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Supplementary Information

Cu-doped $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ as a highly active cathode for solid oxide electrolytic cells

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Experimental procedure

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) and $Sr_2Fe_{1.3}Cu_{0.2}Mo_{0.5}O_{6-\delta}$ (SFCM) powders were synthesized by using the combustion method [1]. Briefly, stoichiometric quantities of $Sr(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 5H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ metal salts were dissolved in an appropriate amount of deionized water and a certain proportion of citric acid. Then, glycine was added as a combustion promoter. The clarified solution was stirred in a water bath at 80 °C until it attained a sol-gel form and, then, the combustion was carried out in an oven at 250 °C for 1 h. After combustion, the as-received powder was ground and calcined in a muffle furnace at 950 °C for 4 h in air.

The crystal structure and phase analysis were performed by using X-ray diffractometer (XRD, Panalytical X'Pert Pro). The XRD data were analyzed by using the Rietveld refinement with GSAS program and EXPGUI interface. The microstructure of the as-prepared powders was observed by scanning electron microscopy (SEM, FEI QUANTA-250). The chemical composition and oxidation states of different atoms were analyzed by X-ray photoelectron spectroscopy (XPS, MULT1LAB2000, VG). The electrical conductivity was measured by using a Keithley 2400 source meter, following a four-probe method in a mixture of CO and CO_2 (1:1 *v*/*v*). Electrical conductivity relaxation (ECR) method was utilized to characterize the CO-CO_2 reactions, at 750 °C, with a digital multimeter (2400, Keithley) by using the four-point technique.[2] Moreover, surrounding atmosphere switching from 33%CO_2-67%CO to 50%CO_2-50%CO at a flow rate of 100 mL min^{-1}. The schematic diagram of the ECR experiment is presented in Fig. S6. CO_2-temperature programmed desorption (TPD) experiments were carried out by using a micromeritics apparatus (Chembet Pulsar TPR/TPD).

The electrochemical performance was measured by using LSGM ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$, Fuel Cell, USA), as the electrolyte, GDC ($Ce_{0.8}Gd_{0.2}0_{1.9}$, Fuel Cell, USA), as the barrier layer, and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFC, Fuel Cell, USA), as the anode. The electrochemical properties were assessed by assembling (GDC/SFCM)|LSGM|(GDC/SFCM) symmetrical cells and (SFCM/GDC)|LSGM| LSCF single-cell. Herein, the electrode materials were prepared by screen printing and sintered at 900 °C for 2 h. Electrochemical impedance spectroscopy (EIS) was carried out by using the symmetrical cell in CO/CO_2 mixture. The electrochemical workstation (Autolab 302N), with an AC amplitude of 10 mV, was used to collect EIS spectra, in the frequency range of 0.01 to 100 kHz, and *I-V* characteristics of a single-cell.

Oxygen ion transfer properties

The chemical bulk diffusion coefficient (D_{chem}) and surface exchange coefficient (k_{chem}) were obtained by fitting the electrical conductivity relaxation curves with Eq. (S1 and S2).

$$f(t) = \frac{\sigma(t) - \sigma(t)}{\sigma(\infty) - \sigma(0)} \tag{S1}$$

$$f(t) = 1 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\sum_{l=1}^{\infty} \frac{2L_x^2 exp(\frac{-\alpha_m^2 D_{chem} t}{x^2})}{\alpha_m^2(\alpha_m^2 + L_x^2 + L_x)} \times \frac{2L_y^2 exp(\frac{-\beta_n^2 D_{chem} t}{y^2})}{\beta_n^2(\beta_n^2 + L_y^2 + L_y)} \times \frac{2L_z^2 exp(\frac{-\gamma_l^2 D_{chem} t}{x^2})}{\gamma_m^2(\gamma_l^2 + L_z^2 + L_z)} \tag{S2}$$

where f (t) refers to the normalized conductivity, while σ (0), σ (t) and σ (∞) represent the initial, time-dependent and final conductivity, respectively. Eq. (S3) presents the calculation process of parameters L_x, L_y and L_z.

$$L_x = x\frac{k_{chem}}{D_{chem}}, L_y = y\frac{k_{chem}}{D_{chem}}, L_z = z\frac{k_{chem}}{D_{chem}} \tag{S3}$$

Herein, α_m, β_n and γ_l represent the mth, nth and 1th positive root of the transcendental Eq. (S4), respectively.

$$\alpha_m \tan \alpha_m = L_x, \beta_n \tan \beta_n = L_y, \gamma_l \tan \gamma_l = L_z \tag{S4}$$

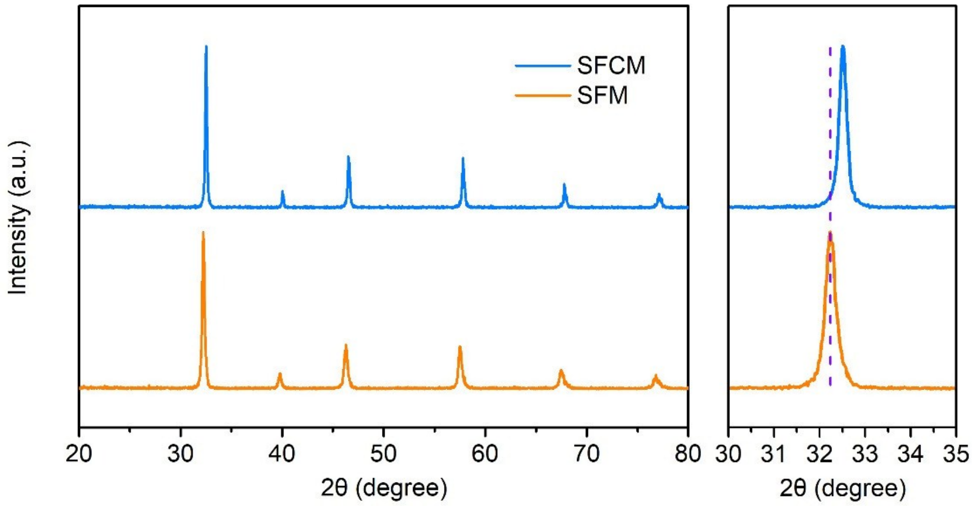

Fig. S1 XRD patterns of SFM and SFCM powders, calcined at 950 ^oC for 4 h.

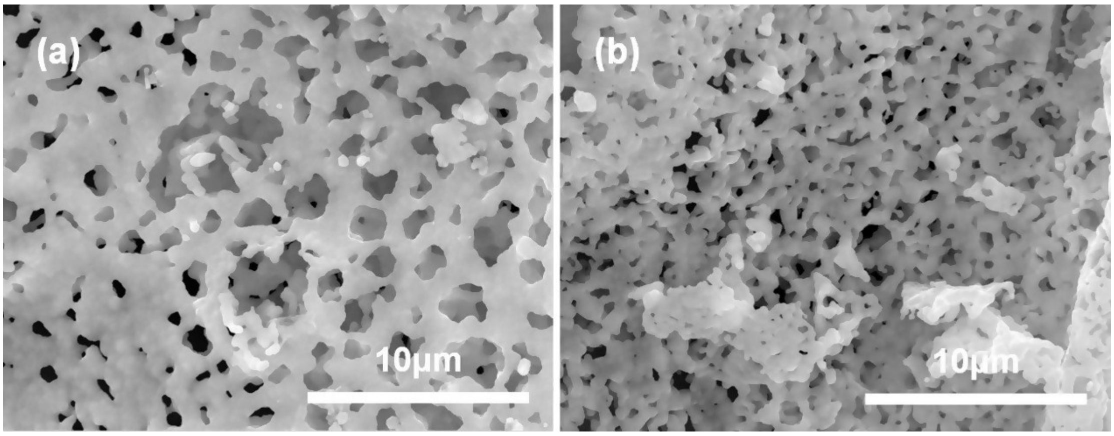

Fig. S2 SEM images of (a) SFCM and (b) SFM powders.

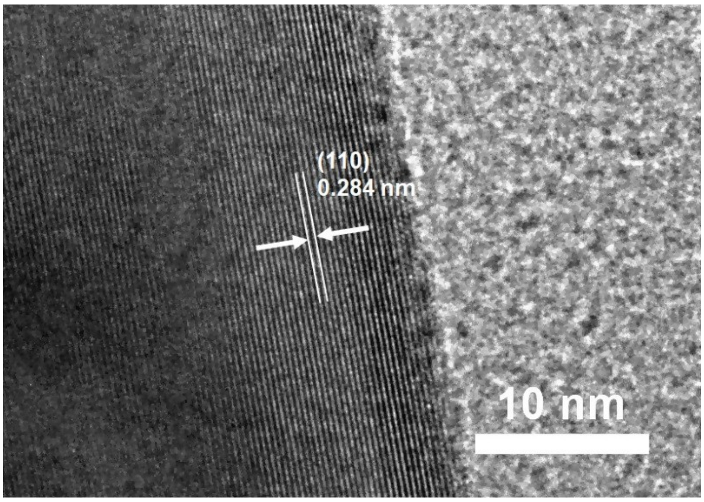

Fig. S3 HRTEM images of SFM powder.

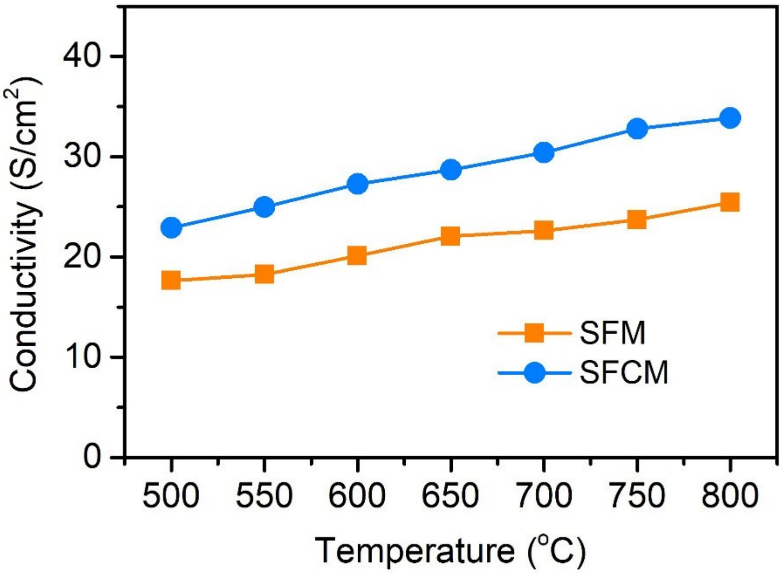

Fig. S4 Temperature-dependent electronic conductivity of SFCM and SFM samples, measured in the temperature range of 500 to 800 ^{o}C under CO/CO_2 environment (1:1 *v*/*v*).

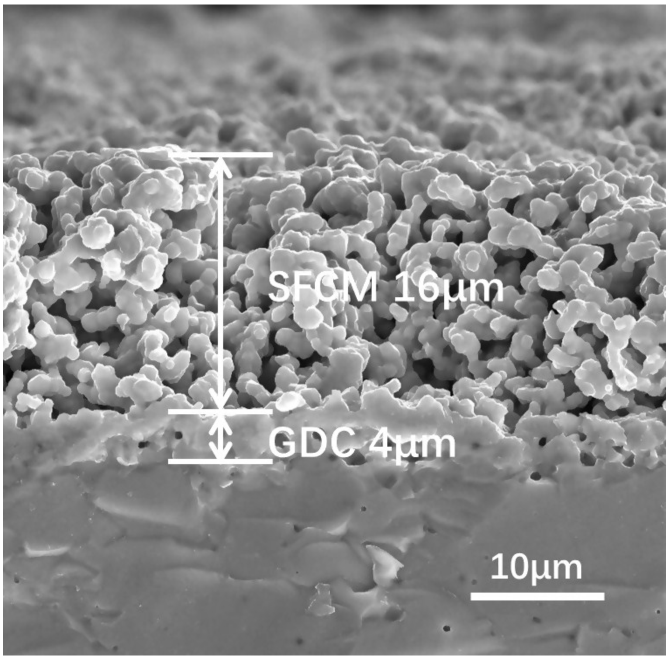

Fig. S5 Cross-sectional SEM image of the single-cell with SFCM cathode.

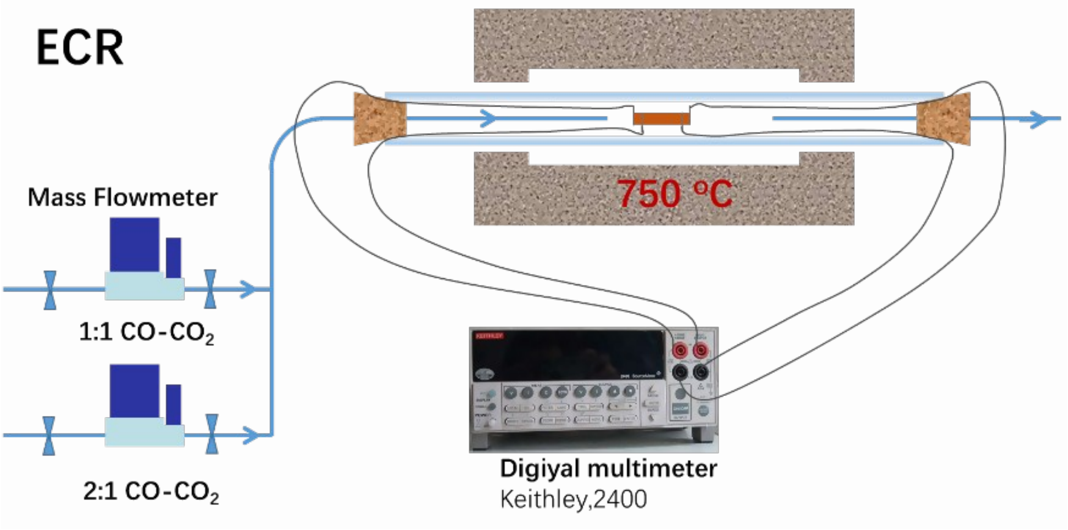

Fig. S6 Schematic illustration of the ECR measurement system.

Table S1 Comparison of the electrolysis current density, measured at 800 °C and 1.5 V, by using different cathode materials, including single-phase oxides and oxide-based composites.

Fuel electrode	**Feeding gas**	**Electrolyte//Oxygen electrode**	**Current density (A cm^{-2})**	**Ref.**
LSFT	CO_2	YSZ//LSFT	0.28	[3]
LSFN	CO_2–30%CO	YSZ//LSCF–GDC	0.75	[4]
LCFN	CO_2–50%CO	YSZ//LSM–YSZ	0.87	[5]
Ce-LSCrF	CO_2–30%CO	YSZ//LSCF	0.9	[6]
F-SFM	CO_2	LSGM//LSCF–SDC	1.36	[7]
GDC- SFM	CO_2	YSZ// LSM–YSZ	0.5	[8]
SFCM	CO_2	LSGM//LSCF–GDC	1.45	This work

LSM = $La(Sr)MnO_{3+\delta}$, SDC = $Ce(Sm)O_{2-\delta}$, LSFT = $La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O_{3+\delta}$, LSFN = $La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$, LCFN = $La_{0.9}Ca_{0.1}Fe_{0.9}Nb_{0.1}O_{3-\delta}$, GDC = $Ce(Gd)O_{2-\delta}$, LSTM = $La_{0.2}Sr_{0.8}Ti_{0.9}Mn_{0.1}O_{3-\delta}$, Ce-LSCrF = $La_{0.65}Ce_{0.05}Sr_{0.3}Cr_{0.5}Fe_{0.5}O_{3-\delta}$, F-SFM = $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}F_{0.1}$, SFM = $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$.

Table S2. Summary of Rietveld refinement results of $Sr_2Fe_{1.5}Cu_{0.2}Mo_{0.5}O_{6-\delta}$.

Sample	$Sr_2Fe_{1.5}Cu_{0.2}Mo_{0.5}O_{6-\delta}$
Space group	Pnma
Cell parameters	a = 5.538 b = 7.850 c = 5.553 $\alpha = \beta = \gamma = 90°$ Density = 5.330 $g \cdot cm^{-3}$
Riveted Refinement Parameters	$R_p = 4.87\%$ $R_{wp} = 7.85\%$ $\chi^2=1.961$

References

1. M. Hou, W. Sun, P. Li, J. Feng, G. Yang, J. Qiao, Z. Wang, D. Rooney, J. Feng and K. Sun, *Journal of Power Sources*, 2014, **272**, 759-765.
2. M. Zheng, W. Shuang, L. Mei and C. Xia, *Journal of Power Sources*, 2017, **345**, 165-175.
3. Z. Cao, B. Wei, J. Miao, Z. Wang, Z. Lü, W. Li, Y. Zhang, X. Huang, X. Zhu, Q. Feng and Y. Sui, *Electrochemistry Communications*, 2016, **69**, 80-83.
4. S. Liu, Q. Liu and J.-L. Luo, *Journal of Materials Chemistry A*, 2017, **5**, 2673-2680.
5. L. Liu, X. Zhou, Y. Wang, S. Li, R. Yin, X. Ji, X. Zhao and B. Li, *Electrochimica Acta*, 2017, **236**, 371-377.
6. Y. Zhang, J. Li, Y. Sun, B. Hua and J. L. Luo, *Acs Applied Materials & Interfaces*, 2016, **8**, 6457.
7. Y. Li, Y. Li, Y. Wan, Y. Xie, J. Zhu, H. Pan, X. Zheng and C. Xia, *Advanced Energy Materials*, 2019, **9**, 1803156.
8. H. Lv, Y. Zhou, X. Zhang, Y. Song, Q. Liu, G. Wang and X. Bao, *Journal of Energy Chemistry*, 2019, **35**, 71-78.