## Supplementary information

## Highly efficient and stable perovskite cathode with *in-situ* exsolved NiFe alloy nanoparticles for CO<sub>2</sub> electrolysis

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**Fig. S1** (a) XRD patterns of LSCrF, LSCrFN and NiFe@LSCrFN. (b) Enlarged XRD patterns at 30-36° of (a).



Fig. S2 XPS spectra of Cr 2p for LSCrFN and NiFe@LSCrFN.



Fig. S3 TPR profiles in hydrogen for LSCrFN and LSCrF sample.



Fig. S4 The impedance spectra of Cell-2 before and after the stability test.





(d) Cathode-3 after stability test.



**Fig. S6** Electrical conductivity relaxation curves of (a) LSCrFN-YSZ and (b) NiFe@LSCrFN-YSZ at 650-800°C

sample	Ni <sup>0</sup> (at%)	Ni <sup>2+</sup> (at%)
LSCrFN	0	100
NiFe@LSCrFN	33.3	72.2

Table S1 XPS analysis of Ni 3p for the LSCrFN and NiFe@LSCrFN.

**Table S2** XPS analysis of Fe 2p for the LSCrFN and NiFe@LSCrFN.

sample	Fe <sup>0</sup> (at%)	Fe <sup>3+</sup> (at%)	Fe <sup>2+</sup> (at%)
LSCrFN	0	61.9	38.1
NiFe@LSCrFN	6.6	54.9	38.5

sample	Cr <sup>6+</sup> (at%)	Cr <sup>4+</sup> (at%)	Cr <sup>3+</sup> (at%)
LSCrFN	28.5%	16.7%	54.8%
NiFe@LSCrFN	0	24.3%	75.7%

 Table S3 XPS analysis of Cr 2p for the LSCrFN and NiFe@LSCrFN.

Table S4 XPS analysis of *O* 1s for the LSCrFN and NiFe@LSCrFN.

sample	O <sub>L</sub> (at%)	O <sub>V</sub> (at%)	O <sub>C</sub> (at%)
LSCrFN	46.3	25.3	28.4
NiFe@LSCrFN	41.0	35.3	23.7

**Table S5** Comparison of performance at 800°C and 1.5 V for direct  $CO_2$  electrolysis of Cell-2 with other SOECs.

Fuel electrode	Exsolved nanoparticles	Electrolyte	Current	Polarization	
		Thickness	density	resistance	Refs
		(µm)	$(A \cdot cm^{-2})$	$(\Omega \cdot cm^2)$	
LSCMC-SDC	Cu	YSZ (50)	0.25	0.50 at 2 V	[1]
LSTMN-YSZ	Ni	YSZ (46)	0.075	2.20 at 1.6V	[2]
LSTCN1-SDC	Ni	YSZ (28)	0.4	0.51 at 1.6 V	[3]
LSTCN2-SDC	Ni	LSGM	0.6	0.43 at 1.6 V	٢/٦
		(55.5)			[4]
LCFN-GDC	NiFe	YSZ (300)	0.9	0.40 at 1.3V	[5]
LSCrFN-YSZ	NiFe	YSZ (13)	1.15	0.27@1.5V	This
					work

Notes: LSCMC =  $(La_{0.75}Sr_{0.25})_{0.9}(Cr_{0.5}Mn_{0.5})_{0.9}Cu_{0.1}O_{3-\delta}$ ,

$$\begin{split} & \text{LSTMN} = (\text{La}_{0.2}\text{Sr}_{0.8})_{0.9}(\text{Ti}_{0.9}\text{Mn}_{0.1})_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}, \\ & \text{LSTCN1} = (\text{La}_{0.2}\text{Sr}_{0.8})_{0.95}\text{Ti}_{0.85}\text{Cr}_{0.1}\text{Ni}_{0.05}\text{O}_{3+\delta}, \\ & \text{LSTCN2} = (\text{La}_{0.2}\text{Sr}_{0.8})_{0.85}\text{Ti}_{0.8}\text{Cr}_{0.1}\text{Ni}_{0.1}\text{O}_{3-\delta}, \\ & \text{LCFN} = \text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}, \\ & \text{SDC} = \text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}, \\ & \text{LSGM} = \text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta} \end{split}$$

## References

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