Supporting Information

Electronic engineering and oxygen vacancy modification of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ perovskite oxide by low-electronegativity sodium doping for efficient reversible CO_2/CO fueled solid oxide cells

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Totally 18 figures and 5 tables

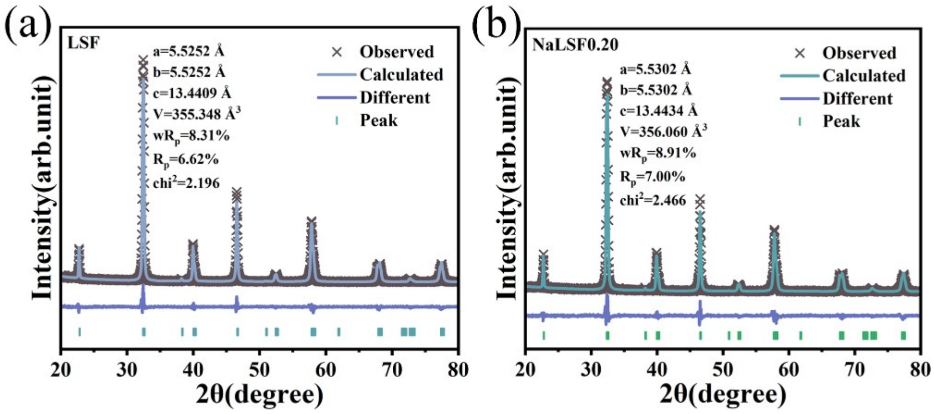

Fig. S1. The profiles of XRD refinement of a) LSF and b) NaLSF0.20 powders.

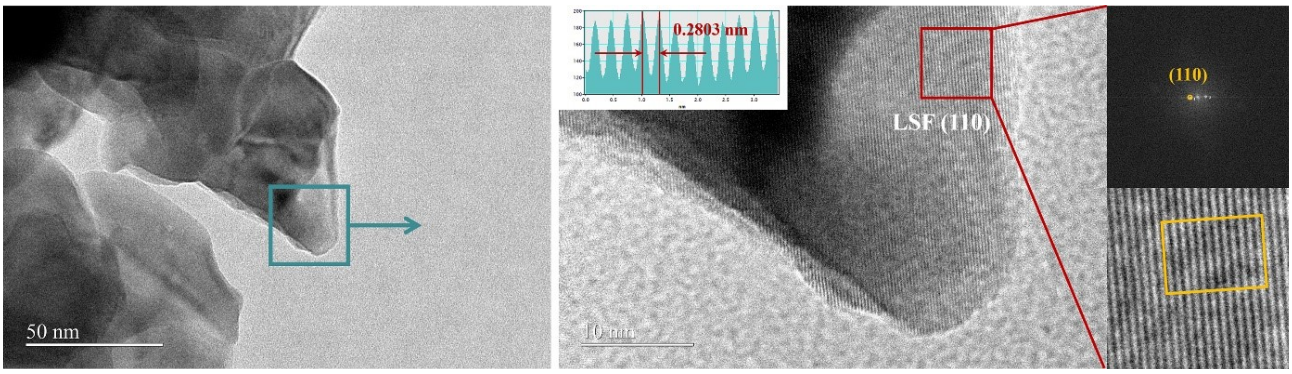

Fig. S2. HR-TEM microscope of LSF powder.

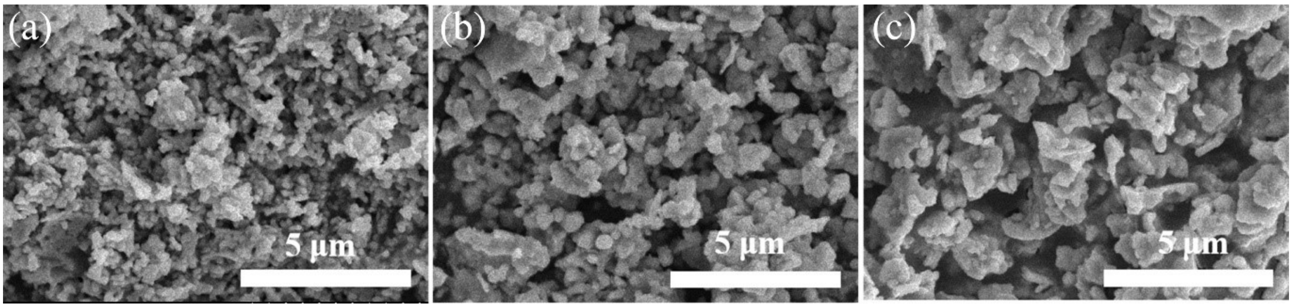

Fig. S3. The SEM of microscope structure of a) LSF, b) NaLF0.10, and c) NaLSF0.20 powders.

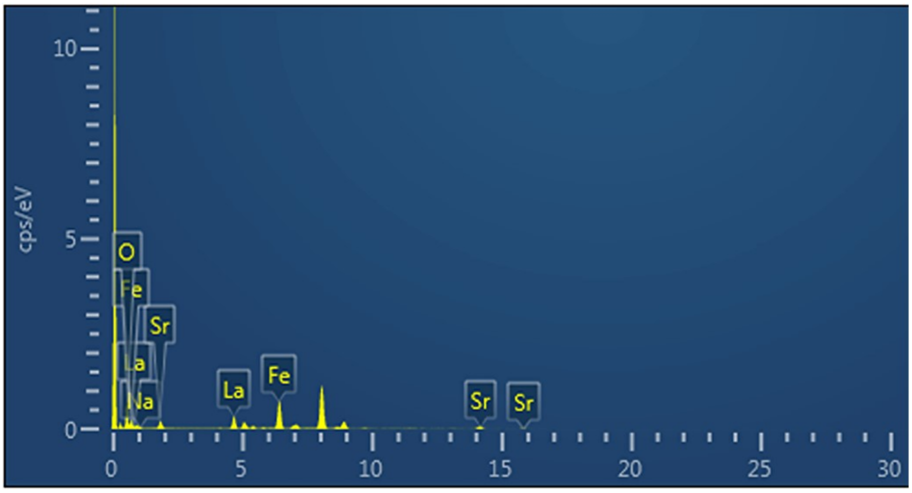

Fig. S4. Elements' content obtained by EDX.

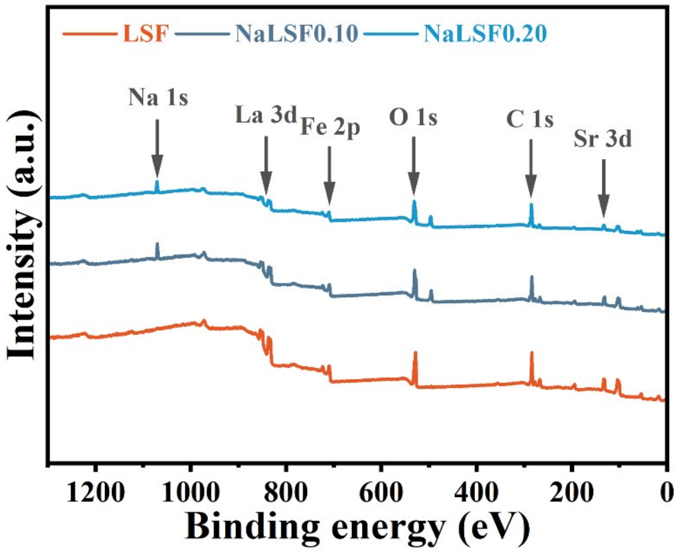

Fig. S5. XPS full survey spectra of all powders.

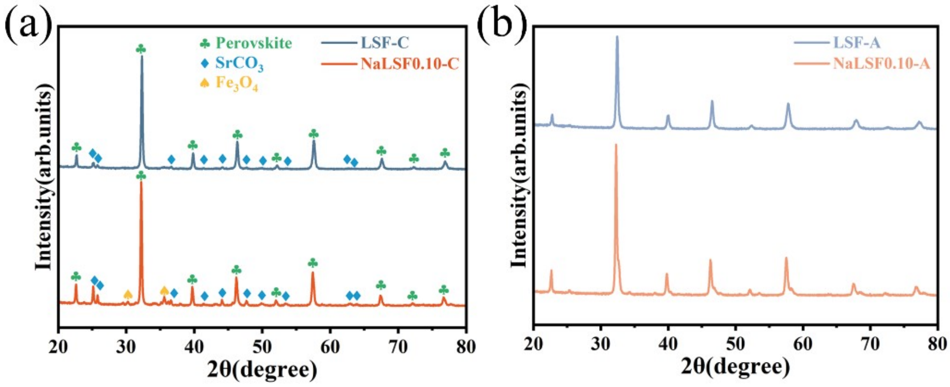

Fig. S6. Physical properties of LSF and NaLSF0.10: a) XRD patterns after sintered at 50% CO-CO_2 atmosphere, b) XRD patterns of both samples in Figure 4a after successively sintered under air atmosphere for 10 h.

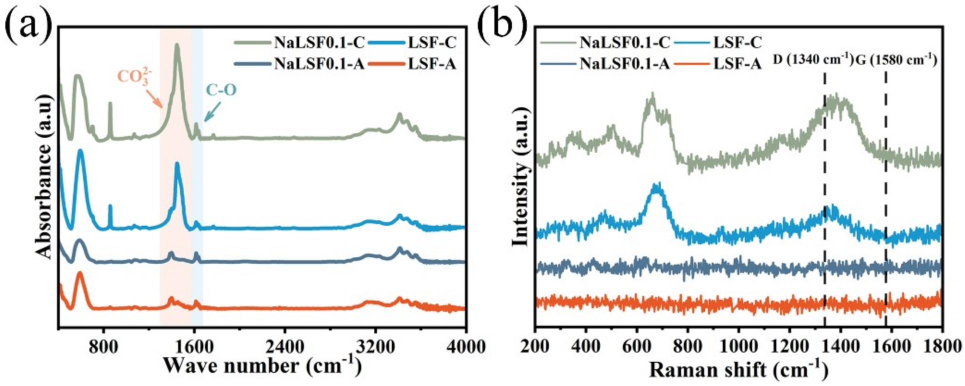

Fig. S7. Chemical properties of LSF and NaLSF0.10 after sintered at 50% CO-CO_2 atmosphere and air atmosphere for 10 h: a) the Fourier infrared spectra, b) Raman spectra.

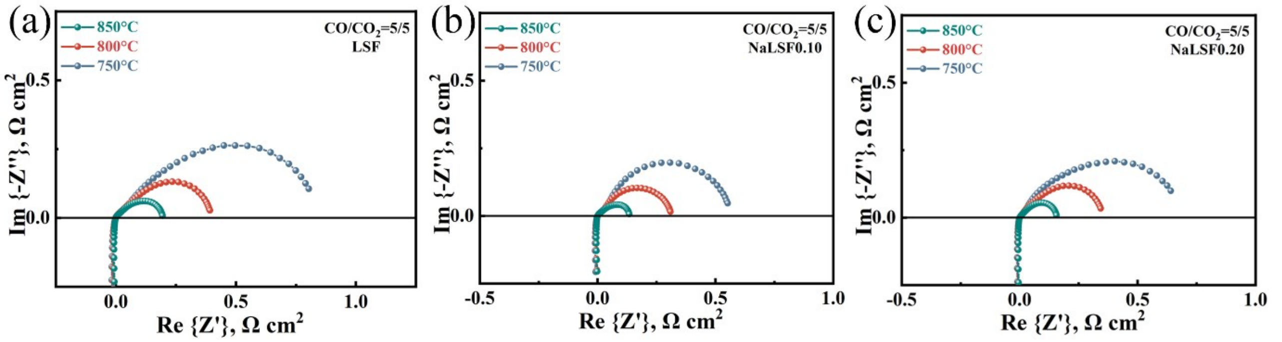

Fig. S8. EIS curves of symmetrical cells with a) LSF, b) NaLSF0.10, and c) NaLSF0.20 cathodes from 750 ℃ to 850 ℃ at 50% CO-CO_2 atmosphere.

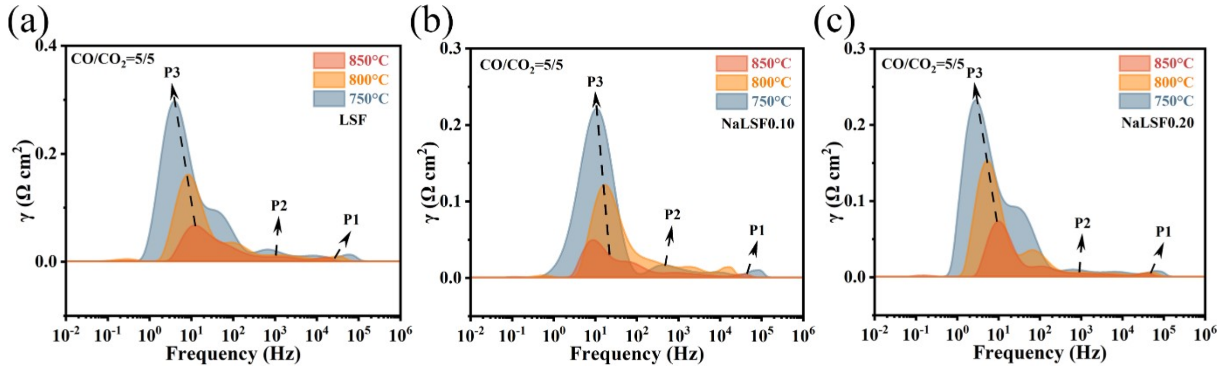

Fig. S9. DRT curves of symmetrical cells with a) LSF, b) NaLSF0.10, and c) NaLSF0.20 cathodes from 750 ℃ to 850 ℃ at 50% CO-CO_2 atmosphere.

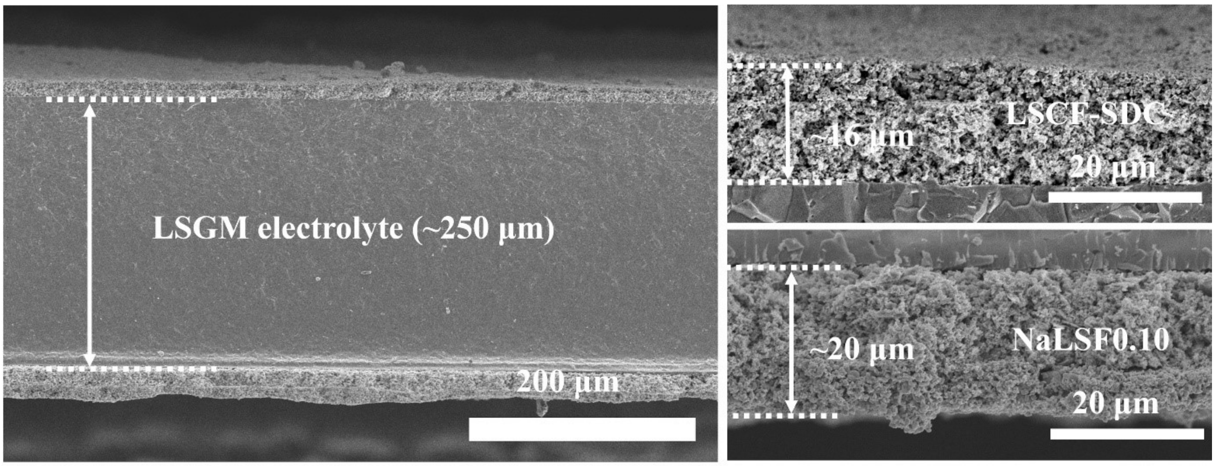

Fig. S10. SEM images of the cross-sectional of SOECs before the test with NaLSF0.10 cathode and LSCF-SDC anode.

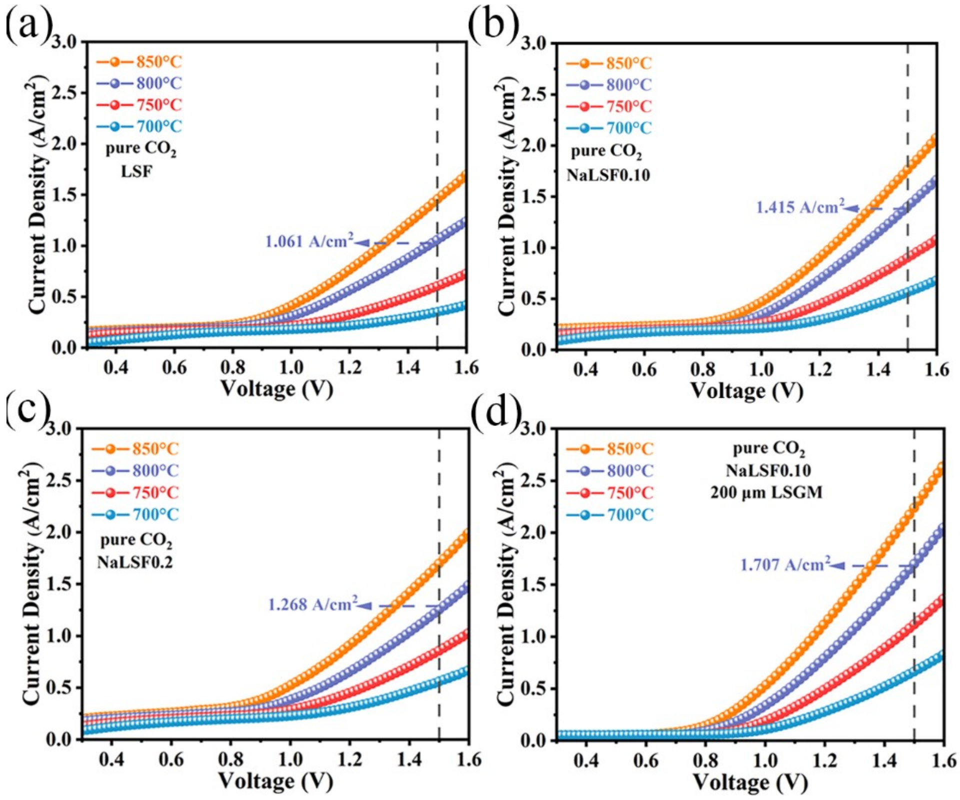

Fig. S11. I-V curves of SOECs with a) LSF, b) NaLSF0.10, c) NaLSF0.20, and d) NaLSF0.10 (200 μm electrolyte) cathodes from 700 ℃ to 850 ℃ in pure CO_2 atmosphere.

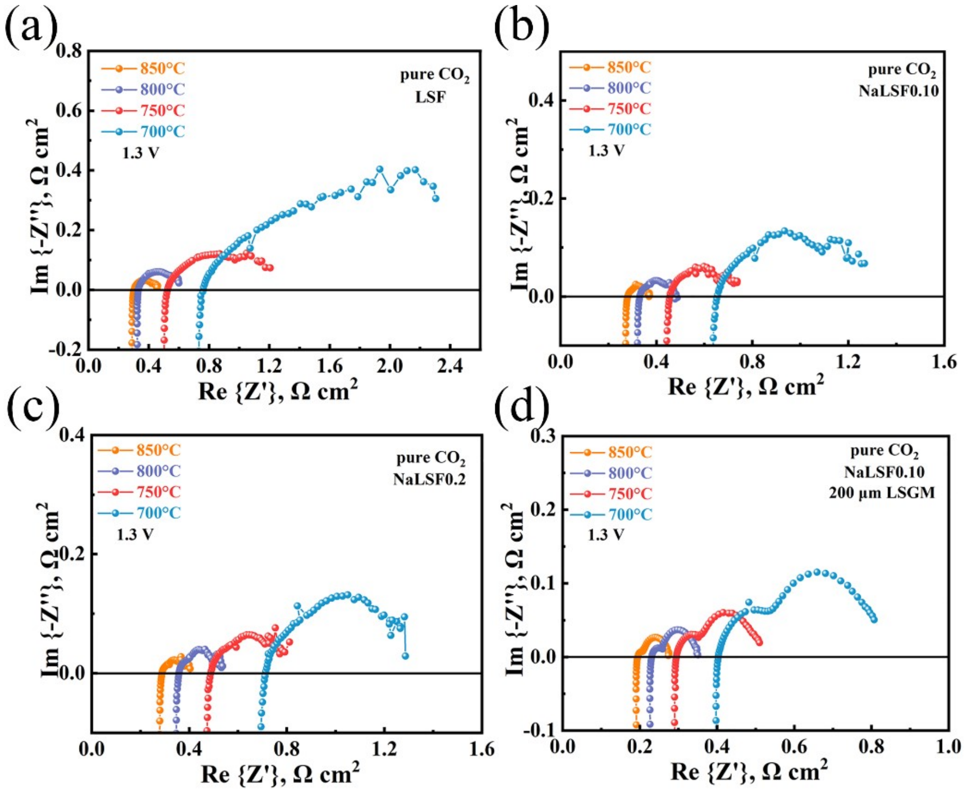

Fig. S12. EIS curves of SOECs with a) LSF, b) NaLSF0.10, c) NaLSF0.20, and d) NaLSF0.10 (200 μm electrolyte) cathodes from 700 ℃ to 850 ℃ at 1.3 V in pure CO_2 atmosphere.

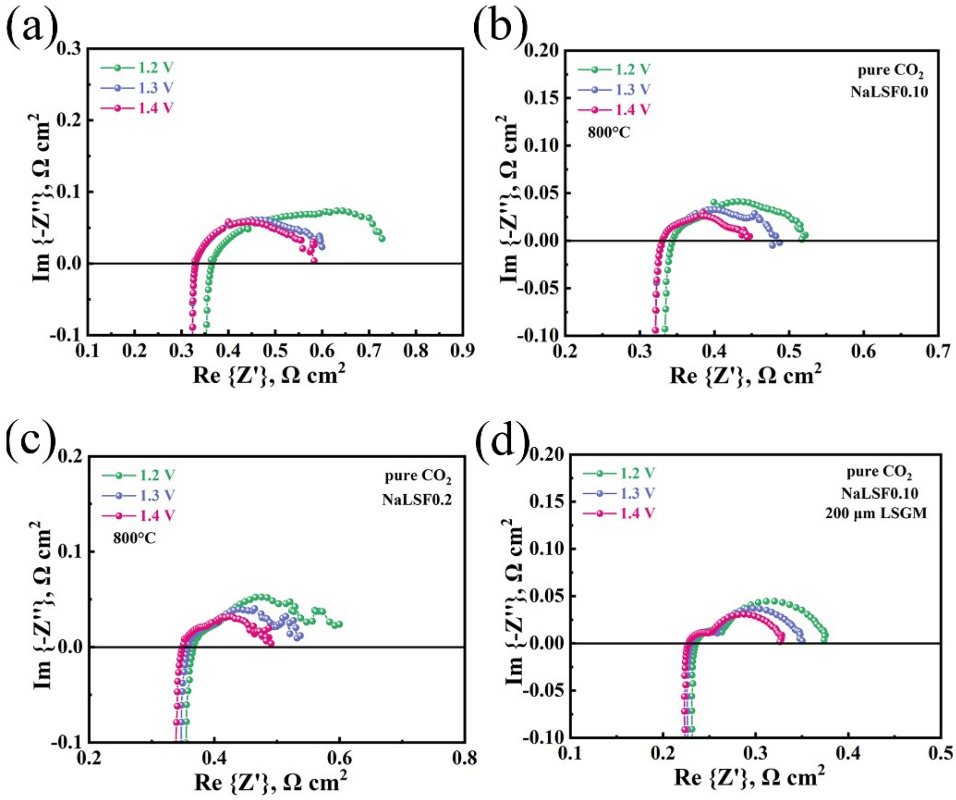

Fig. S13. EIS curves of SOECs with a) LSF, b) NaLSF0.10, c) NaLSF0.20, and d) NaLSF0.10 (200 μm electrolyte) cathodes from 1.2 V to 1.4 V at 800 °C in pure CO_2 atmosphere.

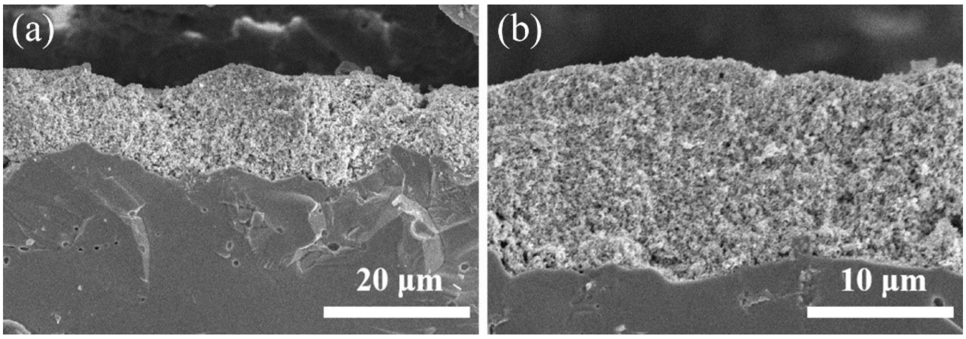

Fig. S14. a) and b) SEM images of the cross-sectional of SOECs with the electrolyte had been polished.

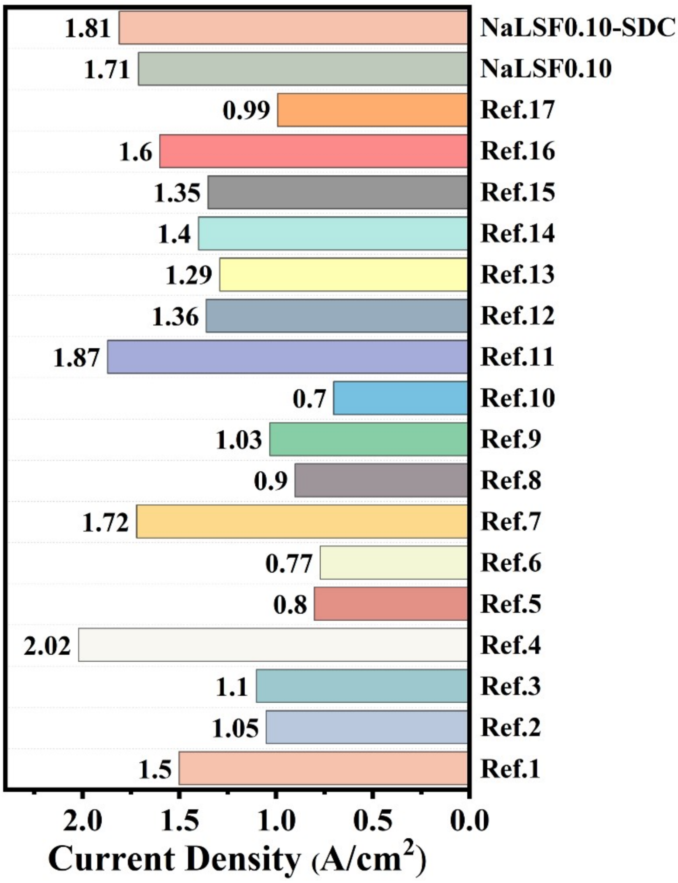

Fig. S15. Comparison of performance for the SOECs with NaLSF0.10 cathode in this work with reported various cathodes at 800 °C and 1.5 V.

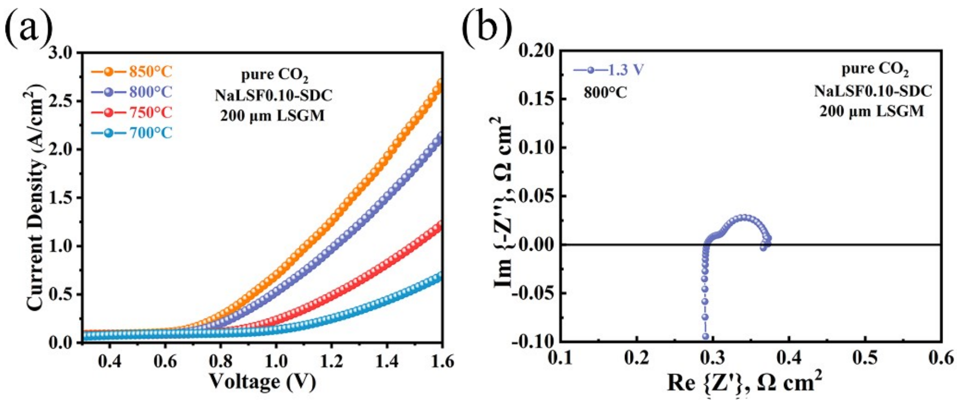

Fig. S16. a) I-V curves, b) EIS at 1.3 and 800 °C.

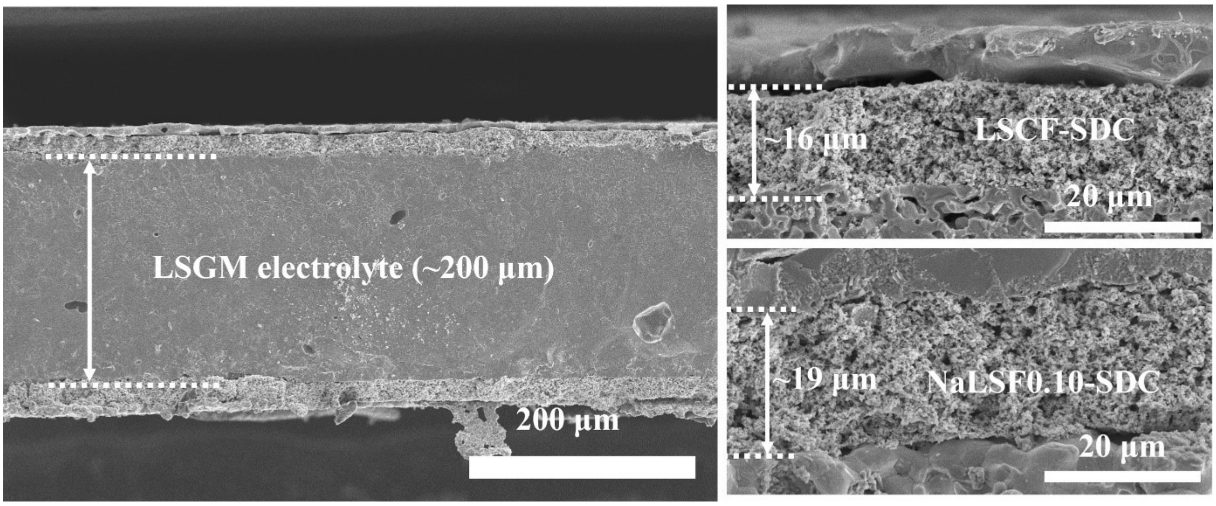

Fig. S17. SEM images of the cross-sectional of RSOCs after the test with NaLSF0.10-SDC cathode and LSCF-SDC anode.

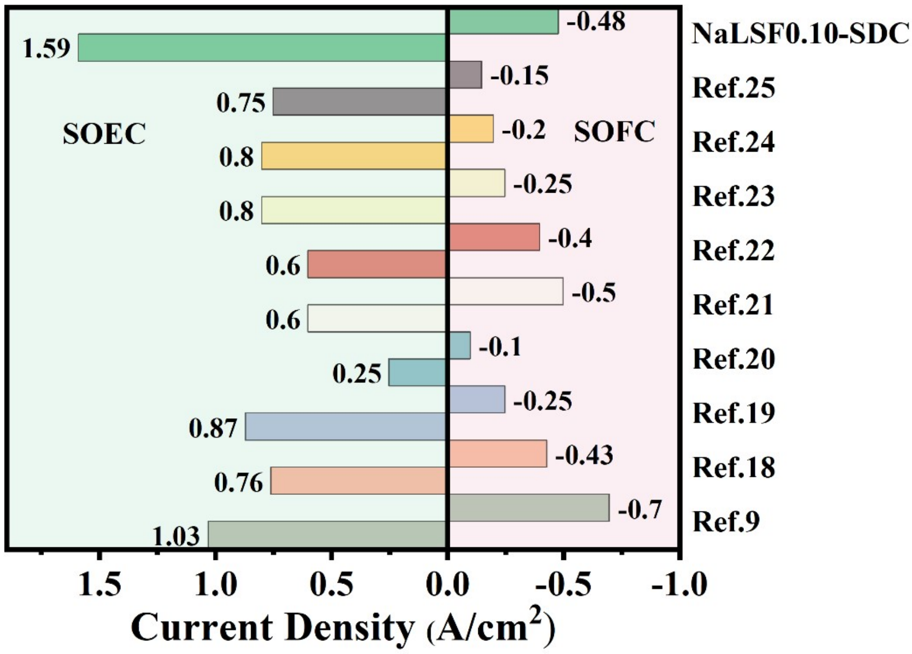

Fig. S18. Comparison of performance for the RSOCs with NaLSF0.10-SDC cathode in this work with reported various cathodes at 800 °C/850 °C and 1.5 V (SOEC mode) or 800 °C/850 °C and 0.6 V (SOFC mode).

Table S1. Structural Refinement Results for LSF, NaLSF0.10, and NaLSF0.20 powders.

	LSF	NaLSF0.10	NaLSF0.20
a (Å)	5.5252	5.5267	5.5302
b (Å)	5.5252	5.5267	5.5302
c (Å)	13.4409	13.4340	13.4434
V ($Å^3$)	355.348	355.359	356.060
wR_p (%)	8.31	8.62	8.91
R_p (%)	6.62	6.67	7.00
Chi^2	2.196	2.389	2.466

Table S2. The composition of lattice oxygen and surface adsorbed oxygen species in LSF, NaLSF0.10, and NaLSF0.20 samples.

Samples	B.E. O *1s* (eV)			O_{lat} (at.%)	O_{ads}+$O_{H/carbonate}$ (at.%)	O_{ads}+$O_{H/carbonate}$/$O_{lat.}$
	O_{lat}	O_{ads}	$O_{H/carbonate}$			
LSF	528.43	530.03 530.08	532.73	50.76	43.65	0.97
NaLSF0.10	528.13	529.28 530.58	531.43	35.08	48.07	1.85
NaLSF0.20	528.08	529.48 530.73	531.38	26.08	48.13	2.62

Table S3. The composition of Fe^{2+}, Fe^{3+}, and Fe^{4+} fitting by Fe *2p* spectra in LSF, NaLSF0.10, and NaLSF0.20 samples.

Concentration (%)	LSF	NaLSF0.10	NaLSF0.20
Fe^{2+}	50.25	51.28	53.19
Fe^{3+}	35.17	35.39	36.17
Fe^{4+}	14.58	13.33	10.64

Table S4. Comparison of current densities for CO_2 electrolysis at 800 °C and 1.5 V.

Cathodes	Electrolytes//anodes	Current densities (A cm^{-2})	References	
$Sr_2Fe_{1.5}Mo_{0.5}O_{3-\delta}$	LDC/LSGM//LSCF-SDC	1.50	*Adv Energy Mater* **2021**, *11*, 2102845	1
$CoFe@Sr_2Fe_{1.35}Co_{0.2}Mo_{0.45}O_{6-\delta}$-GDC	LDC/LSGM//BSCF-GDC	1.05	*Adv Mater* **2020**, *32*, 1906193	2
$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.65}Mn_{0.35}O_{3-\delta}$	LDC/LSGM//LSM	0.60	*Appl Catal B* **2020**, *272*, 118968	3
$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.55}Mn_{0.35}Cu_{0.10}O_{3-\delta}$	LDC/LSGM//LSM	1.10		
CoFe-$La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$	LDC/LSGM//BSCF-GDC	2.02	*Angew Chem Int Ed* **2020**, 59, 15968	4
$FeNi@La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$	GDC/YSZ/GDC//LSCF−GDC	0.80	*J Mater Chem A* **2019**, *7*, 6395	5
$La_{0.43}Ca_{0.37}Ti_{0.94}Ni_{0.06}O_{3-\delta}$-Ce	LDC/LSGM//LSCF-GDC/LSCF	0.77	*J Mater Chem A* **2022**, *10*, 20350	6
$Ni@Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$-Ni@GDC	LSGM//PBSCF-GDC	1.72	*Appl Catal B* **2023**, 337, 122968	7
$Sr_2Fe_{1.3}Zr_{0.2}Mo_{0.5}O_{6-\delta}$	GDC//LSGM//LSCF	0.90	*Appl Catal B* **2022**, *317*, 121754	8
$Sr_{1.97}Fe_{1.5}Mo_{0.5}Ni_{0.1}O_{6-\gamma}$	SDC/LSGM//LSCF-SDC	1.03	*ACS Appl Mater. Interfaces* **2022**, *14*, 9138	9
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$-Pd	YSZ//LSM-YSZ	0.70	*Nano Energy* **2020**, *71*, 104598	10
$RuFe@Sr_2Fe_{1.4}Ru_{0.1}Mo_{0.5}O_{6-\delta}$-GDC	LDC/LSGM/BSCF-GDC	1.87	*Nat Commun*, **2021**, *12*, 5665	11
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}F_{0.1}$	LDC/LSGM//LSCF-SDC	1.36	*Adv Energy Mater* **2019**, *9*,1803156	12
$Sr_2Fe_{1.45}Ir_{0.05}Mo_{0.5}O_{6-\delta}$-GDC	LDC/LSGM//BSCF-GDC	1.29	*Natl Sci Rev* **2023**, *10*, nwad078	13
$Sr_2FeMo_{2/3}Mg_{1/3}O_{6-\delta}$	LDC/LSGM/LDC//LSCF-SDC	1.40	*Nano Energy* **2021**, 82, 105707	14
$La_{0.5}Sr_{0.5}Fe_{0.9}Ti_{0.1}O_{3-\delta}$	LSGM//LSCF-GDC	1.35	*Ceram Inter* **2022**, *48*, 4223	15
$La_{0.55}Sr_{0.45}Fe_{0.9}Mo_{0.1}O_{3-\delta}$	LSGM//LSC	1.60	*Chem Eng J* **2022**, *433*, 133632	16
$La_{0.6-x}Li_xSr_{0.4}Co_{0.7}Mn_{0.3}O_{3-\delta}$	LSGM//LSCF	0.99	*Small* **2023**, 2303305	17
$Ce_{0.9}M_{0.1}O_{2-\delta}$ infiltrated LSCrF-GDC	YSZ//LSM-YSZ	0.60	*J Energy Chem* **2020**, *40*, 46	18
$(La_4Sr_4)_{0.9}Ti_{7.2}Ni_{0.8}O_{26}$	YSZ//LSCF	1.20	*J Energy Chem* **2023,** *84,* 219	19
$Sr_2Fe_{1.4}Zn_{0.1}Mo_{0.5}O_{6-\delta}$	LSGM/BSCF	~1.50	*Green Chem* **2023**, DOI: 10.1039/D3GC03518B	20
NaLSF0.10	LSGM//LSCF-SDC	1.71	**This work**	
NaLSF0.10-SDC	LSGM//LSCF-SDC	1.81		

GDC: $Gd_{0.2}Ce_{0.8}O_{2-\delta}$; LDC: $La_{0.4}Ce_{0.8}O_{2-\delta}$; SDC: $Sm_{0.2}Ce_{0.8}O_{2-\delta}$; LSM: $La_{0.8}Sr_{0.2}MnO_{3-\delta}$; LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$; YSZ (8% nickel-yttria stabilized zirconia), BSCF: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, PBSCF: $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$.

Table S5. Comparison of performance of RSOCs for CO-CO_2 at 800 °C and 1.5 V.

Fuel electrode	Electrolytes//air electrode	Current densities (A cm^{-2})		References	
		SOEC@1.5V	**SOFC@0.6V**		
$Sr_{1.97}Fe_{1.5}Mo_{0.5}Ni_{0.1}O_{6-\gamma}$ Ni-YSZ (70% CO-CO_2)	YSZ//SDC//LSCF	1.03 0.91	0.70 0.95	*ACS Appl Mater. Interfaces* **2022**, *14*, 9138	9
CoFe-$Sr_2Fe_{7/6}Mo_{0.5}Co_{1/3}O_{6-\delta}$ in 2:1 CO-CO_2	SDC/YSZ//LSM-SDC	0.76	0.43	*Sci China Mater* **2021** *64*, 1114	21
$La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$-GDC in 30% CO-$CO_2$	YSZ/GDC//LSCF-GDC	0.87	0.25	*J Mater Chem A* **2017**, *5*, 2673	22
$La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O_{3-\delta}$ in 30% CO-CO_2	SDC/YSZ/SDC//$La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O_3$	0.25	0.10	*Electrochimica Acta* **2020**, *332*, 135464	23
FeNi@$La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$-GDC	GDC/YSZ/GDC//LSCF-GDC	0.60	0.50	*ACS Catalysis* **2016**, *6*, 6219-6228	24
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$-YSZ	YSZ//SFM-YSZ	0.60	0.40	*Solid State Ionics*, **2018**, *319* 98-104	25
CoFe@$Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$-GDC in 30% CO-$CO_2$ $Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$-GDC in 30% CO-$CO_2$	GDC/YSZ/GDC//LSCF-GDC	0.80 (850^{o}C) 0.65 (850^{o}C)	0.25 (850^{o}C) 0.14 (850^{o}C)	*J Mater Chem A* **2016**, *5*, 2673	26
Co@$La_{0.6}Sr_{0.4}Co_{0.7}Mn_{0.3}O_3$ in 30% CO-CO_2	GDC/LSGM//LSCF-GDC	0.80	0.20	*Appl Catal B* **2019**, *272*, 147-156	27
CoNi@$La_{0.6}Sr_{0.4}Co_{0.5}Ni_{0.2}Mn_{0.3}O_3$	GDC/LSGM//LSCF-GDC	0.75	0.15	*J Mater Chem A* **2020**, *8*, 138	28
NaLSF0.10-SDC	LSGM//LSCF-SDC	1.59	0.48	**This work**	

Noted, if not specific statement, the applied fuel electrode gas atmosphere is 50% CO-CO_2

References

1. X. Xi, J. Liu, W. Luo, Y. Fan, J. Zhang, J. Luo and X. Fu, *Adv. Energy Mater.*, 2021, **11**, 2102845.
2. H. Lv, L. Lin, X. Zhang, Y. Song, H. Matsumoto, C. Zeng, N. Ta, W. Liu, D. Gao, G. Wang and X. Bao, *Adv. Mater.*, 2020, **32**, e1906193.
3. X. Yang, K. Sun, M. Ma, C. Xu, R. Ren, J. Qiao, Z. Wang, S. Zhen, R. Hou and W. Sun, *Appl. Catal. B*, 2020, **272**, 118968.
4. H. Lv, T. Liu, X. Zhang, Y. Song, H. Matsumoto, N. Ta, C. Zeng, G. Wang and X. Bao, *Angew. Chem. Int. Ed.*, 2020, **59**, 15968-15973.
5. Y. Tian, L. Zhang, Y. Liu, L. Jia, J. Yang, B. Chi, J. Pu and J. Li, *J. Mater. Chem. A*, 2019, **7**, 6395-6400.
6. Z. Li, M. Peng, Y. Zhu, Z. Hu, C. Pao, Y. Chang, Y. Zhang, Y. Zhao, J. Li and Y. Sun, *J. Mater. Chem. A*, 2022, **10**, 20350-20364.
7. F. Hu, Y. Ling, S. Fang, L. Sui, H. Xiao, Y. Huang, S. Wang, B. He and L. Zhao, *Appl. Catal. B*, 2023, **337**, 122968.
8. L. Zhang, W. Sun, C. Xu, R. Ren, X. Yang, J. Qiao, Z. Wang, S. Zhen and K. Sun, *Appl. Catal. B*, 2022, **317**, 121754.
9. Y. Li, Y. Li, S. Zhang, C. Ren, Y. Jing, F. Cheng, Q. Wu, P. Lund and L. Fan, *ACS Appl. Mater. Interfaces*, 2022, **14**, 9138-9150.
10. Y. Zhou, L. Lin, Y. Song, X. Zhang, H. Lv, Q. Liu, Z. Zhou, N. Ta, G. Wang and X. Bao, *Nano Energy*, 2020, **71**, 104598.
11. H. Lv, L. Lin, X. Zhang, R. Li, Y. Song, H. Matsumoto, N. Ta, C. Zeng, Q. Fu, G. Wang and X. Bao, *Nat. Commun.*, 2021, **12**, 5665.
12. Y. Li, Y. Li, Y. Wan, Y. Xie, J. Zhu, H. Pan, X. Zheng and C. Xia, *Adv. Energy Mater.*, 2019, **9**, 1803156.
13. Y. Shen, T. Liu, R. Li, H. Lv, N. Ta, X. Zhang, Y. Song, Q. Liu, W. Feng, G. Wang and X. Bao, *Natl. Sci. Rev.*, 2023, **10**, nwad078.
14. X. Xi, J. Liu, Y. Fan, L. Wang, J. Li, M. Li, J. Luo and X. Fu, *Nano Energy*, 2021, **82**, 105707.
15. Y. Hou, L. Wang, L. Bian, Q. Zhang, L. Chen and K.-c. Chou, *Ceram. Int.*, 2022, **48**, 4223-4229.

16. D. He, W. Ruan, J. Li, J. Ni and C. Ni, *Chem. Eng. J.*, 2022, **433**, 133632.
17. W. Lin, W. Su, Y. Li, T. Chiu, M. Singh, Z. Pan and L. Fan, *Small*, 2023, **19**, 2303305.
18. Z. Huang, Z. Zhao, H. Qi, X. Wang, B. Tu and M. Cheng, *J. Energy Chem.*, 2020, **40**, 46-51.
19. Z. Liu, J. Zhou, Y. Sun, X. Yue, J. Yang, L. Fu, Q. Deng, H. Zhao, C. Yin and K. Wu, *J. Energy Chem.*, 2023, **84**, 219-227.
20. S. Liu, M. Yang, R. Xu, X. Xiang, G. Yang, H. Xu, G. Xiao, R. Ran, W. Zhou and Z. Shao, *Green Chem.* , 2023, 10.1039/D3GC03518B.
21. Y. Li, M. Singh, Z. Zhuang, Y. Jing, F. Li, K. Maliutina, C. He and L. Fan, *Sci. China Mater.*, 2021, **64**, 1114-1126.
22. S. Liu, Q. Liu and J.-L. Luo, *Journal of Materials Chemistry A*, 2017, **5**, 2673-2680.
23. Z. Cao, Z. Wang, F. Li, K. Maliutina, Q. Wu, C. He, Z. Lv and L. Fan, *Electrochim. Acta*, 2020, **332**, 135464.
24. S. Liu, Q. Liu and J.-L. Luo, *ACS Catalysis*, 2016, **6**, 6219-6228.
25. Y. Li, S. Zou, J. Ju and C. Xia, *Solid State Ion.*, 2018, **319**, 98-104.
26. S. Liu, Q. Liu and J.-L. Luo, *Journal of Materials Chemistry A*, 2016, **4**, 17521-17528.
27. S. Park, Y. Kim, H. Han, Y. Chung, W. Yoon, J. Choi and W. Kim, *Appl. Catal. B*, 2019, **248**, 147-156.
28. S. Park, Y. Kim, Y. Noh, T. Kim, H. Han, W. Yoon, J. Choi, S.-H. Yi, W.-J. Lee and W. B. Kim, *Journal of Materials Chemistry A*, 2020, **8**, 138-148.