Supporting Information

Bimetallic persulfide nanoflake assembled by dealloying and sulfurization: a versatile electro-catalyst for overall water splitting and Zn-air batteries

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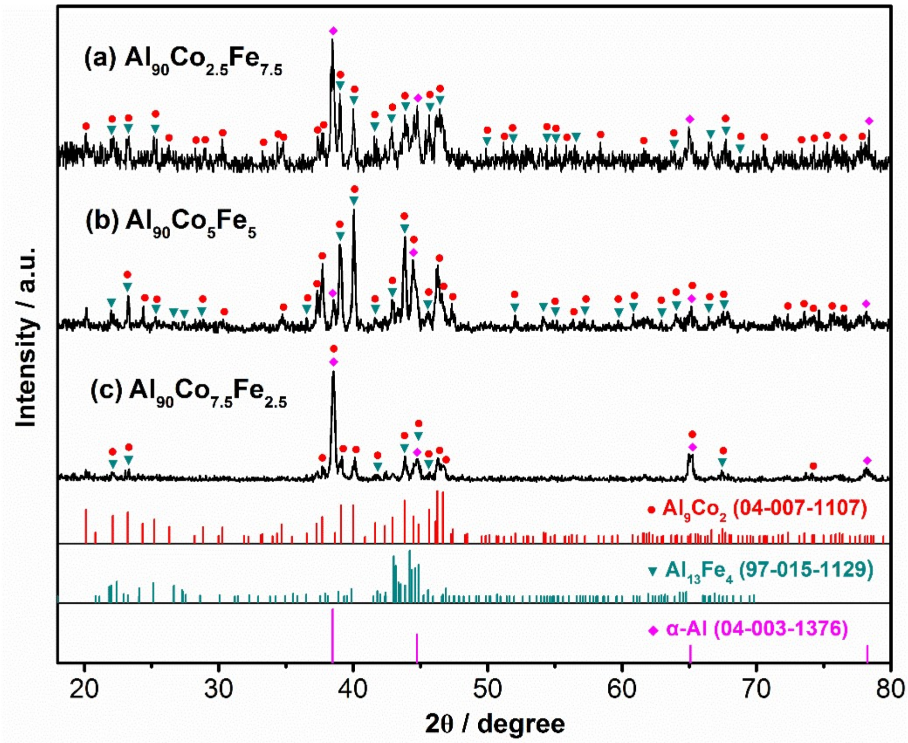

Fig. S1 XRD patterns of (a) $Al_{90}Co_{2.5}Fe_{7.5}$, (b) $Al_{90}Co_5Fe_5$ and (c) $Al_{90}Co_{7.5}Fe_{2.5}$ precursors.

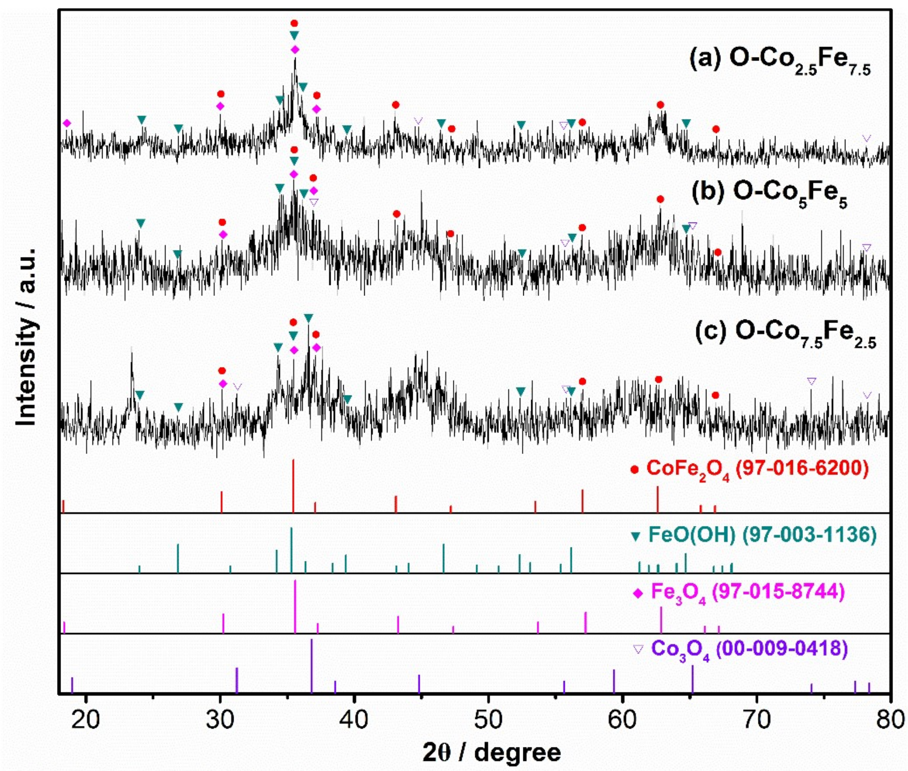

Fig. S2 XRD patterns of (a) O-$Co_{2.5}Fe_{7.5}$, (b) O-Co_5Fe_5 and (c) O-$Co_{7.5}Fe_{2.5}$.

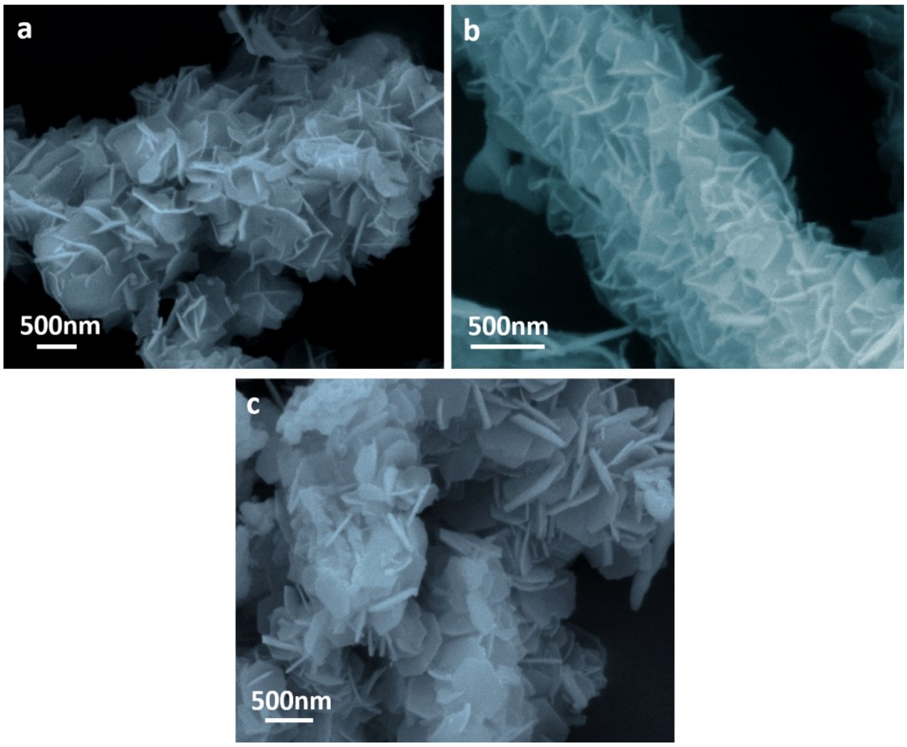

Fig. S3 SEM images of (a) O-$Co_{2.5}Fe_{7.5}$, (b) O-Co_5Fe_5 and (c) O-$Co_{7.5}Fe_{2.5}$.

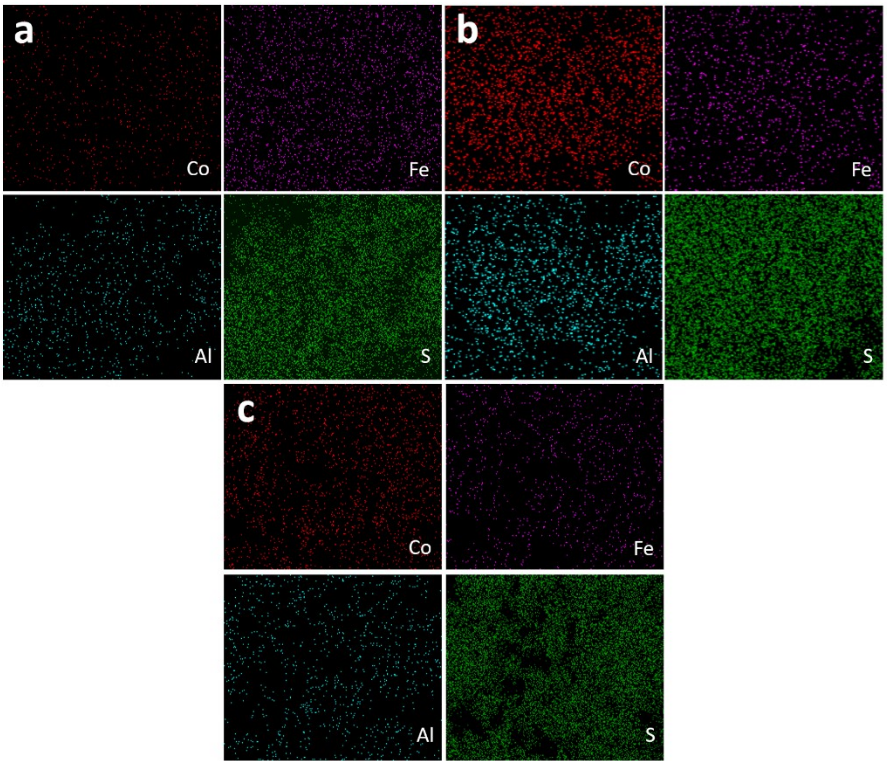

Fig. S4 EDX elemental mappings of Co, Fe, Al and S for (a) S-$Co_{2.5}Fe_{7.5}$, (b) S-$Co_{2.5}Fe_{7.5}$ and (c) S-$Co_{7.5}Fe_{2.5}$.

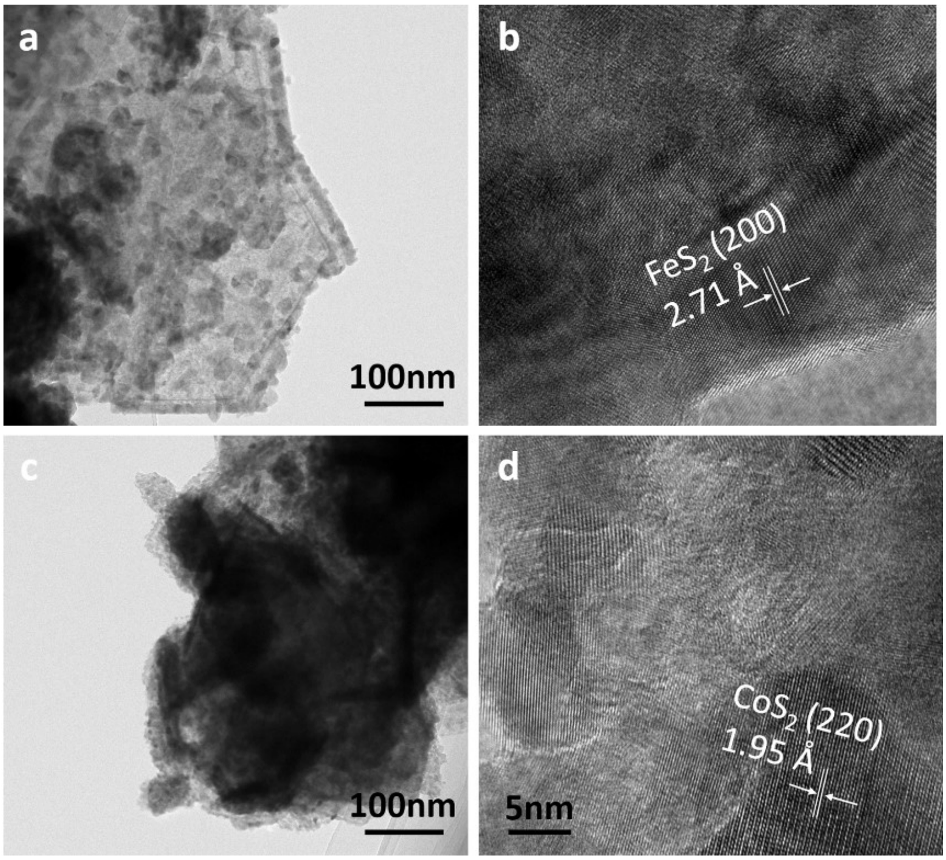

Fig. S5 (a) TEM and (b) HRTEM images of S-$Co_{2.5}Fe_{7.5}$. (c) TEM and (b) HRTEM image of S-$Co_{7.5}Fe_{2.5}$.

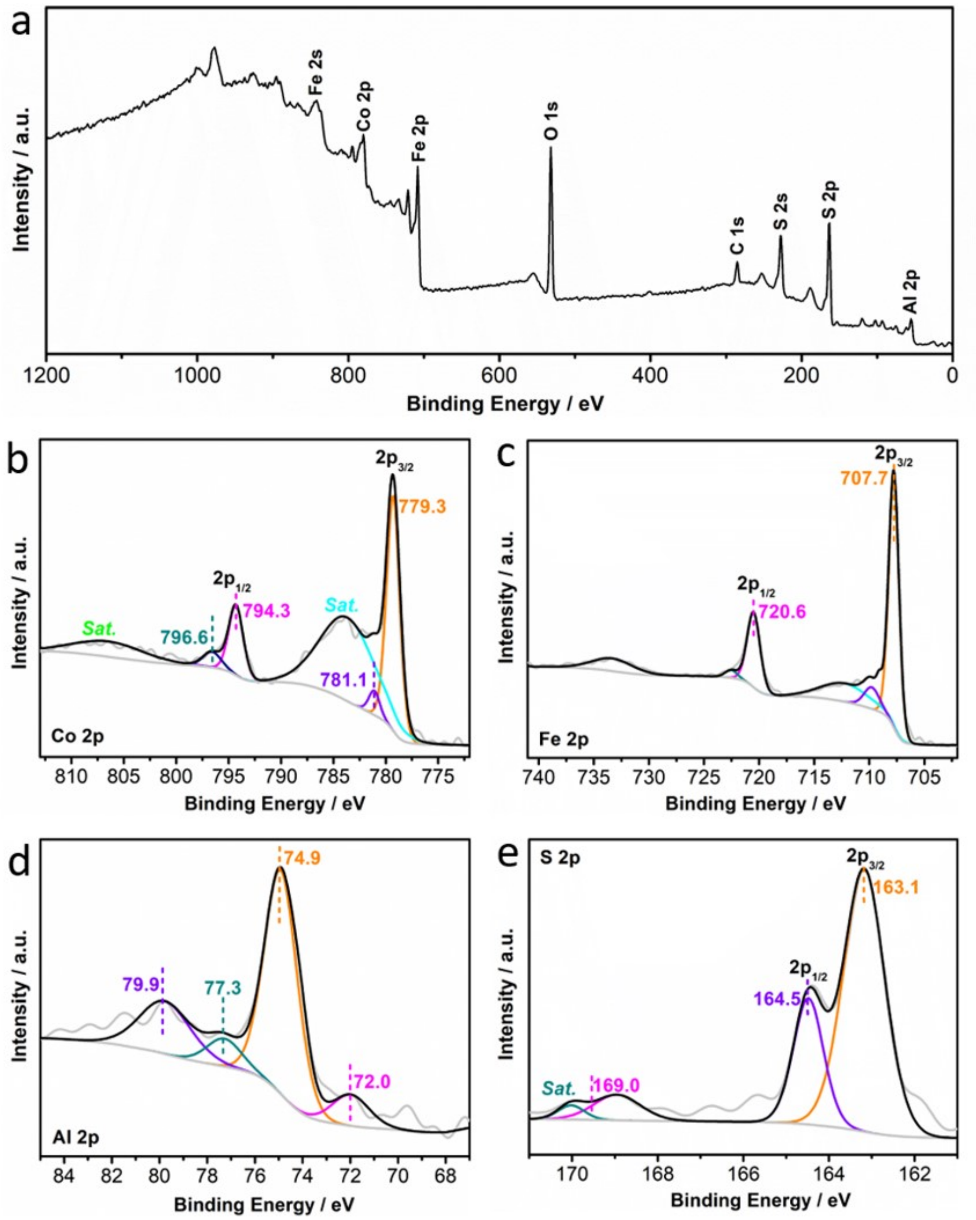

Fig. S6 XPS spectra of S-$Co_{2.5}Fe_{7.5}$ sample. (a) Survey spectrum, (b) Co 2p, (c) Fe 2p, (d) Al 2p, (e) S 2p.

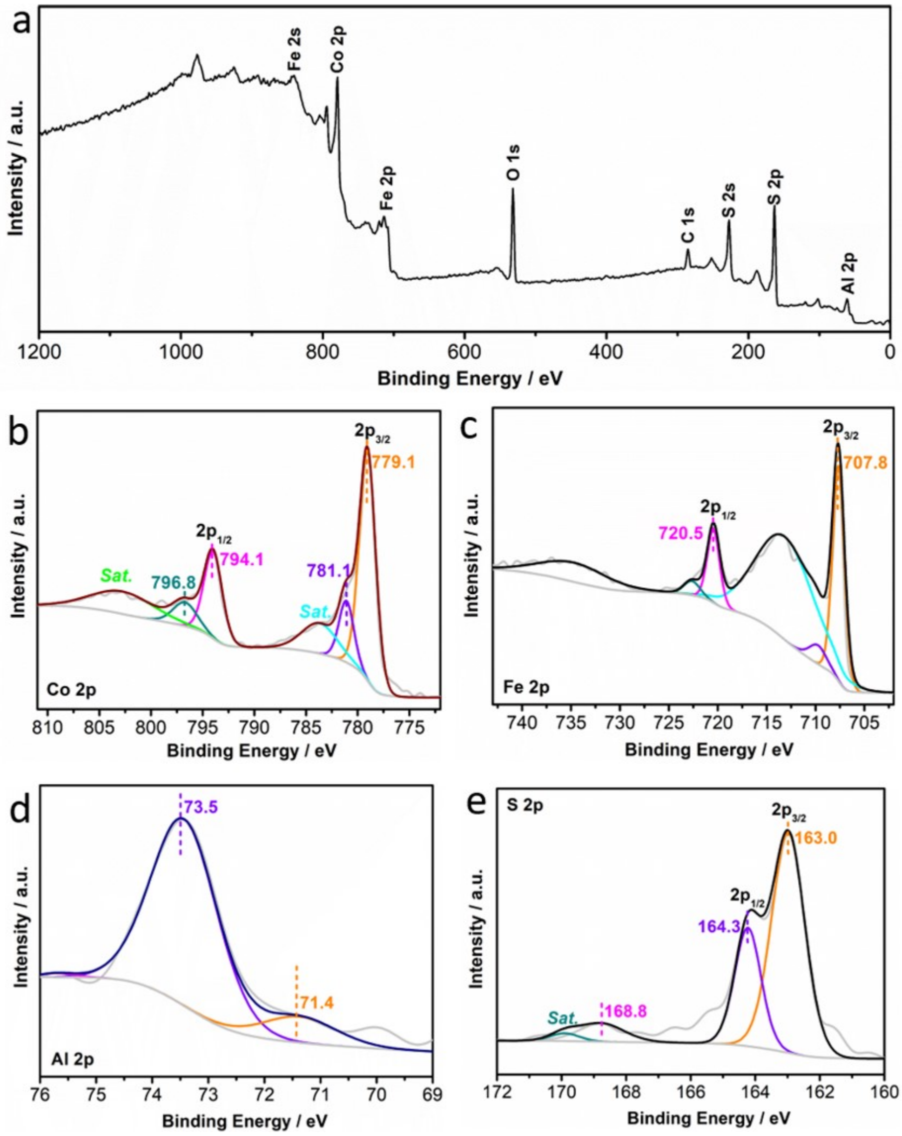

Fig. S7 XPS spectra of S-$Co_{7.5}Fe_{2.5}$ sample. (a) Survey spectrum, (b) Co 2p, (c) Fe 2p, (d) Al 2p, (e) S 2p.

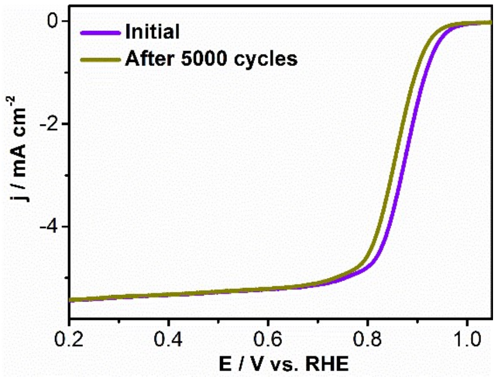

Fig. S8 LSV curves of Pt/C measured before and after 5000 ADT continuous cycles.

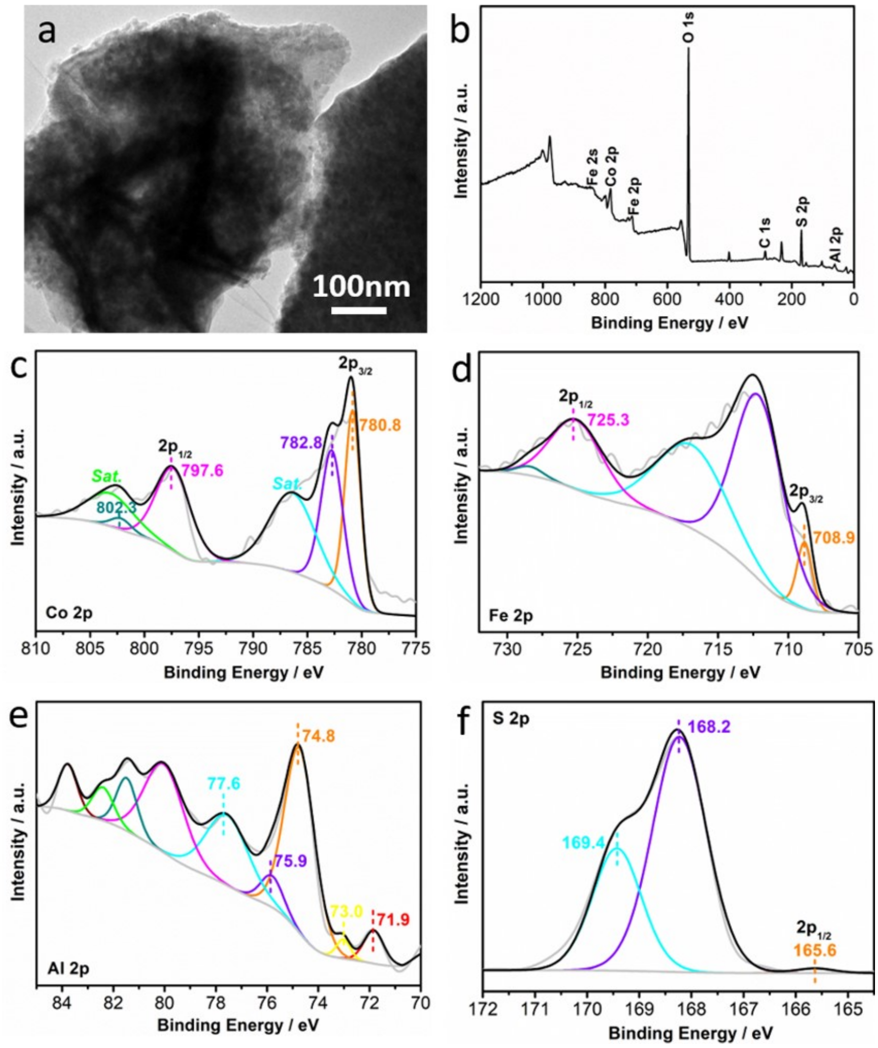

Fig. S9 (a) TEM image and (b-f) XPS spectra of S-Co_5Fe_5 electrode after both ADT and subsequent CA test in 0.1 M KOH solution.

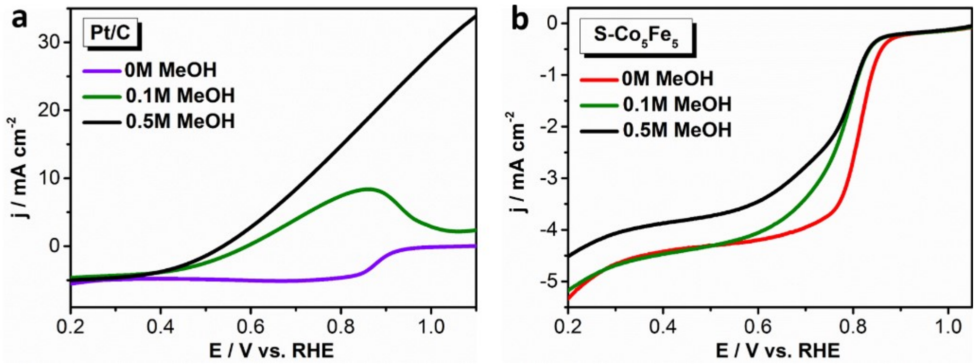

Fig. S10 Methanol tolerance comparison of (a) Pt/C and (b) S-Co_5Fe_5.

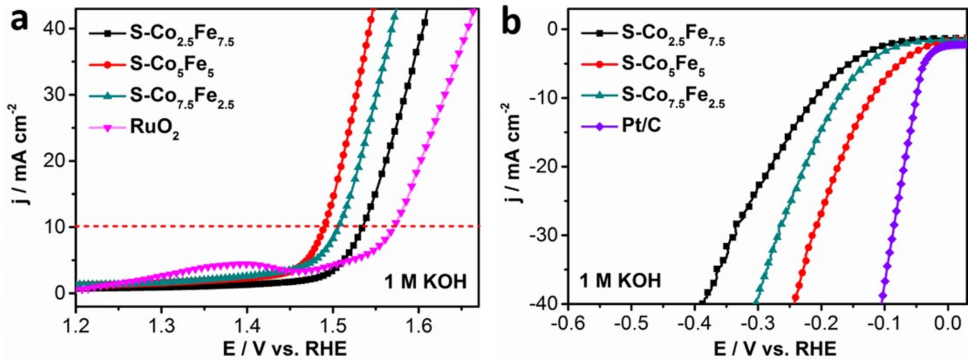

Fig. S11 (a) OER polarization curves of S-$Co_{2.5}Fe_{7.5}$, S-Co_5Fe_5, S-$Co_{7.5}Fe_{2.5}$ and RuO_2 in 1.0 M KOH. (b) HER polarization curves of S-$Co_{2.5}Fe_{7.5}$, S-Co_5Fe_5, S-$Co_{7.5}Fe_{2.5}$ and Pt/C in 1.0 M KOH.

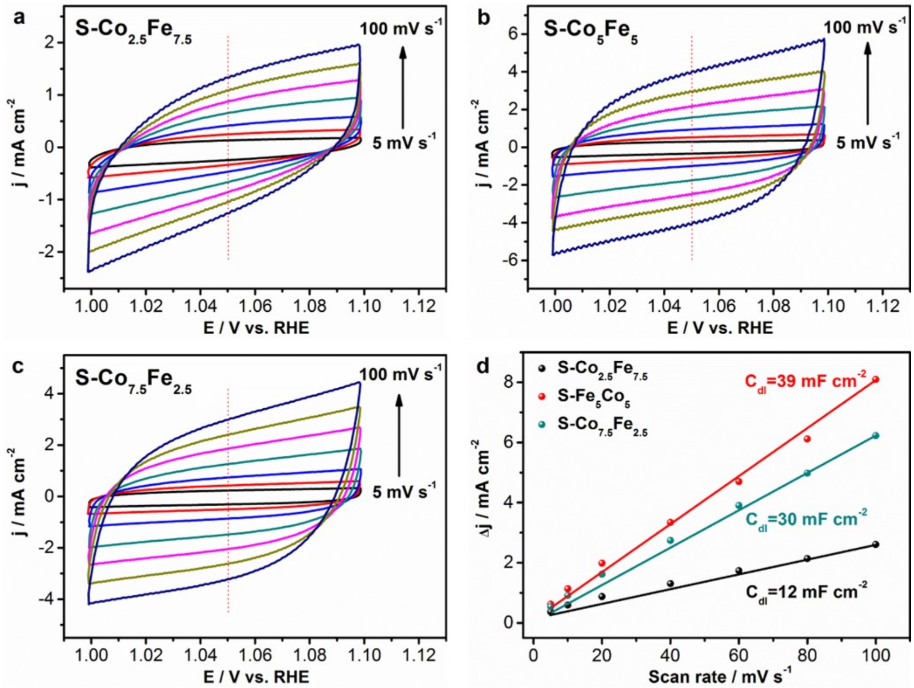

Fig. S12 CV curves of (a) S-$Co_{2.5}Fe_{7.5}$, (b) S-Co_5Fe_5 and (c) S-$Co_{7.5}Fe_{2.5}$ electrodes in the potential range of 1.0～1.1 V vs. RHE under different scan rates. (d) Capacitive currents at the middle of potential window as a function of scan rate.

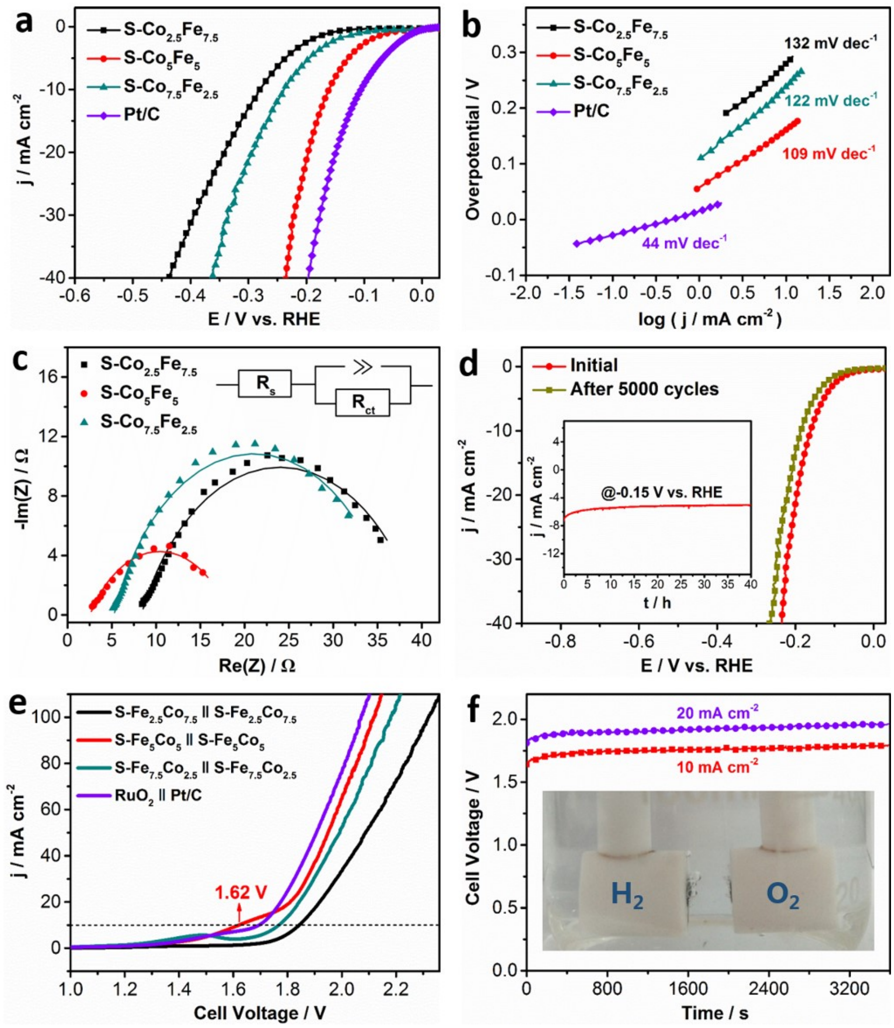

Fig. S13 (a) HER polarization curves of S-$Co_{2.5}Fe_{7.5}$, S-Co_5Fe_5, S-$Co_{7.5}Fe_{2.5}$ and Pt/C in 0.1 M KOH. (b) Tafel plots. (c) Nyquist plots for S-$Co_{2.5}Fe_{7.5}$, S-Co_5Fe_5 and S-$Co_{7.5}Fe_{2.5}$ at -0.1 V vs. RHE (The inset is the equivalent circuit for fitting). (d) LSV curves of S-Co_5Fe_5 measured before and after 5000 ADT continuous cycles (The inset is the *j*-*t* profile recorded at a -0.15 V for 40 h). (e) Polarization curves of two-electrode devices for overall water splitting in 0.1 M KOH. (f) Stability curves of S-Co_5Fe_5 ¦¦ S-Co_5Fe_5 under constant currents of 10 and 20 mA cm^{-2} (The inset is the photograph of overall water splitting).

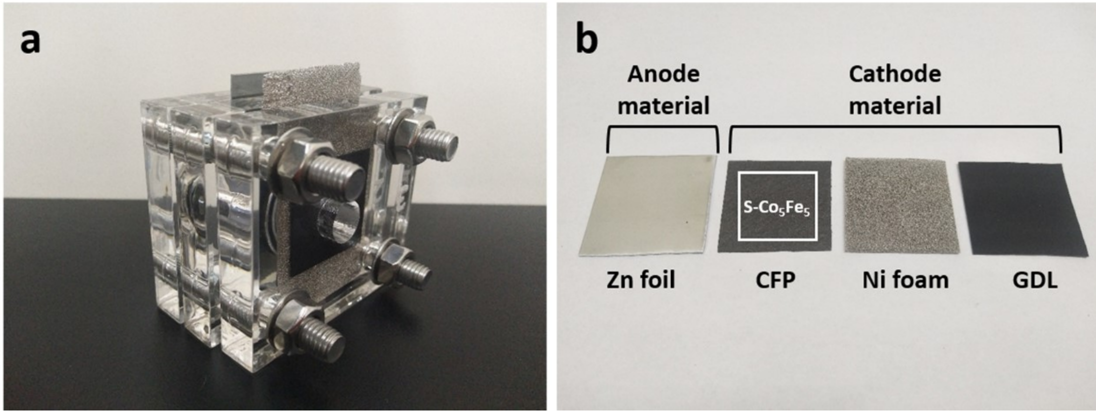

Fig. S14 (a) Photograph of the Zn-air battery device. (b) Photographs of the anode and cathode materials.

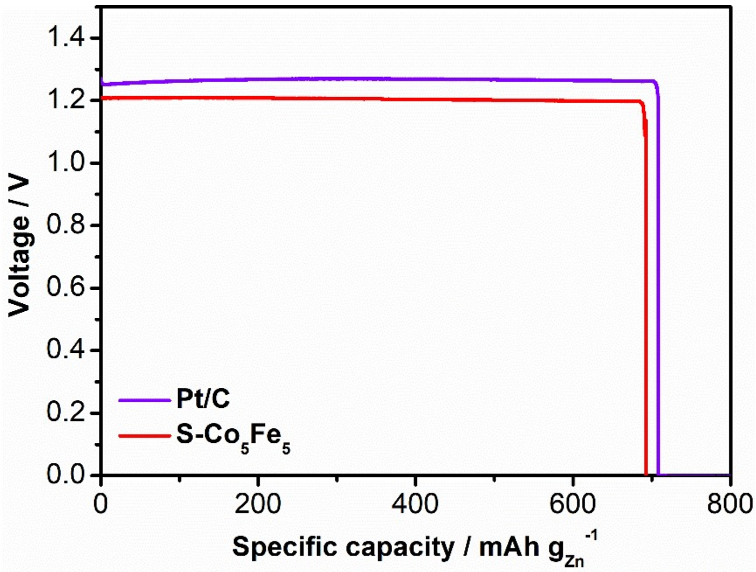

Fig. S15 The discharge specific capacity plots of ZnAB (Zn plate ¦¦ S-Co_5Fe_5) and ZnAB (Zn plate ¦¦ Pt/C) at a current density of 10 mA cm^{-2}.

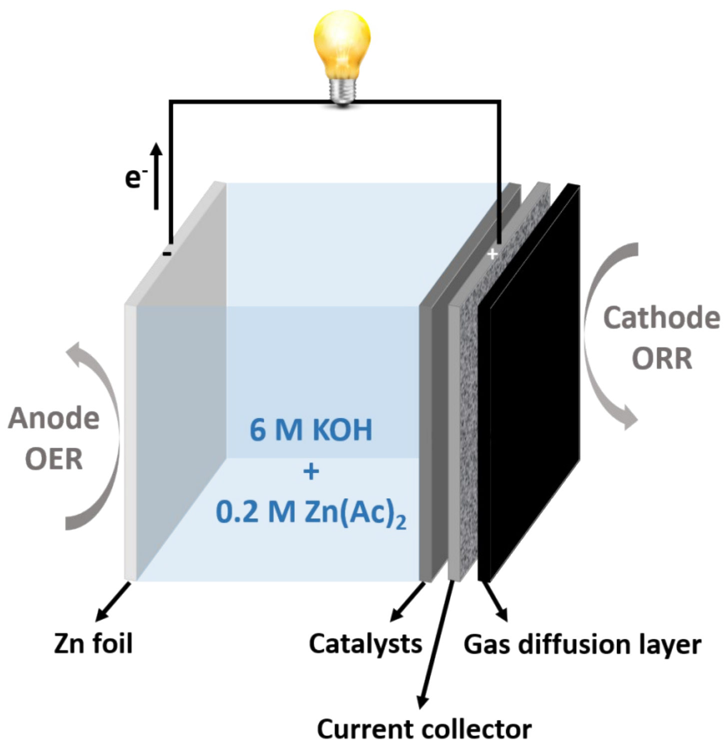

Fig. S16 A schematic of the rechargeable Zn-air battery.

Table S1 ICP analysis for S-Co_xFe_{10-x} (x=2.5, 5, 7.5).

Catalysts	**Element proportion (at. %)**			
	Al	**Co**	**Fe**	**S**
S-$Co_{2.5}Fe_{7.5}$	3.97	11.81	38.07	46.15
S-Co_5Fe_5	2.74	16.12	15.94	65.2
S-$Co_{7.5}Fe_{2.5}$	1.93	37.35	12.74	47.98

Table S2 Comparison of ORR performance in 0.1 M KOH for the as-prepared catalysts in this study with the other reported catalysts in literatures.

Catalysts	E_{onset} (V)	$E_{1/2}$ (V)	Tafel slope (mV dec^{-1})	Reference
S-$Co_{2.5}Fe_{7.5}$	**0.84**	**0.62**	**169**	**This work**
S-Co_5Fe_5	**0.91**	**0.79**	**64**	**This work**
S-$Co_{7.5}Fe_{2.5}$	**0.86**	**0.72**	**85**	**This work**
Pt/C	**0.99**	**0.87**	**61**	**This work**
$NiCo_2O_4$@NiCoFe-OH	0.89	0.77	--	[1]
NiO/$NiCo_2O_4$	0.89	0.73	85.4	[2]
Co/PCNF	--	0.78	--	[3]
$CoSe_2$	0.82	0.75	107	[4]

Table S3 Comparison of OER performance in 0.1 M KOH for the as-prepared catalysts in this study with the other reported catalysts in literatures.

Catalysts	η_{onset} (mV)	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
S-$Co_{2.5}Fe_{7.5}$	**150**	**390**	**114**	**This work**
S-Co_5Fe_5	**70**	**300**	**79**	**This work**
S-$Co_{7.5}Fe_{2.5}$	**130**	**330**	**86**	**This work**
RuO_2	**200**	**370**	**96**	**This work**
W-N/C-4@Co_9S_8@WS_2	--	560	36	[5]
$LaMnNiCoO_3$(1:2:3)	--	370	--	[6]
$ZnCoMnO_4$/N-rGO	340	480	158	[7]
Fe/Ni-N-C	--	322	69	[8]

Table S4 EIS parameters obtained by fitting the Nyquist plots to the equivalent circuit model in 0.1 M KOH at 1.5 V vs. RHE.

Catalysts	R_s (Ω)	R_{ct} (Ω)	Q_1 (F cm^{-2})	n_1
S-$Co_{2.5}Fe_{7.5}$	2.662	12.59	0.0101	0.918
S-Co_5Fe_5	1.104	1.290	0.1078	0.785
S-$Co_{7.5}Fe_{2.5}$	1.820	8.887	0.0229	0.957

Table S5 Comparison of OER/ORR bi-functional activities for the as-prepared catalysts in this study with the other reported catalysts in literatures.

Catalysts	Electrolyte	OER E_{10} (V)	ORR $E_{1/2}$ (V)	$\Delta E = E_{10} - E_{1/2}$ (V)	Reference
S-$Co_{2.5}Fe_{7.5}$	**0.1 M KOH**	**1.62**	**0.62**	**1.00**	**This work**
S-Co_5Fe_5	**0.1 M KOH**	**1.53**	**0.79**	**0.74**	**This work**
S-$Co_{7.5}Fe_{2.5}$	**0.1 M KOH**	**1.56**	**0.72**	**0.84**	**This work**
RuO_2	**0.1 M KOH**	**1.60**	**0.31**	**1.29**	**This work**
Pt/C	**0.1 M KOH**	**1.73**	**0.87**	**0.86**	**This work**
FeCo/Co_2P@NPCF	0.1 M KOH	1.56	0.79	0.77	9
$NiCo_2O_4$	0.1 M KOH	1.64	0.77	0.87	10
CoDNG900	0.1 M KOH	1.613	0.864	～0.75	11
NiO/$NiCo_2O_4$	0.1 M KOH	1.587	0.73	0.857	2
Co@Co_3O_4/NC-1	0.1 M KOH	1.65	0.80	0.85	12
$Co(OH)_2$+N-rGO	0.1 M KOH	1.66	0.79	0.87	13
CoO@Co/N-rGO	0.1 M KOH	1.64	0.73	0.91	14
NiFe-LDH/Fe-N-C (1:1)	0.1 M KOH	1.515	0.728	0.787	15
Fe@N-C-700	0.1 M KOH	1.71	0.83	0.88	16
Co_3O_4/2.7Co_2MnO_4	0.1 M KOH	1.77	0.68	1.09	17
$Co_3FeS_{1.5}(OH)_6$	0.1 M KOH	1.588	0.721	0.867	18
CuS/NiS_2	0.1 M KOH	1.52	0.73	0.79	19
FeCo-Co_4N/N-C	0.1 M KOH	1.51	0.76	0.75	20
PPy/FeTCPP/Co	0.1 M KOH	1.61	0.86	0.75	21
Ni/NiO/$NiCo_2O_4$/N-CNT-As	0.1 M KOH	1.60	0.74	0.86	22

Table S6 Comparison of HER performance in 0.1 M KOH for the as-prepared catalysts in this study with the other reported catalysts in literatures.

Catalysts	η_{onset} (mV)	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
S-$Co_{2.5}Fe_{7.5}$	**160**	**280**	**132**	**This work**
S-Co_5Fe_5	**57**	**161**	**109**	**This work**
S-$Co_{7.5}Fe_{2.5}$	**108**	**238**	**122**	**This work**
Pt/C	**16**	**106**	**44**	**This work**
PPy/FeTCPP/Co	--	240	83	[21]
FeNi/NPC	--	260	112	[23]
Co@Co-N-C	78	314	59	[24]
SHG	230	310	112	[25]

Table S7 EIS parameters obtained by fitting the Nyquist plots to the equivalent circuit model in 0.1 M KOH at -0.1 V vs. RHE.

Catalysts	R_s (Ω)	R_{ct} (Ω)	Q_1 (F cm^{-2})	n_1
S-$Co_{2.5}Fe_{7.5}$	8.250	31.350	0.0307	0.714
S-Co_5Fe_5	2.451	15.970	0.0337	0.622
S-$Co_{7.5}Fe_{2.5}$	5.253	31.560	0.0220	0.766

Table S8 Comparison of HER/OER bi-functional activities for the as-prepared catalysts in this study with the other reported catalysts in literatures.

Catalysts	Electrolyte	Cell voltage E_{10} (V)	Reference
S-$Co_{2.5}Fe_{7.5}$ ¦¦ S-$Co_{2.5}Fe_{7.5}$	**0.1 M KOH**	**1.84**	**This work**
S-Co_5Fe_5 ¦¦ S-Co_5Fe_5	**0.1 M KOH**	**1.62**	**This work**
S-$Co_{7.5}Fe_{2.5}$ ¦¦ S-$Co_{7.5}Fe_{2.5}$	**0.1 M KOH**	**1.76**	**This work**
RuO_2 ¦¦ Pt/C	**0.1 M KOH**	**1.69**	**This work**
CoFe@NC/NCHNSs-700 ¦¦ CoFe@NC/NCHNSs-700	1 M KOH	1.665	[26]
CoFe@N-GCNCs-700 ¦¦ CoFe@N-GCNCs-700	1 M KOH	1.63	[27]
CoFe-N-CNTs/CNFs-900 ¦¦ CoFe-N-CNTs/CNFs-900	1 M KOH	1.66	[28]
Ni_3S_2 ¦¦ Ni_3S_2	1 M KOH	1.63	[29]
$Co_{0.85}Se$/NF ¦¦ $Co_{0.85}Se$/NF	1 M KOH	1.63	[30]

Table S9 Comparison of ZnAB performance using S-Co_5Fe_5 as cathode catalyst with the other reported catalysts in literatures.

ZnAB	OCP (V)	Peak power density (mW cm^{-2})	Reference
Zn plate ¦ S-Co_5Fe_5	**1.46**	**179**	**This work**
Zn plate ¦ CoFe/N-HCSs	1.387	96.5	31
Zn plate ¦ CoFe/FeNC	--	154.1	32
Zn plate ¦ CoFe@NO-CNT	1.45	142	33
Zn plate ¦ NPSC-Co_2Fe_1	1.44	174.6	34
Zn plate ¦ CoFe@N-CNWF	1.46	90	35
Zn plate ¦ CoO_x@NOC	1.44	141.65	36
Zn plate ¦ Co-MOF-800	1.38	144	37
Zn plate ¦ NCFPO-350	1.36	74.6	38
Zn plate ¦ AlFeCoNiMn	1.44	136	39
Zn plate ¦ $CuCo_2S_4$	1.38	123.9	40

REFERENCES

1 S. Li, X. Yang, S. Yang, Q. Gao, S. Zhang, X. Yu, Y. Fang, S. Yang and X. Cai, *J. Mater. Chem. A*, 2020, **8**, 5601-5611.

2 Z. Zhang, X. Liang, J. Li, J. Qian, Y. Liu, S. Yang, Y. Wang, D. Gao and D. Xue, *ACS Appl. Mater. Interfaces*, 2020, **12**, 21661-21669.

3 Q. Lu, H. Wu, X. Zheng, Y. Chen, A. L. Rogach, X. Han, Y. Deng and W. Hu, Adv. Sci., 2021, **8**, 2101438.

4 X. Zheng, X. Han, Y. Cao, Y. Zhang, D. Nordlund, J. Wang, S. Chou, H. Liu, L. Li, C. Zhong, Y. Deng and W. Hu, *Adv. Mater.*, 2020, **32**, 2000607.

5 X. Liu, X. Li, M. An, Y. Gao, Z. Cao and J. Liu, *Electrochim. Acta*, 2020, **351**, 136249.

6 J. Sun, L. Du, B. Sun, G. Han, Y. Ma, J. Wang, H. Huo, P. Zuo, C. Du and G. Yin, *J. Energy Chem.*, 2021, **54**, 217-224.

7 W. Liu, D. Rao, J. Bao, L. Xu, Y. Lei and H. Li, *J. Energy Chem.*, 2021, **57**, 428-435.

8 H. Li, J. Wang, R. Qi, Y. Hu, J. Zhang, H. Zhao, J. Zhang and Y. Zhao, *Appl. Catal. B*, 2021, **285**, 119778.

9 Q. Shi, Q. Liu, Y. Ma, Z. Fang, Z. Liang, G. Shao, B. Tang, W. Yang, L. Qin and X. Fang, *Adv. Energy Mater.*, 2020, **10**, 1903854.

10 J. Béjar, L. Álvarez-Contreras, J. Ledesma-García, N. Arjona and L. G. Arriaga, *J. Mater. Chem. A*, 2020, **8**, 8554-8565.

11 A. Wang, C. Zhao, M. Yu and W. Wang, *Appl. Catal. B,* 2021, **281**, 119514.

12 A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 4087-4091.

13 Y. Zhan, G. Du, S. Yang, C. Xu, M. Lu, Z. Liu and J. Y. Lee, *ACS Appl. Mater. Interfaces*, 2015, **7**, 12930-12936.

14 X. X. Liu, J. B. Zang, L. Chen, L. B. Chen, X. Chen, P. Wu, S. Y. Zhou and Y. H. Wang, *J. Mater. Chem. A*, 2017, **5**, 5865-5872.

15 S. Dresp, F. Luo, R. Schmack, S. Kühl, M. Gliech and P. Strasser, *Energy Environ.*

Sci., 2016, **9**, 2020-2024.

16 J. Wang, H. Wu, D. Gao, S. Miao, G. Wang and X. Bao, *Nano Energy*, 2015, **13**, 387-396.

17 D. Wang, X. Chen, D. G. Evans and W. Yang, *Nanoscale*, 2013, **5**, 5312-5315.

18 H. F. Wang, C. Tang, B. Wang, B. Q. Li and Q. Zhang, *Adv. Mater.*, 2017, **29**, 1702327.

19 L. An, Y. Li, M. Luo, J. Yin, Y.-Q. Zhao, C. Xu, F. Cheng, Y. Yang, P. Xi and S. Guo, *Adv. Funct. Mater.*, 2017, **27**, 1703779.

20 X. Zhu, T. Jin, C. Tian, C. Lu, X. Liu, M. Zeng, X. Zhuang, S. Yang, L. He, H. Liu and S. Dai, *Adv. Mater.*, 2017, **29**, 1704091.

21 J. Yang, X. Wang, B. Li, L. Ma, L. Shi, Y. Xiong and H. Xu, *Adv. Funct. Mater.*, 2017, **27**, 1606497.

22 N. Ma, Y. Jia, X. Yang, X. She, L. Zhang, Z. Peng, X. Yao and D. Yang, *J. Mater. Chem. A*, 2016, **4**, 6376-6384.

23 H.-X. Zhong, J. Wang, Q. Zhang, F. Meng, D. Bao, T. Liu, X.-Y. Yang, Z.-W. Chang, J.-M. Yan and X.-B. Zhang, *Adv. Sustainable Syst.*, 2017, **1**, 1700020.

24 Y. Wang, Y. Nie, W. Ding, S. G. Chen, K. Xiong, X. Q. Qi, Y. Zhang, J. Wang and Z. D. Wei, *Chem. Commun.*, 2015, **51**, 8942-8945.

25 C. Hu and L. Dai, *Adv. Mater.*, 2017, **29**, 1604942.

26 S. Wang, H. Wang, C. Huang, P. Ye, X. Luo, J. Ning, Y. Zhong and Y. Hu, *Appl. Catal. B*, 2021, **298**, 120512.

27 H.-J. Niu, Y.-P. Chen, R.-M. Sun, A.-J. Wang, L.-P. Mei, L. Zhang and J.-J. Feng, *J. Power Sources*, 2020, **480**, 229107.

28 S. Wang, J. Wang, X. Wang, L. Li, J. Qin and M. Cao, *J. Energy Chem.*, 2021, **53**, 422-432.

29 X. Zheng, X. Han, Y. Zhang, J. Wang, C. Zhong, Y. Deng and W. Hu, *Nanoscale*, 2019, **11**, 5646-5654.

30 W. Ding, Y. Cao, H. Liu, A. Wang, C. Zhang and X. Zheng, *Rare Met.*, 2021, **40**, 1373-1382.

31 J. Li, Y. Kang, W. Wei, X. Li, Z. Lei and P. Liu, *Chem. Eng. J.*, 2021, **407**, 127961.

32 Z. Peng, H. Wang, X. Xia, X. Zhang and Z. Dong, *ACS Sustainable Chem. Eng.*, 2020, **8**, 9009-9016.

33 M. Li, S. Chen, B. Li, Y. Huang, X. Lv, P. Sun, L. Fang and X. Sun, *Electrochim. Acta*, 2021, **388**, 138587.

34 K. He, J. Zai, X. Liu, Y. Zhu, A. Iqbal, T. Tadesse Tsega, Y. Zhang, N. Ali and X. Qian, *Appl. Catal. B*, 2020, **265**, 118594.

35 Q. Zhou, L. Ai, Q. Li, S. Hou, L. Xu, D. Sun, H. Pang, K. Huang and Y. Tang, *Chem. Eng. J.*, 2021, **417**, 127895.

36 M. E. Hilal, H. A. Younus, S. Chaemchuen, S. Dekyvere, X. Zen, D. He, J. Park, T. Han and F. Verpoort, *Catal. Sci. Technol.,* 2021, **11**, 4149-4161.

37 X. Duan, N. Pan, C. Sun, K. Zhang, X. Zhu, M. Zhang, L. Song and H. Zheng, *J. Energy Chem.*, 2021, **56**, 290-298.

38 D.-S. Pan, P. Chen, L.-L. Zhou, J.-H. Liu, Z.-H. Guo and J.-L. Song, *J. Power Sources*, 2021, **498**, 229859.

39 S. Li, X. Zhou, G. Fang, G. Xie, X. Liu, X. Lin and H.-J. Qiu, *ACS Appl. Energy Mater.*, 2020, **3**, 7710-7718.

40 R. Zhang, Z. Hu, S. Cheng, W. Ke, T. Ning, J. Wu, X. Fu and G. Zhu, *Inorg. Chem.*, 2021, **60**, 6721-6730.