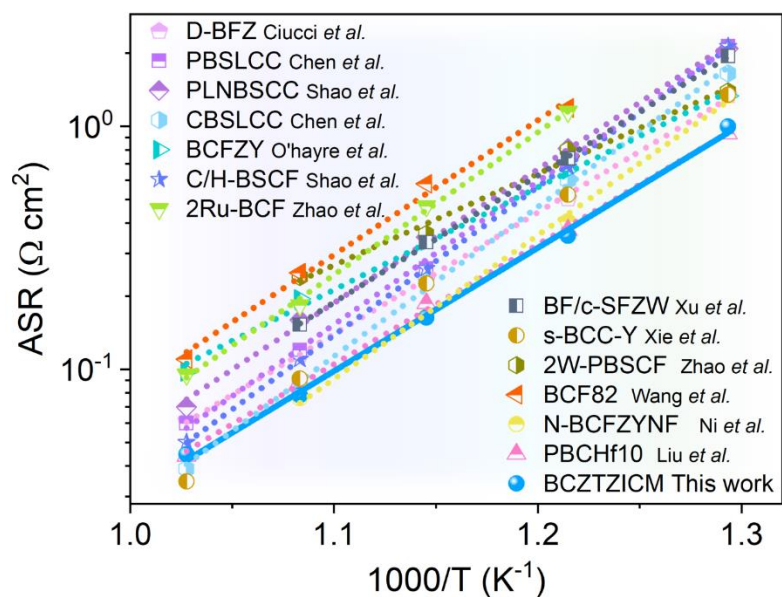
Supplementary Fig. 26.

EIS curves of BZCYYb based-supported symmetrical cell with (a) BSCF, and (b) BCFZY measured at 500, 550, 600, 650, and 700 °C at 5% H₂O atmosphere.



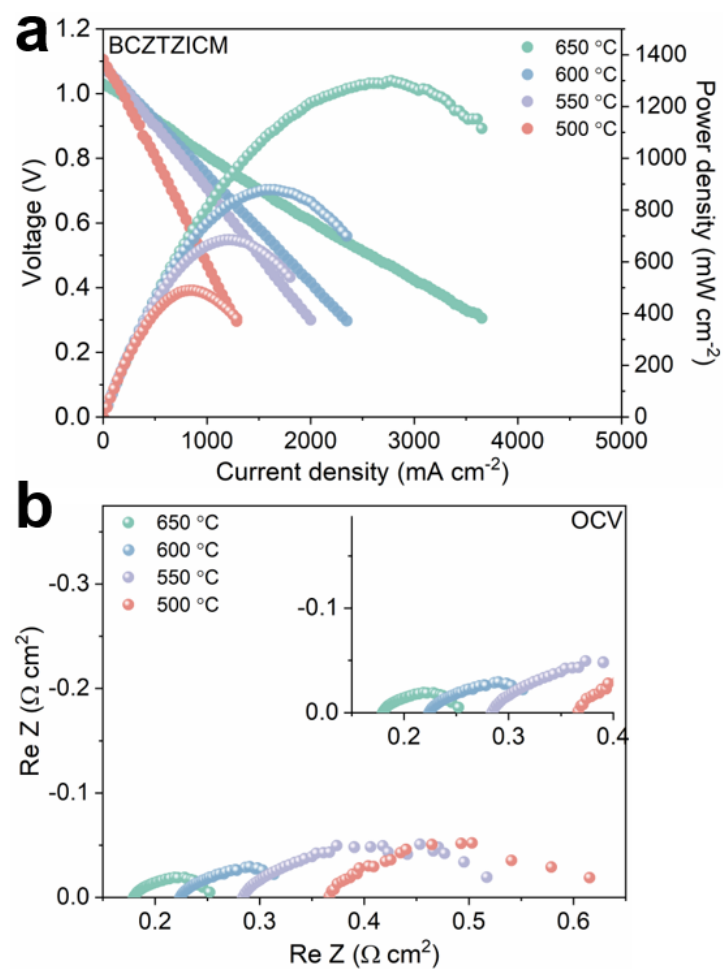
Supplementary Fig. 27.

(a) Arrhenius plots of different electrodes in dry air based on BZCYYb symmetric cells. The EIS plot of the BZCYYb symmetric cell of the (b) BCZTZICM, (c) BCFZY, and (d) BSCF at temperatures between 500 and 700 °C in a dry atmosphere.



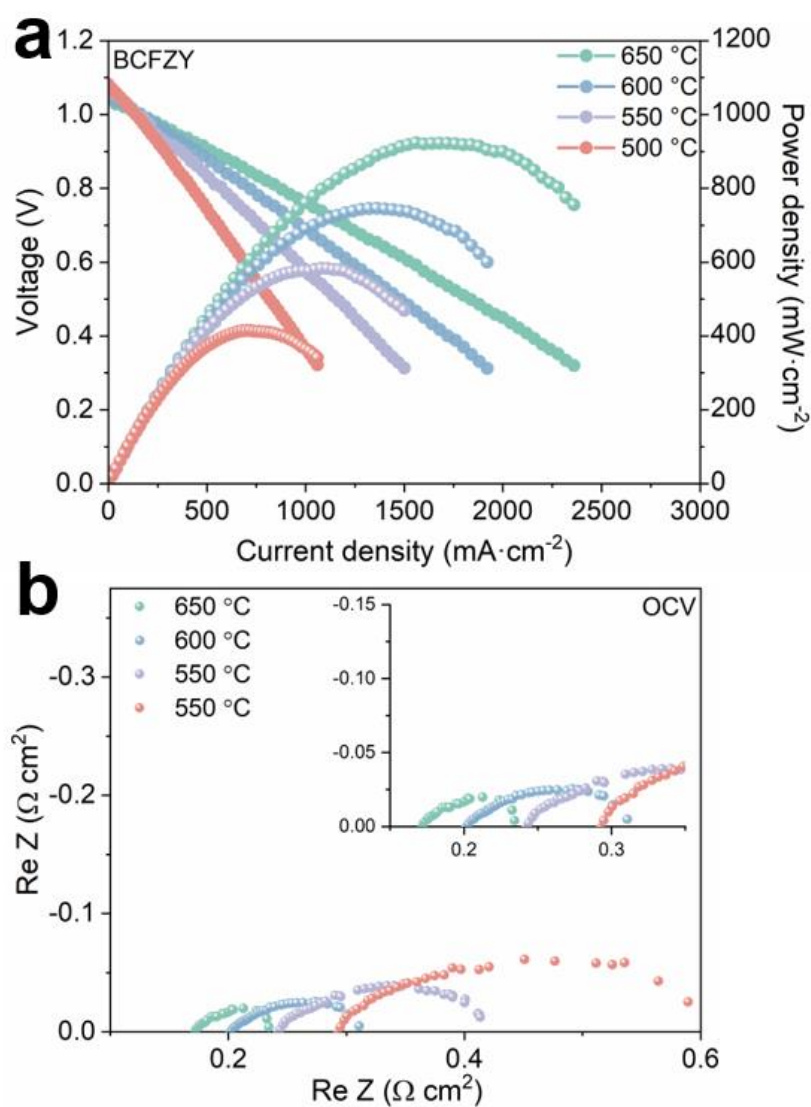
Supplementary Fig. 28.

Arrhenius plots of the ASRs of the D-BFZ, PBSLCC, PLNBSCC, CBSLCC, BCFZY, C/H-BSCF, 2Ru-BCF, BF/C-SFZW, s-BCC-Y, 2W-PBSCF, BCF82, N-BCFZYNF, PBCHf10 and BCZTZICM electrodes^{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13}.



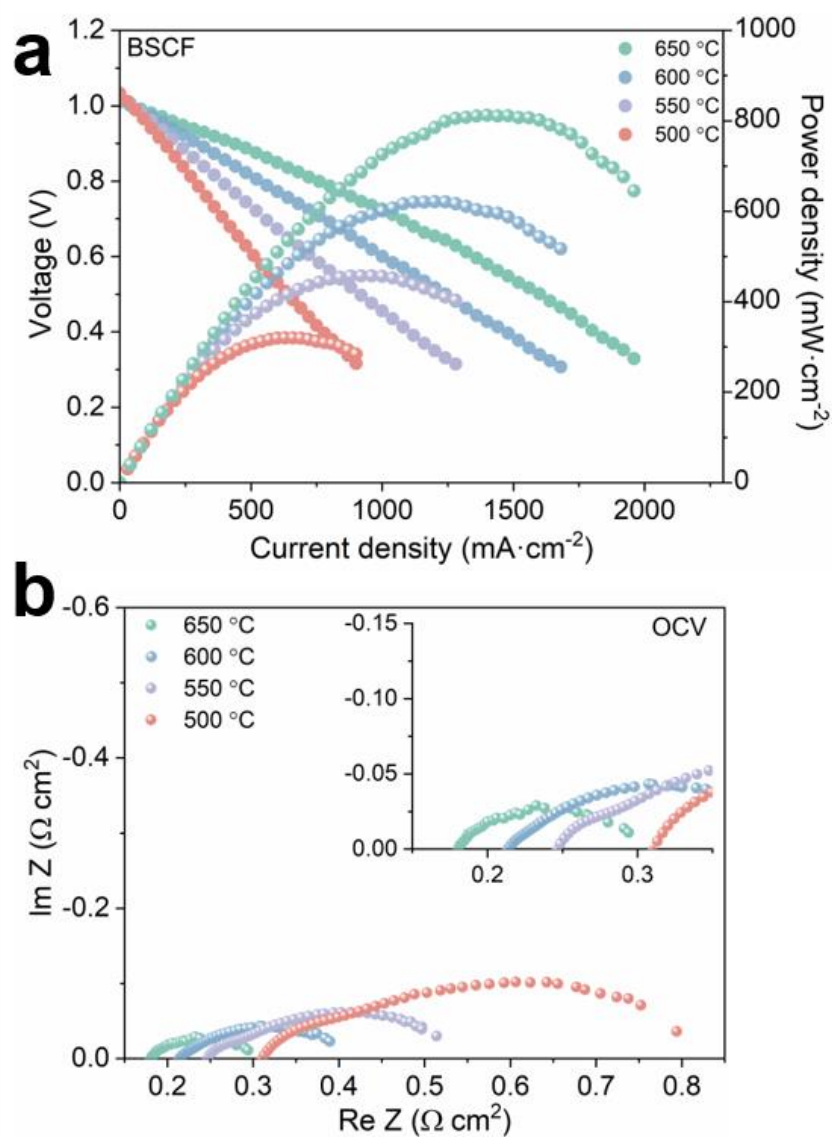
Supplementary Fig. 29.

(a) I - V - P curve and corresponding (b) impedance in fuel cell mode at open circuit configured as a Ni-BZCYYb|BZCYYb|BCZTZICM.



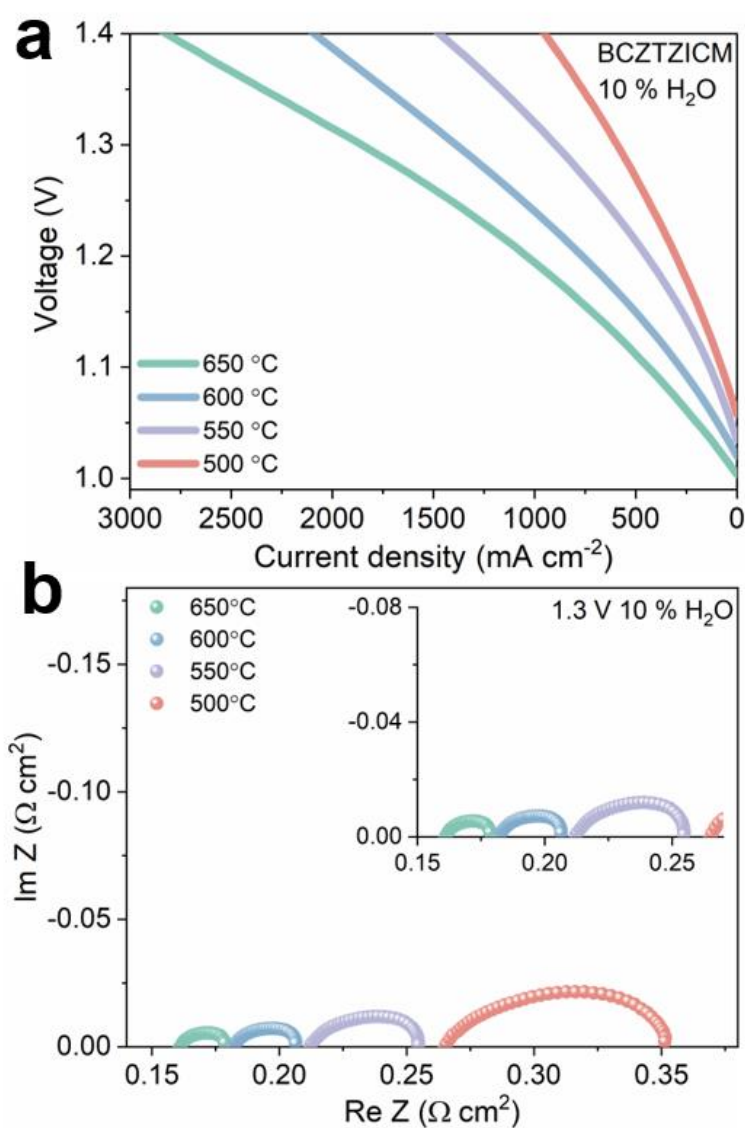
Supplementary Fig. 30.

(a) I - V - P curve and corresponding (b) impedance in fuel cell mode at open circuit configured as a Ni-BZCYYb|BZCYYb|BCFZY.



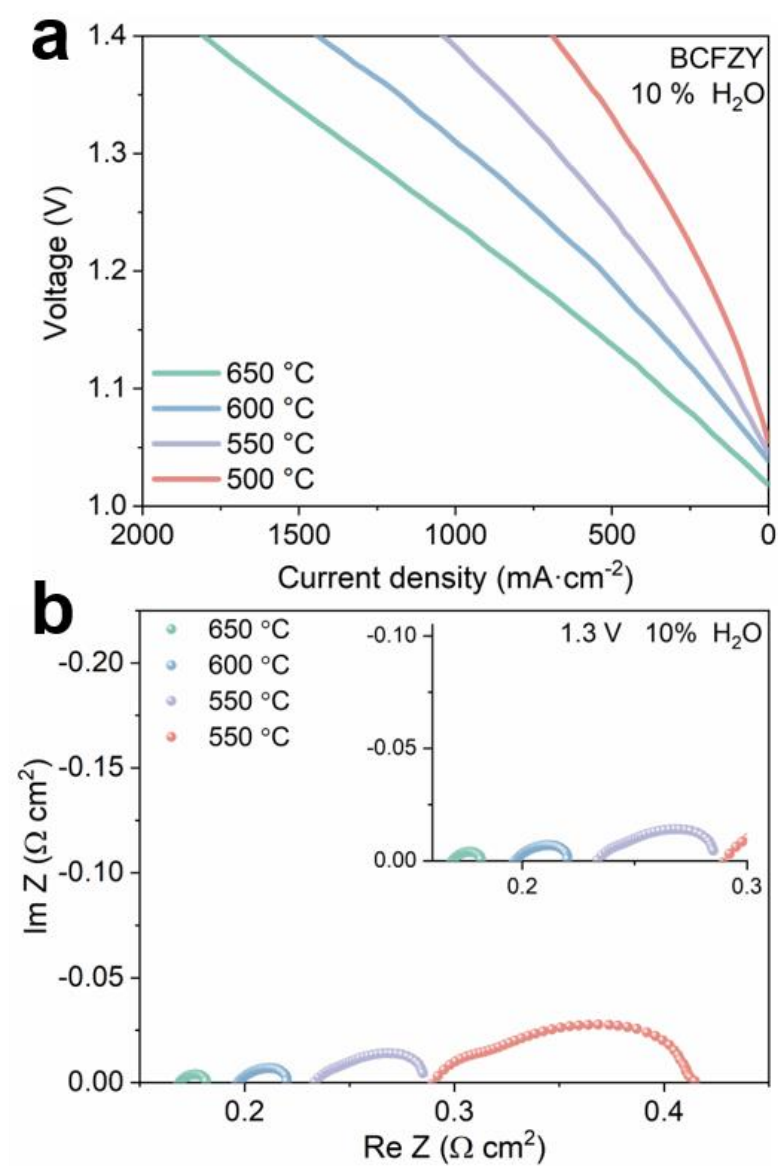
Supplementary Fig. 31.

(a) I - V - P curve and corresponding (b) impedance in fuel cell mode at open circuit configured as a Ni-BZCYYb|BZCYYb|BSCF.



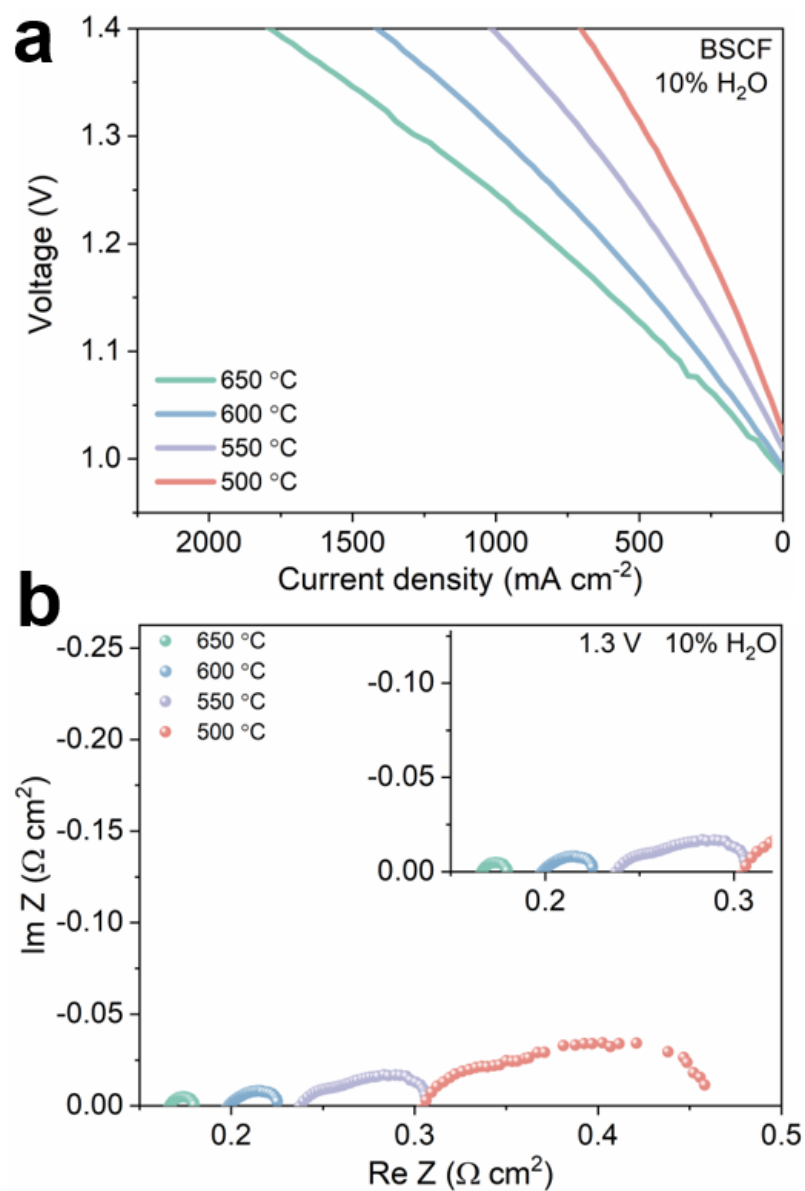
Supplementary Fig. 32.

(a) I - V curve and corresponding (b) impedance in electrolysis mode at 1.3V configured as a Ni-BZCYYb|BZCYYb|BCZTZICM.



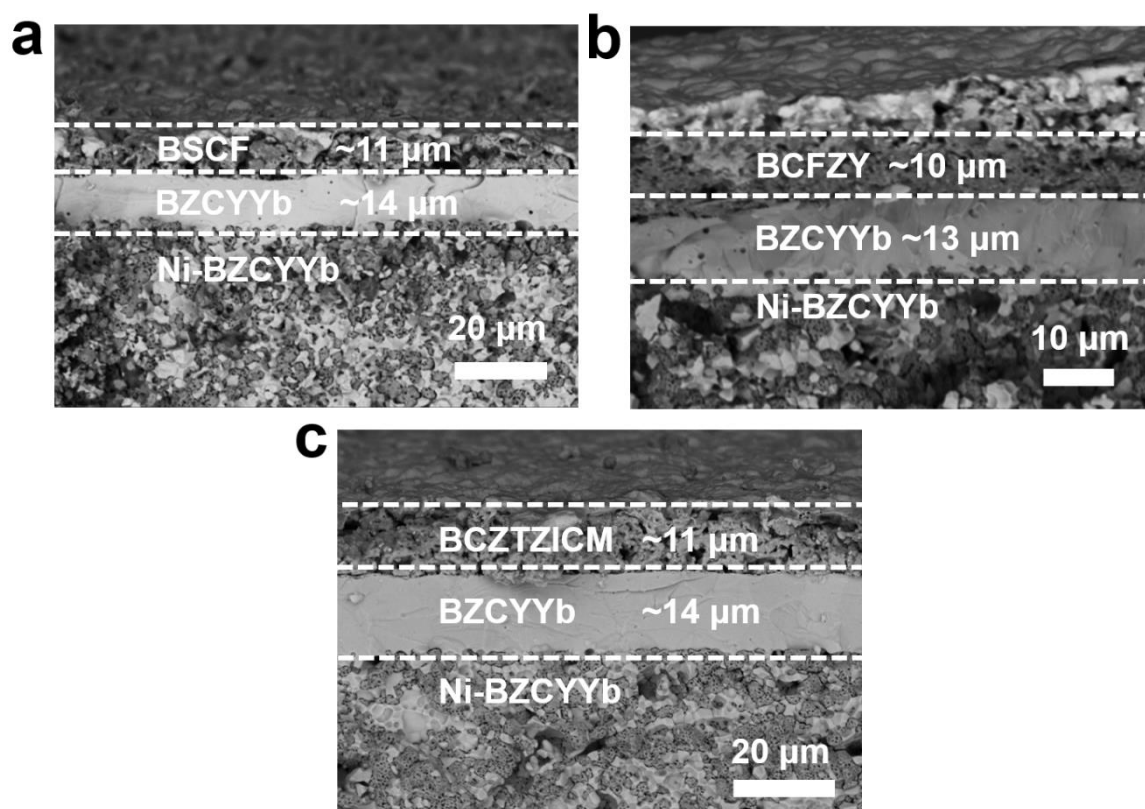
Supplementary Fig. 33.

(a) I - V curve and corresponding (b) impedance in electrolysis mode at 1.3V configured as a Ni-BZCYYb|BZCYYb|BCFZY.



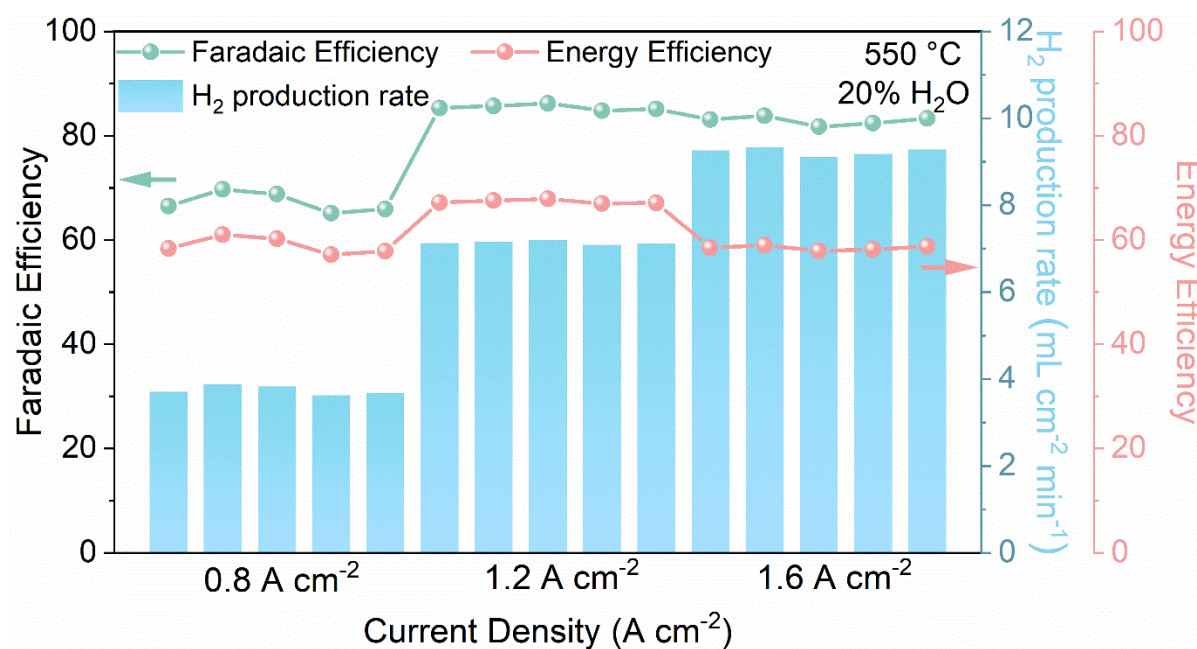
Supplementary Fig. 34.

(a) I - V curve and corresponding (b) impedance in electrolysis mode at 1.3V configured as a Ni-BZCYYb|BZCYYb|BSCF.



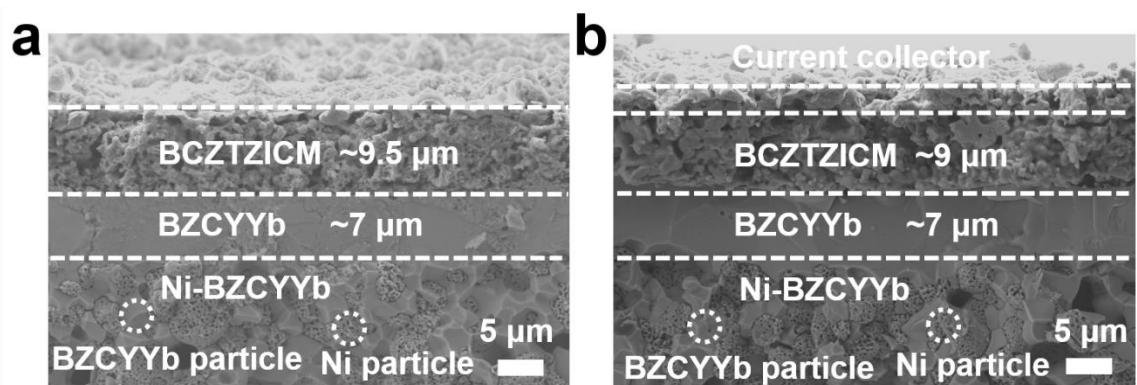
Supplementary Fig. 35.

Cross-sectional morphology of single cells prepared by co-pressing method after testing, with the air electrode configured as (a) BSCF, (b) BCFZY, and (c) BCZTZICM.



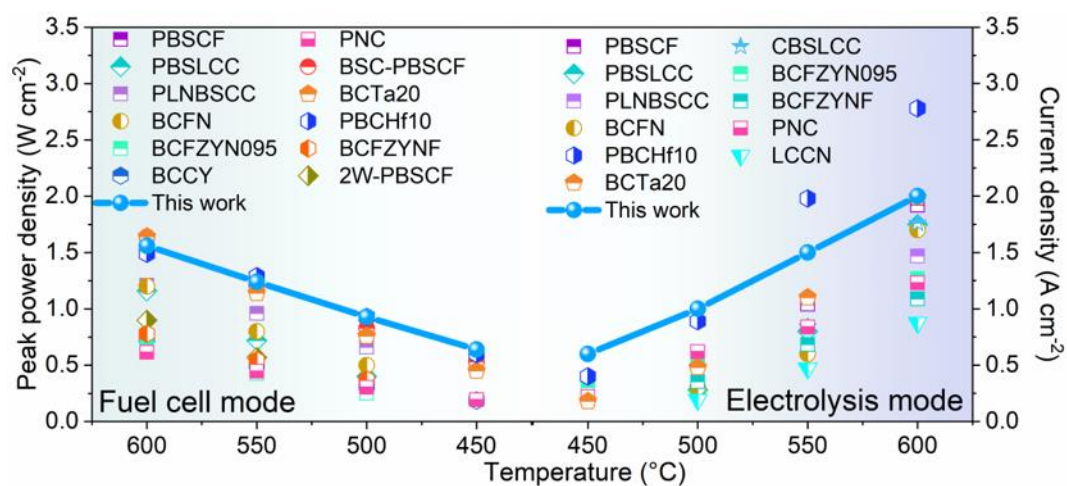
Supplementary Fig. 36.

The faraday efficiency, corresponding H₂ production rate and energy efficiency of tested hydrogen electrode-supported ultrathin BZCYYb electrolyte single cell with BCZTZICM oxygen electrode.



Supplementary Fig. 37.

Tested hydrogen electrode-supported ultrathin electrolyte (~7 μm) BZCYYb single cell with oxygen electrode thickness of 9-10 μm, hydrogen electrode consists of porous Ni metal particles and BZCYYb.



Supplementary Fig. 38.

Performance comparison with leading oxygen electrodes (peak power density in fuel cell mode; current density at 1.3 V in electrolysis mode) ^{2, 3, 4, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22}.

Supplementary Table 1. TEC of oxygen electrodes.

Oxygen electrode	TEC($\times 10^{-6}$ K $^{-1}$)	Temperature range (°C)	References
PBSCF ^a	21.3	250-900	23
PBSLCC ^b	23.8	300-800	2
PBCC ^c	24.5	300-800	2
PNC ^d	17.6	100-800	24
BCF82 ^e	21.77	25-800	11
D-SFN ^f	17.1	100-1000	25
BCFZY ^g	22.56	300-800	This work
BSCF ^h	26.08	300-800	This work
BCZTZICM ⁱ	17.68	300-800	This work
BZCYYb ^j	11.98	300-800	This work
c-SYNC ^k	12.9	100-800	26
BSCF-YMO ^l	16.56	25-900	27
s-BCC-Y ^m	17.06	300-800	9
BSC-PBSCF ⁿ	18	100-650	19
BCCY ^o	15.7	300-800	17
C/H-BSCF ^p	19.7	40-1000	6
PBCHf10 ^q	24.1	400-800	12
SCFN ^r	16.8	200-800	28
BB-OPS ^s	20.6	100-700	29
BCFZYN-095 ^t	18.7	25-800	16
BGCO0.1 ^u	20.46	25-800	30
NSTF0.3 ^v	19.9	300-700	31
PNCO64 ^w	18.5	25-1000	32
^a PrBa _{0.5} Sr _{0.5} Co _{1.5} Fe _{0.5} O _{5+δ} (PBSCF). ^b Pr _{0.2} Ba _{0.2} Sr _{0.2} La _{0.2} Ca _{0.2} CoO _{3-δ} (PBSLCC). ^c			

$\text{Pr}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_2\text{O}_{5+\delta}$ (PBCC). ^d $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (PNC). ^e $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (BCF82). ^f $\text{Sr}_{2.8}\text{Fe}_{1.8}\text{Nb}_{0.2}\text{O}_{7-\delta}$ (D-SFN). ^g $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY). ^h $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). ⁱ $\text{BaCo}_{0.8}(\text{Zr}_{1/6}\text{Ti}_{1/6}\text{Zn}_{1/6}\text{In}_{1/6}\text{Cu}_{1/6}\text{Mo}_{1/6})_{0.2}\text{O}_{3-\delta}$ (BCZTZICM). ^j $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb). ^k $\text{SrNb}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}$ -20 wt.% $\text{Y}_2\text{W}_3\text{O}_{12}$ (c-SYNC). ^l $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -30 wt.% $\text{Y}_2\text{Mo}_3\text{O}_{12}$ (BSCF-YMO). ^m $\text{BaCo}_{0.7}\text{Ce}_{0.15}\text{Y}_{0.15}\text{O}_{3-\delta}$ composites (s-BCC-Y). ⁿ $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$ - $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ (BSC-PBSCF). ^o $\text{BaCo}_{0.7}(\text{Ce}_{0.8}\text{Y}_{0.2})_{0.3}\text{O}_{3-\delta}$ composites (BCCY). ^p $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{Co}_{1.6}\text{Fe}_{0.4}\text{O}_{7-\delta}$ composites (C/H-BSCF). ^q $\text{Pr}_0\text{BaCo}_{1.9}\text{Hf}_{0.1}\text{O}_{5+\delta}$ composites (PBCHf10). ^r $\text{Sr}_{0.9}\text{Ce}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ composites (SCFN). ^s $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ - $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ in molar ratio of 7:3 via sol-gel (BB-OPS). ^t $\text{Ba}_{0.95}(\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1})_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ composites (BCFZYN-095). ^u $\text{Ba}_{1.1}\text{Gd}_{0.9}\text{Co}_2\text{O}_{6-\delta}$ composites (BGCO0.1). ^v $\text{Na}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ composites (NSTF0.3). ^w $\text{Pr}_4\text{Ni}_{1.8}\text{Co}_{1.2}\text{O}_{10-\delta}$ composites (PNCO64).

Supplementary Table 2. TEC of oxygen electrodes and crack width of electrode after thermal cycling.

Oxygen electrode materials	TEC ($\times 10^{-6} \text{ K}^{-1}$)	Thermal cycle conditions			Crack width (μm)	References
		Heating rate ($^{\circ}\text{C min}^{-1}$)	Cooling rate ($^{\circ}\text{C min}^{-1}$)	Cycle number		
SNC						
(based on SDC symmetric cell)	20.5	30	7.5	40	~1/0.6	²⁶
BSCF						
(based on SDC symmetric cell)	22.4	30	6	40	~0.9	³³
BCC						
(based on BZCYYb symmetric cell)	25.89	10	6.7	35	~0.78/0.6	⁹
BCFZY						
(based on BZCYYb symmetric cell)	22.56	20	10	40	1.38/1.54	This work
BSCF						
(based on BZCYYb symmetric cell)	26.08	20	10	40	1.89	This work
SF						
(based on BZCYYb symmetric cell)	30	30	10	35	~0.82/0.75	⁸
PBCF		1.6	1.6	5		
(based on BZCYYb single cell)	18.5	10	5	15	~4.2	³⁴
		20	10	50		

Supplementary Table 3. Performance and impedance comparison of oxygen electrodes in fuel cell and electrolysis modes at 600 °C.

Oxygen electrode	Peak power density (mW cm ⁻²)	Polarization resistance at OCV (Ω cm ²)	Current density at 1.3 V (mA cm ⁻²)	References
CBSLCC	1660	0.112	1760	4
PBSLCC	1160	0.112	1750	2
BCZTZICM	1560	0.11	2000	This work
PLNBSCC	1210	0.17	1950	3
BCT20 with PLD layer	1640	0.12	1600	35
BSC-PBSCF	1640	0.04	/	19
PBCHf10	1490	0.07	2780	12
BCCY	743	0.113	/	17
PNMCFC-PBC	1720	0.08	2170	36
N-XFN	790	0.167	1700	37
BCFN	1207	0.197	1511	15
C/H-BSCF	1670	0.157	1230	6
BSCF-RC _x	1100	0.13	1490	38
NAUP-PNC	1501	0.07	1316	39
PBN-BCZYYb CCS	1160	0.25	1460	40

Supplementary Table 4. Performance comparison of oxygen electrodes in fuel cell and electrolysis modes at 450 °C.

Oxygen electrode	Electrolyte (μm)	Peak power density (mW cm^{-2})	Current density at 1.3 V (mA cm^{-2})	Test condition at electrolysis	References
NCCO ^a	BZCYYb ^b (8)	180	560@1.4 V	20% H_2O -80%Air	41
PNC ^c	BZCYYb4411 ^d (15)	195	220	10% H_2O -Air Dry H_2	18
BCZTZICM ^e	BZCYYb (7)	648	600	10% H_2O -Air Dry H_2	This work
D-SFN ^f	BZCYYb (23)	165	170	Humidified air	25
3D-PNC73 ^g	BZCYYb (16)	651	640	30% H_2O - O_2 Dry H_2	42
BCT20 with PLD layer ^h	BZCYYb (10)	450	200	3% H_2O -Air 3% H_2O - H_2	20
BSC-PBSCF ⁱ	BZCYYb4411 (3)	530	640	40% H_2O - 60% N_2	19
PBCHf10 ^j	BSCYb172 ^k (7)	600	400	30% H_2O -70%Air 3% H_2O -97% H_2	12
BCFZYN ^l	BZCYYb (19)	252	300	5% H_2O -Air Dry H_2	16
KBCFZY ^m	BZCYYb (7)	210	1100@1.4 V	20% H_2O -80%Air	43
BCCY ⁿ	BZCYYb (16.1)	178	/	/	17
PNMCFC-PBC ^o	BZCYYb (16.1)	640	320	3% H_2O -Air	36
GCCCO- BCZYYb ^p	BZCYYb (~15)	280	/	/	44
PBSCF With PLD layer ^q	BZCYYb (15)	370	/	/	35

^a $\text{Na}_{0.15}\text{Ca}_{2.85}\text{Co}_4\text{O}_{9-\delta}$ (NCCO). ^b $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb). ^c $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (PNC). ^d $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb4411). ^e $\text{BaCo}_{0.8}(\text{Zr}_{1/6}\text{Ti}_{1/6}\text{Zn}_{1/6}\text{In}_{1/6}\text{Cu}_{1/6}\text{Mo}_{1/6})_{0.2}\text{O}_{3-\delta}$

(BCZTZICM). ^f $\text{Sr}_{2.8}\text{Fe}_{1.8}\text{Nb}_{0.2}\text{O}_{7-\delta}$ (D-SFN). ^g three-dimensional $\text{PrNi}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ mesh (3D-PNC73). ^h $\text{BaCo}_{0.8}\text{Ta}_{0.2}\text{O}_{3-\delta}$ (BCT20 with PLD layer). ⁱ $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$ - $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ composites (BSC-PBSCF). ^j $\text{PrBaCo}_{1.9}\text{Hf}_{0.1}\text{O}_{5+\delta}$ composites (PBCHf10). ^k $\text{BaSn}_{0.1}\text{Ce}_{0.7}\text{Yb}_{0.2}\text{O}_{3-\delta}$ (BSCYb172). ^l $\text{Ba}_{0.95}(\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1})_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ composites (BCFZYN). ^m $\text{K}_{0.05}\text{Ba}_{0.95}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.18}\text{Y}_{0.02}\text{O}_{3-\delta}$ (KBCFZY). ⁿ $\text{BaCo}_{0.7}(\text{Ce}_{0.8}\text{Y}_{0.2})_{0.3}\text{O}_{3-\delta}$ composites (BCCY). ^o $\text{PrNi}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{Cu}_{0.2}\text{O}_{3-\delta}$ coating $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PNMCFC-PBC). ^p $\text{Gd}_{0.3}\text{Ca}_{2.7}\text{Co}_{3.82}\text{Cu}_{0.18}\text{O}_{9-\delta}$ - $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ composites (GCCCCO-BZCYYb). ^q $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ with PBSCF PLD film (PBSCF With PLD layer).

Supplementary Table 5. Stability and degradation rate comparison of oxygen electrodes in fuel cell and electrolysis modes.

Oxygen electrode	Electrolyte	Degradation rate	Current density (mA cm ⁻²)	Time (h)	Test condition	Ref
BCFZY	BZCYYb	< 30 mV per 1000 h	-1385	600	20% H ₂ O-Air	45
			-1385	1200	10% H ₂ O-Air	
BSC-PBSCF	BZCYYb4411	< 0.07 mV h ⁻¹	300	100	H ₂ -Air	19
		< 0.15 mV h ⁻¹	-600	260	/	
PNC55	BZCYYb	1.98%	1.4 V	200	30%H ₂ O-O ₂	42
BCZTZICM	BZCYYb	19.3 μV h ⁻¹	300/500	780	80 mL 10% H ₂ O-Air 60 mL Dry H ₂	This work
		16.9 μV h ⁻¹	-300/-500		80 mL Dry Air 60 mL Dry H ₂	
PrO _x -PNC	BZCYYb4411	0.077 mA cm ⁻² h ⁻¹ (0.35%)	0.75 V	80	20 sccm H ₂ 40 sccm O ₂	46
		0.134 mA cm ⁻² h ⁻¹ (0.57%)	1.25 V	80	Humidified O ₂	
NAUP-PNC	BZCYYb4411	1.03 %	1.3 V	105	20%H ₂ O-O ₂	39
		1.24 %	1.4 V			
PBNO-BCZYYb CCS	BZCYYb	slight activation	400	1018	10% H ₂ O-Air Dry H ₂	40
		9 μV h ⁻¹		759	20% H ₂ O-Air Dry H ₂	
		1 μV h ⁻¹		5013		
PBNO-BCZYYb441 1 CCS	BZCYYb	3 μV h ⁻¹	-1000	2616	40% H ₂ O-Air Dry H ₂	
PBNO-BCY CCS		10 μV h ⁻¹		1041		

Supplementary Note 1

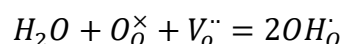
For $A_nB_mO_\delta$ -type oxides, we calculated the change in lattice oxygen content by testing the change in its ion valence and normalizing it using the following equation.

$$n(O) = \frac{\Delta A * n + \Delta B * m}{2}$$

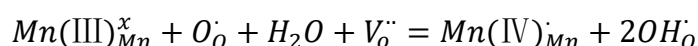
Where $n(O)$ represents the change in lattice oxygen content, ΔA and ΔB are the changes in the valence state of A and B ions, respectively.

Supplementary Note 2

The proton uptake has the beneficial effect of enhancing the absorption of protons by the electrode, thereby strengthening the proton transport capacity. In general, proton defects can be generated by hydration reactions with oxygen vacancies, as illustrated by the following formula:



Where $O_O^\times$ represents lattice oxygen, $V_O^{\bullet\bullet}$ is oxygen vacancies, and $OH_O^\bullet$ represents proton defects. Beyond classical hydration pathways, PCEC oxygen electrodes can generate protonic defects through transition metal oxide mediated routes^{47, 48}.



Where $h^\bullet$ represents electronic holes, $Mn(III)_{Mn}^x$ is Mn^{3+} ion. The proposed mechanisms, extendable to Fe/Co/Ni systems based on their redox activity^{1, 31}. This mechanism is derived from lowering of antibonding O 2p states that hybridize with transition metal 3d orbitals, coupled with the influence of incorporated protonic defects on the local coordination environment of transition metal ions. It also has been experimentally validated in relevant perovskite electrodes. It should be noted that this oxidative proton uptake mechanism is not universally observed across all perovskite compositions, depending on the degree of metal-oxygen covalency, the position of the Fermi level relative to the oxygen 2p band, and the local coordination flexibility around B-site cations⁴⁹.

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