Supporting Information

Effect of Fe doping on the oxygen reduction reaction activity of a $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ cathode for protonic ceramic fuel cells

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Supplementary experimental details

Materials Preparation

All PNC55, PNCF541, PNCF532, PNCF523, PNCF514 and PNF55 samples were prepared by a sol-gel complexing method. Taking PNCF532 as an example, firstly, stoichiometric amounts of metal nitrates $Pr(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were mixed with citric acid (CA) and glycine in DI water with the molar ratio of metal ions: CA: glycine = 1: 0.75: 0.75. After continuously heating and stirring the solution to evaporate the water, a dark purple gel was obtained. Subsequently, the gel was put into a drying oven at 260 °C for 4 h to get the precursor. Then, the precursor was calcined at 1000 °C for 2 h to obtain the final powder.

$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte powder was produced by a traditional solid-state reaction process.[1] Say it carefully, raw $BaCO_3$, ZrO_2, CeO_2, Y_2O_3 and Yb_2O_3 according to the desired BCZYYb stoichiometry were mixed in absolute ethanol and ball-milled at 220 rpm for 24 h. After drying completely, the preliminary powder was uniaxially pressed into a pellet at 10 MPa and calcined at 1100 °C for 12 h. Then, the fired pellet was ball-milled with a certain amount of absolute ethanol at 400 rpm for 4 h. The pressing, calcination and ball-milling procedures were repeated twice to get a pure perovskite phase.

Cell Fabrication

Symmetrical cells were fabricated by coating cathode slurry on BZCYYb pellets. To prepare dense BZCYYb substrates, the BZCYYb powder was first mixed with 1 wt% NiO (as a sintering aid) and adequate absolute ethanol, then ball-milled for 24 h, and followed uniaxially pressed into some pellets after being dried, sieved, and finally sintered at 1450°C for 5 h. After polishing the sintered pellets, the cathode slurry was painted on both sides of the dense electrolyte pellets. The slurry was made by mixing the sample powder and terpinol (with 5 wt% ethyl cellulose) with a mass ratio of 1:0.8. The cells were then co-fired at 950 °C for 2 h to form porous cathodes (with an active area of ~0.2826 cm^2). Besides, the Ag paste was covered on the surface of cathodes for EIS tests.

The NiO-BZCYYb anode -supported half-cells were manufactured by tape casting and co-sintering. More details about the fabrication process can be found in our previous work.[2] The cathode slurry was painted onto the electrolyte surface of the half-cells (with an active area of ~0.196 cm^{-2}), and then co-fired at 950 °C for 2 h to obtain the single cells. Also, the Ag paste and wires were used as current collectors.

Characterization and electrochemical tests

The phase compositions of samples were detected by X-ray diffraction (XRD, Germany Bruker D8 Advance) with Cu Ka radiation. The microstructure and micromorphology of the cathodes and cells were observed by a cold field emission scanning electron microscopy (SEM, Hitachi SU8010). Further, a transmission electron microscope (TEM, American FEI Tecnai G2 F20) equipped with energy-dispersive spectrum (EDS) analysis was performed to detect the crystal structure and elemental distribution of PNCF532 sample. To investigate the valence changes of Co and Fe in samples, X-ray photoelectron spectroscopy (XPS, American Thermo Scientific K-Alpha) were conducted.

To measure the conductivity of PNC55 and PNCF532, the as-synthesized sample powder was mixed with 1% polyvinyl butyral and then uniaxially pressed into a rectangular bar. The bar can be used for testing after sintering at 1150 °C for 10 h. The conductivity curves of PNC55 and PNCF532 were tested in the air by the four-probe DC method. For cells testing, a multi-channel electrochemical workstation (AMETEK PARSTAT MC) was employed to perform the electrochemical impedance spectra (EIS), current density-voltage curves and long-term stability performance. Specifically, EIS curves were tested under open-circuit voltage (OCV) conditions in humidified air (3 vol% H_2O). IV curves, as well as impedance spectra and stability of single cells were obtained by feeding 3 vol% H_2O humidified hydrogen (at a rate of 30 mL min^{-1}) in the anode and ambient air in the cathode. The humidity of 3 vol% is controlled by flowing the gas through a water-bubbler at room temperature (about 25 °C).

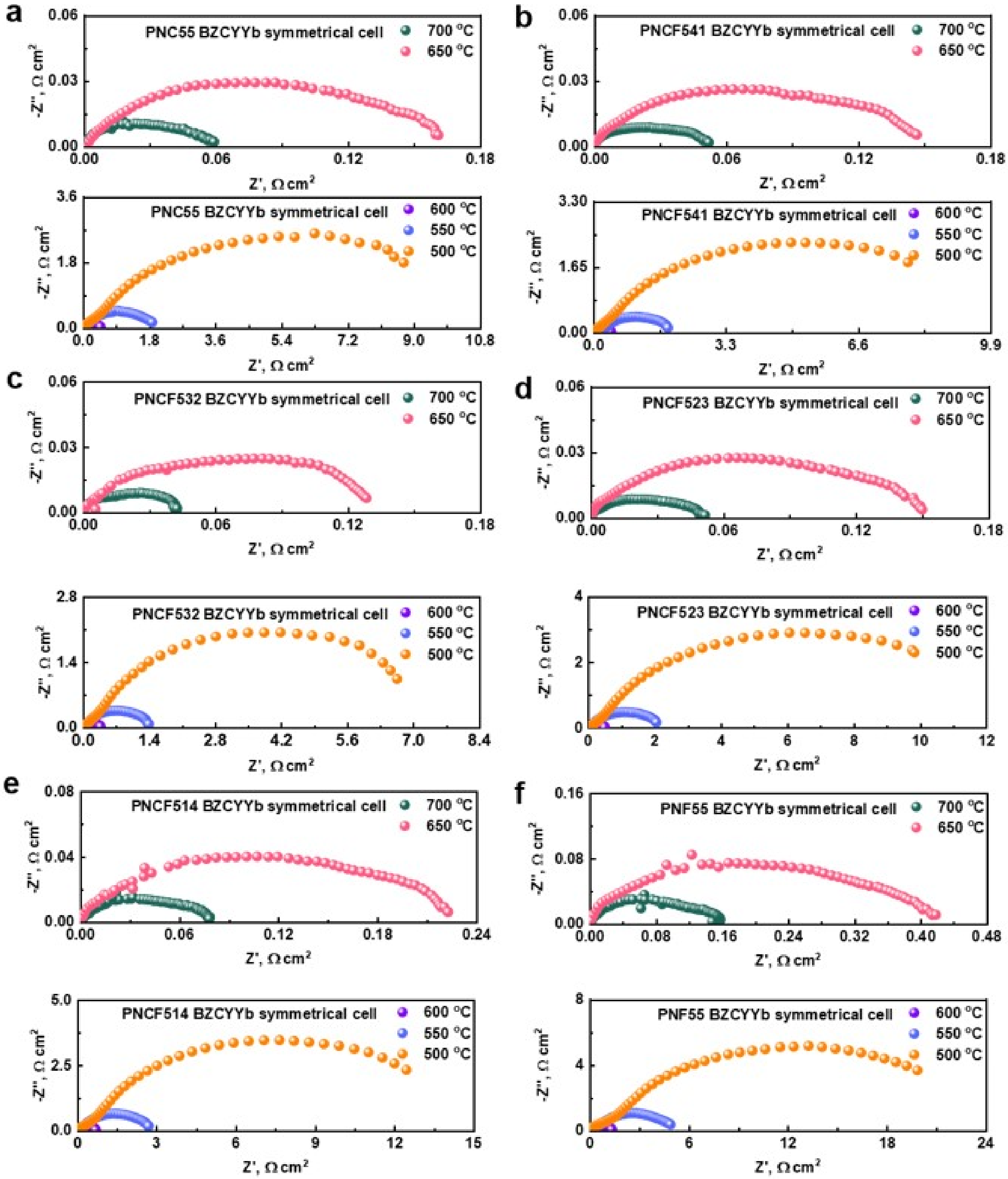

Figure S1. EIS of the BZCYYb-based symmetrical cells with PNC55, PNCF541, PNCF532, PNCF523, PNCF514 and PNF55 cathodes at a temperature range from 500 to 700 °C in wet air with 3 vol% H_2O.

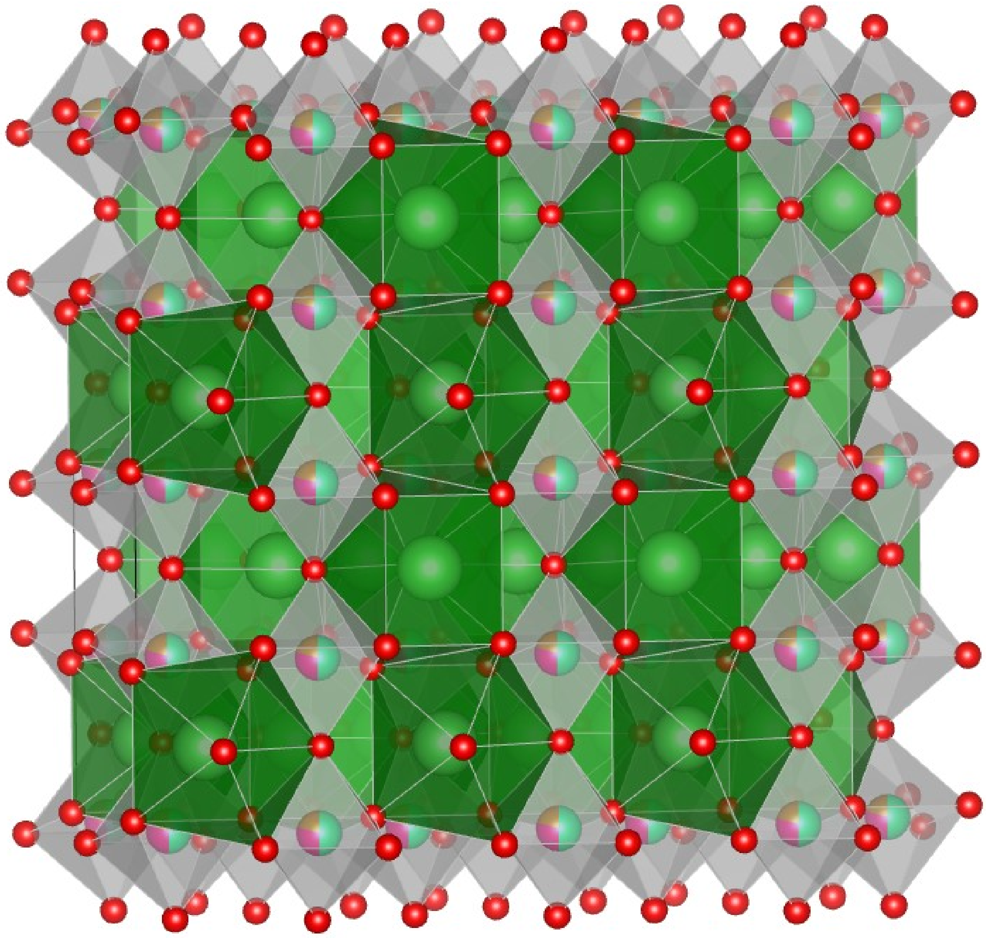

Figure S2. The polyhedral crystal structure of orthorhombic perovskite PNCF532(Pbnm(62)).

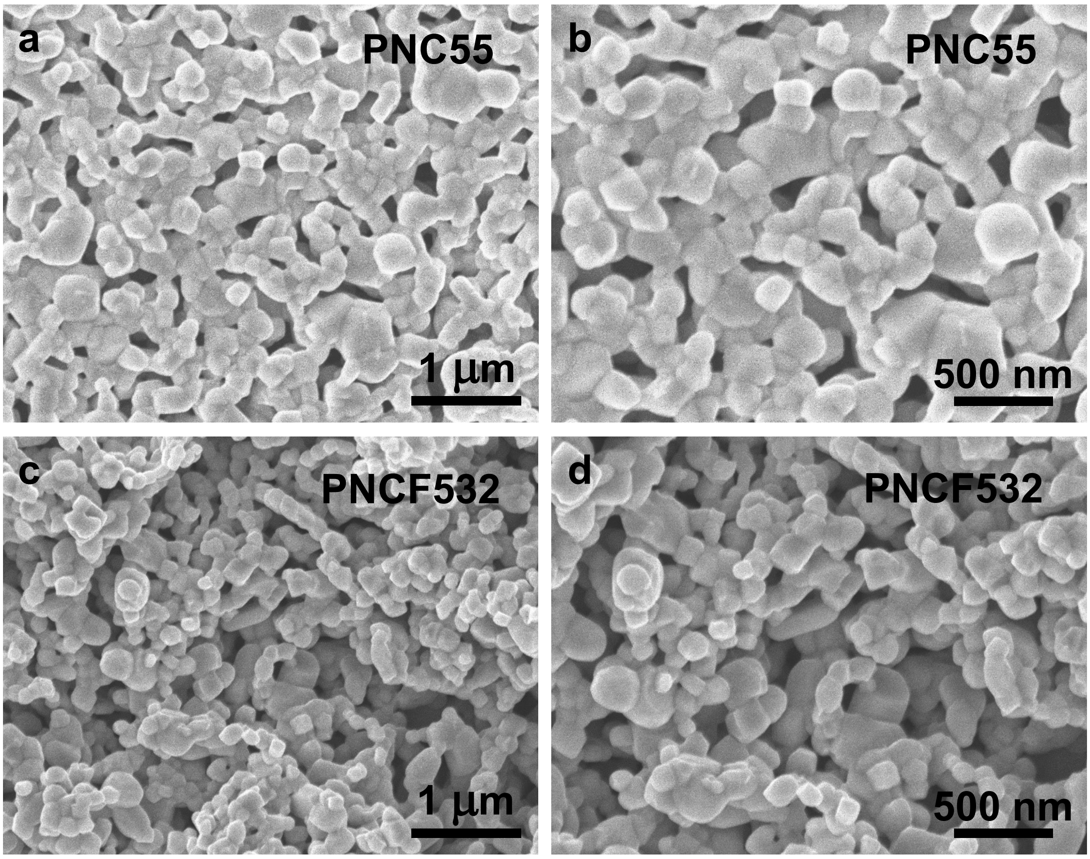

Figure S3. The SEM images of PNC55 and PNCF532 cathodes.

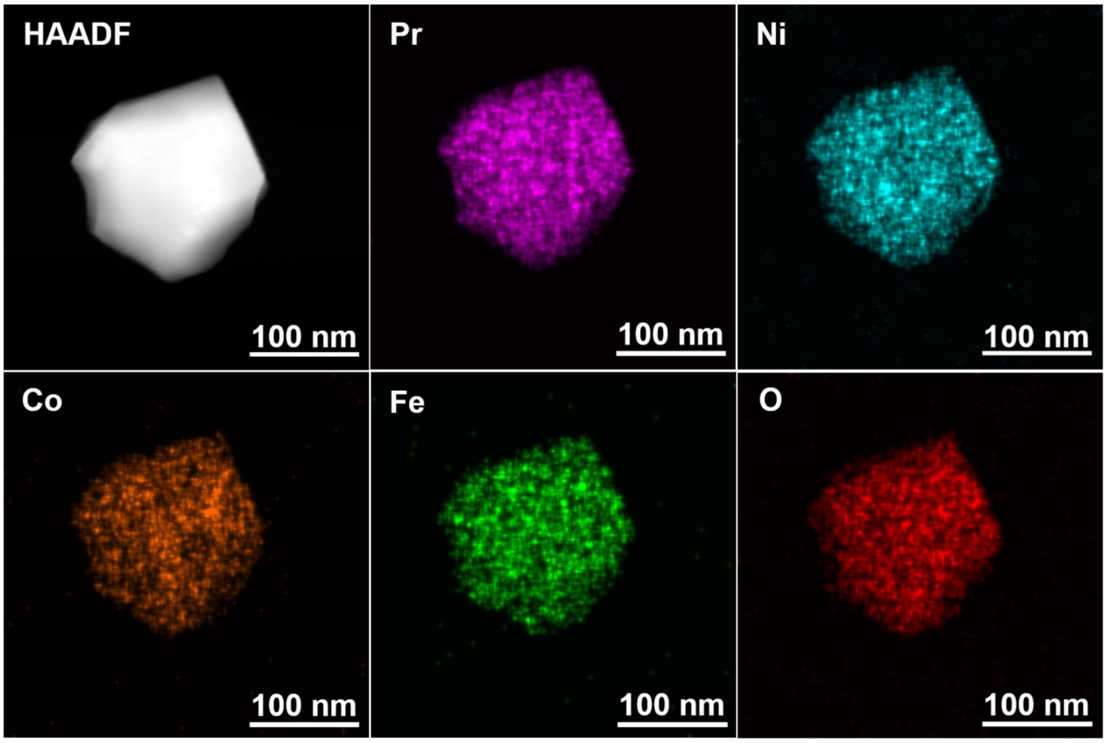

Figure S4. HAADF and the X-ray EDS mapping of Pr, Ni, Co, Fe and O from the PNCF532 grain.

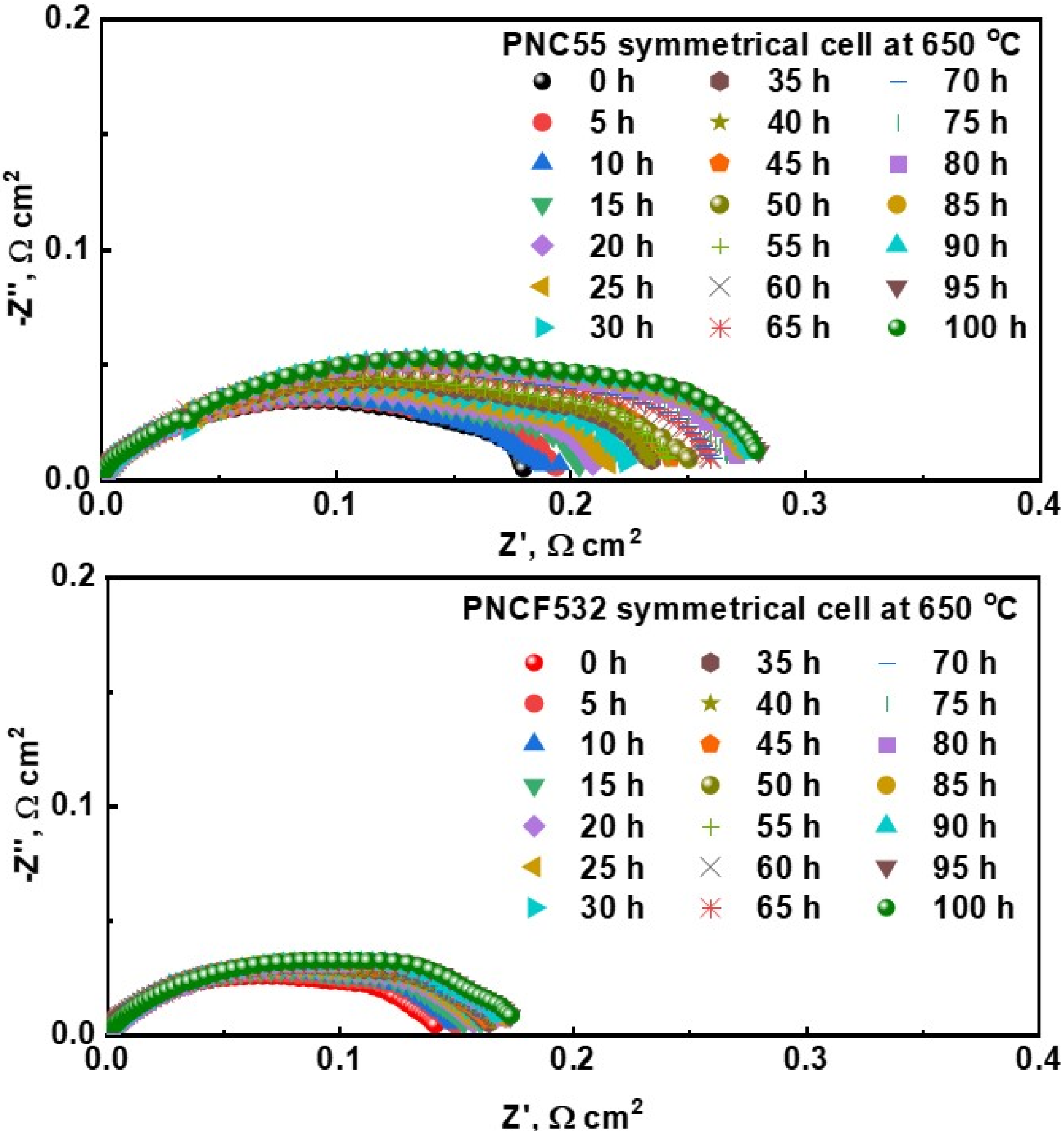

Figure S5. Short stability (100 h) of R_p of BZCYYb symmetrical cells with PNC55 and PNCF532 cathode, tested at 650 °C under flowing air with 3 vol.% H_2O.

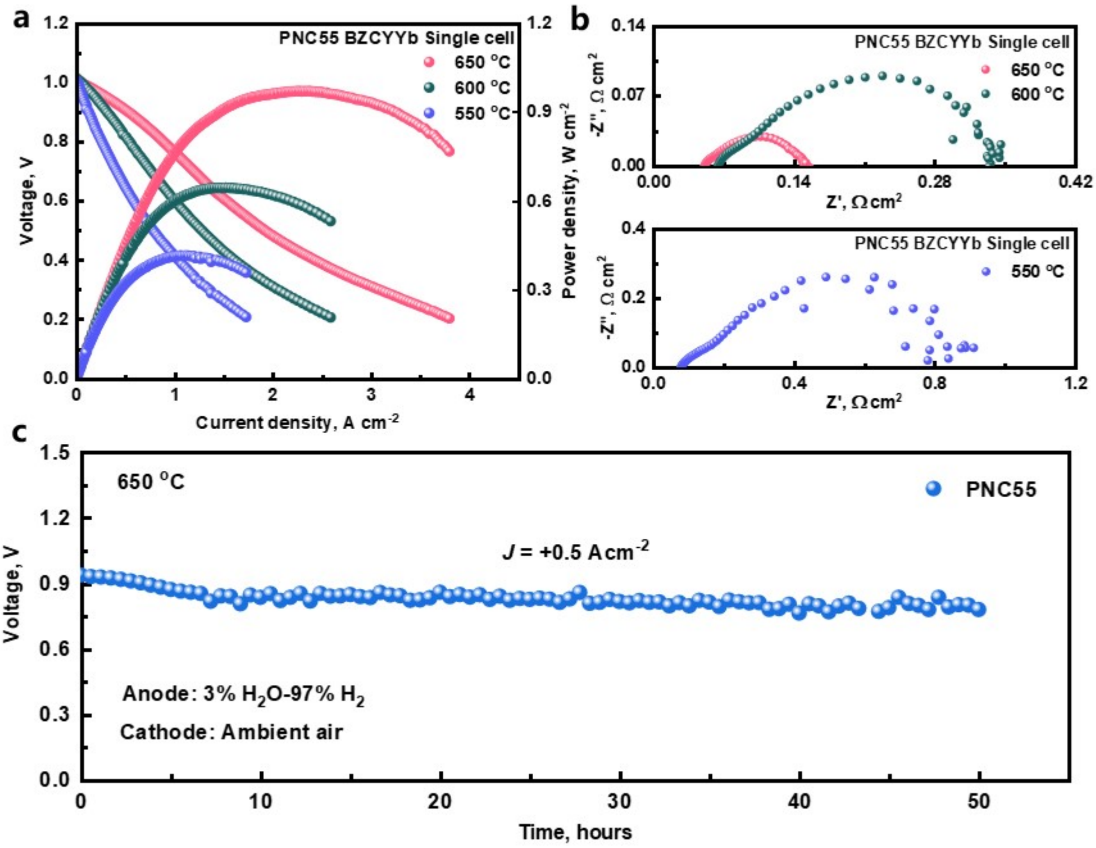

Figure S6. (**a**) Typical I-V-P curves of a single cell with PNC55 cathode measured at 650-550 °C (**b**) Typical EIS curves of the single cell measured at 650-550 °C under OCV conditions. (**c**) A short-term (~50 h) stability evaluation of the PNC55 single-cell measured at the constant current density of 0.5 A cm^{-2} and 650 °C.

Table S1. The abbreviations of samples.

Sample composition	Abbreviation
$PrNi_{0.5}Co_{0.5}O_{3-\delta}$	PNC55
$PrNi_{0.5}Co_{0.4}Fe_{0.1}O_{3-\delta}$	PNCF541
$PrNi_{0.5}Co_{0.3}Fe_{0.2}O_{3-\delta}$	PNCF532
$PrNi_{0.5}Co_{0.2}Fe_{0.3}O_{3-\delta}$	PNCF523
$PrNi_{0.5}Co_{0.1}Fe_{0.4}O_{3-\delta}$	PNCF514
$PrNi_{0.5}Fe_{0.5}O_{3-\delta}$	PNF55

Table S2. XRD standard card and result of XRD refinement.

Sample	PDF number	Proportion (wt. %)	Space group	a (Å)	b (Å)	c (Å)	Volume	GOF[a]
$PrNiO_3$	79-2453	---	Pbnm(62)	5.413	5.383	7.623	222.12	---
PNCF532	---	100	Pbnm(62)	5.423	5.413	7.655	224.67	1.099

[a] GOF stands for the goodness of fitting in XRD refinement, where a value of GOF less than 2 is a reliable fitting result.[3]

Table S3. Performance comparisons of the peak power densities of the representative cathodes reported recently and PNCF532 (this work).

Cathode	Electrolyte	Anode	Electrolyte thickness(μm)	Temperature, °C	Pmax, W/cm^2	Authors, Years
$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) [4]	BCZYYb1711[a]	NiO-BCZYYb1711	14.1	700	1.374	Seong et al.,2018
				650	1.048	
				600	0.704	
$PrNi_{0.5}Mn_{0.5}O_{3-\delta}$(PNM) + PrO_x [5]	BCZYYb1711	NiO-BCZYYb1711	30	700	0.800	Chen et al.,2018
				650	0.441	
$BaCo_{0.7}(Ce_{0.8}Y_{0.2})_{0.3}O_{3-\delta}$(BCCY) [6]	BCZYYb1711	NiO-BCZYYb1711	16.1	650	0.993	Song et al.,2019
				600	0.730	
$Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Ni_{0.05}O_{3-\delta}$ (BCFZYN) [7]	BCZYYb1711	NiO-BCZYYb1711	15	650	0.930	Liang et al., 2021
				600	0.660	
				550	0.450	
$PrCo_{0.5}Ni_{0.5}O_{3-\delta}$ nanofiber [8]	BCZYYb4411[b]	NiO-BCZYYb4411	10	600	0.607	Ding et al.,2020
				550	0.444	
$Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) [9]	BCZYYb1711	NiO-BCZYYb1711	10	650	1.710	Pei et al., 2022
				600	1.210	
				550	0.820	
				500	0.550	
$PrNi_{0.7}Co_{0.3}O_{3-\delta}$ (PNC73) [10]	BCZYYb4411	NiO-BCZYYb4411	~10	600	0.950	Tang et al., 2022
				550	0.680	
				500	0.450	
				450	0.320	
				400	0.230	
				350	0.140	
$PrNi_{0.4}Co_{0.4}Fe_{0.2}O_{3-\delta}$ (PNCF) [11]	BCZYYbF[c]	NiO-BCZYYbF	15	700	0.790	Zhu et al., 2022
				650	0.620	
				600	0.420	
PNCF532	BCZYYb1711	NiO-BCZYYb1711	~8	650	1.230	**This work**
				600	0.740	
				550	0.410	

[a] BZCYYb1711: $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$.

[b] BZCYYb4411: $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3-\delta}$.

[c] BZCYYbF: $BaZr_{0.3}Ce_{0.48}Y_{0.1}Yb_{0.1}Fe_{0.02}O_{3-\delta}$.

References

1. L. Y. Yang, S. Wang, K. Blinn, M. Liu, Z. L. Liu, Z. Cheng and M. Liu, *Science*, 2009, **326**, 126-129.
2. H. Gao, F. He, F. Zhu, J. Xia, Z. Du, Y. Huang, L. Zhu and Y. Chen, *Advanced Functional Materials*, 2024, **34**, 2401747.
3. D. Guan, G. Ryu, Z. Hu, J. Zhou, C.-L. Dong, Y.-C. Huang, K. Zhang, Y. Zhong, A. C. Komarek, M. Zhu, X. Wu, C.-W. Pao, C.-K. Chang, H.-J. Lin, C.-T. Chen, W. Zhou and Z. Shao, *Nature Communications*, 2020, **11**, 3376.
4. A. Seong, J. Kim, J. Kim, S. Kim, S. Sengodan, J. Shin and G. Kim, *Journal of The Electrochemical Society*, 2018, **165**, F1098-F1102.
5. Y. Chen, S. Yoo, K. Pei, D. Chen, L. Zhang, B. deGlee, R. Murphy, B. Zhao, Y. Zhang, Y. Chen and M. Liu, *Advanced Functional Materials*, 2017, **28**, 1704907.
6. Y. Song, Y. Chen, W. Wang, C. Zhou, Y. Zhong, G. Yang, W. Zhou, M. Liu and Z. Shao, *Joule*, 2019, **3**, 2842-2853.
7. M. Liang, F. He, C. Zhou, Y. Chen, R. Ran, G. Yang, W. Zhou and Z. Shao, *Chemical Engineering Journal*, 2021, **420**, 127717.
8. H. Ding, W. Wu, C. Jiang, Y. Ding, W. Bian, B. Hu, P. Singh, C. J. Orme, L. Wang, Y. Zhang and D. Ding, *Nature Communications*, 2020, **11**, 1907.
9. K. Pei, Y. Zhou, K. Xu, H. Zhang, Y. Ding, B. Zhao, W. Yuan, K. Sasaki, Y. Choi, Y. Chen and M. Liu, *Nature Communications*, 2022, **13**, 2207.
10. W. Tang, H. Ding, W. Bian, C. Y. Regalado Vera, J. Y. Gomez, Y. Dong, J. Li, W. Wu, W. Fan, M. Zhou, C. Gore, B. M. Blackburn, H. Luo and D. Ding, *Small*, 2022, **18**, 2201953.
11. Z. Zhu, M. Zhou, K. Tan, Z. Fan, D. Cao, Z. Liu, M. Chen, Y. Chen, M. Chen and J. Liu, *ACS Applied Materials & Interfaces*, 2023, **15**, 14457-14469.