

Supplementary Material

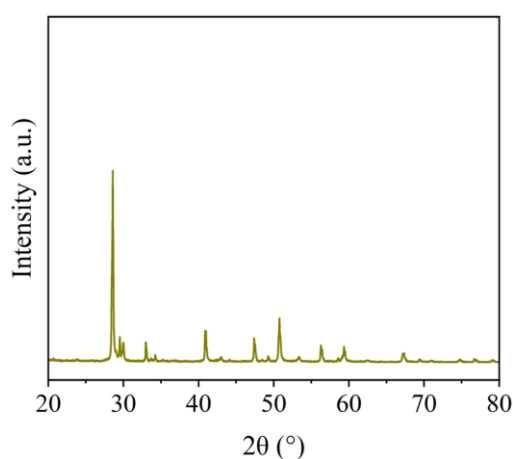
**High-performance novel anode-supported microtubular protonic ceramic fuel cells via highly efficient and simplified extrusion technology**

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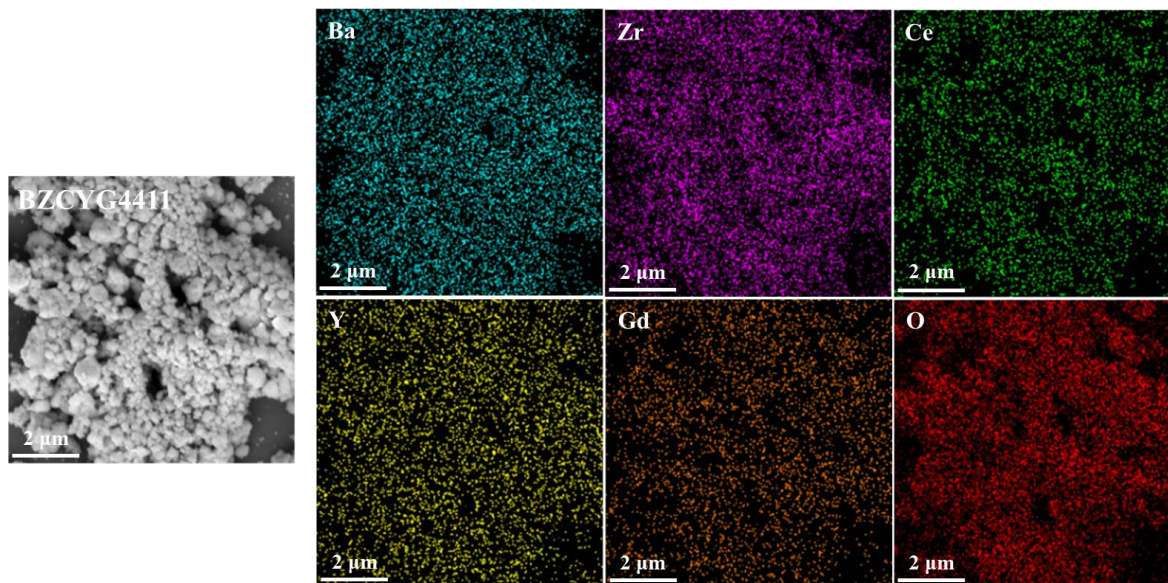
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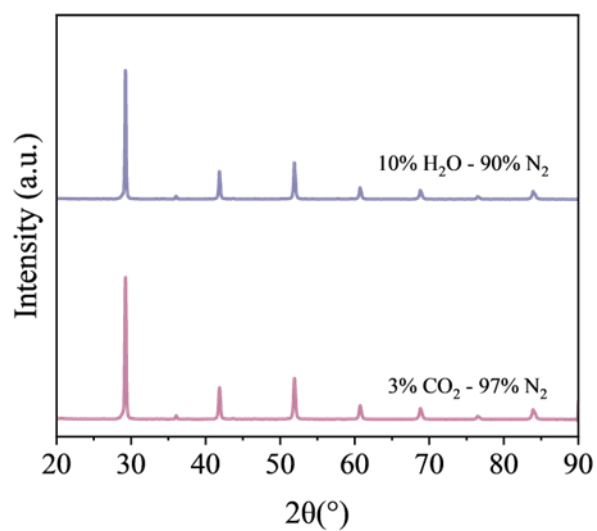
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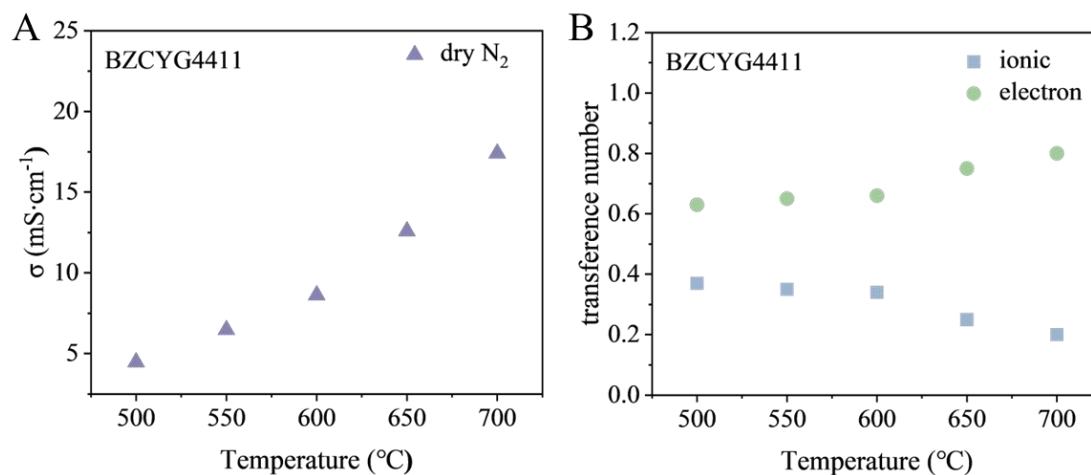
**Supplementary Figure 1.** XRD pattern of the BZCYG4411 powder synthesized by the type 2 method.



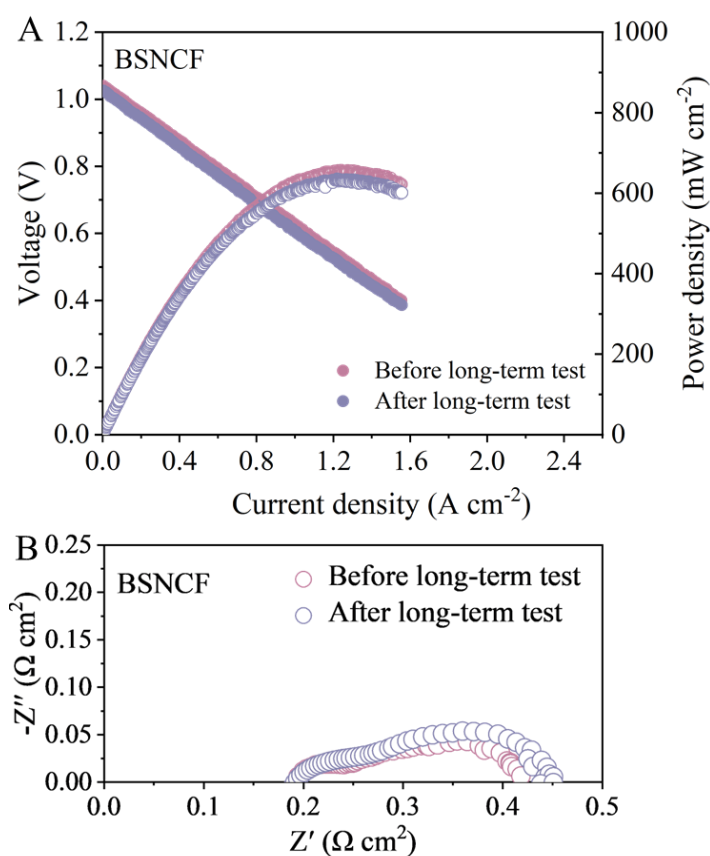
**Supplementary Figure 2.** EDX-mapping images of BZCYG4411 powder (type 1).



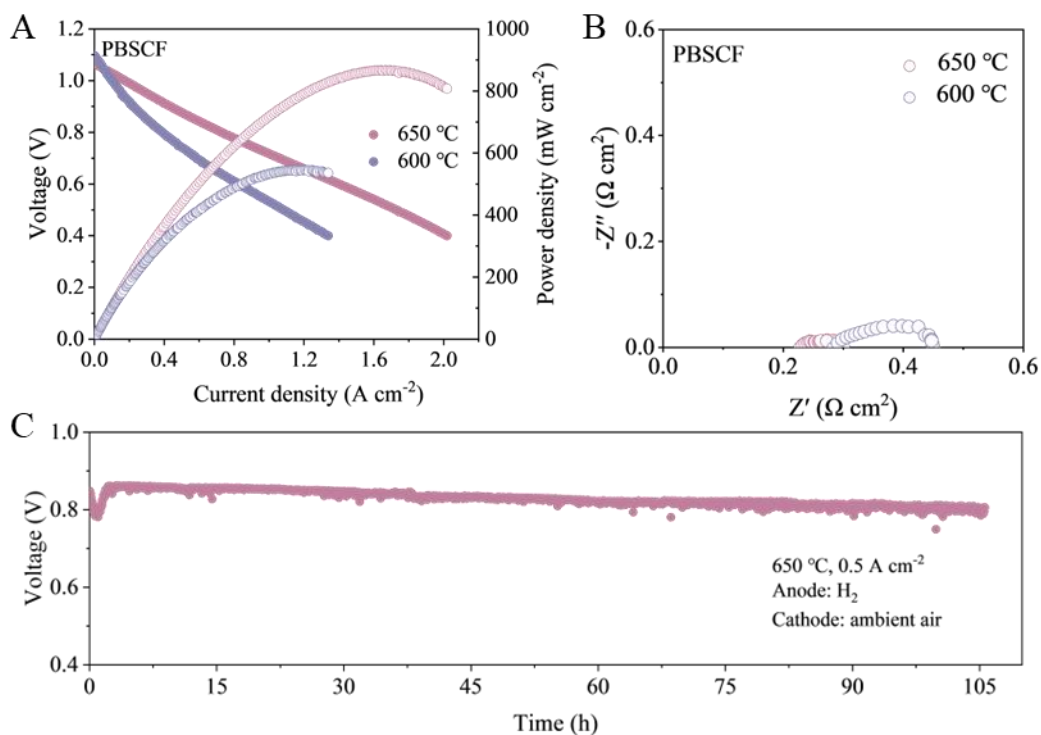
**Supplementary Figure 3.** XRD patterns of BZCYG4411 pellets after exposure to 10% H<sub>2</sub>O-90% N<sub>2</sub> and 3% CO<sub>2</sub> - 97% N<sub>2</sub> at 650 °C for 50 h, respectively.



**Supplementary Figure 4.** (A) The electrical conductivity of BZCYG4411 measured at 500-700 °C in dry N<sub>2</sub>; (B) The transference number of ionic and electron of BZCYG4411.



**Supplementary Figure 5.** Comparison of (A) I-V-P and (B) EIS curves of the cell using BSNCF cathode before and after long-term test.



**Supplementary Figure 6.** The electrochemical performance of the microtubular PCFC with PBSCF cathode. (A) I-V-P curves; (B) EIS curves; (C) Stability test at 650 °C.

**Supplementary Table 1.** Refined lattice parameters of BZCYG4411 using one-step SSR.

Sample	Space group	R <sub>p</sub> (%)	R <sub>wp</sub> (%)	a (Å)	b (Å)	c (Å)	α	β	γ
BZCYG4411	<i>Imma</i>	7.92	10.57	6.08	8.61	6.11	90°	90°	90°

**Supplementary Table 2. PPDs of tubular PCFCs in previous literature.**

Fabrication technique	Electrolyte	Cathode	Temperature (°C)	PPDs (mW cm <sup>-2</sup> )	Ref
Extrusion	BZCYYb	BSNCF	600	449.94	This work
Extrusion	BZCYYb	PBSCF	600	546.61	This work
3D Printing	BCZY27	BCFZY	600	281	[1]
Phase inversion	BZCYYb	LSCF- BZCYYb	600	530	[2]
Phase inversion	BZCYYb	SSC- BZCYYb	600	150	[3]

BCZY27: BaCe<sub>0.2</sub>Zr<sub>0.7</sub>Y<sub>0.1</sub>O<sub>3-δ</sub>; BCFZY: BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>O<sub>3-δ</sub>; LSCF: La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>; SSC: Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub>.

### Supplementary References

- [1] Zou M, Conrad J, Sheridan B, et al. 3D Printing Enabled Highly Scalable Tubular Protonic Ceramic Fuel Cells. *Acs Energy Lett* 2023;8:3545-51. [DOI: 10.1021/acseenergylett.3c01345].
- [2] Chen C, Liu M, Bai Y, Yang L, Xie E, Liu M. Anode-supported tubular SOFCs based on BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub> electrolyte fabricated by dip coating. *Electrochem. Commun.* 2011;13:615-618. [DOI: 10.1016/j.elecom.2011.03.025].
- [3] Zhao L, Zhang X, He B, Liu B, Xia C. Micro-tubular solid oxide fuel cells with graded anodes fabricated with a phase inversion method. *J. Power Sources* 2011;196:962-967. [DOI: 10.1016/j.jpowsour.2010.08.074].