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Synergistic Ce/In Dual-Doping in La_{0.3}Sr_{0.7}FeO_{3-δ}: Breaking the Activity-Stability Trade-Off in SSOFCs Electrodes

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1. Experimental section

1.1. Materials synthesis

LSCeFIn-0.1 were synthesized by the sol-gel method. Briefly, the precursors of $La(NO_3)_3 \cdot 6H_2O$ (99.9% Aladdin, China), $(C_2H_3O_2)_2Sr$ (AR Aladdin, China), $Ce(NO_3)_3 \cdot 6H_2O$ (99.9% Aladdin, China), Fe(NO_3)_3 \cdot 9H_2O (99.9% Aladdin, China), and $In(NO_3)_3$ (99.9% Aladdin, China) were weighed in stoichiometric ratios and then dissolved in deionized water, and a small amount of anhydrous citric acid and EDTA was added subsequently. The obtained solution was magnetic stirred at 80°C until it became a gel. The prepared gel was dried at 200°C for 5 h and then ground into powder. Finally, the obtained powder was pre-calcined at 600°C in air for 4 h and then sintered at 1000°C for 5 h in a muffle furnace LSF, $La_{0.3}Sr_{0.7}Fe_{0.9}In_{0.1}O_{3-\delta}$ (LSFIn-0.1) was synthesized using the same method as LSCeFIn-0.1.

The electrolytes were prepared by dry compression. Commercial LSGM (WOW MATERIALS) powder was placed in a 15 mm mold, compressed at 2.5 MPa, and then fired in air at 1450°C for 5 h to form dense LSGM electrolytes.

1.2. Cell fabrication

In the fabrication of symmetric cells, powders of LSF, LSFIn-0.1, and LSCeFIn-0.1 were mixed with a binder solution (4 wt% hydroxyethyl cellulose) at a weight ratio of 1:1.5. The mixture was then manually milled for 30 minutes, resulting in the formation of a viscous slurry. To fabricate the SSOFCs, the prepared slurry uniformly applied to both sides of the LSGM electrolyte. The cells were then subjected to sintering at 1000°C for 2 h in ambient air. After sintering, Ag paste was applied to both surfaces of the electrolyte to ensure efficient current collection.

1.3. Characterization

X-ray diffraction (XRD, Rigaku TTR-III diffractometer Cu K α radiation, 40 kV, 40 mA) in the 2 θ range of 5° < 2 θ < 80°. The powdered LSF, LSFIn-0.1, and LSCeFIn-0.1 were reduced in an Ar-5% H₂ atmosphere at 800°C for 10 h, followed by XRD analysis to investigate phase stability. The fine structure of LSCeFIn-0.1 powders was observed using high-resolution transmission electron microscopy (HRTEM, JEM-2100). The microstructure of the single cell was observed by scanning electron microscopy (SEM, Zeiss, Gemini SEM500). Transmission electron microscopy (TEM, Talos F200X) was employed to examine the microstructure of the powders. Elemental surface analysis was performed by X-ray photoelectron spectroscopy (XPS,

Thermo Fisher Scientific ESCALAB 250Xi). Thermogravimetric analysis (TGA) was performed using a HITACHI STA7300, with a heating rate of 10°C ⋅min⁻¹, from room temperature to 1000°C under an air atmosphere. Electron Paramagnetic Resonance (EPR) was carried out on a Bruker EMXplus-6/1.

1.4. Electrochemical test

Electrochemical impedance spectroscopy (EIS), current-voltage-power (I-V-P) were conducted on a GAMRY INTERFACE 5000E electrochemical workstation. The symmetric cells were studied in hydrogen and air atmospheres, respectively, and the two electrodes were tested for AC impedance plots in the frequency range of 10^6 to 10^{-2} Hz with an amplitude of 10 mV at a fixed voltage to determine their catalytic performances for the anodic and cathodic reactions, The symmetric cell was further investigated in a single-cell model in which the cathodic side was exposed to ambient air while the anodic side was exposed to humidified hydrogen gas (3 vol% H₂O), at a flow rate of 50 mL·min⁻¹.



2. Figures and Supporting Table

Figure S1. Refined XRD patterns of (a) LSF and (b) LSFIn-0.1.



Figure S2. XRD patterns of LSFIn-0.1-LSGM composites.



Figure S3. XRD patterns of LSF, LSFIn-0.1, LSCeFIn-0.1 in 5% H₂/Ar.



Figure S4. a TGA curves of LSF, LSFIn-0.1 and LSFIn-0.1 powders in gas. b EPR spectra of $V_o^{"}$ in LSF, LSFIn-0.1, and LSCeFIn-0.1.



Figure S5. X-ray photoemission spectroscopy of LSF, LSFIn-0.1, LSCeFIn-0.1 samples before and after reduction in Ar-5% H_2 atmosphere in terms of O 1s.



Figure S6. X-ray photoemission spectroscopy of LSF, LSFIn-0.1, LSCeFIn-0.1 samples before and after reduction in Ar-5% H_2 atmosphere in terms of Fe 2p.



Figure S7. X-ray photoemission spectroscopy of LSCeFIn-0.1 samples before and after reduction in Ar-5% H_2 atmosphere in terms of Ce 3d.



Figure S8. Nyquist plot LSFIn-0.1 in 3% H₂O/H₂ atmosphere.



Figure S9. Nyquist plot of LSFIn-0.1 in air.



Figure S10. I-V-P curves of a LSFIn-0.1, b LSCeFIn-0.05, and c LSCeFIn-0.15, d contrasting line graph.



Figure S11. SEM image a anode b cathode after long-term operation.



Figure S12. LSCeFIn-0.1 XRD image after 300 h of operation.



Figure S13. LSCeFIn-0.1 EDS mapping image after 300 h of operation.

composition	Rp(%)	Rwp(%)	χ^2	Space group	a(Å)	b(Å)	c(Å)	Volume(Å ³)
LSF	2.13	3.22	2.04	R-3c	5.4802	5.4802	13.4053	348.66
LSFIn-0.1	6.54	8.53	1.62	R-3c	5.4974	5.4974	13.4717	351.72
LSCeFIn-0.1	6.57	8.27	1.39	R-3c	5.4739	5.4739	13.438	349.57

Table. S1 Refinement paraments of LSF, LSFIn-0.1 and LSCeFIn-0.1.

Table. S2 EIS for symmetric cell at 800-650°C and 3% H_2O/H_2 atmosphere

Sample	800°C	750°C	700°C	650°C
LSF	$0.322 \ \Omega \cdot cm^2$	$0.500 \ \Omega \cdot cm^2$	$0.808 \ \Omega \cdot cm^2$	$0.163 \ \Omega \cdot cm^2$
LSFIn-0.1	$0.188 \ \Omega \cdot cm^2$	$0.275 \ \Omega \cdot cm^2$	$0.540 \ \Omega \cdot cm^2$	$1.115 \ \Omega \cdot cm^2$
LSCeFIn-0.1	$0.097 \ \Omega \cdot cm^2$	$0.138 \ \Omega \cdot cm^2$	$0.308 \ \Omega \cdot cm^2$	$0.866 \ \Omega \cdot cm^2$

Table. S3 Fitting results of EIS for symmetric cell at 800°C and 3% H₂O/H₂ atmosphere

Sample	$\operatorname{Rp}(\Omega \cdot \operatorname{cm}^2)$	$R_L \left(\Omega \cdot cm^2 \right)$	$R_{I}(\Omega \cdot cm^{2})$	$R_{\rm H} \left(\Omega \cdot cm^2 \right)$
LSF	0.322	0.095	0.192	0.033
LSFIn-0.1	0.188	0.109	0.065	0.014
LSCeFIn-0.1	0.097	0.023	0.059	0.015

Table. S4 EIS for symmetric cell at 800-650°C and air atmosphere

Sample	800°C	750°C	700°C	650°C
LSF	$0.058 \ \Omega \cdot cm^2$	$0.12 \ \Omega \cdot cm^2$	$0.25 \ \Omega \cdot cm^2$	$0.6 \ \Omega \cdot cm^2$
LSFIn-0.1	$0.037 \ \Omega \cdot cm^2$	$0.063 \ \Omega \cdot cm^2$	$0.14 \ \Omega \cdot cm^2$	$0.33 \ \Omega \cdot cm^2$
LSCeFIn-0.1	$0.037 \ \Omega \cdot cm^2$	$0.066 \ \Omega \cdot cm^2$	$0.167 \ \Omega \cdot cm^2$	$0.404 \ \Omega \cdot cm^2$

Table. S5 Fitting results of EIS for a symmetric cell at 800°C and air atmosphere

Sample	$\operatorname{Rp}(\Omega \cdot \operatorname{cm}^2)$	$R_L \left(\Omega \cdot cm^2 \right)$	$R_{I} \left(\Omega \cdot cm^{2} \right)$	$R_{\rm H} \left(\Omega \cdot cm^2 \right)$
LSF	0.058	0.008	0.022	0.028
LSFIn-0.1	0.037	0.001	0.016	0.011
LSCeFIn-0.1	0.037	0.009	0.017	0.011

Cell configuration (Air electrode Electrolyte Fuel electrode)	Electrolyte thickness (µm)	PPD at 800°C (mWcm ⁻²)	Reference
LSF LSGM LSF	260	579	This work
LSFIn-0.1 LSGM LSFIn-0.1	260	832	This work
LSCeFIn-0.1 LSGM LSCeFIn-0.1	260	1049	This work
$Ce_{0.2}Sr_{0.8}Fe_{0.95}Ru_{0.05}O_{3-\delta} LSGM Ce_{0.2}Sr0_{.8}Fe_{0.95}Ru_{0.05}O_{3-\delta}$	320	846	1
$Pr_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta} LSGM Pr_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$	400	692 _(850°C)	2
$La_{0.3}Sr_{0.7}Fe_{0.9}Ti_{0.1}O_{3-\delta} LSGM La_{0.3}Sr_{0.7}Fe_{0.9}Ti_{0.1}O_{3-\delta}$	300	847	3
$SrCo_{0.2}Fe_{0.8}O_{3-\delta} LSGM SrCo_{0.2}Fe_{0.8}O_{3-\delta}$	300	719 _(850°C)	4
$Sr_2Ti_{0.8}Co_{0.2}FeO_6 LSGM Sr_2Ti_{0.8}Co_{0.2}FeO_6 $	270	555	5

Table S6. Comparison of the electrochemical performance of LSGM electrolyte-supported

 SSOFCs reported in the literature and in the present study

References

- 1. B. Li, S. He, J. Li, X. Yue, J. T. S. Irvine, D. Xie, J. Ni and C. Ni, ACS Catal., 2020, **10**, 14398-14409.
- 2. X. Sun, Y. Xia, B. Wang, B. Li, L. Ma, J. Chen and B. Chi, *Chem. Eng. J.*, 2024, **479**.
- 3. Y. Hou, L. Wang, L. Bian, Y. Wang and K.-c. Chou, *ACS Appl. Mater. Interfaces*, 2021, **13**, 22381-22390.
- 4. P. Li, B. Yang, J. Chen, B. Li, L. Ma, M. Wang, X. Sun, Y. Tian and B. Chi, *J. Mater. Chem. A*, 2024, **12**, 31895-31901.
- B. Niu, C. Lu, W. Yi, S. Luo, X. Li, X. Zhong, X. Zhao and B. Xu, *Appl. Catal. B Environ.*, 2020, 270, 118842.