

## Supporting Information

# In situ construction A-site high-entropy Perovskite with interfacial CeO<sub>2</sub> for high performance IT-SOFC air-electrode

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## 1. Experimental Section

### 1.1 Preparation of La<sub>0.2</sub>Ba<sub>0.2</sub>Sr<sub>0.2</sub>Ca<sub>0.2</sub>Ce<sub>0.2-x</sub>CoO<sub>3-δ-x</sub>CeO<sub>2</sub> material

All perovskite materials were prepared by citric acid-ethylenediaminetetraacetic acid sol-gel method. La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ba(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in a certain amount of deionized water according to the stoichiometric ratio. Subsequently, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were added to it to complex the metal ions to induce homogeneous mixing of the metal cations at the atomic level according to the molar ratio of CA : EDTA : total metal ions = 2:1:1. The pH was adjusted between 7~8 using NH<sub>3</sub>·H<sub>2</sub>O weak base. Then, the solution was stirred and heated at 80 °C until the water evaporated to produce a viscous homogeneous gel. The obtained gel was dried at 200 °C for 5 h to remove nitrate ions, and then black fluffy precursor powder was obtained, next the powder was ground moderately and calcined at 1000 °C for 5 h in a muffle furnace to obtain La<sub>0.2</sub>Ba<sub>0.2</sub>Sr<sub>0.2</sub>Ca<sub>0.2</sub>Ce<sub>0.2-x</sub>CoO<sub>3-δ-x</sub>CeO<sub>2</sub> (LBSCCC-CeO<sub>2</sub>). In addition, La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> (LSC) material was prepared by the same method for comparison.

### 1.2 Cell fabrication

The NiO-YSZ|YSZ|SDC fuel-pole-supported half-cell was prepared by co-tape casting process. The electrolyte layer slurry consisted of 2.5 g YSZ powder, 0.12 g triethanolamine (TEA),

0.12 g dibutyl phthalate (DBP), 0.12 g polyethylene glycol (PEG), 0.12 g poly (vinyl butyral) (PVB), and 40 g anhydrous ethanol. The fuel electrode functional layer slurry consisted of 0.6 g nickel oxide, 0.4 g yttrium oxide stabilized zirconia (YSZ), and 0.1 g polymethylmethacrylate (PMMA). The isolation buffer layer is similar to the electrolyte layer paste. It consisted of 2.5 g of SDC powder, 0.12 g of triethanolamine (TEA), 0.12 g of dibutyl phthalate (DBP), 0.12 g of polyethylene glycol (PEG), 0.12 g of polyvinyl butyral (PVB), and 40 g of anhydrous ethanol. The above medicines were purchased from Aladdin. Weigh the above slurry according to the proportion, put them in a polyethylene plastic bottle, add a certain amount of zirconium beads, and ball-mill it for 48 h to make them mix evenly. The ball-milled fuel electrode layer slurry, electrolyte layer slurry, and isolation layer slurry are sequentially flowed onto the template. After forming, then is pressed into a 15 mm diameter front half-cell. The former half-cell was calcined in a muffle furnace at 1300 °C for 5 h. The NiO-YSZ|YSZ|SDC half-cell was obtained. The prepared LBSCCC-CeO<sub>2</sub> powder was wet milled (with anhydrous ethanol) in a ball mill at 400 rpm for 24 h. 1.5 g of LBSCCC-CeO<sub>2</sub> powder was mixed with 1 g of terpinol (containing 6% ethyl cellulose) and ground thoroughly to obtain the air electrode slurry. Screen printing was used to brush onto the La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM) electrolyte (symmetric cell), and the isolation layer side of the half-cell (single cell). The porous air electrodes were obtained by co-firing at 1000 °C for 2 h under air atmosphere in a muffle furnace. During electrochemical testing, silver paste was coated on both sides of the electrode (fuel, air) for current collection.

### 1.3 Electrochemical measurement

The symmetric cell impedance was conducted on an Energy-lab XM electrochemical workstation in an atmospheric environment. The resulting single cell was sealed on an alumina tube coated with silver paste. During single-cell testing, wet H<sub>2</sub> (3% H<sub>2</sub>O) was supplied to the fuel electrode at a rate of 50 ml/min, and the air electrode side was exposed to atmospheric conditions. The current-voltage and impedance of single cell were performed on the Gamry electrochemical workstation. For the impedance measurement of the symmetric cell and single-cell, the frequency ranged from 0.1 Hz to 10 kHz with an amplitude AC of 10 mV.

### 1.4 Other characterization

The XRD patterns were conducted by a Bruker D8 advance (Germany Bruker) instrument using Cu K $\alpha$  radiation ( $\lambda=0.15406$  nm). Thermal field emission scanning electron microscope

(SEM, Hitachi SU8010, Japan) and transmission electron microscope (JEOL 4000EX) with energy spectrum analysis were used to observe the microstructure and microforms of the samples. Thermal gravimetric analysis (TGA) was performed in the air with a heating rate of 10 °C/min using a Netzsch STA 2500 thermogravimetric analyzer. XPS measurements were performed by a device (Thermo Scientific K-Alpha). Electron paramagnetic resonance (EPR) testing was performed using a Bruker EMX Plus instrument from Germany. Accurately weigh 10 mg sample and put it into a quartz tube, which is centered in the resonance chamber. The relative peak intensity represents concentration of oxygen vacancy. Inductively coupled plasma (ICP) analysis (Agilent 5110) was used to elucidate the equimolar nature of the high-entropy perovskite composite cathode. Electrical conductivity relaxation (ECR) technique was used for surface exchange coefficients ( $K^*_{\text{chem}}$ ) and bulk diffusion coefficients ( $D^*_{\text{chem}}$ ) of the electrode materials, which were tested by a digital source meter (Keithley 2450). In this work, 0.5 g of LBSCCC-CeO<sub>2</sub> and LSC powders were pressed under 1 Mpa pressure in a long bar model (20 mm long and 6 mm wide) and sintered in air at 1125 °C for 10 h to make the bars dense for measurement of electrical conductivity relaxation (ECR) and electrical conductivity. To test the SOFC performance, the fuel electrode was streamed with wet hydrogen (3% H<sub>2</sub>O) at a rate of 100 mL min<sup>-1</sup>, while the air electrode was exposed to ambient air.

## 2. Supporting Table and Figures

**Supporting Table. 1** Refinement parameters of LBSCCC-CeO<sub>2</sub> and LSC.

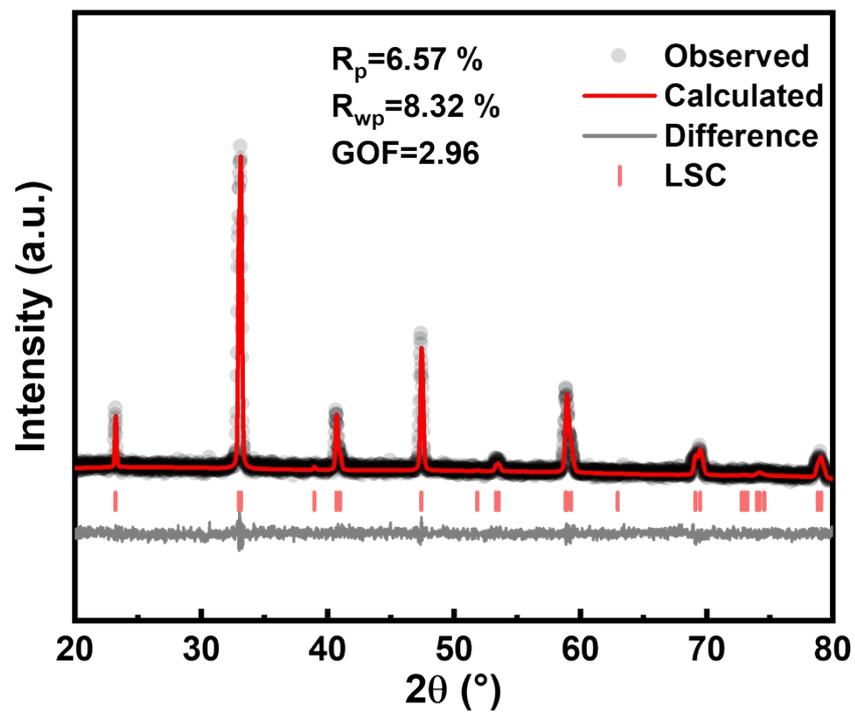
Composition	R <sub>p</sub> (%)	R <sub>wp</sub> (%)	χ <sup>2</sup>	Space group	a(Å)	b(Å)	c(Å)
LBSCCC	5.61	7.10	1.08	Pm $\bar{3}$ m	3.84884	3.84884	3.84884
CeO <sub>2</sub>	5.61	7.10	1.08	Fm $\bar{3}$ m	5.41423	5.41423	5.41423
LSC	6.57	8.32	2.96	R3-C	5.43464	5.43464	13.21422

**Supporting Table. 2** The refined results of coordinate and occupancy for each atom in LBSCCC-CeO<sub>2</sub> and LSC.

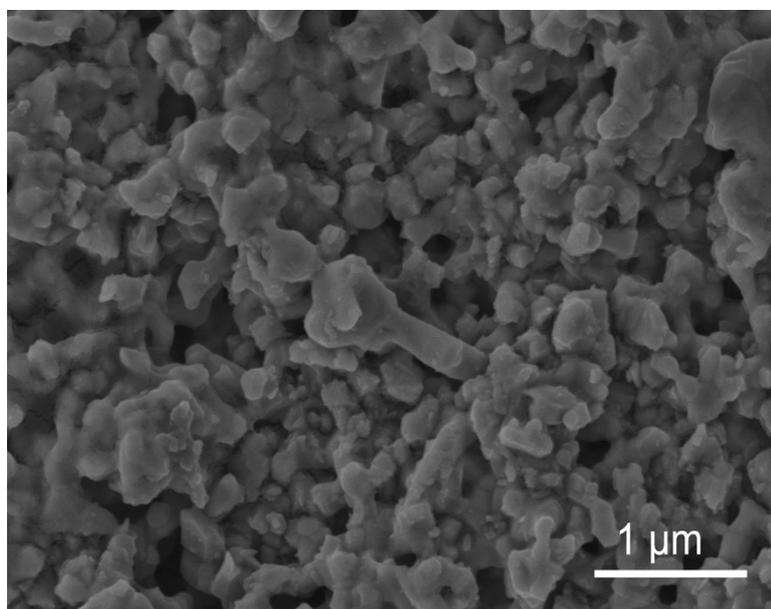
Samples	Element	x	y	z	frac
Phase 1 (LBSCCC, 85.2 wt.%)					
LBSCCC-CeO <sub>2</sub>	La 1	0	0	0	0.2000
	Ba 1	0	0	0	0.2000
	Sr 1	0	0	0	0.2000
	Ca 1	0	0	0	0.2000
	Ce 1	0	0	0	0.1824
	Co 1	0.5	0.5	0.5	1.0000
	O 1	0.5	0.5	0	0.8695
Phase 2 (CeO <sub>2</sub> , 14.8 wt.%)					
LBSCCC-CeO <sub>2</sub>	Ce 1	0	0	0	1.0000
	O 1	0.25	0.25	0.25	0.9751
Phase (LSC)					
LSC	La 1	0	0	0.25	0.595
	Sr 1	0	0	0.25	0.400
	Co 1	0	0	0	1.0000
	O 1	0.46246	0	0.25	0.882

**Supporting Table. 3** The atomic ratio of each element in the as-synthesized LBSCCC-CeO<sub>2</sub>, measured by inductively coupled plasma (ICP).

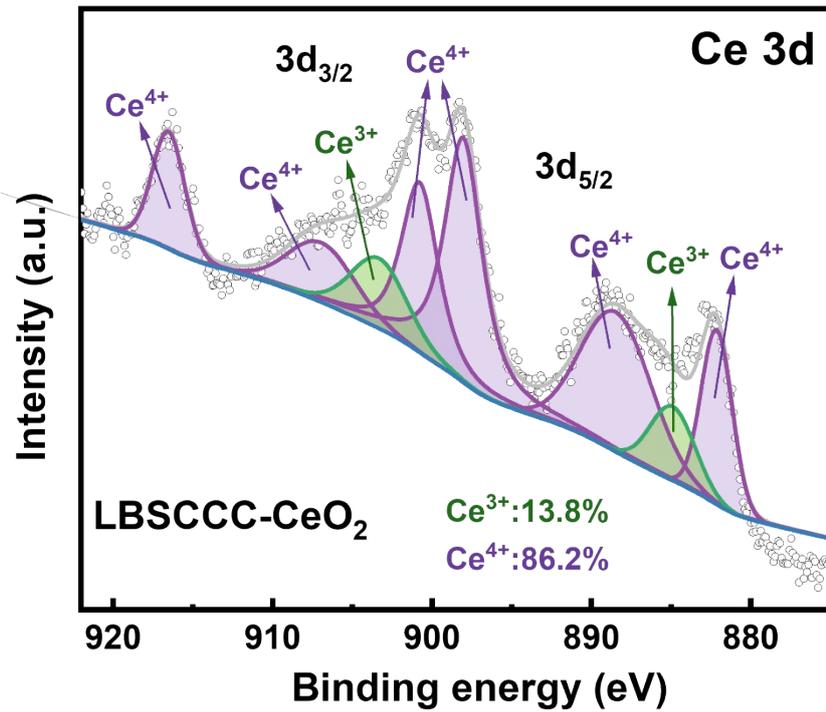
Samples	La	Ba	Sr	Ca	Ce	Co
LBSCCC-CeO <sub>2</sub>						
mg/kg	152018.6	146192.1	93827.5	38342.2	150481.5	347507.2
mol%	0.099	0.095	0.096	0.086	0.096	0.528



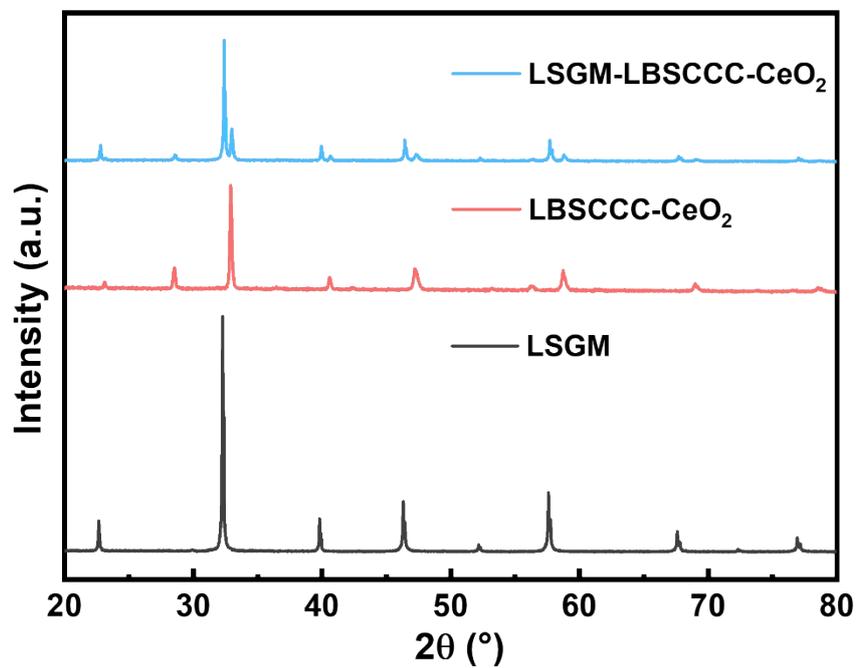
**Figures S1.** Refined XRD patterns of as-synthesized LSC powder at room temperature.



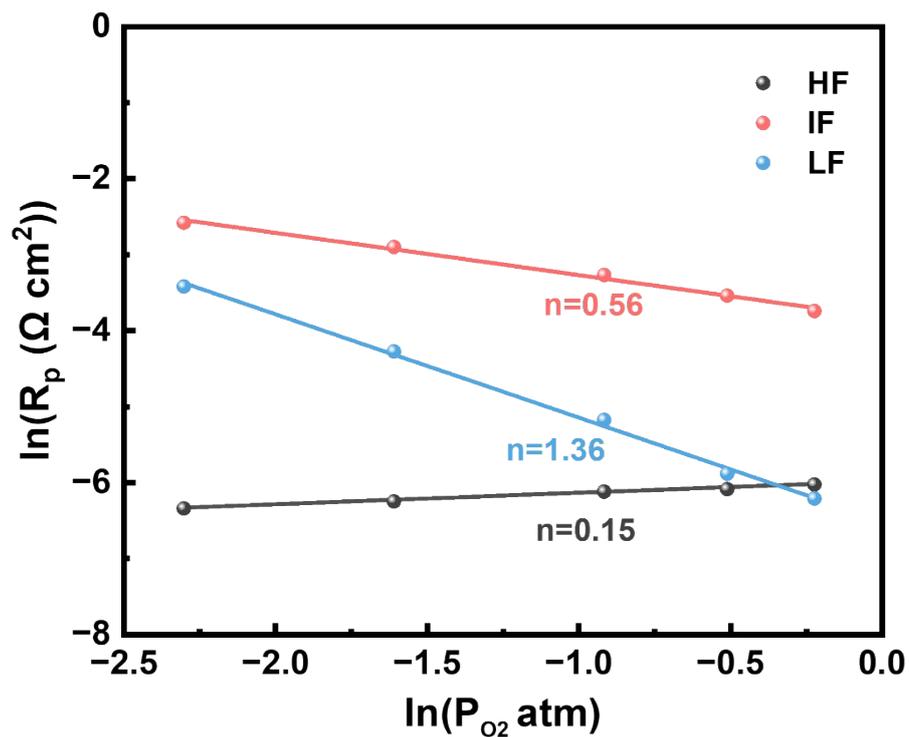
**Figures S2.** SEM image of synthesized  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) air electrode material.



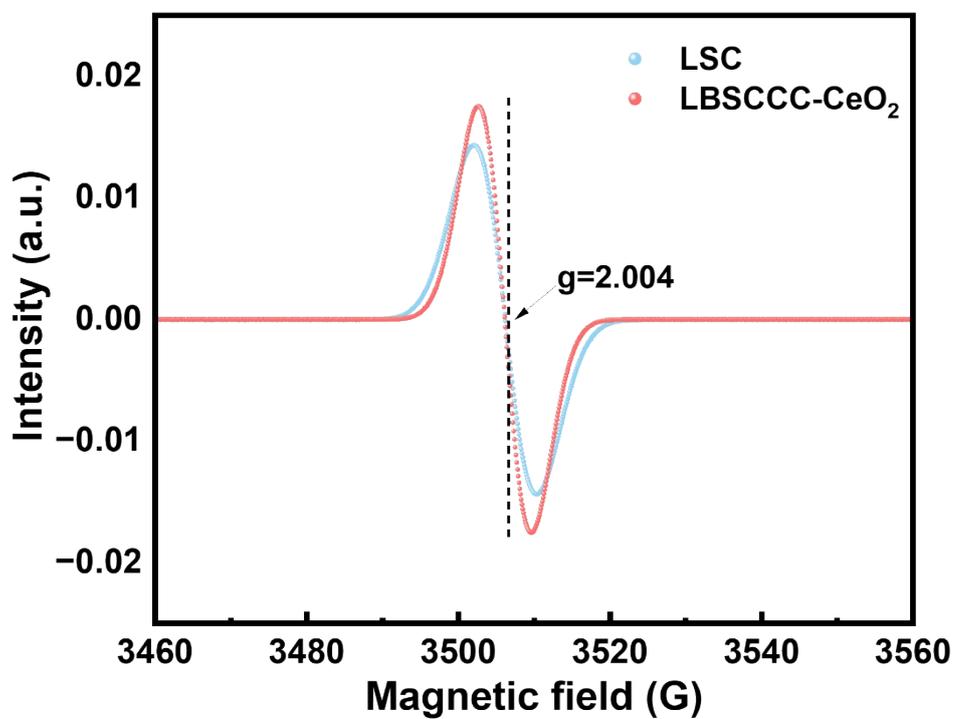
Figures S3. XPS spectrum of Ce 3d of LBSCCC-CeO<sub>2</sub>.



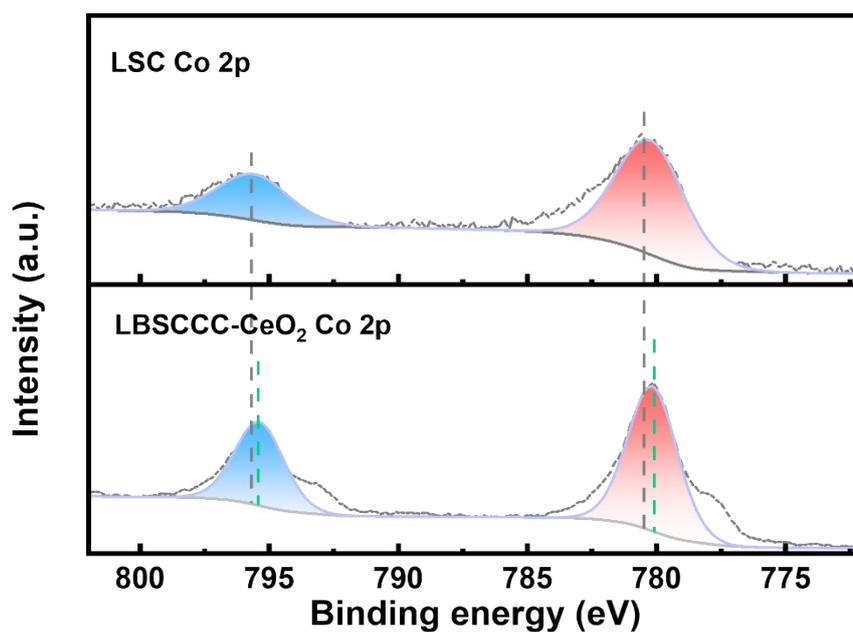
Figures S4. LBSCCC-CeO<sub>2</sub> has good chemical compatibility with conventional La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM) electrolyte.



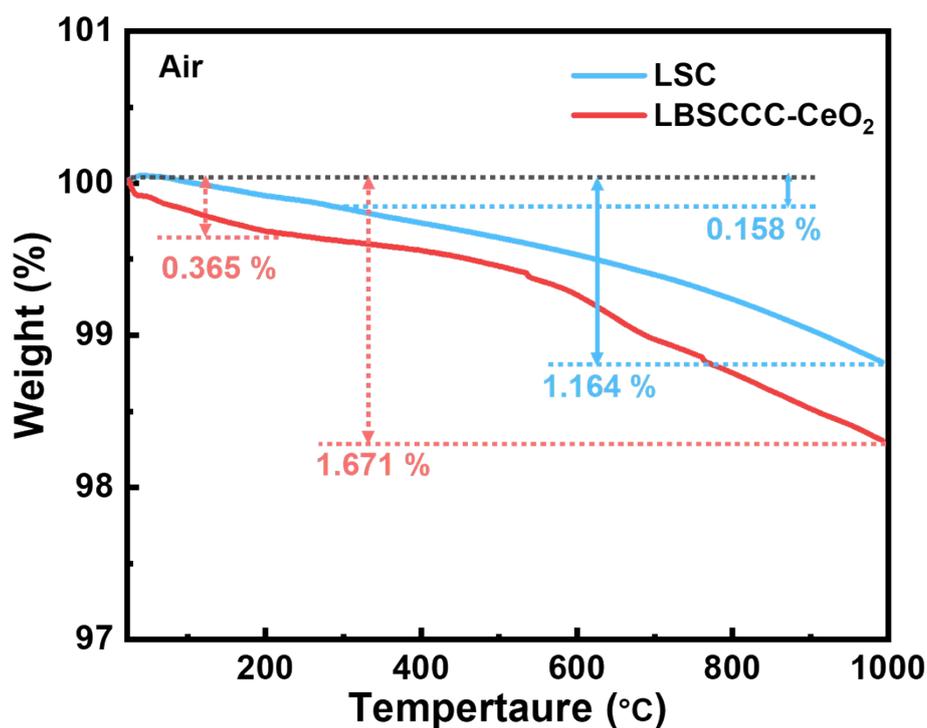
Figures S5. Dependence of  $R_p$  of LSC at different frequency range at 750 °C, as a function of  $P_{O_2}$ .



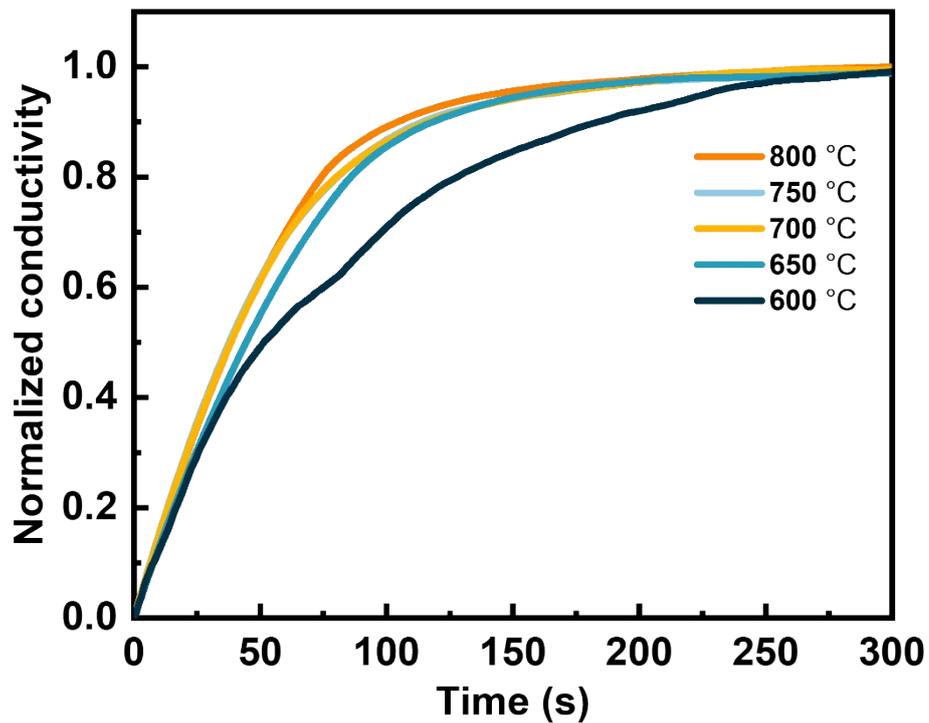
Figures S6. Fitted curves of electron paramagnetic resonance (EPR) for LBSCCC-CeO<sub>2</sub> and LSC electrodes.



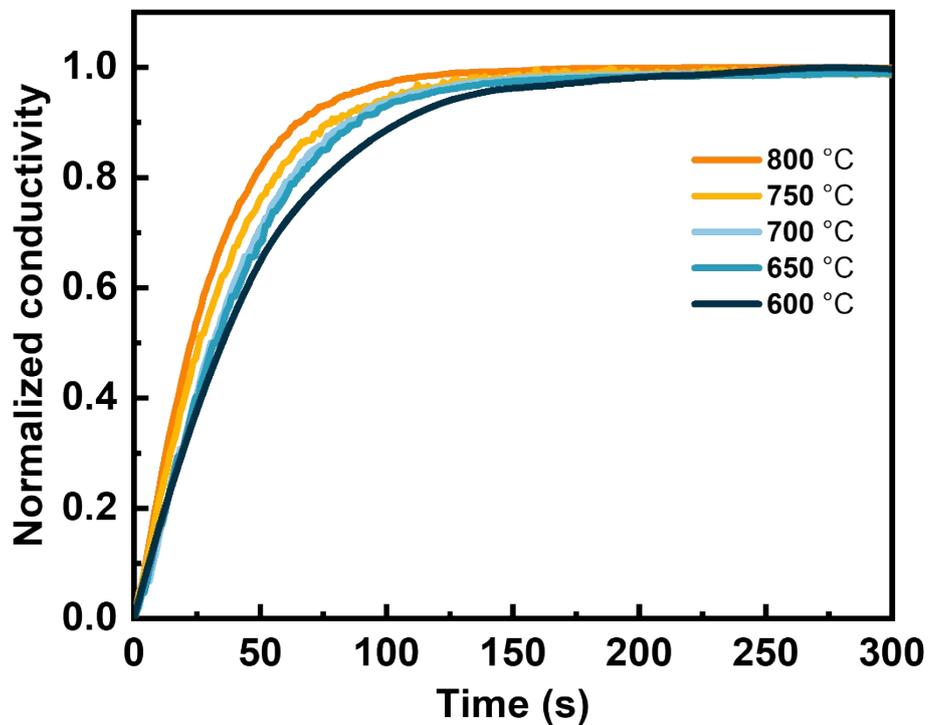
Figures S7. XPS spectra of Co 2p of LBSCCC-CeO<sub>2</sub> and LSC.



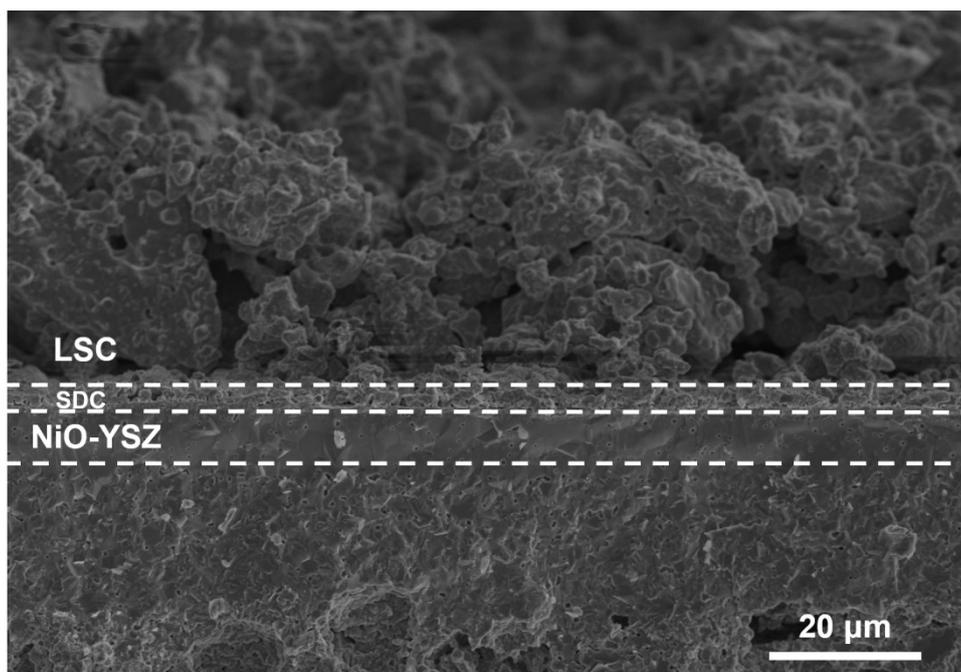
Figures S8. TG curves of LSC and LBSCCC-CeO<sub>2</sub> samples from room temperature to 1000 °C.



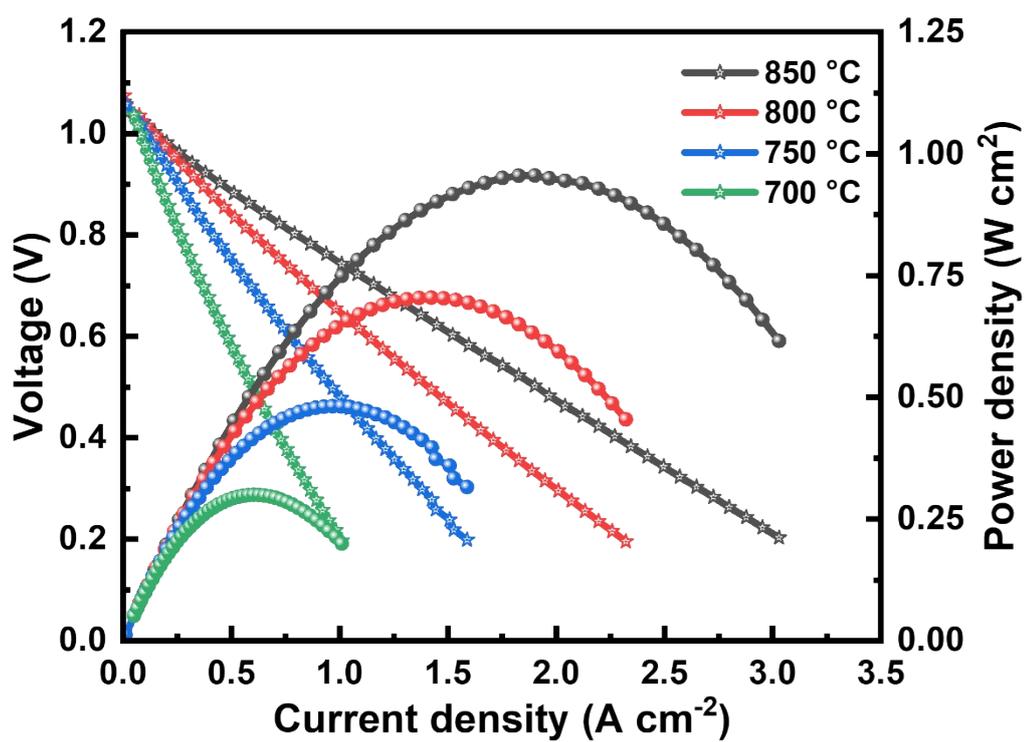
Figures S9. Electrical conductivity relaxation testing (ECR) for LSC materials.



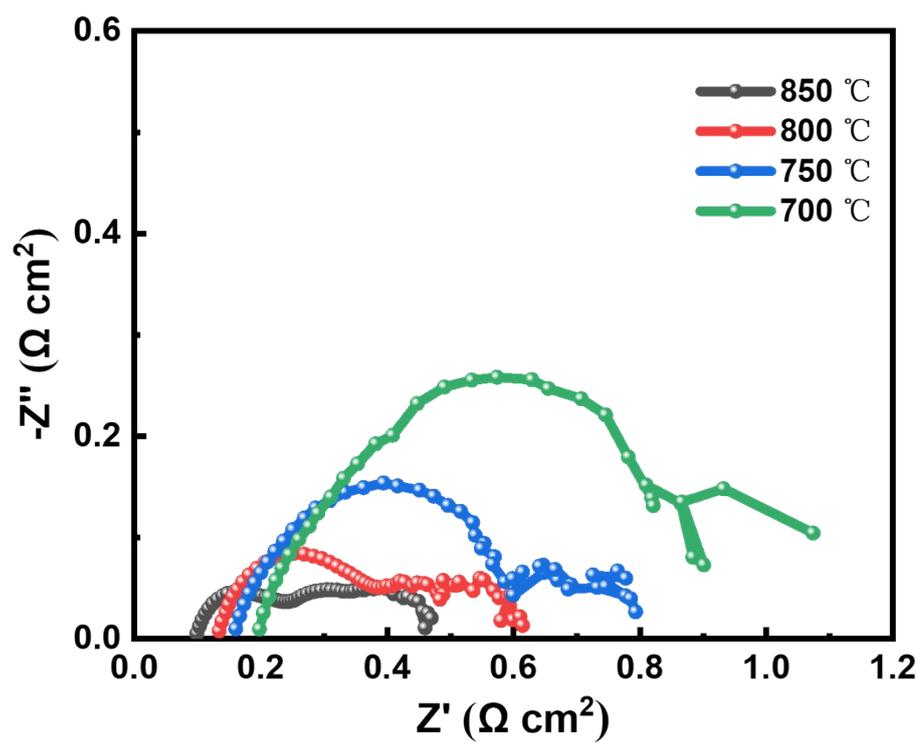
Figures S10. Electrical conductivity relaxation testing (ECR) for LBSCCC-CeO<sub>2</sub> materials.



Figures S11. Cross-sectional SEM image of single cell with LSC.



Figures S12. Peak power density (PPD) of single cell with LSC at 700-850 °C



**Figures S13.** Electrochemical impedance spectroscopy (EIS) of single cell with LSC at 700-850 °C.