Supporting Information

Highly efficient CO₂ electrolysis to CO on Ruddlesden popper perovskite oxide with *in situ* exsolved Fe nanoparticles

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Table S1. Comparison of CO ₂ electro-conversion performance to CO over ceramic-based
cathodes with exsolved metal nanoparticles.

Catalyst	Exsolved element	Gas condition	Current density at 1.5 V (A·cm ⁻²)	Faraday efficiency (%)	Reaction time (hour)	Ref
La _{0.6} Sr _{0.4} Mn _{0.2} Fe _{0.8} O ₃	Fe	30% CO/CO ₂	2.04 (850 °C)	97.9	100	This work
$Sr_{1.9}Fe_{1.5}Mo_{0.4}Ni_{0.1}O_{6-\delta}$	Ni-Fe	100% CO ₂	ca. 2.16 (800°C)	98	500	[S1]
$La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$	Ni-Fe	30% CO/CO ₂	ca. 1.49 (850°C)	70	100	[S2]
$(La_{0.65}Sr_{0.3}Ce_{0.05})_{0.9}(Cr_{0.5}Fe_{0.5})_{0.85}Ni_{0.15}O_{3-\delta}$	Ni-Fe	30% CO/CO ₂	ca. 1.43 (850°C)	90.9	100	[S3]
$La_{0.6}Sr_{0.4}Co_{0.5}Ni_{0.2}Mn_{0.3}O_{3}$	Co-Ni	30% CO/CO ₂	1.08 (850°C)	97.8	90	[S4]
$La_{0.6}Sr_{0.4}Co_{0.7}Mn_{0.3}O_{3}$	Со	30% CO/CO ₂	1.03 (850°C)	97.4	12	[S5]
Sr ₂ Fe _{1.35} Mo _{0.45} Ni _{0.2} O _{6-δ}	FeNi ₃	5% N ₂ /CO ₂	ca. 0.890 (800°C)	97.5	40	[S6]
Sr ₂ Fe _{1.58} Mo _{0.5} O _{6-δ}	Fe	100 % CO ₂	ca. 0.860 (850°C)	85	100	[S7]
$Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$	Co-Fe	100 % CO ₂	ca. 0.830 (850°C)	87	100	[S8]
$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.85}Mn_{0.1}Ni_{0.05}O_{3+\delta}$	Ni	100 % CO ₂	ca. 0.440 (800°C)	96	100	[S9]
$(La_{0.75}Sr_{0.25})_{0.9}(Cr_{0.5}Mn_{0.5})_{0.9}Cu_{0.1}O_{3-\delta}$	Cu	100 % CO ₂	ca. 0.235 (800°C)	65	-	[S10]
$(La_{0.75}Sr_{0.25})_{0.9}(Cr_{0.5}Mn_{0.5})_{0.9}Ni_{0.1}O_{3-\delta}$	Ni	100 % CO ₂	ca. 0.190 (800°C)	80	21	[S11]

Temperature (°C)	$\frac{R_1}{(\Omega \cdot cm^2)}$	$\frac{R_2}{(\Omega \cdot cm^2)}$		
850	0.033	0.169		
800	0.120	0.218		
750	0.288	0.324		

 Table S2. Values of polarization resistance component in fitted equivalent circuit at OCV.



Fig S1. The SEM image of (a) cross-section of button cell (LSMF-GDC|LSGM|LSCF-GDC) and (b) porous structure of LSMF-GDC electrode.



Fig S2. XRD pattern of grounded LSGM pellet measured after twice-sintered process (XRD measurement condition: 40kV and 30 mA).



Fig S3. Schematic diagram of SOEC test reactor for high temperature CO_2 electrolysis.



Figure S4. XRD pattern of oxidized Fe-R.P.LSMF in the 2θ range from 20 ° to 40 °.



Fig S5. First derivatives of (a) Fe K-edge and (b) Mn K-edge XANES spectra of reference oxides, LSMF and Fe-R.P.LSMF.



Fig S6. XRD patterns of LSMF after treated in 20% H_2/N_2 atmosphere from room temperature to 900 °C.



Figure S7. The cross-sectional SEM image of button cell after reduction process.



Fig S8. EIS profiles and its fitted data of inserted equivalent circuit at OCV with respect to temperatures of (a) 850 °C, (b) 800 °C, and (c) 750 °C.



Fig S9. EIS profiles under OCV and operating voltage of 1.5 V at temperatures of (a) 850 °C, (b) 800 °C, and (c) 750 °C.



Fig S10. The voltage profile of the button cell during 13h operation with an applied constant current of $1.8 \text{ A} \cdot \text{cm}^{-2}$ in a pure CO₂ at 850 °C.

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