

Electronic Supplementary Information

In-situ passivation of Fe nanoparticles exsolved from perovskite cathodes through Zinc doping for CO₂ electrolysis

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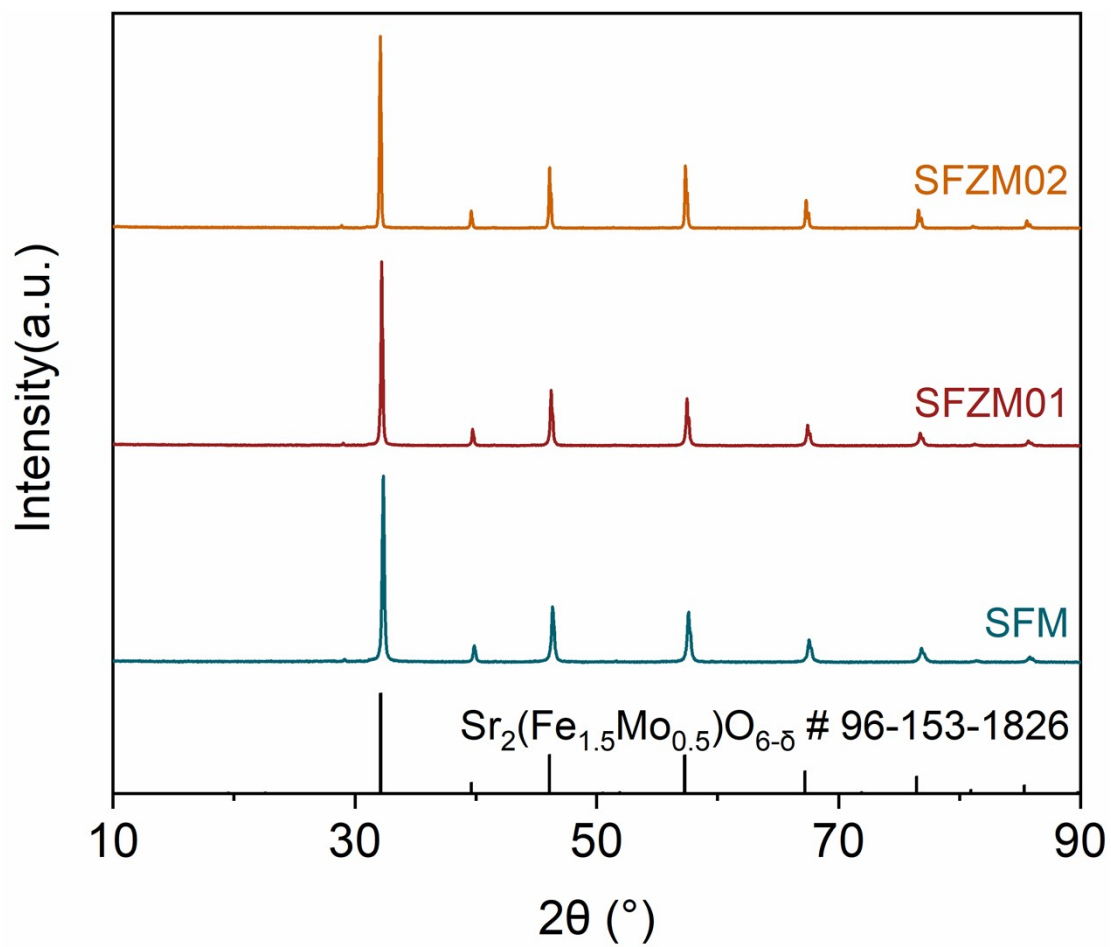


Fig. S1. XRD patterns of as-synthesized SFM, SFZM01, and SFZM02 powders.

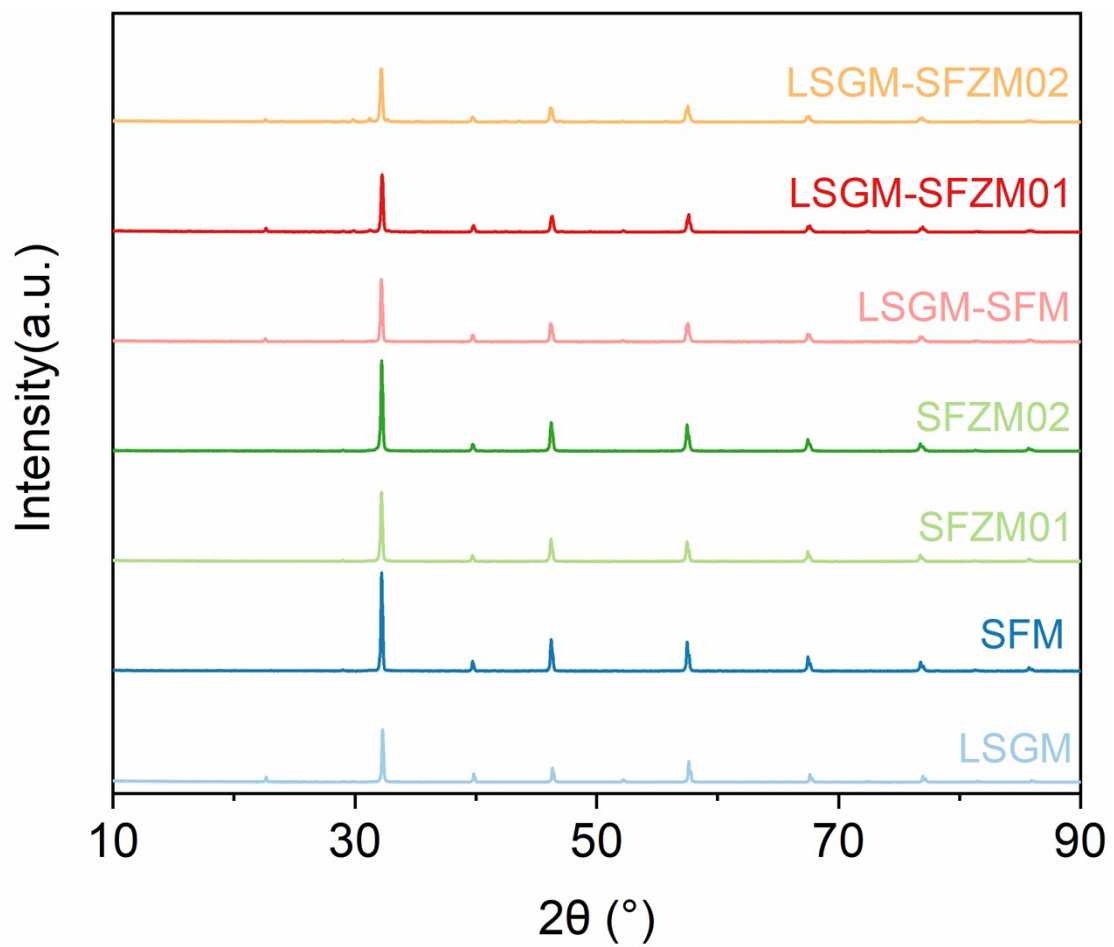


Fig. S2. XRD patterns of LSGM and SFZM_x powders with mass ratio of 1:1 after sintering in air for 10 hours.

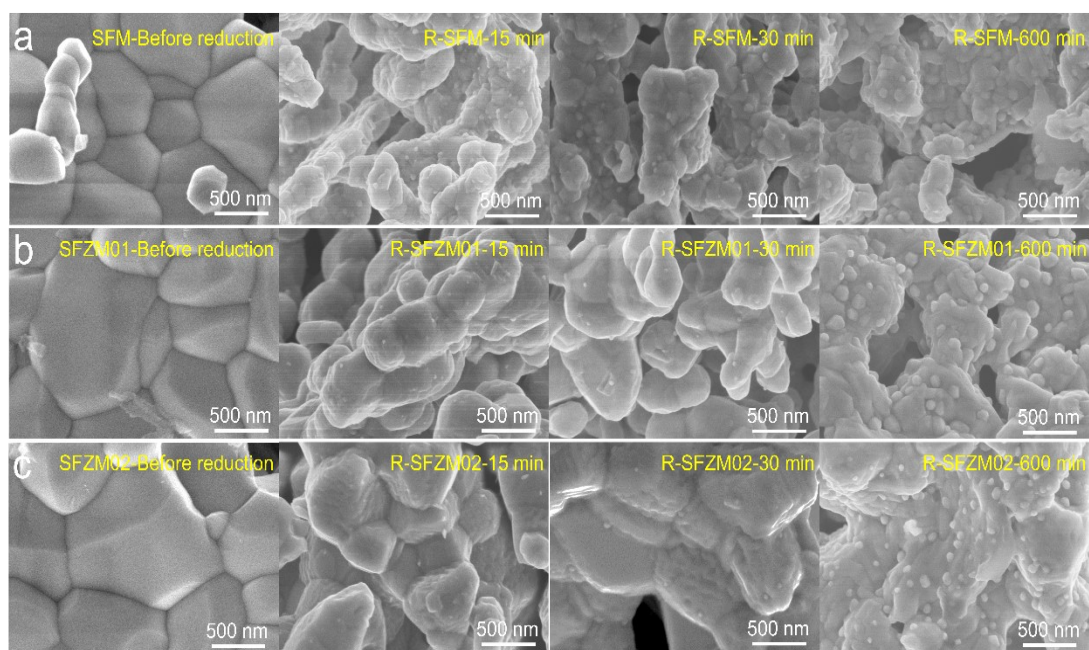


Fig. S3. SEM images of (a) SFM, (b) SFZM01, (c) SFZM02 powders before and after treatment under 10% H₂-Ar for different time (15, 30, 600 min)

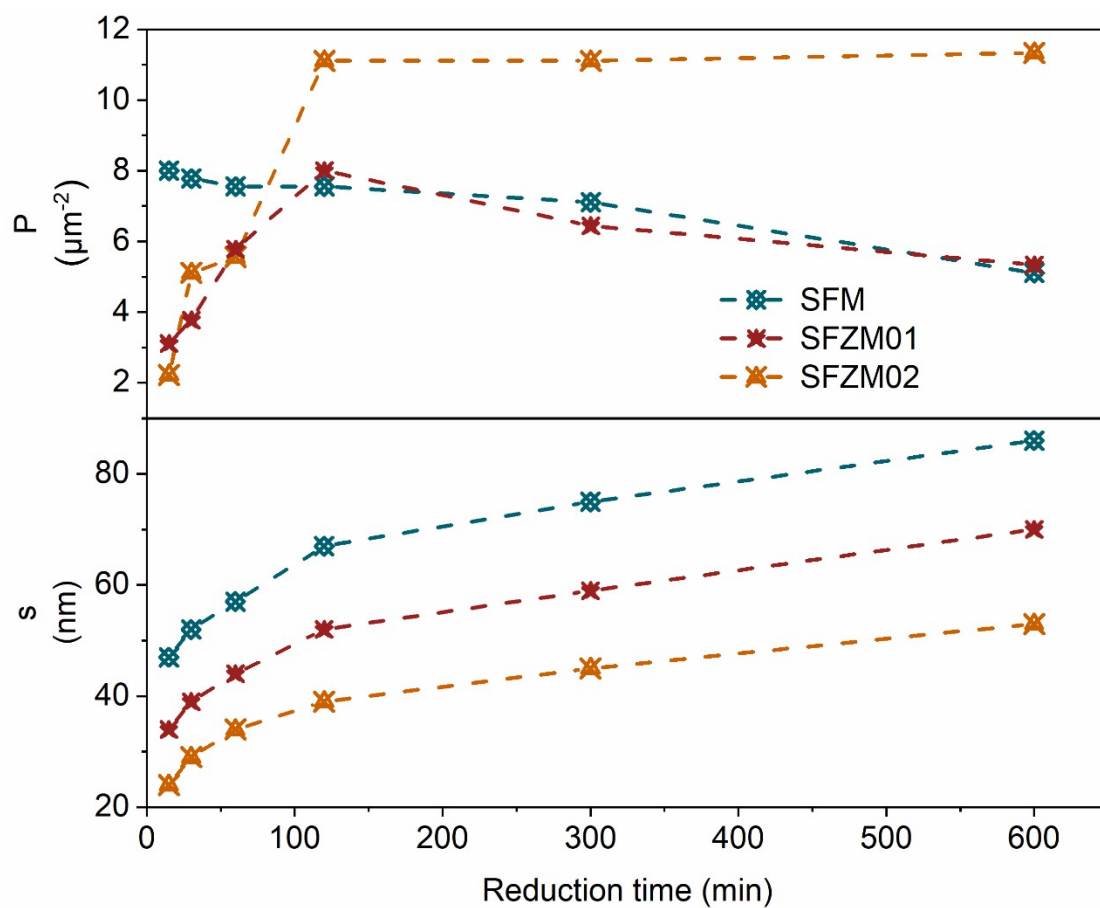


Fig. S4. Particle average diameter size and population density of exsolved NPs determined by SEM image analysis for various time (from 15 to 600 min).

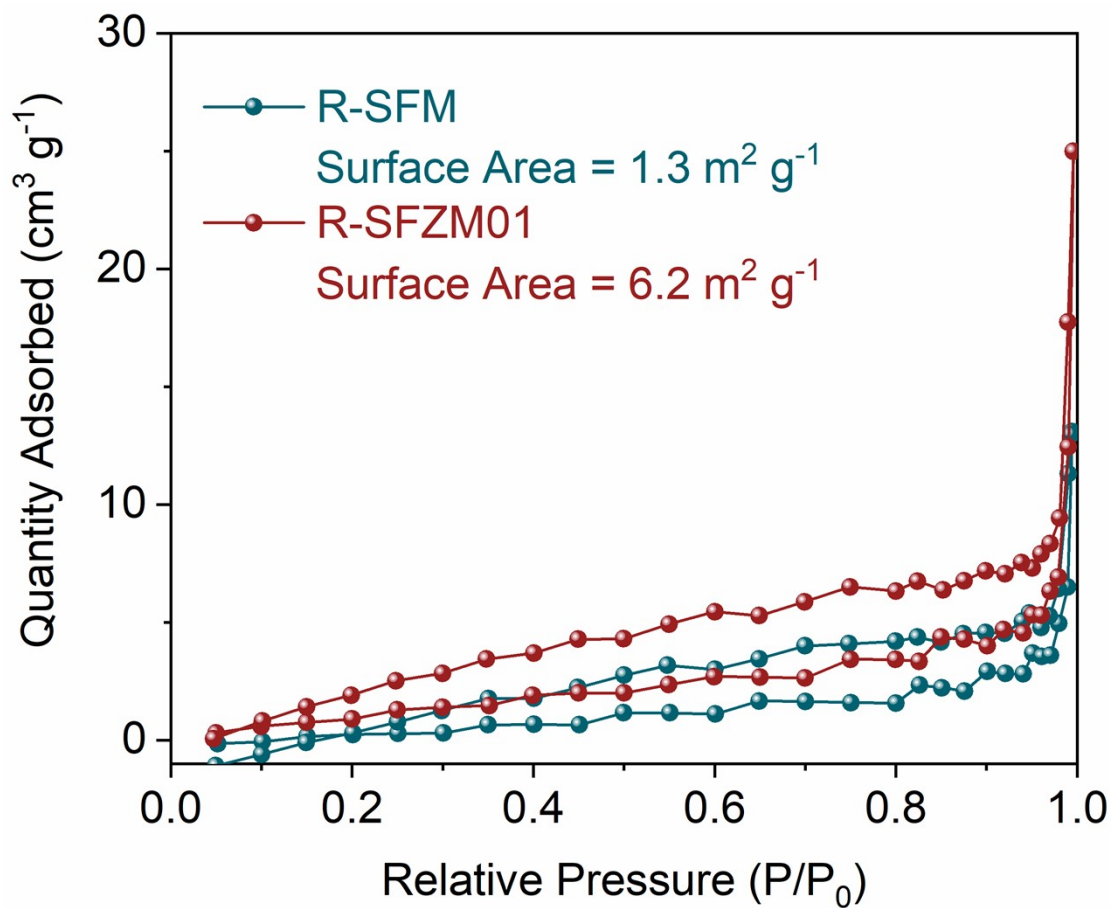


Fig. S5. N₂ adsorption/desorption isotherms of SFM and SFZM01 after reduction under 10% H₂-Ar at 800 °C for 120 min.

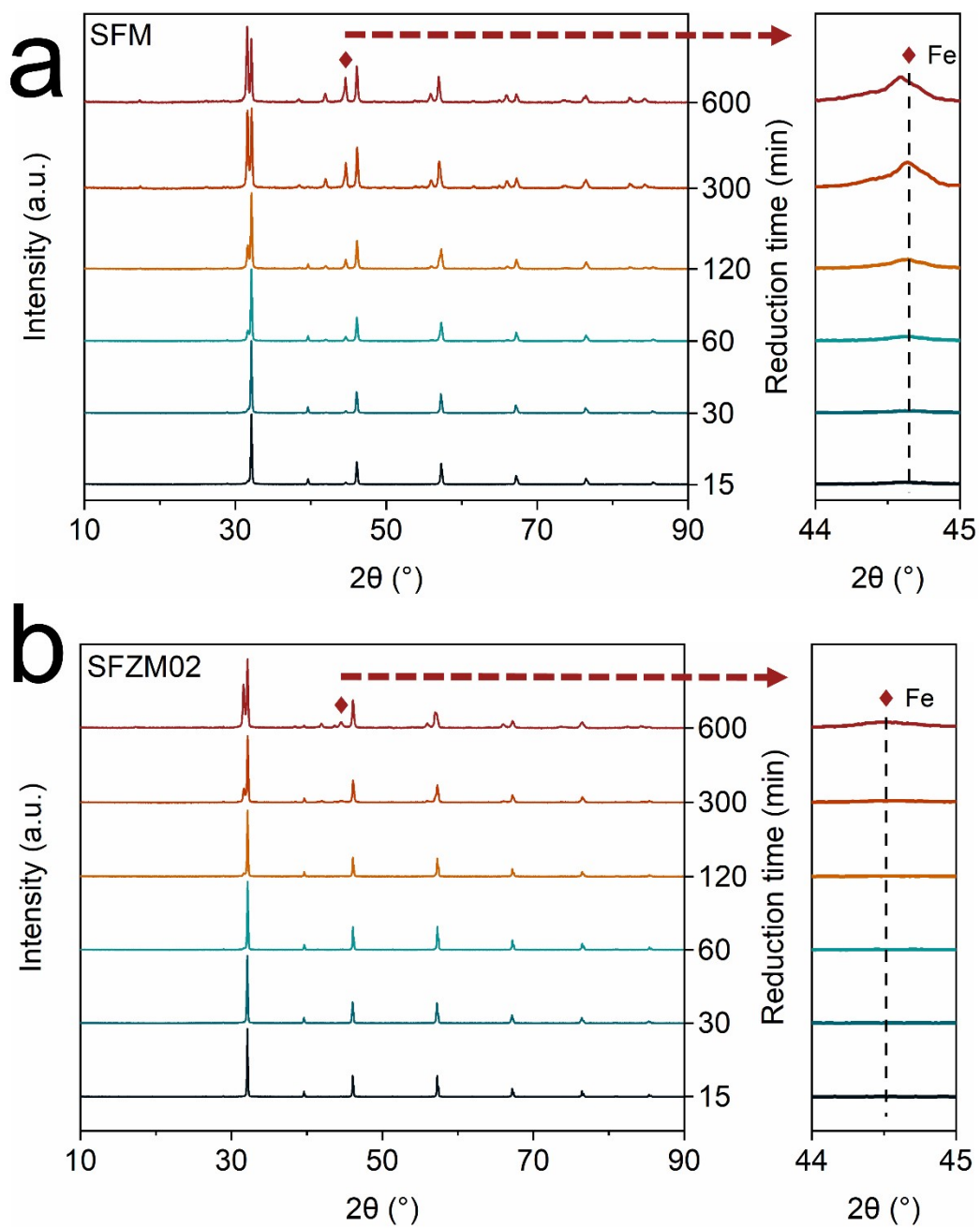


Fig. S6. XRD patterns of (a) SFM and (b) SFZM02 after reduction treatments (annealing from 15 to 600 min).

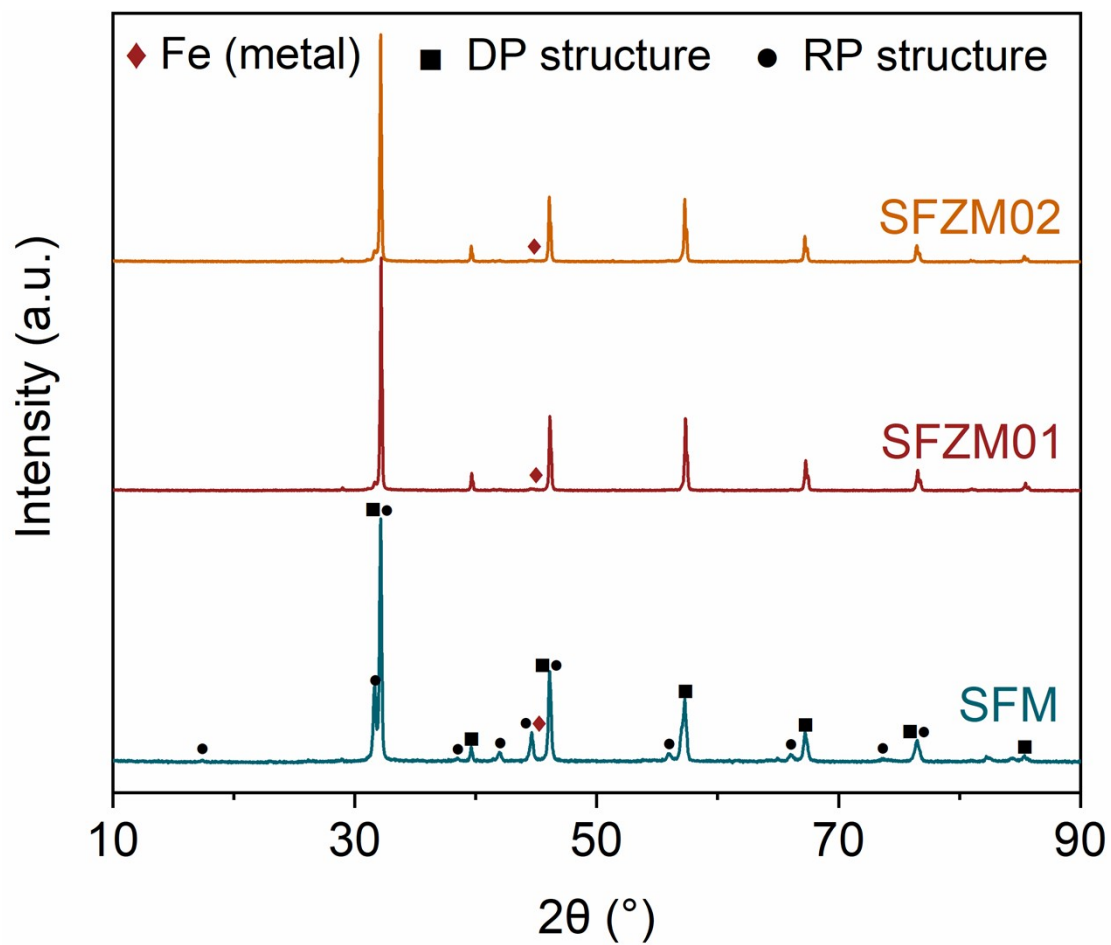


Fig. S7. XRD patterns of the SFM, SFZM01, and SFZM02 after reduction under 10% H_2/N_2 atmosphere at 800 °C for 2 h.

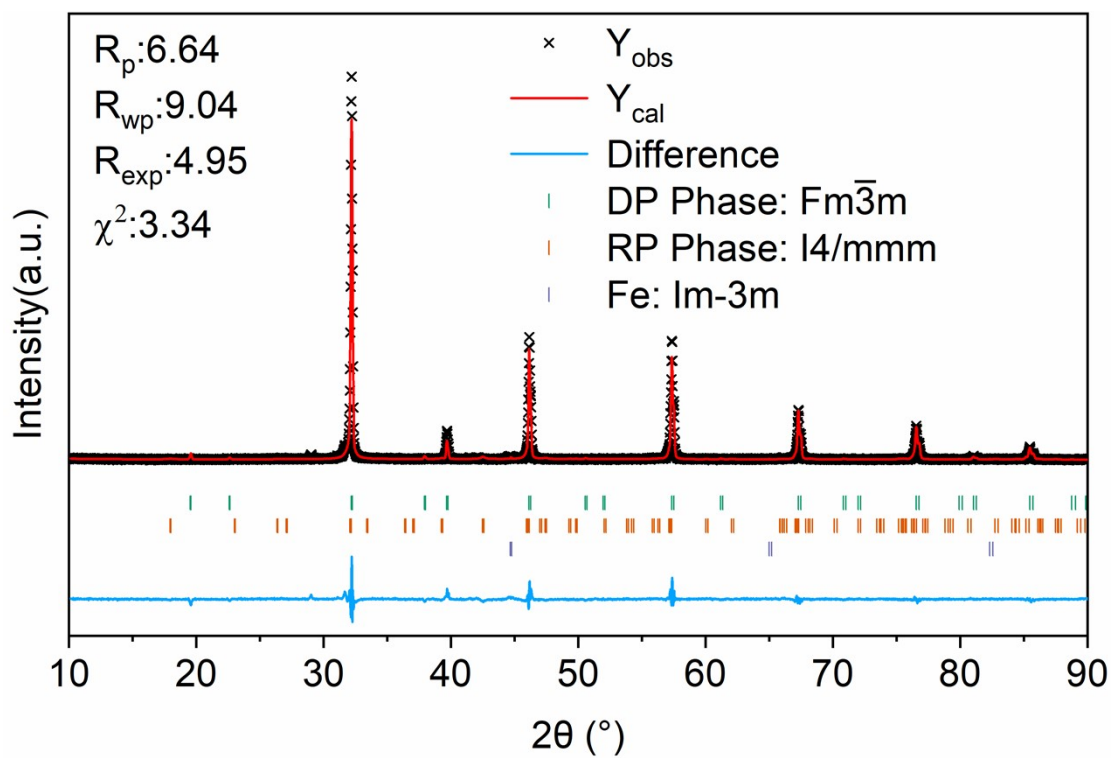


Fig. S8. Rietveld refinement of the reduced SFZM01 after reduction under 10% H₂/N₂ atmosphere at 800 °C for 2 h.

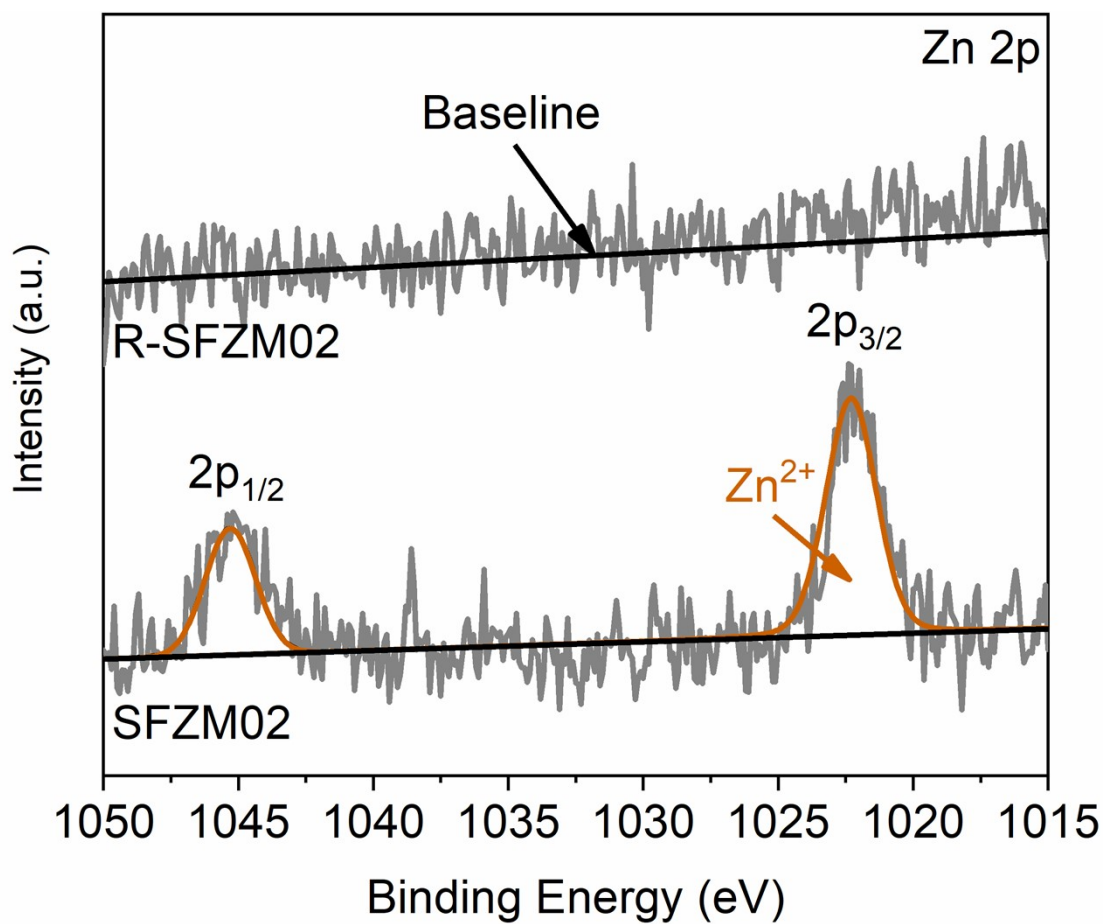


Fig. S9. XPS spectra of Zn 2p for oxidized and reduced SFZM02 samples.

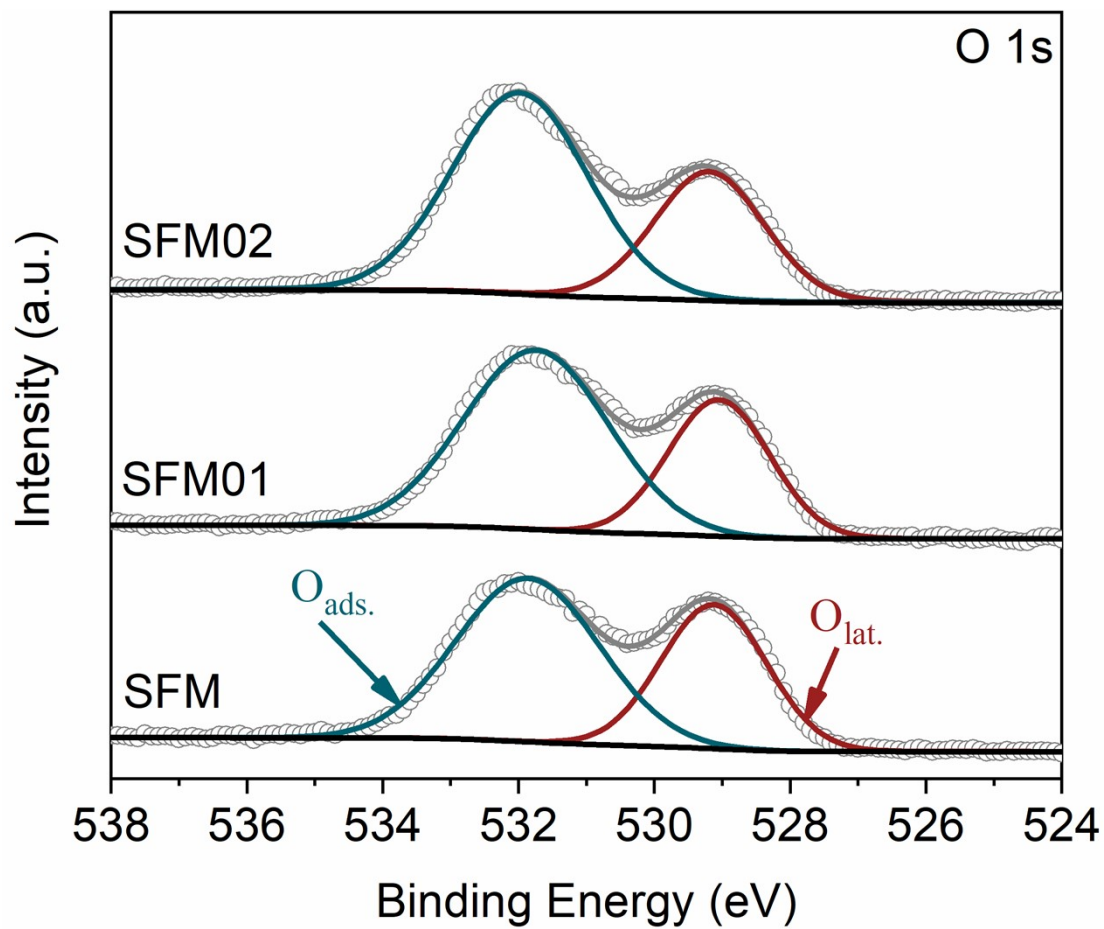


Fig. S10. XPS spectra of O 1s of SFZMx.

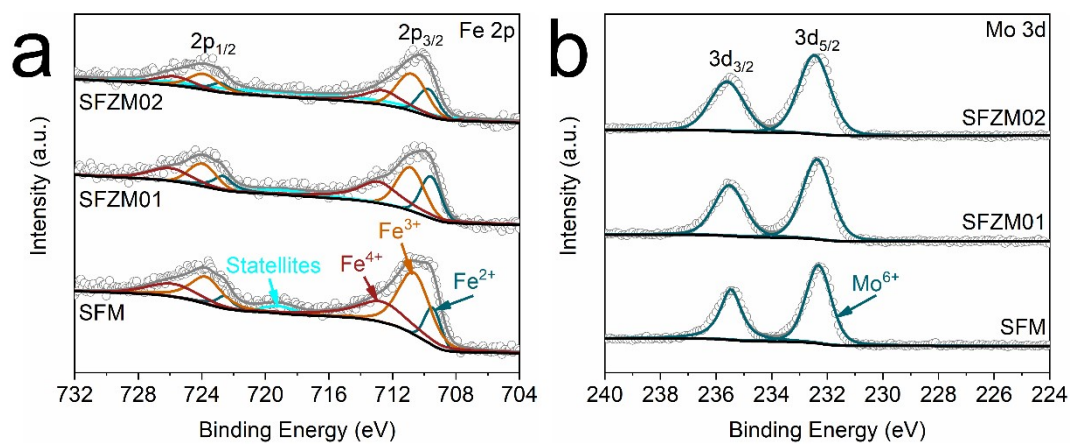


Fig. S11. XPS spectra of (a) Fe 2p, (b) Mo 3d of SFZMx.

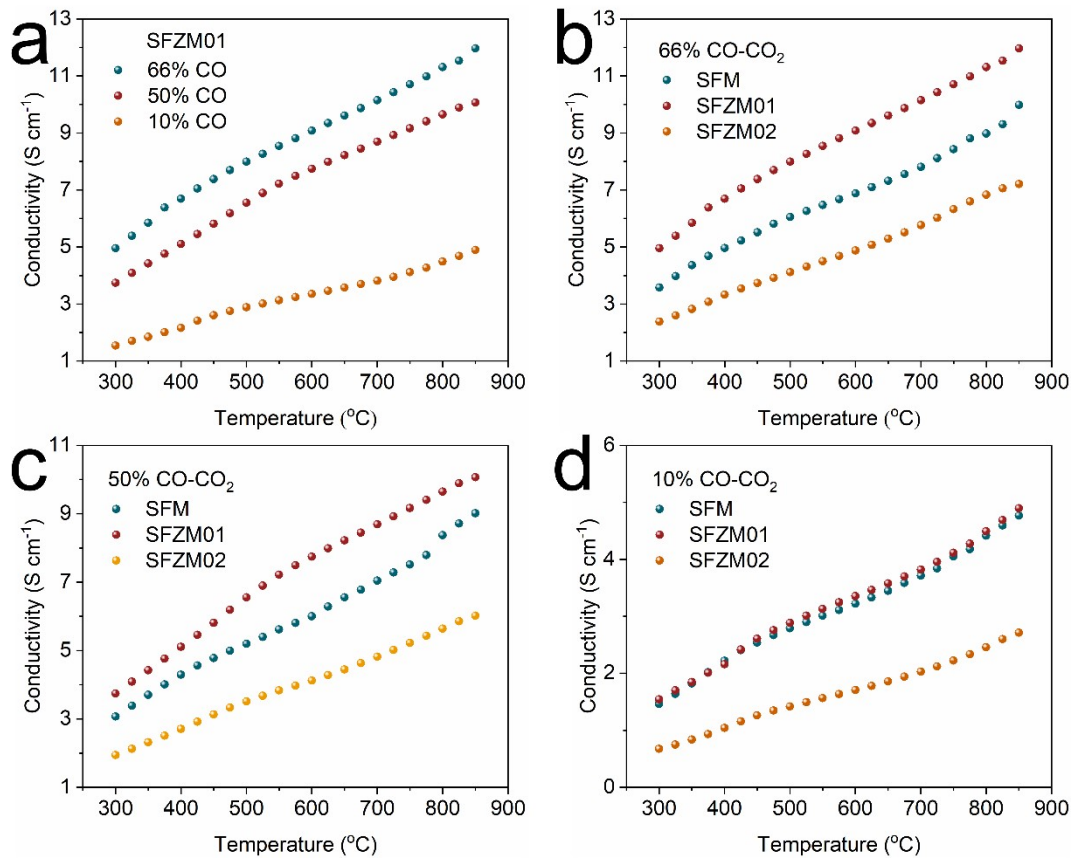


Fig. S12. Conductivity of the R-SFM, R-SFZM01 and R-SFZM02 in different CO partial pressures at 300-850 °C.

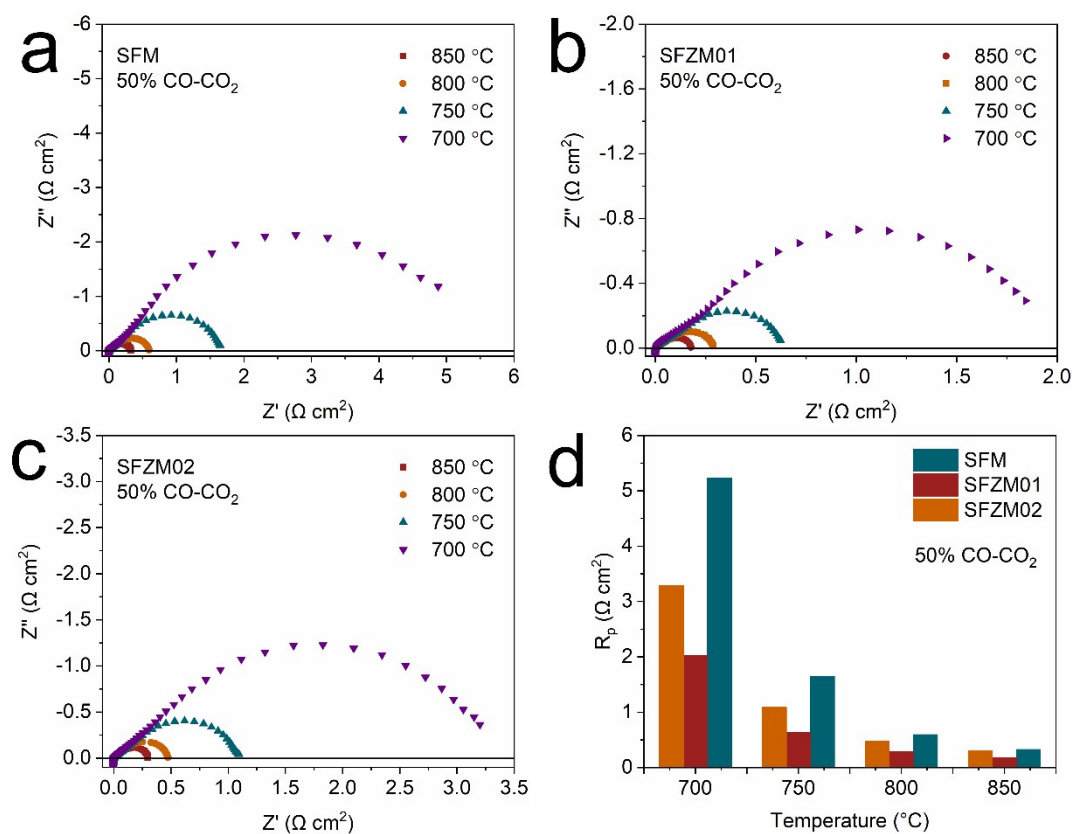


Fig. S13. EIS of the symmetrical cells with (a) SFM, (b) SFZM01, and (c) SFZM02 electrodes at 700-850 °C in 50% CO-CO₂. (d) Comparison of polarization impedance of three cathodes at different temperatures.

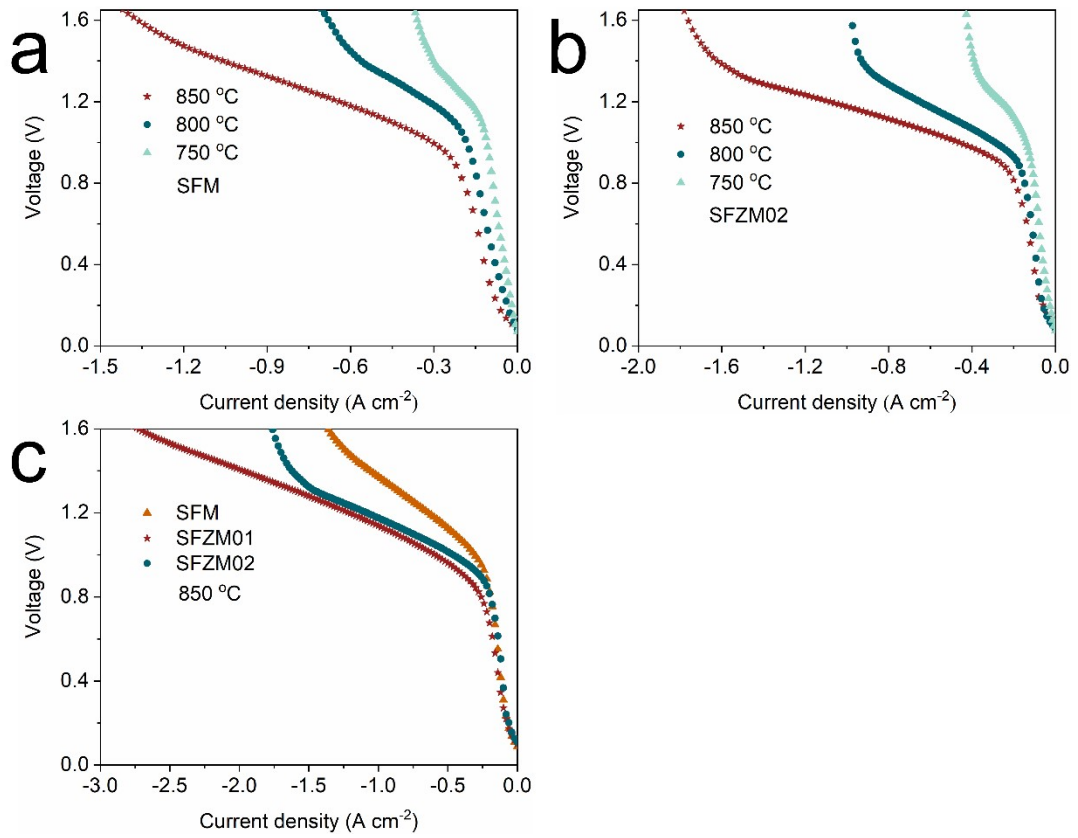


Fig. S14. (a, b) I-V curves from 750 to 850 °C of SFM/SFZM02|LSGM|BSCF single cells. (c) Comparison of I-V curves of three single cells at 850 °C.

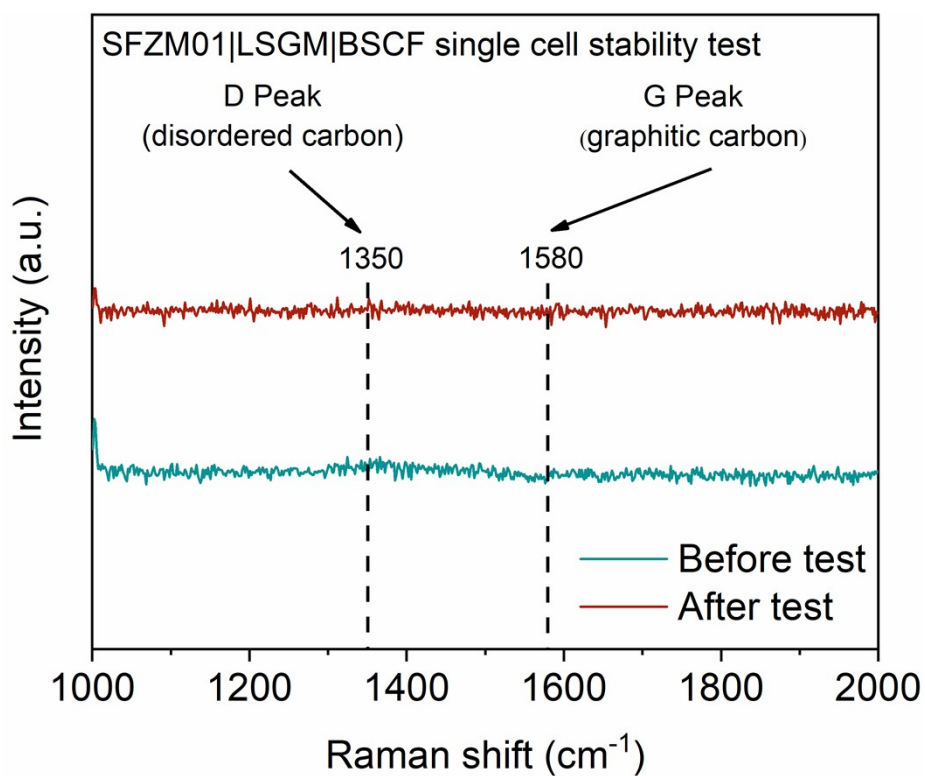


Fig. S15. Raman spectra of the surface of SFZM01 cathode before and after the durability test.

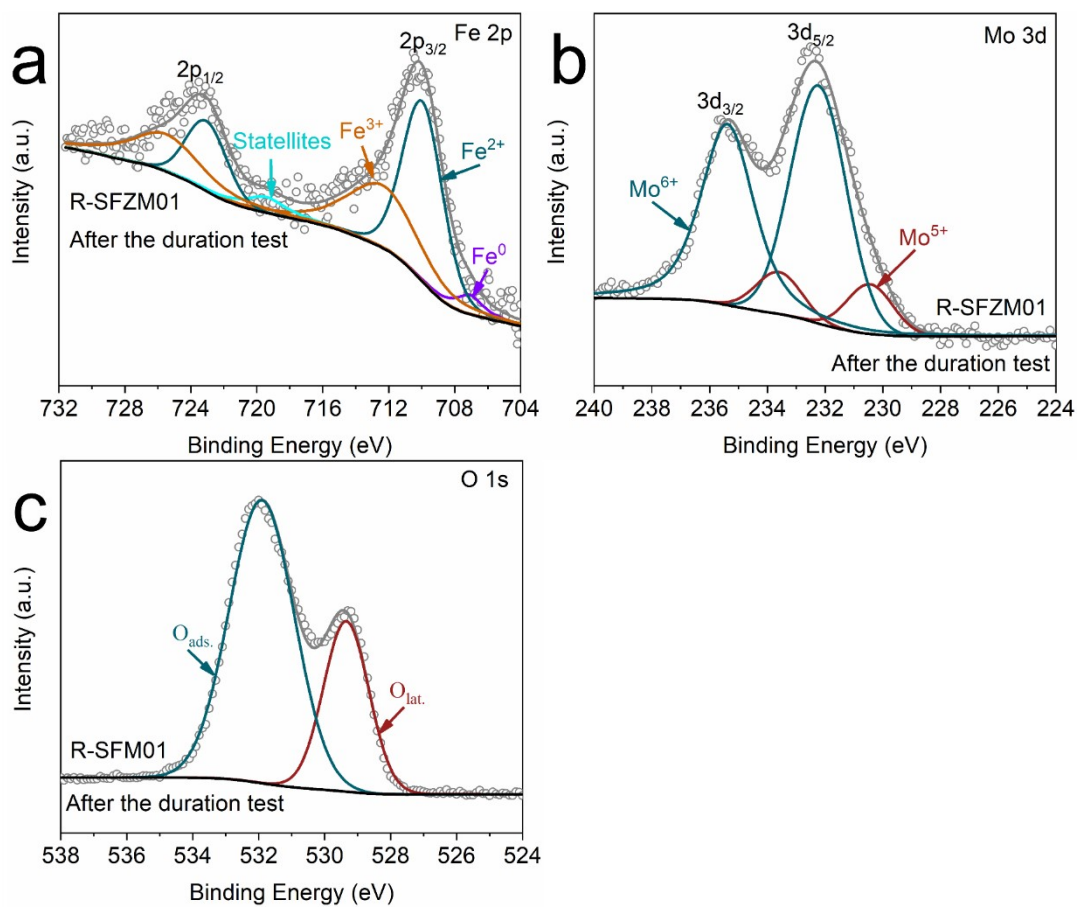


Fig. S16. XPS spectra of (a) Fe 2p, (b) Mo 3d, and (c) O 1s of R-SFZM01 cathode after the duration test.

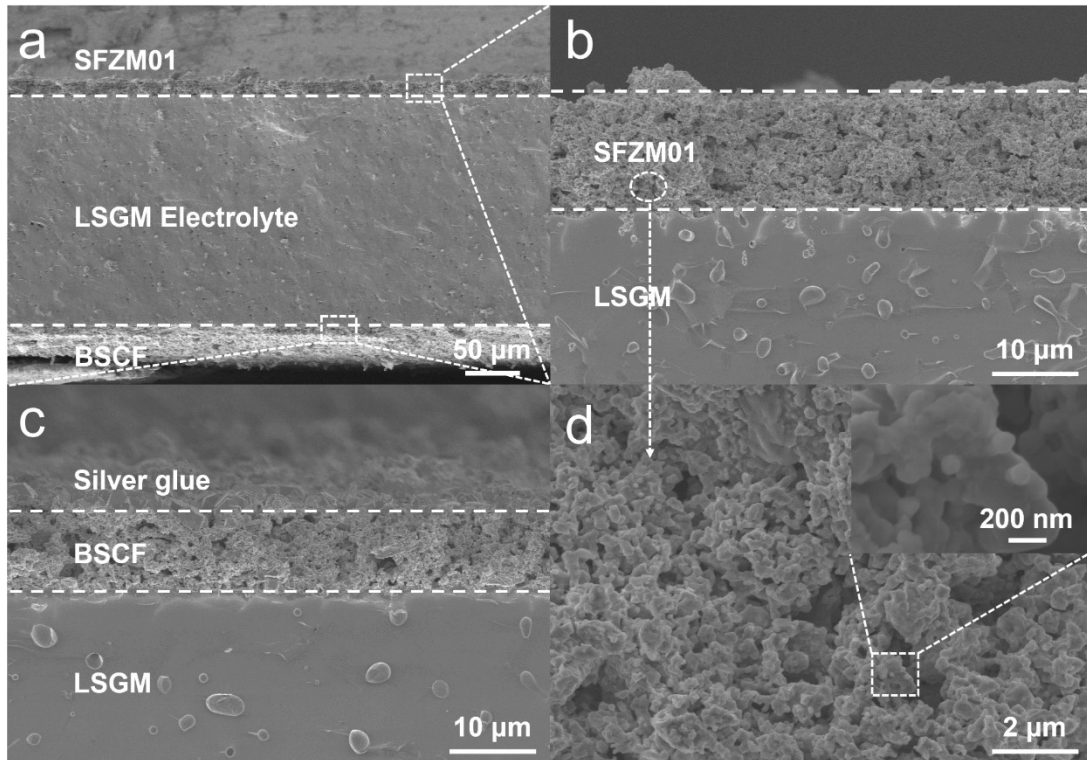


Fig. S17. SEM images of single cell after stability test. (a) Full view of single cell with SFZM01|LSGM|BSCF configuration. Detailed morphology of the interface between electrolyte with (b) SFZM01 cathode and (c) BSCF anode. (d) The morphology of SFZM01 cathode.

Table S1. Refinement parameters of SFZM01 powder and the reduced SFZM01.

Sample	Composition	R_p	R_{wp}	χ^2	Space group	a (Å)	b (Å)	c (Å)
SFZM01	-	5.49	7.83	2.98	Fm-3m	7.84384	7.84384	7.84384
Reduced SFZM01	DP-SFZM01	6.64	9.04	3.34	Fm-3m	7.86391	7.86391	7.86391
	RP-SFZM01	6.64	9.04	3.34	I4/mmm	3.94044	3.94044	19.74541
	Fe	6.64	9.04	3.34	Im-3m	2.86665	2.86665	2.86665

Table S2. XPS fitting results of Fe 2p_{3/2}, Mo 3d_{5/2} and O 1s for the SFM, SFZM01 and SFZM02 powders.

Samples	SFM	SFZM01	SFZM02
Fe ⁰ (at.%)	0	0	0
Fe ²⁺ (at.%)	13.76	24.77	22.59
Fe ³⁺ (at.%)	51.33	36.54	45.48
Fe ⁴⁺ (at.%)	34.91	38.69	31.93
Average valence of Fe	+3.21	+3.14	+3.09
Mo ⁵⁺ (at.%)	0	0	0
Mo ⁶⁺ (at.%)	1	1	1
Average valence of Mo	+6	+6	+6
O _S / (O _L + O _S) (at.%)	60.59	65.04	65.52

Table S3. XPS fitting results of Fe 2p_{3/2}, Mo 3d_{5/2} and O 1s for R-SFM, R-SFZM01, and R-SFZM02 powders.

	R-SFM	R-SFZM01	R-SFZM02
Fe ⁰ (at.%)	9.55	5.64	3.14
Fe ²⁺ (at.%)	39.93	53.34	51.36
Fe ³⁺ (at.%)	50.52	41.02	45.51
Average valence of Fe	+2.31	+2.30	+2.39
Mo ⁵⁺ (at.%)	10.83	12.37	11.54
Mo ⁶⁺ (at.%)	89.17	87.63	88.46
Average valence of Mo	+5.89	+5.88	+5.88
O_S/ (O_L + O_S) (at.%)	67.05	70.10	67.30

Table S4. XPS fitting results of Fe 2p_{3/2}, Mo 3d_{5/2} and O 1s for R-SFZM01 cathode after the duration test.

	R-SFZM01
Fe ⁰ (at.%)	5.69
Fe ²⁺ (at.%)	55.18
Fe ³⁺ (at.%)	39.13
Average valence of Fe	+2.28
Mo ⁵⁺ (at.%)	14.54
Mo ⁶⁺ (at.%)	85.46
Average valence of Mo	+5.85
O_S/ (O_L + O_S) (at.%)	70.21