Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

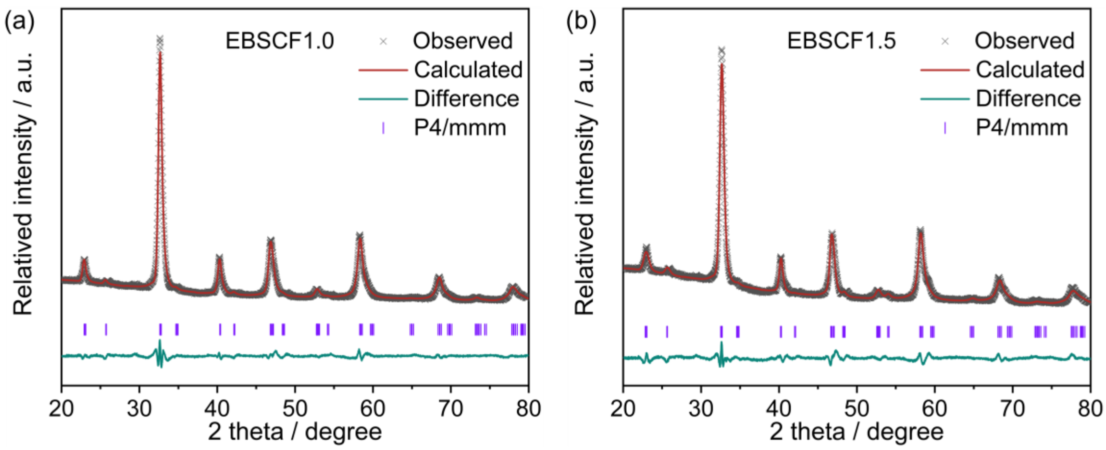

Fig. S1 Rietveld refinement XRD patterns of (a) EBSCF1.0 and (b)EBSCF1.5.

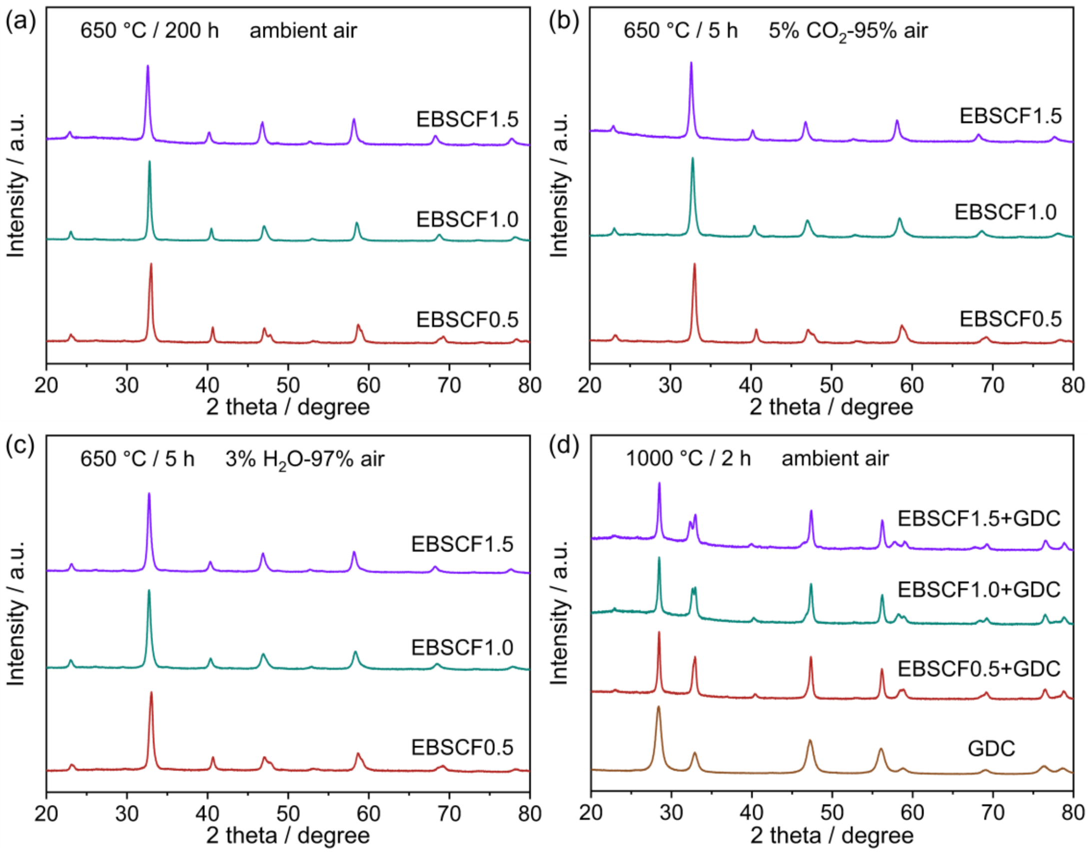

Fig. S2 XRD patterns of EBSCFx (x = 0.5, 1.0, and 1.5) treaded under different conditions: (a) 650 °C for 200 h in air, (b) 650 °C for 5 h in 5% CO_2-95% air, (c) 650 °C for 5 h in 3% H_2O-97% air, and (d) EBSCF-GDC composite with a mass ratio of 1:1 at 1000 °C for 2 h in air.

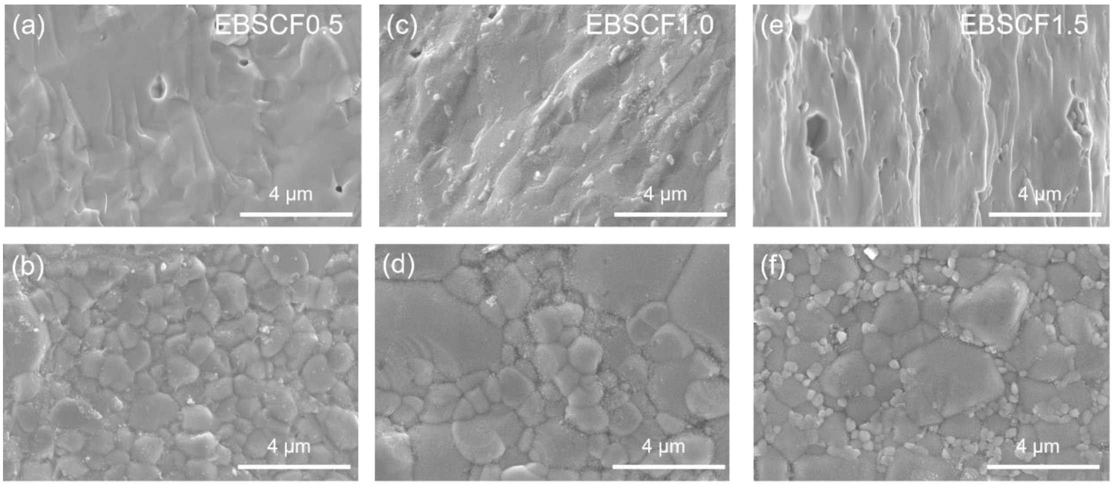

Fig. S3 Cross-section and surface morphologies of dense bar samples sintering at 1250 ℃ for 5 h. (a)(b) EBSCF0.5, (c)(d) EBSCF1.0, and (e)(f) EBSCF1.5.

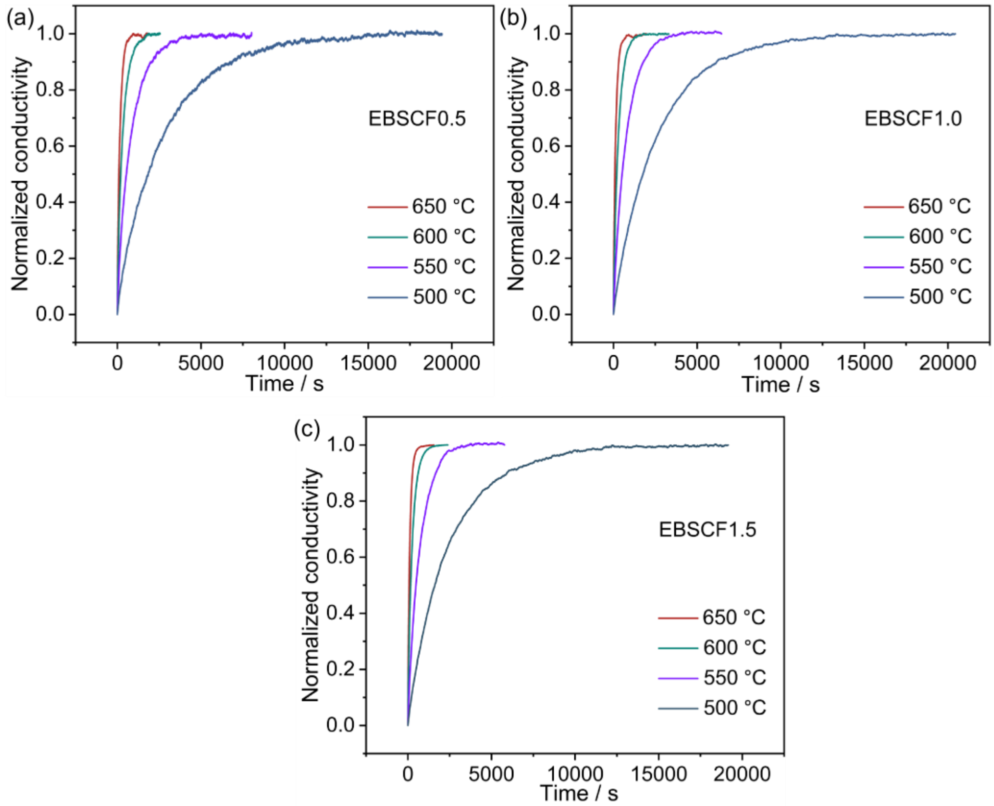

Fig. S4 Normalized ECR curves of (a) EBSCF0.5, (b) EBSCF1.0, and (c) EBSCF1.5 obtained at various temperatures.

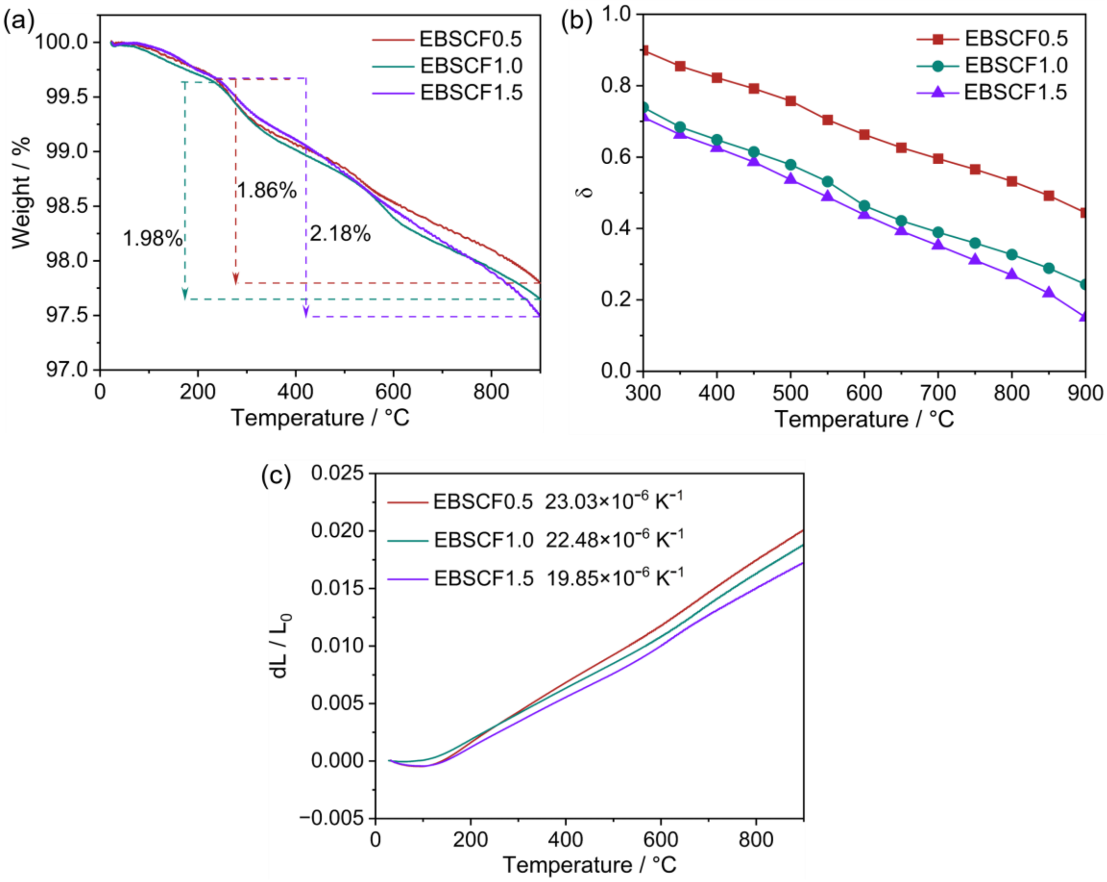

Fig. S5 Thermal analysis for EBSCFx. (a) TGA curves for powder samples, (b) oxygen stoichiometry at the temperature from 300 to 900 °C, and (c) thermal expansion curves for dense bar samples.

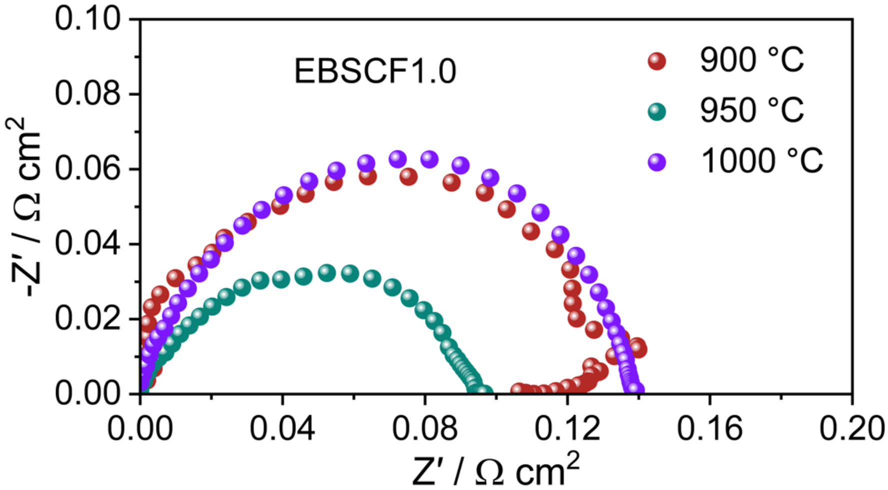

Fig. S6 EIS plots of EBSCF1.0 symmetric cells tested at 650 °C under different sintering temperatures.

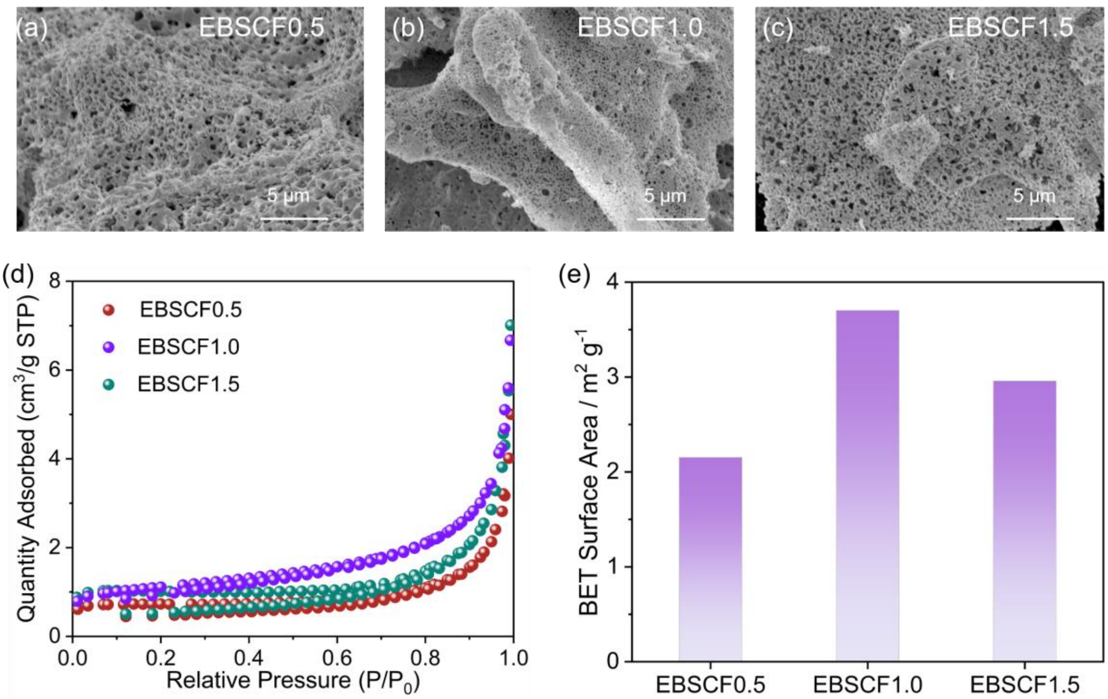

Fig. S7 The SEM morphologies for the prepared powders of (a) EBSCF0.5, (b) EBSCF1.0, (c) EBSCF1.5. (d) N_2 adsorption-desorption isotherms of the EBSCFx samples. (e) BET surface areas of EBSCFx.

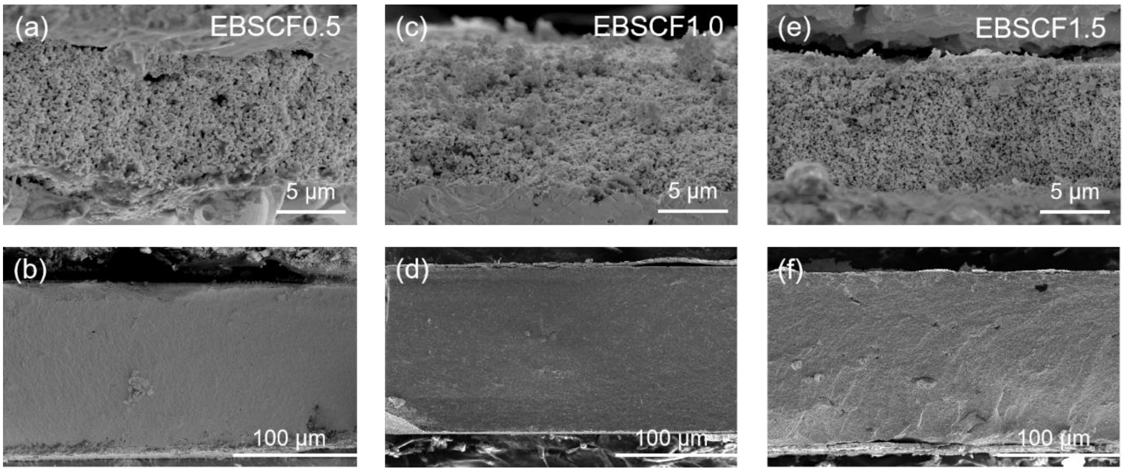

Fig. S8 The section morphology of symmetrical cells after EIS measurement. (a)(c)(e) The full morphologies, and (b)(d)(f) the magnified morphologies of the EBSCFx electrode and GDC electrolyte.

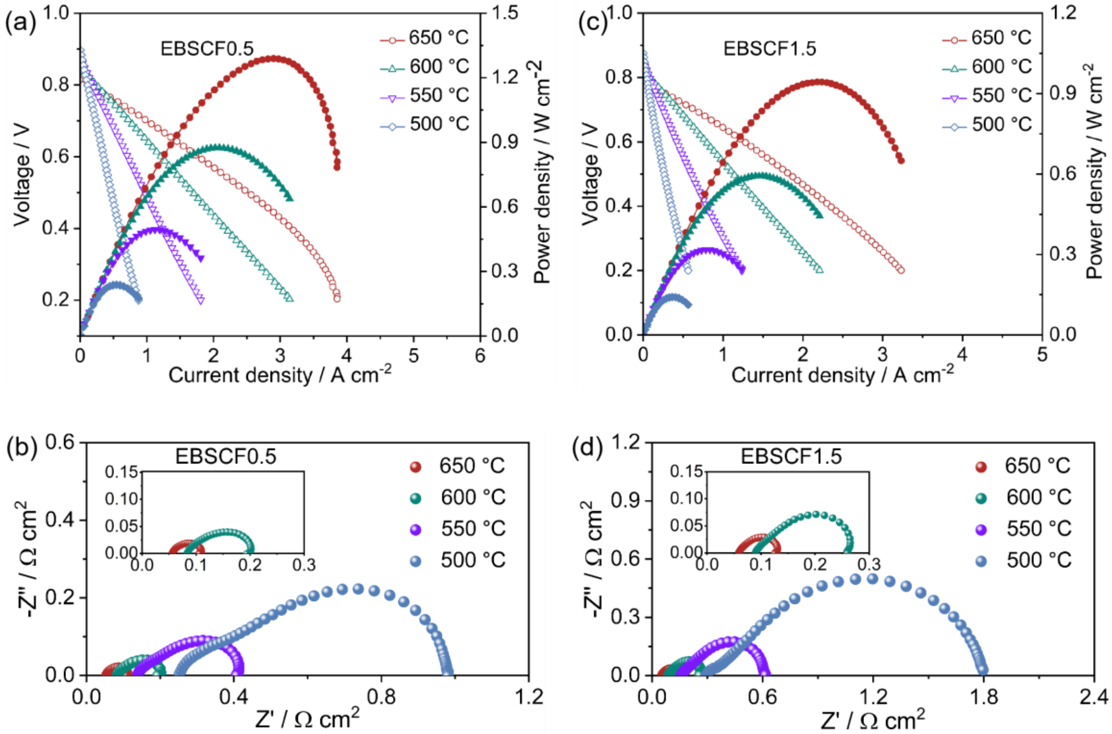

Fig. S9 (a) *I-V* and *I-P* curves for a single cell using EBSCF0.5 cathode. (b) EIS of EBSCF0.5 cell. (c) *I-V* and *I-P* curves for a single cell using EBSCF1.5 cathode. (d) EIS of EBSCF1.5 cell.

Table S1 XRD Rietveld refinement results of EBSCFx (x = 0.5, 1.0, and 1.5).

Sample		EBSCF0.5	EBSCF1.0	EBSCF1.5
Space group		P4/mmm	P4/mmm	P4/mmm
	a= b (Å)	3.8700(8)	3.8781(5)	3.8906(8)
Lattice	c (Å)	7.6571(4)	7.7131(5)	7.7345(2)
parameters	V ($Å^3$)	114.68	116.01	117.08
	α/β/γ (deg)		α= β= γ= 90	
Refinement	R_p (%)	1.86	1.93	2.44
parameters	R_{wp} (%)	2.30	2.59	3.13

Table S2 The density of the measured bars for EBSCFx.

Sample	w_1	w_2	w_3	D_b
EBSCF0.5	0.2351	0.2355	0.1960	99.0%
EBSCF1.0	0.2240	0.2245	0.1858	98.7%
EBSCF1.5	0.2242	0.2248	0.1849	98.5%

The subsequent equations (known as Archimedes' relations) are employed for the determination of the open porosity (P_O) and density (D_b) of the bars. Here, w_1 represents the weight of the dry sample, w_2 denotes the weight upon saturation, and w_3 is the weight of the sample when immersed in distilled water.

$$P_O = \frac{w_2 - w_1}{w_2 - w_3} \times 100\%$$

$$D_b = 1 - P_O$$

Table S3 The relative proportion of oxygen species for EBSCFx.

Oxygen Species	EBSCF0.5 %	EBSCF1.0 %	EBSCF1.5 %
O^{2-}	23.6	29.1	33.1
O_2^{2-} and O^-	23.5	23.6	25.8
OH^- and CO_3^{2-}	37.5	20.0	26.6
H_2O	15.4	17.3	14.5

Table S4 The relative proportion of the Co^{3+} and Co^{4+} for EBSCFx.

Valence State	EBSCF0.5 %	EBSCF1.0 %	EBSCF1.5 %
Co^{4+}	58.8	42.6	28.0
Co^{3+}	41.2	57.4	72.0
Average valence state	3.59	3.43	3.28

Table S5 The relative proportion of the Fe^{3+} and Fe^{4+} for EBSCFx.

Valence State	EBSCF0.5 %	EBSCF1.0 %	EBSCF1.5 %
Fe^{4+}	64.9	46.1	43.1
Fe^{3+}	35.1	53.9	56.9
Average valence state	3.65	3.46	3.43

Table S6 The average valence of B site elements for EBSCFx.

Sample	Average valance of Co	Average valance of Fe	Average valence of B site
EBSCF0.5	3.59	3.65	3.60
EBSCF1.0	3.43	3.46	3.44
EBSCF1.5	3.28	3.43	3.39

Table S7 ORR elementary reaction and process.[S1-S2]

n	ORR elementary reaction	ORR process
1	$O_2(g) \rightarrow O_{2,\,ads}$	gas diffusion and oxygen adsorption
0.5	$O_{2,ads} \rightarrow 2O_{ads}$	oxygen surface adsorption dissociation
0.375	$O_{ads} + e^{'} + V_{O,\,S}^{\cdot\cdot} \rightarrow O_{O,\,S}^{\cdot}$	the first charge transfer process
0.125	$O_{O,\,S}^{\cdot} + e^{'} \rightarrow O_{O,\,S}^{\times}$	the second charge transfer process
0.25	$O_{ads} + 2e^{'} + V_{O(S)}^{\cdot\cdot} \rightarrow O_{O,\,S}^{\cdot}$	the total charge transfer process
0	$O_{O,\,Cat}^{\times} \rightarrow O_{O,\,Ele}^{\times}$	the migration of oxygen ions from the cathode to the electrolyte

Table S8 R_p values of R_H, R_I, and R_L under different oxygen partial pressures.

R_p ($\Omega \cdot cm^2$)	Oxygen partial pressure (atm)				
	0.21	0.30	0.50	0.70	1.00
R_H	0.00688	0.00669	0.00614	0.00693	0.00690
R_I	0.10488	0.11132	0.10192	0.09545	0.08776
R_L	0.01293	0.00558	0.00416	0.00264	0.00138

Table S9 Average binding energy of metal-oxygen for EBSCF.

Sample	<A-O> (kJ mol^{-1})			<B-O> (kJ mol^{-1})		<ABE> (kJ mol^{-1})
	<Eu-O>	<Ba-O>	<Sr-O>	<Co-O>	<Fe-O>	
EBSCF0.5	-76.8	-20.4	-21.0	-132.9	-50.1	-301.2
EBSCF1.0	-76.8	-20.4	-21.0	-88.6	-100.2	-307.0
EBSCF1.5	-76.8	-20.4	-21.0	-44.3	-150.3	-312.8

The values of ABE are calculated by the following equations

$$\langle ABE \rangle = \langle A\text{-}O \rangle + \langle B\text{-}O \rangle \quad (1)$$

$$\langle A\text{-}O \rangle = \frac{x_A}{n \times CN_A} \times \left(\Delta H_{A_nO_m} - n\Delta H_A - \frac{m}{2} \times D_{O_2}\right) \quad (2)$$

$$\langle B\text{-}O \rangle = \frac{x_B}{n \times CN_B} \times \left(\Delta H_{B_nO_m} - n\Delta H_B - \frac{m}{2} \times D_{O_2}\right) \quad (3)$$

Where x_A and x_B are the molar ratios of A and B metals. $CN_{A(B)}$ is the coordination number of cations on the A and B sites (CN_{Eu} = 9, $CN_{Sr(Ba)}$ = 12, and $CN_{Co(Fe)}$ = 6). $\Delta H_{A(B)_nO_m}$ is the standard molar enthalpies of formation one mole of $A(B)_mO_n$ oxides, $\Delta H_{A(B)}$ is the sublimation energy of A(B) metal, and D_{O_2} (= 500.2 kJ mol^{-1}) is the dissociation energy of gaseous oxygen.[S3] $\Delta H_{Eu_2O_3}$ = −1657.9, ΔH_{BaO} = −548, ΔH_{SrO} = −592, $\Delta H_{Co_3O_4}$ = −910.0, $\Delta H_{Fe_2O_3}$=-823, ΔH_{Eu} = 178, ΔH_{Ba} = 179.1, ΔH_{Sr} = 164, ΔH_{Co} = 426.7, ΔH_{Fe}= 415.3 kJ mol^{-1}.

S1. M. Li, Y. Ren, Z. Zhu, S. Zhu, F. Chen, Y. Zhang and C. Xia, *Electrochim. Acta*, 2016, **191**, 651-660.

S2. L. Shen, Z. Du, Y. Zhang, X. Dong, and H. Zhao, *Applied Catalysis B: Environmental*, 2021, **295**, 120264.

S3. X. Ding, Z. Gao, D. Ding, X. Zhao, H. Hou, S. Zhang, G. Yuan,*Applied Catalysis B: Environmental*, 2019, **243**, 546-555.