Electronic Supplementary Information (ESI) for Chemical Communications. This journal is (c) The Royal Society of Chemistry 2022.

Electronic Supplementary Information (ESI)

A flexible self-healing $Zn_3V_2O_7(OH)_2·2H_2O$-based Zn-ion battery under continuous folding and twisting

Yajun Zhu[a], Xirong Lin[b], Xin Jin[c], Tianli Han[a,], Huigang Zhang[c,*], Jinyun Liu[a,*]*

Experimental

All chemicals were analytical reagent grade purchased from Aladdin and used without purification.

Synthesis of 3D ZVO/CC cathode: Firstly, a piece of CC was cut into 10 mm×10 mm, and soaked in acid (nitric acid: hydrochloric acid = 3:1) for 24 h, followed by ultrasonication with acetone and ethanol, and finally cleaned with deionized water. ZVO/CC cathode was prepared by a solvothermal method. 7.5 mmol NH_4VO_3 was added in 40 mL deionized water. Then, 5 mmol glycine was added. 5 mmol $Zn(NO_3)_2·6H_2O$ was dissolved in 20 mL deionized water, which was added to the above solution. The solution was put into an autoclave with a piece of CC. It was heated at 170 °C for 10 h. At last, CC with ZVO nanosheets growing on the surface was washed and dried for use.

Preparation of hydrogel electrolyte: 2.1 g PVA was dissolved in a 10 mL solution containing 2.2 g $Zn(CH_3COO)_2·2H_2O$ and 0.2 g $Mn(CH_3COO)_2·4H_2O$ under stirring slowly at 90 °C. After 1.5 h, viscous solution was put into a dish and left overnight. PZM hydrogel electrolyte was formed. Pure PVA hydrogel was prepared without adding Zn^{2+} and Mn^{2+} ions.

Characterization: SEM (Hitachi S-8100, 5 kV), TEM (Hitachi HT-7700), XRD (Bruner D8 Advance), XPS (ESCALAB 250), FTIR spectroscopy (IR-21IR), Raman spectroscopy (Renishaw), and BET analyzer (ASAP 2460) were used for characterizing morphology, structure and composition. Ionic conductivity and mechanical properties were measured on ORION ST2643 and INSTRON 3367, respectively.

Battery construction and electrochemical tests: Zn-ion batteries prepared with PZM hydrogel electrolyte, ZVO/CC, and a Zn anode were sealed using polyethylene. The batteries were bent to 30°, 60°, 90°, 120° and 150°, and their voltages during cutting/healing were measured using a multimeter. In addition, 2032-typed coin cells were also assembled using the cathode, Zn foil and glass fiber separator for comparison, along with electrolyte containing 2.2 g $Zn(CH_3COO)_2·2H_2O$ and 0.2 g $Mn(CH_3COO)_2·4H_2O$ in 10 mL deionized water. CV profiles and EIS spectra were tested by using an electrochemical workstation (Chi-660E).

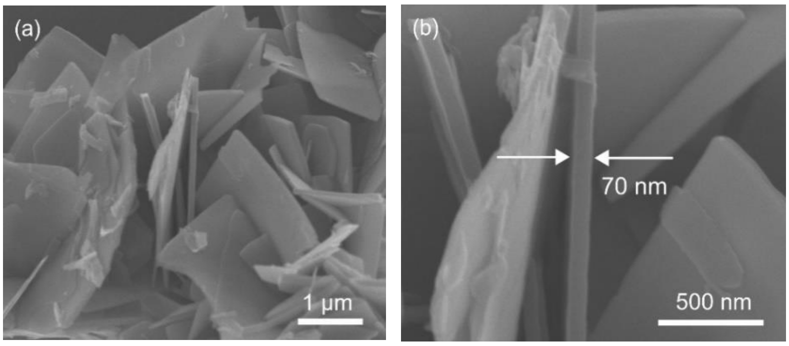

Fig. S1 (a,b) SEM images of ZVO nanosheets with different magnifications.

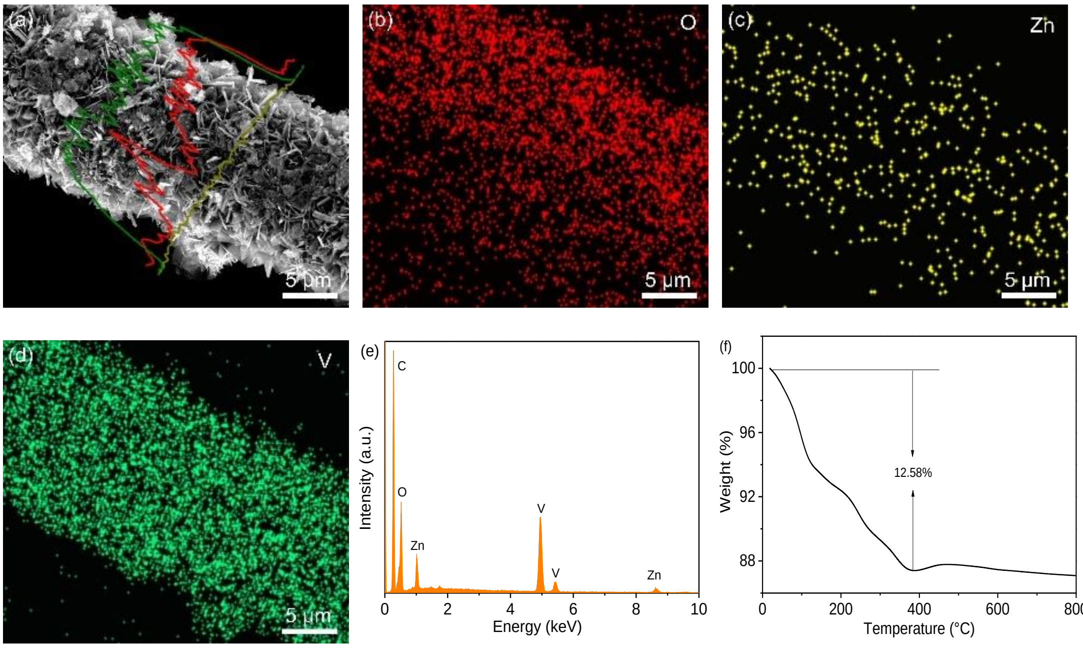

Fig. S2 (a) SEM and (b-d) elemental mapping image of ZVO/CC. (e) EDS spectrum and (f) TGA curve.

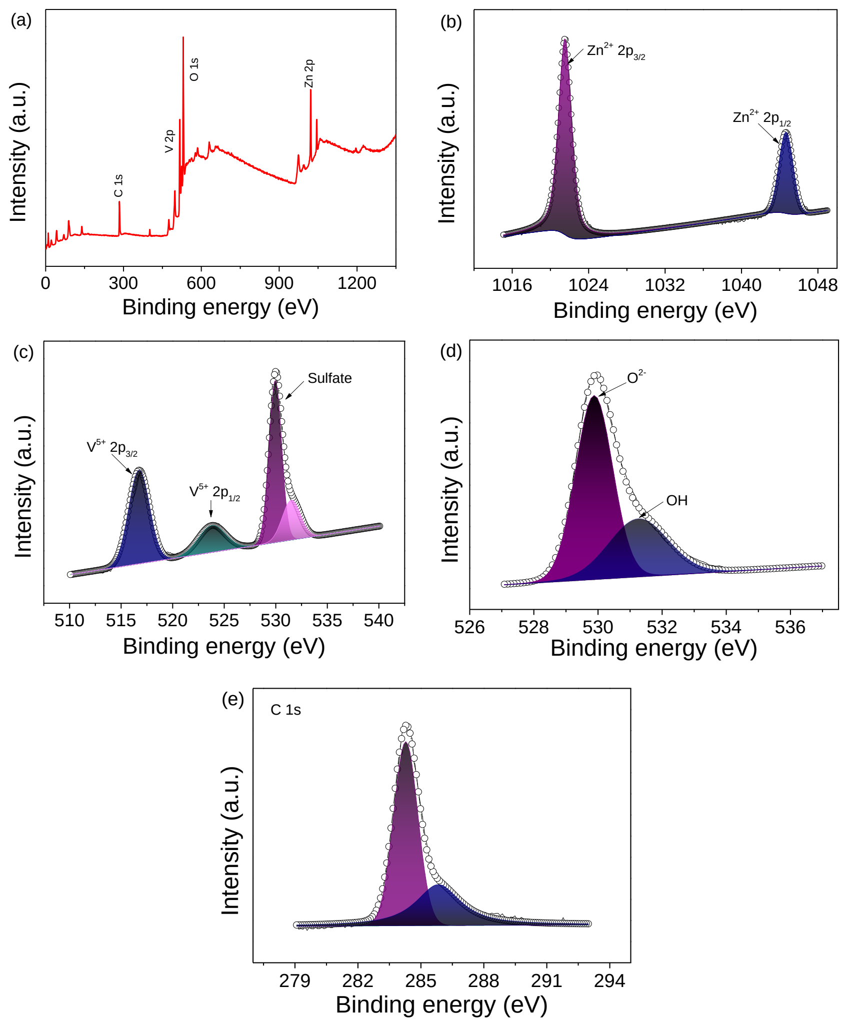

Fig. S3 (a) XPS survey spectrum of ZVO/CC. High-resolution XPS spectra of (b) Zn 2p, (c) V 2p, (d) O 2p, and (e) C 1s.

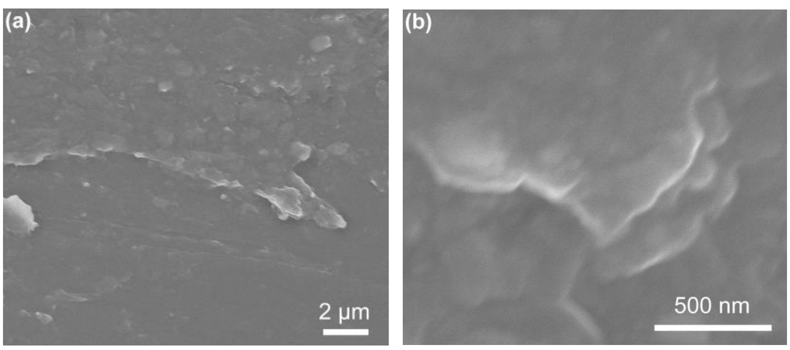

Fig. S4 (a,b) SEM images of pure PVA gel electrolyte with different magnifications.

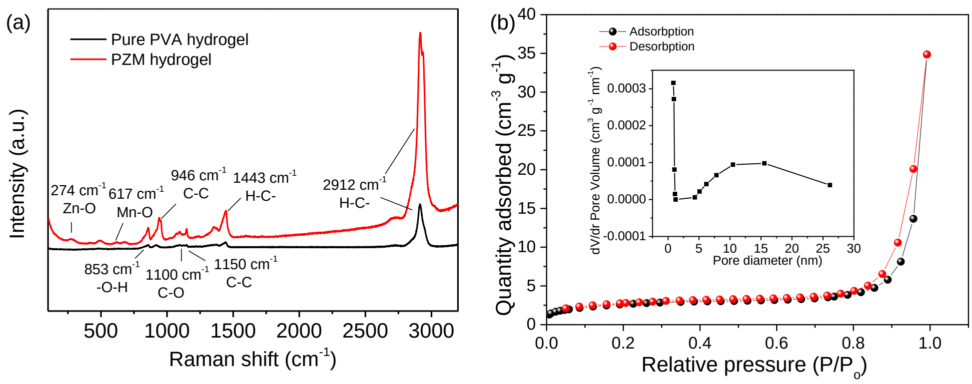

Fig. S5 (a) Raman spectra of PZM and pure PVA hydrogels. (b) N_2 adsorption-desorption isotherm of ZVO, inset shows the pore-size distribution.

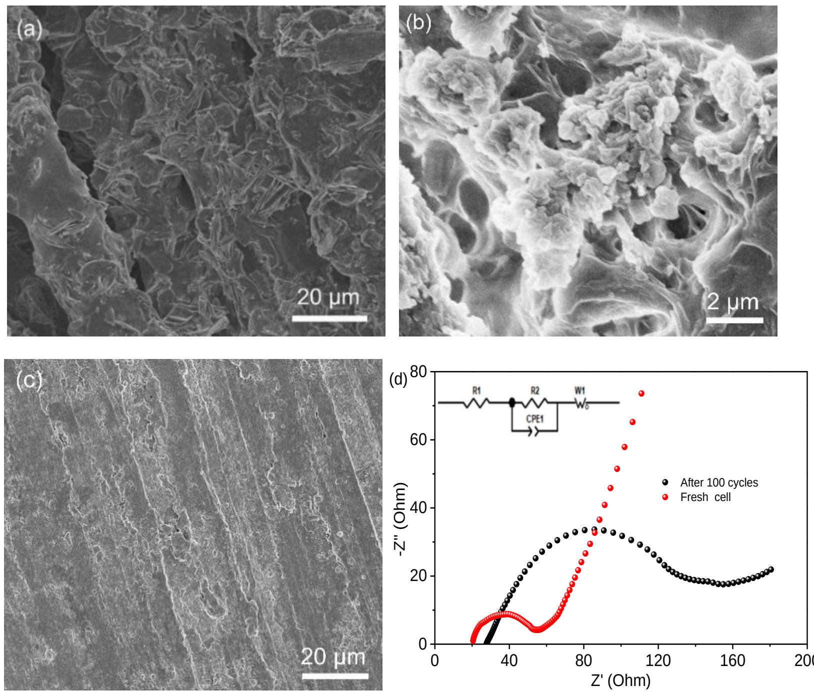

Fig. S6 SEM images of the (a) cathode, (b) PZM hydrogel, and (c) anode after 100 cycles. (e) Impedance spectra of the battery before and after cycling 100 times. The inset shows the equivalent circuit for fitting.

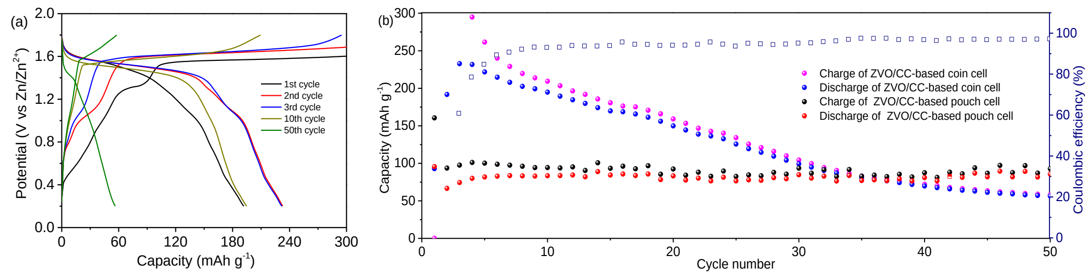

Fig. S7 (a) Charge-discharge curves ZVO/CC-based coin cell. (b) Cycling performances of the ZVO/CC-based coin cell and pouch cell at100 mA g^{-1}.

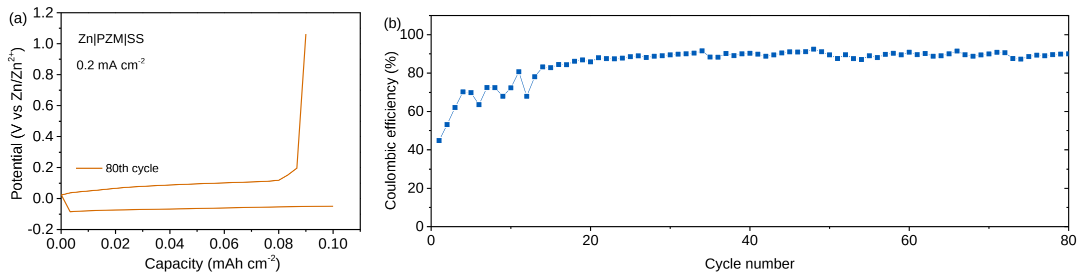

Fig. S8 (a) Charge-discharge curves at the 80th cycle, and (b) Coulombic efficiency of Zn|PZM|stainless steel (SS) half cell at 0.2 mA cm^{-2}.

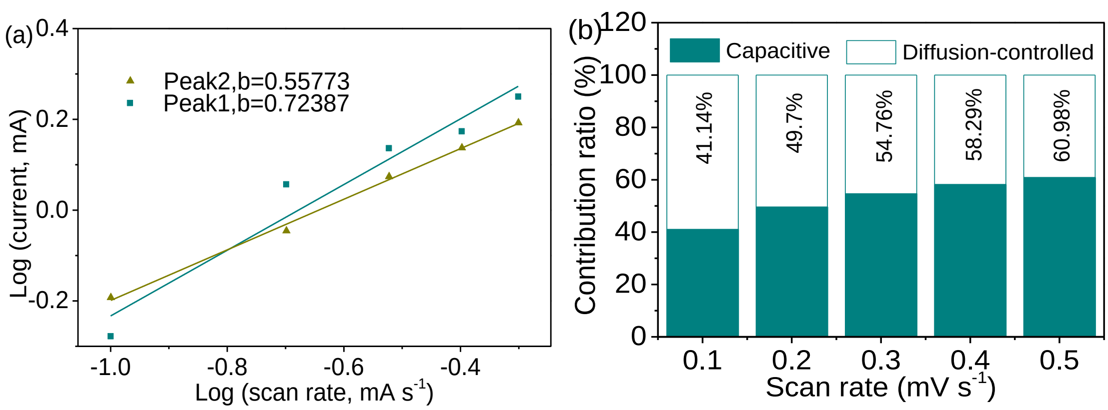

Fig. S9 (a) Fitted line plot of log(i) versus log(v). (b) Ratio of capacitance to diffusion-controlled contribution.

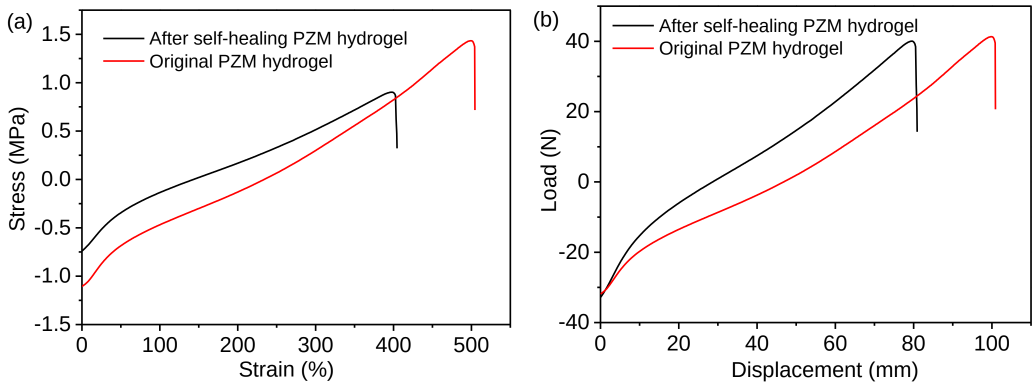

Fig. S10 (a) Stress-strain curves of fresh PZM hydrogel and the one after self-healing. (b) Load-displacement curves.

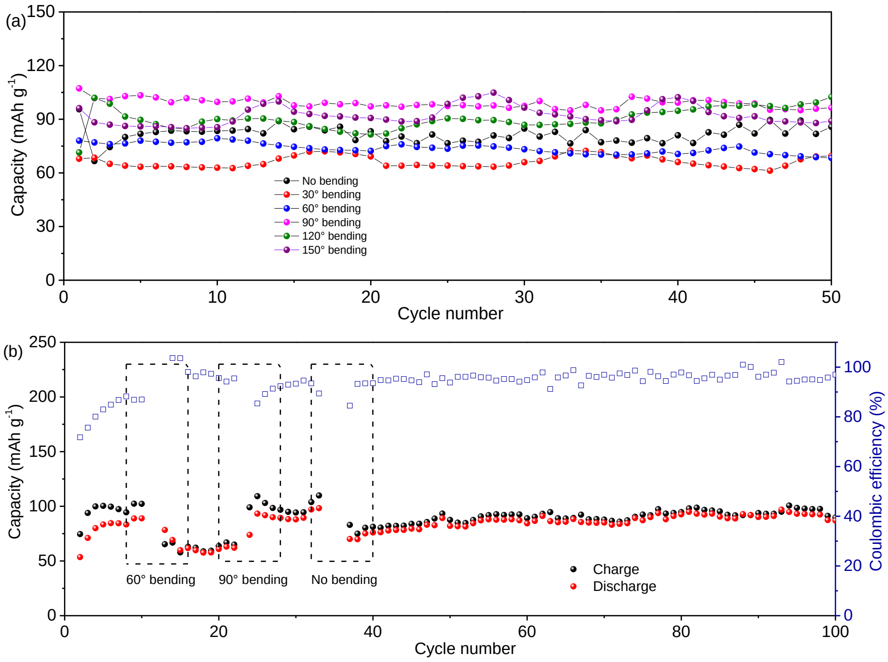

Fig. S11 (a) Capacities when being folded at different angles at 100 mA g^{-1}. (b) Capacities when the battery is folded 60°, 90°, and back to 0°.

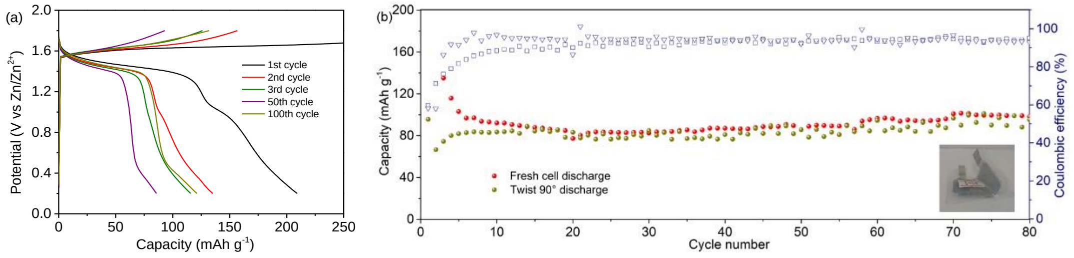

Fig. S12 (a) Charge-discharge curves and (b) cycling performance after the battery was twisted at 90°at 100 mAh g^{-1}. The inset displays the photo of battery after being twisted.

Table S1. Comparison on the electrochemical performance of some Zn-ion batteries.

Cathode	Electrolyte	Capacity /mAh g^{-1}	Rates /A g^{-1}	Cycle numbers	Ref.
Ce-MnO_2	2.0 M $ZnSO_4$ + 0.1 M $MnSO_4$	78	1.5	100	1
KMn_8O_{16}	1.0 M $ZnSO_4$ + 0.05 M $MnSO_4$	77	0.1	100	2
Phenazine	2.0 M $ZnSO_4$	28	0.1	200	3
α-MnO_2	2.0 M $ZnSO_4$	96.8	0.1	50	4
$ZnMnCoO_4$	2.0 M $ZnSO_4$ + 0.1 M $MnSO_4$	39	0.2	120	5
Mn (BTC)	2.0 M $ZnSO_4$ + 0.1 M $MnSO_4$	27	0.1	50	6
Layered MnO_2	1 M $ZnSO_4$	97	0.1	50	7
Prussian blue analogue	1M choline acetate-water + zinc acetate	54	0.1	50	8
$ZnMn_2O_4$	2.0 M ZnSO4 + 0.1 M MnSO4	67	0.1	40	9

MnO_2	1 M $ZnSO_4$ + 0.05 M H_2SO_4	89.5	0.3	55	10
δ-MnO_2	0.3 M $ZnCl_2$	39	0.1	150	11
Perylene-3,4,9,10-tetracarboxy-lic diimide	3.0 M $ZnSO_4$	73	0.1	200	12
V_2O_5	Solid Zn-ion conductors	58	0.02	300	13
PANI/CNT	PVA-based gel electrolyte	50	0.1	480	14
MnO_2/CC	PAM/$ZnSO_4$-$MnSO_4$	91.7	0.1	30	15
ZVO/CC	PZM hydrogel	96	0.1	100	This work

References

1 J. Wang, X. Sun, H. Zhao, L. Xu, J. Xia, M. Luo, Y. Yang, Y. Du, *J. Phys. Chem. C* **2019**, *123*, 22735-22741.

2 J. Cai, X. Wu, S. Yang, C. Li, F. Tang, J. Chen, Y. Chen, Y. Xiang, X. Wu, Z. He, *Front. Chem.* **2018**, *6*, 352.

3 Q. Wang, Y. Liu, P. Chen, *J. Power Sources* **2020**, *468*, 228401.

4 X. Guo, J. Zhou, C. Bai, X. Li, G. Fang, S. Liang, *Mater. Today Energy* **2020**, *16*, 100396.

5 A. Baby, B. Senthilkumar, P. Barpanda, *ACS Appl. Energy Mater.* **2019**, *2*, 3211-3219.

6 X. Pu, B. Jiang, X. Wang, W. Liu, L. Dong, F. Kang, C. Xu, *Nano-Micro Lett.* **2020**, *12*, 152.

7 M. H. Alfaruqi, S. Islam, D. Y. Putro, V. Mathew, S. Kim, J. Jo, S. Kim, Y. K. Sun, K.

Kim, J. Kim, *Electrochim. Acta* **2018**, *276*, 1-11.

8 Z. Liu, P. Bertram, F. Endres, *J. Solid State Electr.* **2017**, *21*, 2021-2027.

9 J. W. Lee, S. D. Seo, D. W. Kim, *J. Alloy. Compd.* **2019**, *800*, 478-482.

10 C. Wu, H. Tan, W. Huang, W. Li, K. N. Dinh, C. Yan, W. Wei, L. Chen, Q. Yan, *Adv. Funct. Mater.* **2020**, *30*, 2003187.

11 W. Kao-ian, R. Pornprasertsuk, P. Thamyongkit, T. Maiyalagan, S. Kheawhom, *J. Electrochem. Soc.* **2019**, *166*, 1063-1069.

12 N. Liu, X. Wu, Y. Zhang, Y. Yin, C. Sun, Y. Mao, L. Fan, N. Zhang, *Adv. Sci.* **2020**, *7*, 2000146.

13 J. Wang, Z. Zhao, G. Lu, Y. Zhang, Q. Kong, J. Zhao, G. Cui, *Mater. Today Energy* **2021**, *20*, 100630.

14 W. Du, J. Xiao, H. Geng, Y. Yang, Y. Zhang, E. H. Ang, M. Ye, C. Li, *J. Power Sources* **2020**, *450*, 227716.

15 F. Wu, X. Gao, X. Xu, Y. Jiang, X. Gao, R. Yin, W. Shi, W. Liu, G. Lu, X. Cao, *ChemSusChem* **2020**, *13*, 1537-1545.