## **Supplementary Materials**

## Composite of Perovskite and Fluorite Fuel Electrodes for Efficient Carbon Dioxide electrolysis in Solid Oxide Electrolyzer Cells

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Fig. S1 - XPS spectra of O 1s on (a) SFM-SDC, (b) SFM-CMF, (c) CMF electrodes.



Fig. S2 - XPS spectra of Mn 2p on (a) SFM-CMF, (b) CMF electrodes.



Fig. S3 - XPS spectra of Ce 3d on (a) SFM-SDC, (b) SFM-CMF, (c) CMF electrodes.



Fig. S4 - XPS spectra of Fe  $2p_{3/2}$  on (a) SFM-SDC, (b) SFM-CMF, (c) CMF electrodes.



Fig. S5 - XPS spectra of Mo  $3d_{5/2}$  on (a) SFM-SDC, (b) SFM-CMF electrodes.

 Table S1 - Atomic ratio of Fe ions at different valence-states in SFM-CMF (weigh ratio = 6:4) electrodes.

	Fe <sup>4+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Average valence
Theoretical	44 at. %	34 at. %	22 at. %	3.2
Practical	56 at. %	29 at. %	15 at. %	3.4

Theoretical: Mathematical calculation, data from XPS results of SFM  $^{1}$  and CMF (Fig. - S5)

Practical: XPS characterization result. (Fig. 3d)



**Fig. S6** - EIS of cells from OCV to1.4 V at 1073 K with **(a)** SFM-CMF, **(b)**SFM-SDC, **(c)**CMF, **(d)** SDC as cathode

Cells configuration	R <sub>p</sub> (Ω cm <sup>-2</sup> )	Current Density (A cm <sup>-2</sup> )	Durability	References
Ni-YSZ YSZ RuO2@LSM-YSZ	~0.4	0.927	Unstable.	2
FeNi3@SFMN-GDC LDC/LSGM	0.42	0.93	18% degradation under 0.934 A cm <sup>-2</sup> for 20min	3
LSCF-GDC				
SFM-SDC LDC/LSGM LSCF-SDC	0.19@1.5V	1.09	Relatively stable under ~1 A cm <sup>-2</sup> for 20min	1
CoFe@SFMC-GDC LDC/LSGM	0.12	1.20	Stable under ~1 A cm <sup>-2</sup> for 20min	4
BSCF-GDC				
SFNM+1.2Fe-GDC GDC/LSGM	0.2453	1.13	~30% degradation under ~1 A cm <sup>-2</sup> for 40 hour	5
LSCF-GDC (850℃)	(CO/CO <sub>2</sub> )			
RuFe@SFRuM-GDC LSGM  BSCF-	0.11	2.25	~30% degradation under ~0.6 A cm <sup>-2</sup> for 100 hour	6
GDC				
Ni-Fe-LSFM LSGM BLC	~2	2.32	Conduct 100h electrolysis at 0.5A	7
CoFe@LSCFM-GDC LDC/LSGM	0.15	2.40	~30% degradation under ~0.6 A cm <sup>-2</sup> for 100 hour	8
BSCF-GDC				
SFM-CMF LSGM  SSC-SDC	0.089	3.02	13.4% degradation under ~1.0 A cm <sup>-2</sup> for 40 hour	This work
	(CO/CO <sub>2</sub> )			

**Table S2.** Comparison of the properties with state-of-the-art electolyzers for pure  $CO_2$  electrolysis at 1073K. Polarization resistances ( $R_p$ ) was collected at 1.2 V, and current density at 1.6 V.

## References

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