Supporting Information

Robust CO_2 Electrolysis via In-situ Interfacial Engineering with Exsolved Fe Nanoparticles on a Perovskite Cathode

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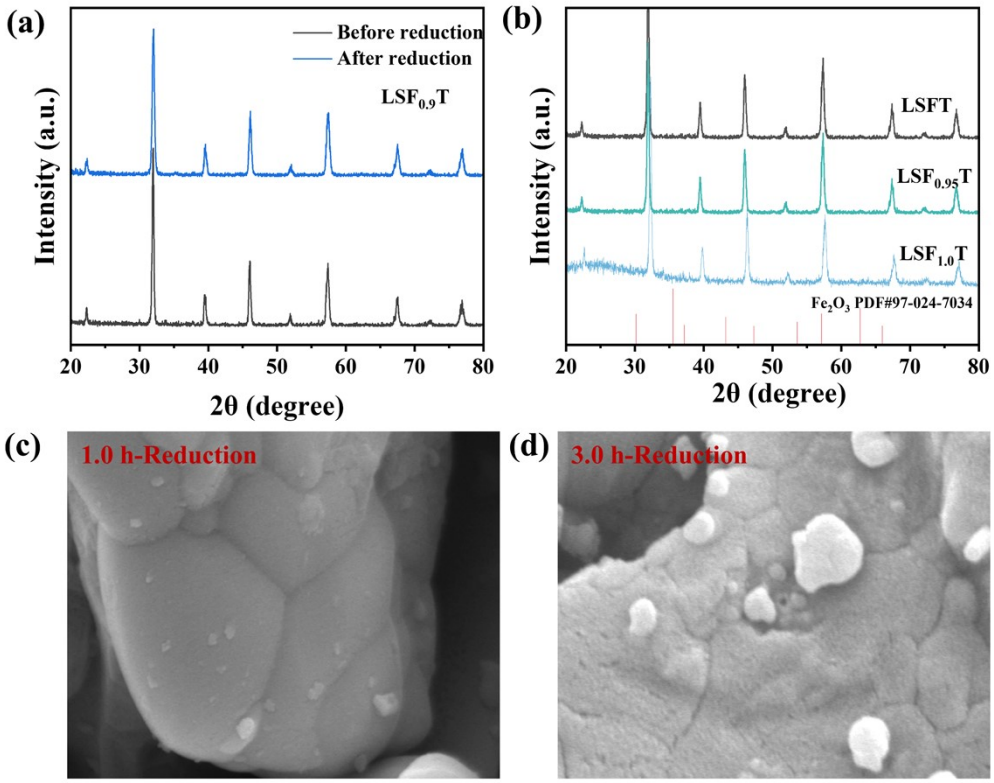

Fig. S1 (a) XRD patterns of $La_{0.6}Sr_{0.4}Fe_{0.9}Ti_{0.2}O_{3-\delta}$ ($LSF_{0.9}T$) before and after reduction. (b) XRD patterns of $La_{0.6}Sr_{0.4}Fe_{0.8}Ti_{0.2}O_{3-\delta}$ (LSFT), $La_{0.6}Sr_{0.4}Fe_{0.95}Ti_{0.2}O_{3-\delta}$ ($LSF_{0.95}T$) and $La_{0.6}Sr_{0.4}Fe_{1.0}Ti_{0.2}O_{3-\delta}$ ($LSF_{1.0}T$). SEM images of $LSF_{0.95}T$ after (c) 1h and (d) 3 h reduction under 20% H_2-80% Ar at 850 °C.

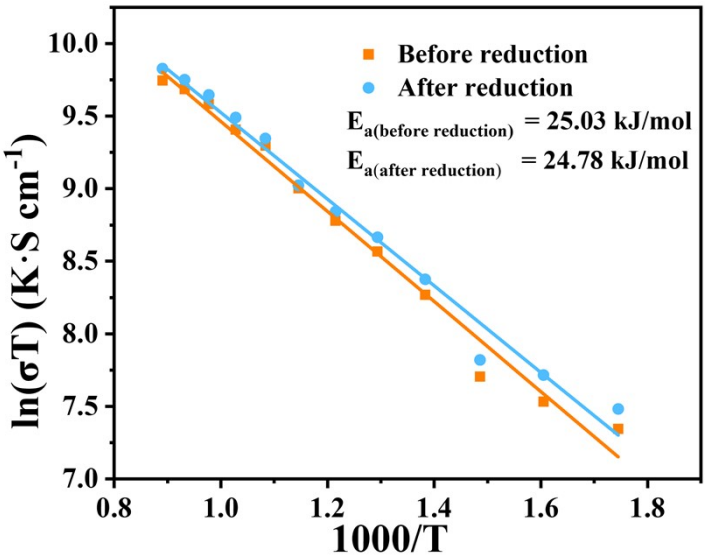

Fig. S2 Arrhenius plots of electrical conductivity for $LSF_{0.95}T$ and R-$LSF_{0.95}T$ in CO_2:CO = 1:1

Table S1 Percentages of Fe valence distribution determined by Fe $2p_{3/2}$ XPS fitting.

Sample	Percentage				Average valence
	Fe^{4+}	Fe^{3+}	Fe^{2+}	Fe^{0}	
$LSF_{0.95}T$	22.70%	52.76%	24.54%	/	2.98
R-$LSF_{0.95}T$	21.34%	35.90%	41.19%	1.57%	2.75

Table S2 Percentages of relative content of oxygen species determined by O 1s XPS fitting.

Sample	Percentage			
	O1	O2	O3	O2/O1
$LSF_{0.95}T$	43.87%	49.05%	7.08%	1.12
R-$LSF_{0.95}T$	39.25%	52.87%	7.88%	1.35

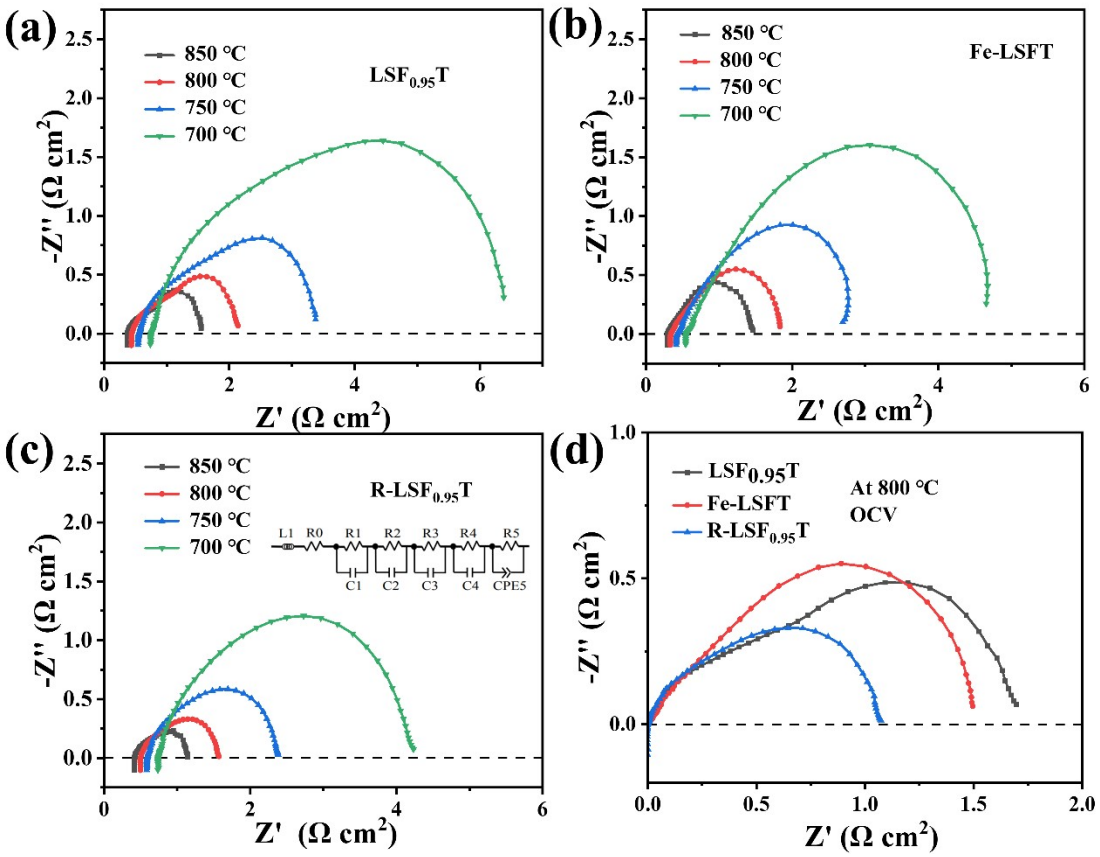

Fig. S3 EIS curves of cells (LSGM electrolyte, LSCF anode) with (a) $LSF_{0.95}T$, (b) Fe-LSFT or (c) R-$LSF_{0.95}T$ cathodes at 700-850℃and (d) at 800℃.

Table S3 Values of polarization resistance components obtained by equivalent circuit fitting (Ω cm^2).

samples	R_1	R_2	R_3	R_4	R_5
$LSF_{0.95}T$	0.018	0.088	0.236	0.327	1.009
Fe-LSFT	0.018	0.080	0.163	0.202	1.093
R- $LSF_{0.95}T$	0.014	0.063	0.120	0.186	0.671

Table S4 Current densities of SOECs with in-situ exsolved cathodes for CO_2 electrolysis at 800 °C and 1.5 V.

Cathode	Electrolyte//Anode	Current density (A cm^{-2})	Ref.
Cu-$(La_{0.75}Sr_{0.25})_{0.9}Cr_{0.45}Mn_{0.45}Cu_{0.1}O_{3-\delta}$	YSZ (400μm)// LSCrM-SDC	0.24	[38]
$FeNi_3$-$La_{0.67}Sr_{0.33}Fe_{0.6}Ni_{0.067}Ti_{0.33}O_{3-\delta}$	LSGM (330μm)//LSC	0.38	[39]
Ni-$(La_{0.75}Sr_{0.25})_{0.9}(Cr_{0.5}Mn_{0.5})_{0.9}Ni_{0.1}O_{3-\delta}$	YSZ (300μm)// LSM-SDC	0.2	[40]
Ni-$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.85}Mn_{0.1}Ni_{0.05}O_{3+\delta}$	YSZ (300μm)//LSM-SDC	0.45	[15]
Fe-$(Ce_{0.08}La_{0.52}Sr_{0.3})C_{0.5}Fe_{0.5}O_{3-\delta}$	YSZ(120μm)//LSCF-SDC	1.05	[41]
Fe-$La_{0.5}Sr_{0.5}FeO_{3-\delta}$	LSGM (250μm)//LSCF	1.13	[42]
CoFe- $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$	LSGM (250μm)//BSCF	1.21	[12]
CoFe-$Sr_2Fe_{1.35}Mo_{0.45}Co_{0.2}O_{6-\delta}$	LSGM (300μm)//BSCF	0.82	[43]
R-$LSF_{0.95}T$	LSGM (300μm)//LSCF	0.78	This work

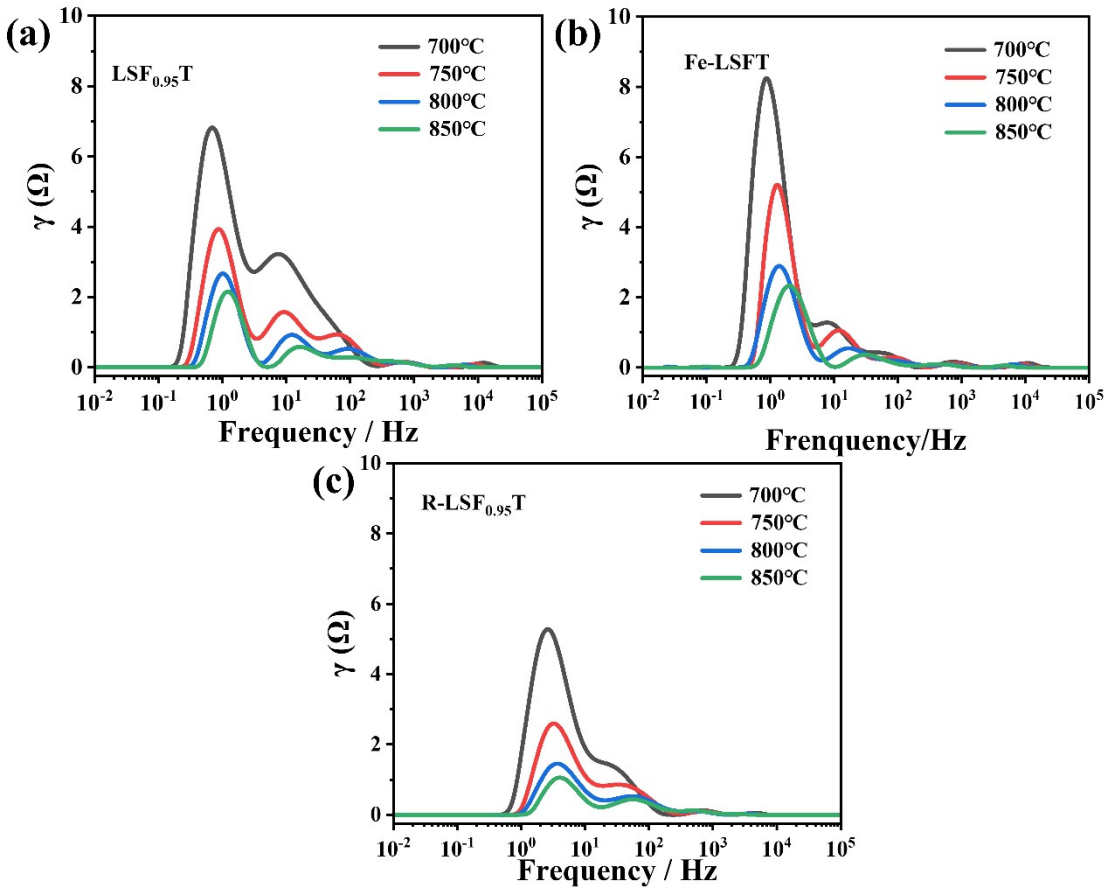

Fig. S4 DRT analysis on R_p of (a) $LSF_{0.95}T$, (b) Fe-LSFT or (c) R-$LSF_{0.95}T$ at 700-850 °C.

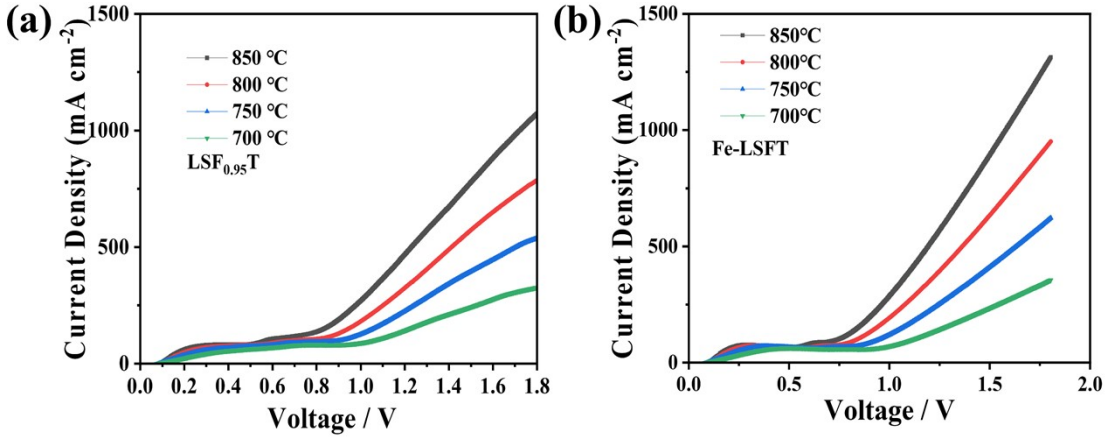

Fig. S5 LSV curves of cells with (a) $LSF_{0.95}T$ and (b) Fe-LSFT cathode at 700-850 °C.