Supporting Information

Ce^{3+} -induced in situ reconstruction of $LaFe_{0.7}Ni_{0.3}O_{3-\delta}$ into threephase nanocomposite cathode for IT-SOFCs

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1. Material and methods

1.1 Electrode powder preparation

La_{1-x}Ce_xFe_{0.7}Ni_{0.3}O_{3- δ} (x =0, 0.1, 0.2, 0.3, labeled as LFN, LCFN0.1, LCFN0.2, LCFN0.3, respectively), were synthesized by using ethylenediaminetetraacetic acid (EDTA)-citric acid (CA) sol-gel complexation method combined with high-temperature sintering. Nitrate was selected as the raw material for the cation source. Typically, La (NO₃)₃·6H₂O (Aladdin, 99.99%), Ce (NO₃)₃·6H₂O (Aladdin, 99.95%), Fe (NO₃)₃·9H₂O (Aladdin, 99.99%), and Ni (NO₃)₂·6H₂O (Aladdin, 98%) according to stoichiometric ratio were mixed and dissolved in 150 mL deionized water to obtain clear solution. Subsequently, EDTA and CA as the complexing agents were added into the above mixture with the molar ratio of the total metal ions/EDTA/CA of 1:1:2. The solution was thoroughly mixed at room temperature to ensure homogeneity. Following this, NH₃·H₂O was added dropwise for adjusting the pH of the solution to 8. After stirring at 80 °C for about 3 h, the dark purple gel was formed. The gel was then dried at 200 °C for 5 h to obtain the electrode powder.

The $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte was prepared by the co-precipitation method and more details have been reported in our previous work.

1.2 Cell Fabrication

The fabrication process of the symmetric cell for electrochemical impedance spectroscopy (EIS) measurements is described below. The SDC electrolyte was first pressed into disc with a diameter of 13 mm and a thickness of 0.4 mm, and then sintered at 1450 °C for 5 h in air. The synthesized electrode powder was mixed with organic additives (terpinol and ethyl cellulose) at a mass ratio of

1: 1.5 to form black slurry, which was then uniformly brushed to the electrolyte surface with an effective area of 0.39 cm², followed by calcination at 850 °C for 2 h in air. A silver paste (current collector) is applied to both sides of electrode surfaces and a silver wire is selected as the current lead.

In order to investigate the discharge characteristics of the synthesized cathode powders, a single cell supported by NiO-YSZ anode was prepared. NiO, 8YSZ and polymethyl methacrylate (99 %, M = 100) were firstly ball-milled according to a mass ratio of 6:4:1, and pressed to form pellets, which were then heated at 800 °C for 2 h in air to obtain mechanical strength as an anode support. The YSZ electrolyte layer was prepared by dip-coating method. The YSZ suspension was added dropwise to the surface of the anode support and sintered at 1400 °C for 5 h to form a dense electrolyte thin layer. Subsequently, the Gadolinia-Doped Ceria (GDC) solution was coated on the electrolyte YSZ surface and sintered at 1200 °C for 2 h to produce the GDC intermediate layer. Similarly, the cathode was prepared as the symmetrical cell and silver wires were attached to the cathode side using silver paste for current collector.

1.3 Electrochemical Measurements

Electrical conductivity relaxation (ECR) is utilized to determine the oxygen exchange coefficient (k_{chem}) and bulk diffusion coefficient (D_{chem}) for evaluating the ORR kinetics and understanding the oxygen transport properties of electrode materials in SOFC. To investigate the conductivity and conductivity relaxation of LFN and LCFN0.2 powders, a dense sample rod was prepared as follows: Firstly, polyvinyl alcohol (PVA) as a binder was added to the corresponding sample powders and milled for 2 h (the mass ratio of sample powder/PVA is 1:0.01). A rectangular stainless-steel mold at 2 MPa pressure was then used to uniaxially compress the ground powders to form long black strip, and sintered at 1400 °C in air for 5 h. Finally, the dense strip with a relative density of more than 97 % was prepared. Conductivity was measured in air by means of the DC four-probe method. The surface exchange coefficients (k_{chem}), which represent the reaction rate constants for ORR, and the chemical oxygen diffusion coefficients (D_{chem}) were estimated by ECR, which was measured using a Keithley 2450 digital source meter. This data was achieved by rapidly switching the atmosphere from air to pure oxygen, with a gas flow rate of 200 mL·min⁻¹.

The electrochemical characteristics of both symmetric and single cells were evaluated through the Energy-lab XM electrochemical workstation. To determine cathode performance, symmetrical cells were tested by exposing them to an in-air atmosphere. To evaluate the single-cell performance, the cell was sealed on an alumina ceramic tube, with the cathode surface exposed to ambient air, while the anode side was connected to a humidified H₂ stream (3 % H₂O). The fuel gas flow rate was 60 mL·min⁻¹. For (EIS) measurements, the frequency range was set to 1×10^{-6} to 1×10^{-1} Hz, and the bias voltage was established at 10 mV.

1.4 Characterizations

The physical structure of the prepared electrode powder was measured by X-ray diffraction (XRD, Bruker D8 advance (Germany Bruker)) using Cu-K α (λ =0.15406 nm) radiation in the range 20° to 80°. The chemical compatibility between the cathode and the electrolyte was demonstrated using a mixture of powders calcined in air at 1000 °C for 5 h. Transmission electron microscopy (TEM, JEOL 4000EX) was used to study the refined structure of the powders. The corresponding energy dispersive Spectrometer (EDS) maps were obtained using the equipped EDS analyzer. Thermo-gravimetric-analysis (TGA) is performed in air at a heating rate of 10 °C·min⁻¹ using a Thermal Gravimetric Analyzer (Netzsch STA 2500). The electron paramagnetic resonance (EPR) tests were carried out using a Bruker EMX Plus instrument from Germany. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo-Scientific K-Alpha device.

2. Supporting Figures and Table



Figure S1: (a) XRD of freshly prepared LFN and (b) refinement mapping; (c) LCFN0.1 and (d) LCFN0.3

refinement patterns.



Figure S2: Compatibility analysis of LCFN0.2 with electrolyte SDC after co-calcination at 1000 °C for 5 h.



Figure S3: SEM image of LFN



Figure S4: Particle distribution histogram of LCFN0.2.



Figure S5: EDS scanning results of LCFN0.2.



Figure S6: XPS spectra of O1s for (a) LFN and (b) LCFN0.2.



Figure S7: EIS of LFN and $La_{1-x}Ce_xFe_{0.7}Ni_{0.3}O_{3-\delta}$ (x = 0.1, 0.2, 0.3) at 700 °C & 650 °C



Figure S8: SEM image of single cell structure.



Figure S9: Compatibility analysis of LCFN0.2 with electrolyte GDC after co-calcination at 1000 °C for 5 h.

Table S1

	$\chi^{2=}$	=1.61, R _p =7.84%, R _{wp} =9.93	%
phase	phase 1 (M-LCFN)	Phase 2 (NiO)	Phase 3(CeO ₂)
Space group	P b n m	Fm - 3m	Fm - 3m
a (Å)	5.54663	4.17875	5.44901
b (Å)	5.56272	4.17875	5.44901
c (Å)	7.83755	4.17875	5.44901
V (Å ³)	241.823	72.969	161.79
quality ratio (%)	84.29	2.49	13.22

Refined lattice parameters of the LCFN0.2 samples.

Table S2

Refined lattice parameters of the LFN samples.

sample	LFN
Space group	P b n m
a (Å)	5.55571
b (Å)	7.84602
c (Å)	5.56036
V (Å ³)	242.377

Table S3

XPS fitting results of O1s in LFN and LCFN0.2 samples

sample	lattice oxygen (Olat) Area	surface oxygen defect (O _{ads}) Area	O_{ads} / $(O_{ads} + O_{lat})$ (at. %)
LFN	47811.26	80080.89	62.5
LCFN0.2	44616.94	81931.15	64.9

Table S4

Proportion of Ce, Ni and Fe valence states in LFN and LCFN0.2 samples, average valence states of Ce, Ni and Fe and approximate values of δ .

	Sample		LFN	LCFN0.2
	Ni 2p	Ni ²⁺	46.6	64.9
		Ni ³⁺	53.4	35.1
		Fe ²⁺	28.3	34.5
Quality ratio (%)	Fe 2p	Fe ³⁺	44.8	50.0
		Fe ⁴⁺	26.9	15.5
	Ce 3d	Ce ³⁺		15.8
		Ce^{4+}		84.2
	Ν	i	+2.53	+2.35
Average valence	F	e	+2.99	+2.70
	С	e		+3.84
	δ		0.07	0.12

Table S5

The R_{HF} , R_{IF} and R_{LF} values of LCFN0.2 cathodes were determined at 700 °C for different oxygen partial pressures.

Po2 (atm)	$R_{LF} (\Omega \cdot cm^2)$	$R_{IF} (\Omega \cdot cm^2)$	$R_{\rm HF} \left(\Omega \cdot cm^2 \right)$
0.1	0.0205	0.1920	0.1368
0.2	0.0134	0.1344	0.1144
0.4	0.0081	0.0933	0.0911
0.6	0.0064	0.0788	0.0859
0.8	0.0051	0.0679	0.0777

Table S6

ASR (Ω ·cm²) values corresponding to LFN and LCFN0.2 single-cell tests.

Sample	800 °C/ (Ω ·cm ²)	750 °C/ (Ω ·cm ²)	700 °C/ ($\Omega \cdot cm^2$)	650 °C/ (Ω ·cm ²)
LFN	0.212	0.326	0.654	1.292
LCFN0.2	0.134	0.190	0.285	0.507

Table S7

Peak power density of SOFC cathode perovskite materials reported to date.

Cathode	structure	peak power	Ref.
		density(W·cm ⁻²)	
Pr2Ni0.5Mn0.5O4-8	NiO+YSZ YSZ (10.5 $\mu m) GDC$ (6.7 $\mu m) cathode$	0.96(800 °C)	[1]
$La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_{3\text{-}\delta}$	NiO+YSZ YSZ (7.24 $\mu m) GDC$ (2.8 $\mu m) cathode$	0.91(750 °C)	[2]
$La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}\text{-}GDC$	NiO+YSZ YSZ (13.5 $\mu m) GDC$ (5.8 $\mu m) cathode$	0.73(750 °C)	[3]
La0.6Sr0.4Co0.2Fe0.8O3-8-	NiO+YSZ YSZ GDC cathode	1.6(800 °C)	[4]
$La_{0.6}Sr_{0.4}CoO_{3\text{-}\delta}$			
$La_{0.6}Sr_{0.4}Co_{0.4}Fe_{0.54}Ta_{0.06}O_{3}$	NiO+YSZ YSZ (11 µm) GDC (5.1 µm) cathode	1.11(750 °C)	[5]
Sm0.5Sr0.5Co0.93Bi0.07O3-8	NiO+SDC SDC (30.6 µm) cathode	1.16(800 °C)	[6]
Nd-doped SrFeO _{3-δ}	NiO+SDC SDC LSGM cathode	0.78(750 °C)	[7]
$Sr_{0.8}Fe_{0.8}Mo_{0.8}In_{0.1}O_{0.8}$	NiO+YSZ YSZ (7.9 μ m) SDC (1.72 μ m) cathode	1.46(800 °C)	[8]
$La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.3}O_{3\text{-}\delta}$	NiO+YSZ YSZ(11 μ m) GDC(3 μ m) cathode	2.36(800 °C),	This
		1.31(750 °C)	work

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