Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Ultrafast and cation insertion-selected zinc hexacyanoferrate for 1.9 V K-Zn hybrid aqueous battery

Meng Huang,[a] Jiashen Meng,[a] Zijian Huang,[a] Xuanpeng Wang[b] and Liqiang Mai*[a]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China

[b] Department of Physical Science & Technology, School of Science, Wuhan University of Technology, Wuhan 430070, P. R. China

*Corresponding Author: E-mail: mlq518@whut.edu.cn

Table S1. Crystallographic data and powder XRD Rietveld refinement results for $K_{0.336}Zn_{2.486}[Fe(CN)_6]_2\cdot 3.09H_2O$ (ZnHCF): atomic coordinates, site occupancies, isotropic displacement parameters and reliability factors at room temperature.

Crystal System	**Trigonal**
Space Group	*R -3 c*
Lattice Parameter	a=12.6148(5), b=12.6148, c=33.0495(22)

Atoms	x	y	z	Wyckoff	Occupancy	Uiso
Zn1	0.28920	0.0	0.25	18e	0.829	18
Fe1	0.0	0.0	0.1468	12c	1.0	12
C1	0.008	0.136	0.1857	36f	1.0	36
C2	0.14	0.14	0.1116	36f	1.0	36
N1	0.027	0.218	0.2069	36f	1.0	36
N2	0.23	0.197	0.0969	36f	1.0	36
K1	-0.006	0.19	0.026	36f	0.056	36
O1	0.364	-0.055	0.07	36f	0.167	36
O2	0.09	0.09	0.028	36f	0.167	36
O3	0.334	-0.05	-0.004	36f	0.167	36

* Rp =7.935, Rwp = 11.445, Rexp = 6.455, R(F2) =13.318, χ2 = 1.7729

Table S2. ICP analysis of ZnHCF.

Element	Fe	Zn	K
Ratio	2.000	2.486	0.336

Table S3. The battery performance comparison of our work and other K and Zn ion aqueous batteries reported previously. The specific capacity is based on the active cathode materials.

Cathode material	Carrier	Rate capability	Discharge plateau	Discharge capacity	cyclability	electrolyte	
$Zn_3[Fe(CN)_6]_2$	Zn^{2+}	32.3 mAh g^{-1} (1.2 A g^{-1})	1.7 V	65.4 mAh g^{-1} (60 mA g^{-1})	100 cycles 81%, retention	1 M $ZnSO_4$	Ref. 3
$FeFe(CN)_6$	Zn^{2+}	30 mAh g^{-1} (60 mA g^{-1})	1.1 V	120 mAh g^{-1} (10 mA g^{-1})	10 cycles 94% retention	1.0 M $Zn(OAc)_2$ in [Ch]OAc + water	Ref. 4
$Na_3V_2(PO_4)_2F_3$	Zn^{2+}	33 mAh g^{-1} (3 A g^{-1})	1.62 V	64.7 mAh g^{-1} (80 mA g^{-1})	4000 cycles, 95% retention	2 M $Zn(CH_3F_3SO_3)_2$	Ref. 5
$K_2NiFe(CN)_6$	K^+/Na^+	35.4 mAh g^{-1} (12 A g^{-1})	1.4 V	67.2 mAh g^{-1} (800 mA g^{-1})	300 cycles, 97.2% retention	K^+/Na^+ (molar ratio 1:1) hybrid electrolyte	Ref. 6
$Zn_3[Fe(CN)_6]_2$	K^+/Zn^{2+}	46.7 mAh g^{-1} (5.16 A g^{-1})	1.937 V	69.1 mAh g^{-1} (172 mA g^{-1})	100 cycles, 86.4% retention	0.5 M $ZnSO_4$+0.25 M K_2SO_4 electrolyte	This work

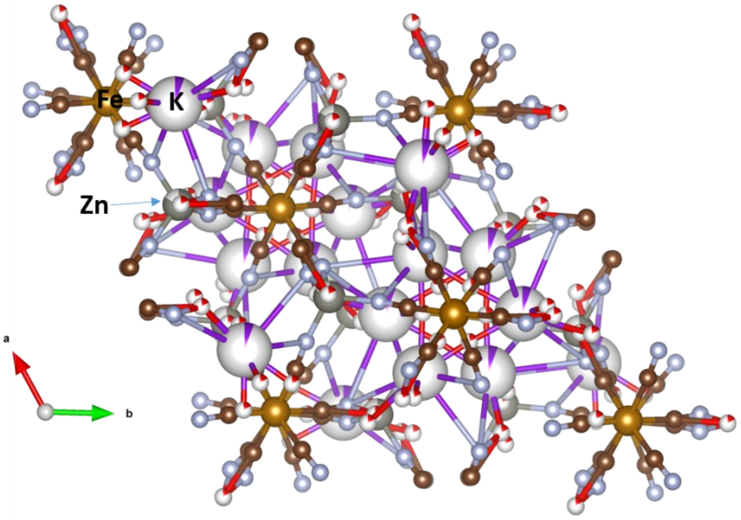

Fig. S1. (010) views of the local structure of ZnHCF.

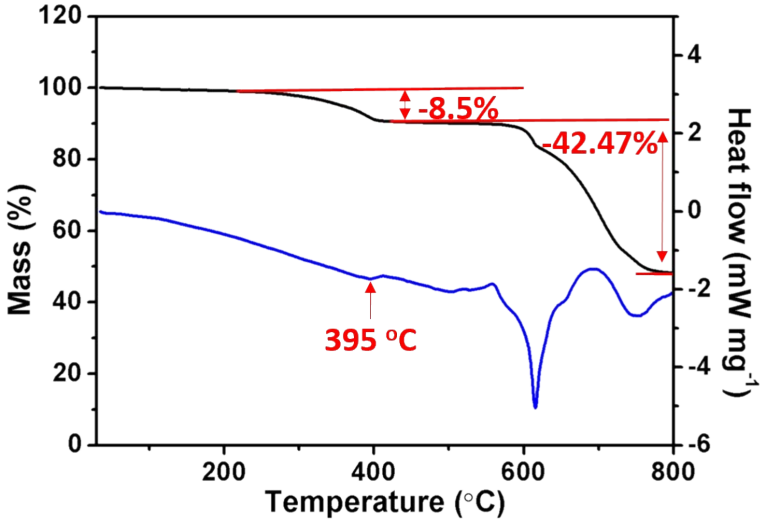

Fig. S2. DTG and DSC profiles of ZnHCF under Ar atmosphere (CHNO (wt%) is 50.97%) with temperature rate of 10 °C min^{-1}.

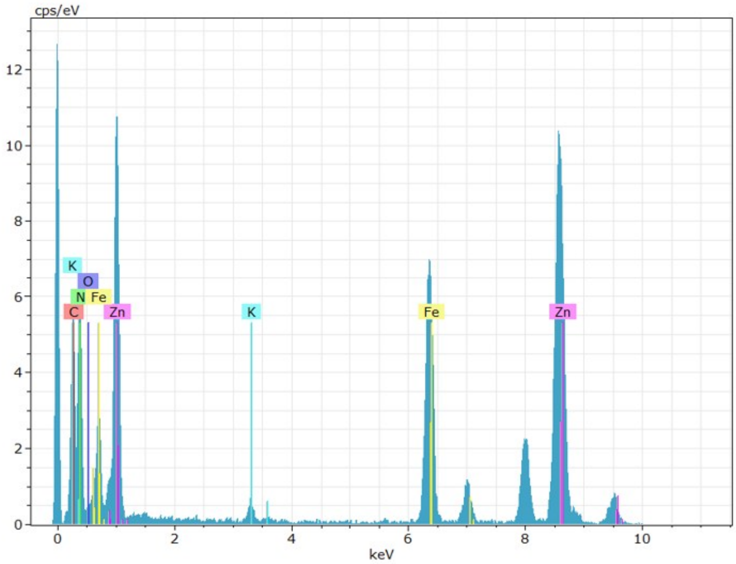

Fig. S3. EDX spectrum of ZnHCF.

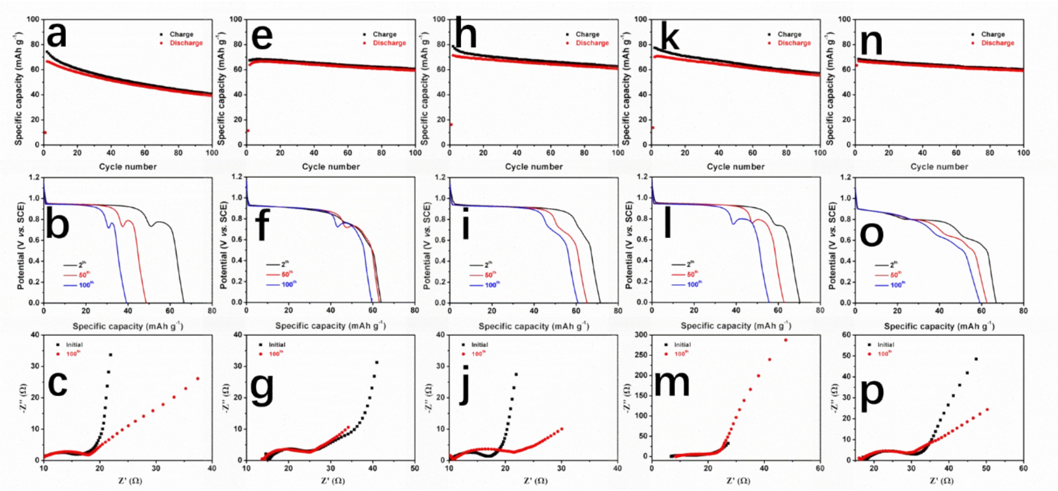

Fig. S4. Cycling performances of ZnHCF at 20 C in 10.0 ml different electrolytes, the corresponding discharge profiles at the 2th, 50th and 100th cycles, and EIS data at the initial state and after 100 cycles: (a-c) 0.05 M $ZnSO_4$+0.5 M K_2SO_4 (0.812 mg active materials), (e-g) 0.5 M $ZnSO_4$+0.25 M K_2SO_4 (0.924 mg active materials), (h-j) 0.25 M $ZnSO_4$+0.25 M K_2SO_4 (0.756 mg active materials), (k-m) 0.25 M $ZnSO_4$+0.5 M K_2SO_4 (0.791 mg active materials), (n-p) 0.5 M $ZnSO_4$+0.05 M K_2SO_4 (0.875 mg active materials).

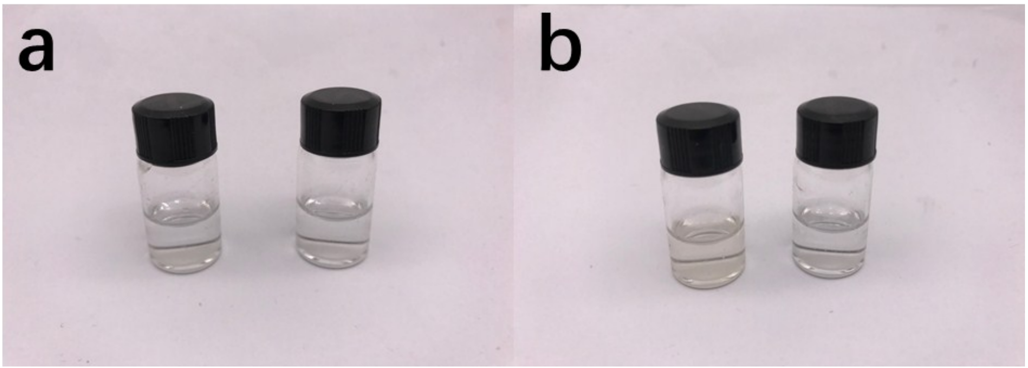

Fig. S5. The 0.05 M $ZnSO_4$+0.5 M K_2SO_4 (left) and 0.5 M $ZnSO_4$+0.25 M K_2SO_4 (right) electrolyte (a) before and (b) after cycling at 20 C.

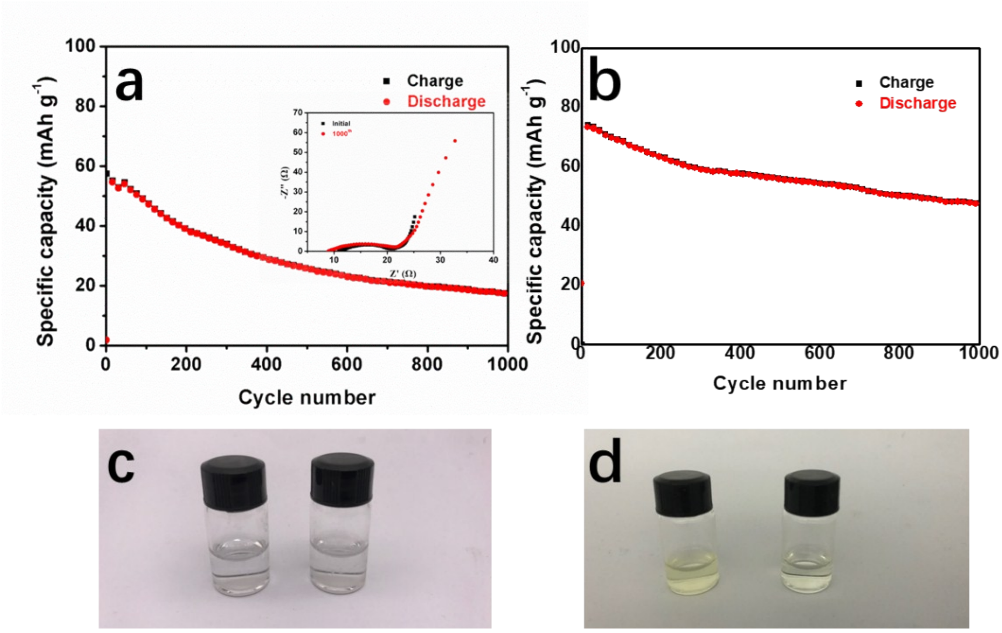

Fig. S6. Cycling performances of ZnHCF at 50 C in (a) 1.5 ml 0.05 M $ZnSO_4$+0.5 M K_2SO_4 electrolytes (1.337 mg active materials), (b) 1.5 ml 0.5 M $ZnSO_4$+0.25 M K_2SO_4 electrolytes (1.526 mg active materials), inset of (a) is the EIS data at the initial state and after 1000 cycles. After cycling for 1000 cycles, the capacity fade of the ZnHCF is 69.0% in condition (a) and 36.1% in condition (b) based on the second discharge capacity. The 0.05 M $ZnSO_4$+0.5 M K_2SO_4 (left) and 0.5 M $ZnSO_4$+0.25 M K_2SO_4 (right) electrolyte (c) before and (d) after cycling at 50 C in different electrolytes.

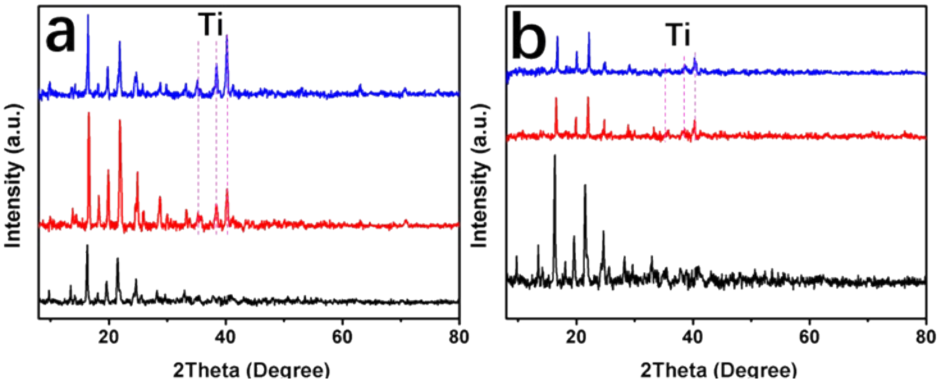

Fig. S7. XRD patterns of fresh and after cycling electrode paste films. (a): fresh electrode paste film (black), after cycling in 0.05 M $ZnSO_4$+0.5 M K_2SO_4 (red) at 20 C for 100 times, and after cycling in 0.5 M $ZnSO_4$+0.25 M K_2SO_4 (blue) at 20 C for 100 times. (b): fresh electrode paste film (black), after cycling in 0.05 M $ZnSO_4$+0.5 M K_2SO_4 (red) at 50 C for 1000 times, and after cycling in 0.5 M $ZnSO_4$+0.25 M K_2SO_4 (blue) at 50 C for 1000 times.

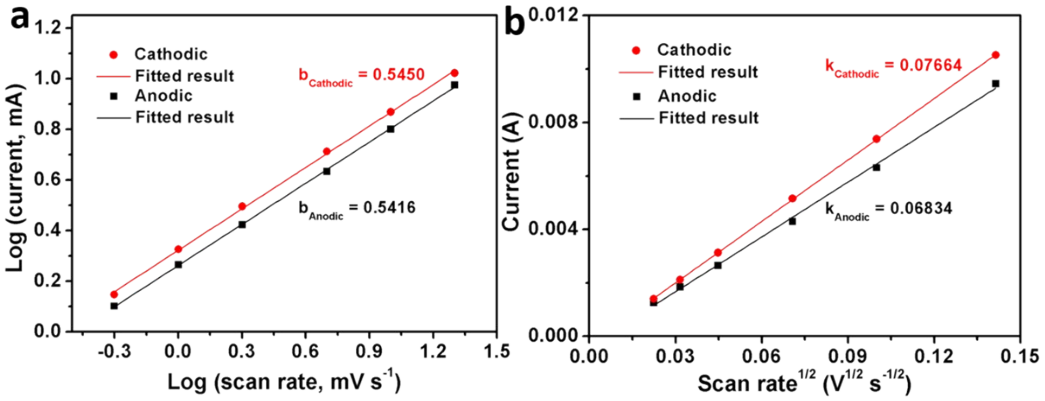

Fig. S8. (a) Log (i) versus log (v) plots at specific peak currents. (b) The relation between the square root of the scan rate ($v^{1/2}$) and the corresponding currents for anodic and cathodic peaks. It is found that the peak currents for both electrodes display a linear relation with the square root of the scan rate ($v^{1/2}$).

Calculation of K^+ apparent diffusion coefficients through CV results[1,2]: The diffusion coefficient value (D) can be calculated from the Eq. (1):

$$Ip = 2.69 \times 10^5\, n^{3/2} A D^{1/2}\, C v^{1/2} \qquad (1)$$

where I_p is the peak current (A), n is the number of electrons per molecule during the intercalation, A is the surface area of the cathode (cm^2), C is the concentration of K ions in the electrode (mol cm^{-3}), and v is the scanning rate (V s^{-1}).

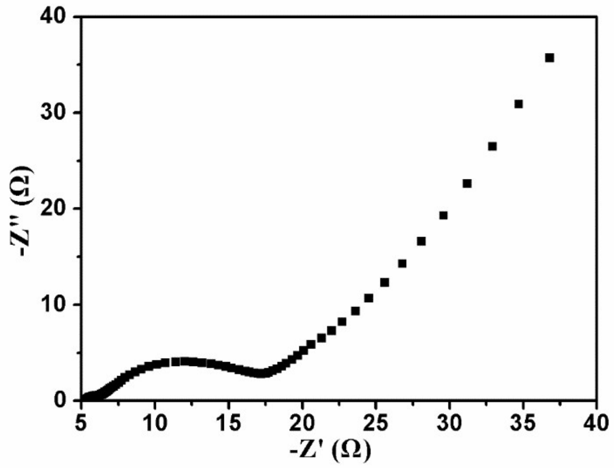

Fig. S9. EIS of ZnHCF at 0.5 M $ZnSO_4$+0.25 M K_2SO_4 electrolyte using a three-electrode cell setup (Zn plates were employed as reference and counter electrodes).

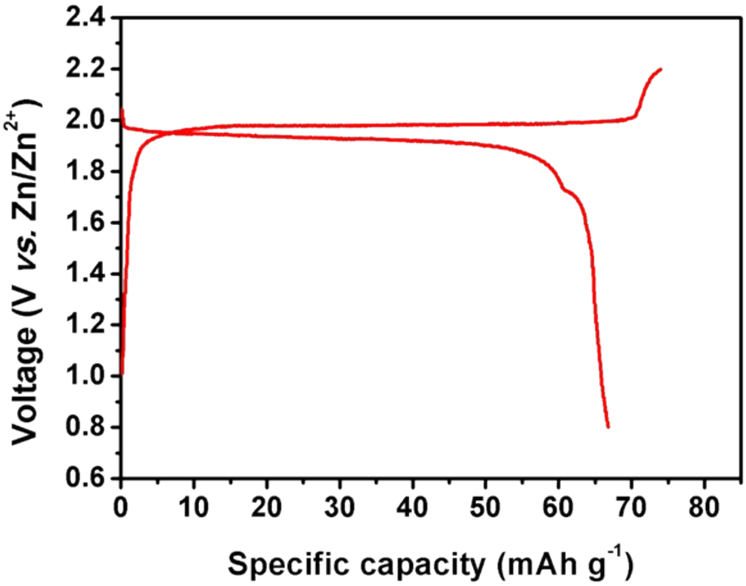

Fig. S10. Charge/discharge profiles of ZnHCF//Zn (mass ratio of active materials at approximate 1:1) cell when the rate returns to 2 C.

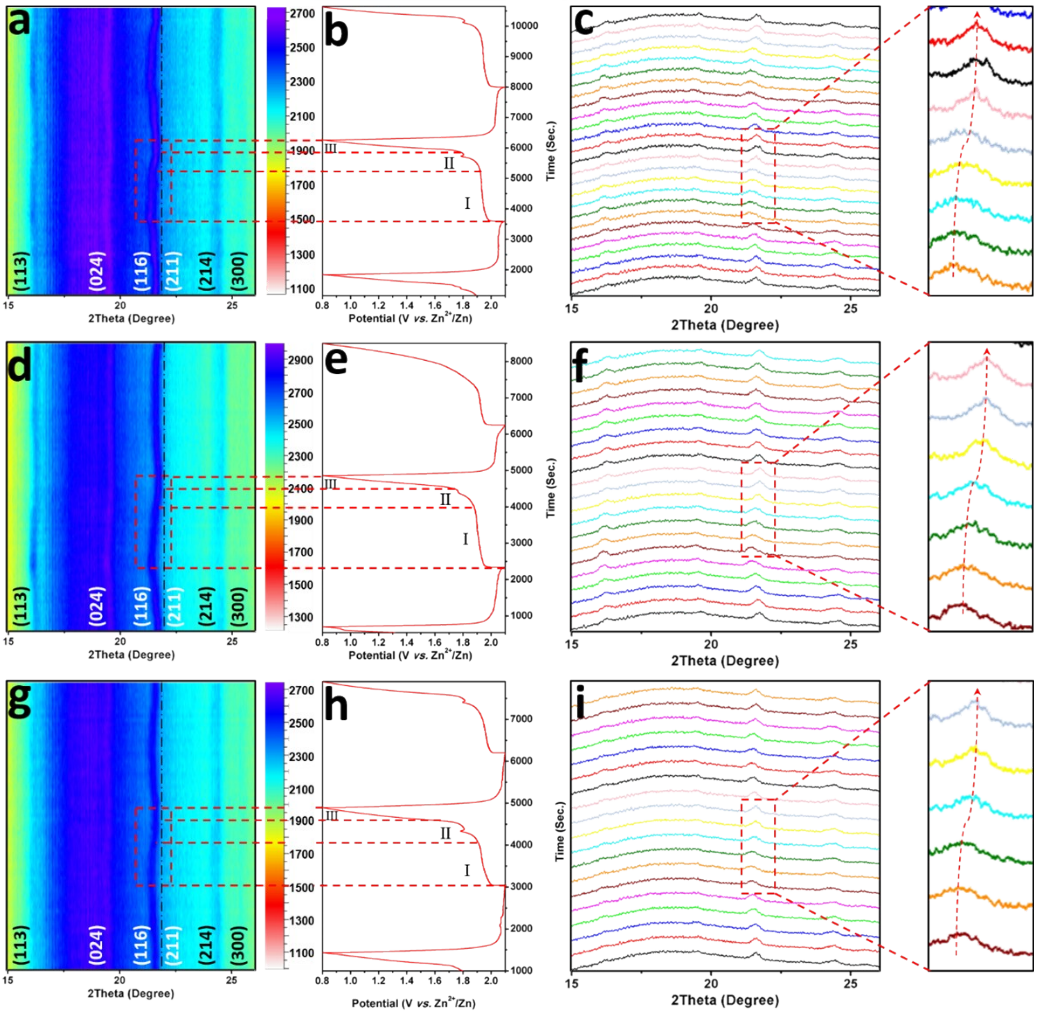

Fig. S11. In situ XRD characterizations of ZnHCF in (a-c) 0.25 M $ZnSO_4$+0.5 M K_2SO_4 electrolyte, (d-f) 0.25 M $ZnSO_4$+0.25 M K_2SO_4 electrolyte and (g-i) 0.05 M $ZnSO_4$+0.5 M K_2SO_4 electrolyte: (a, d, and g) 2D XRD pattern; (b, e, and h) Corresponding charge-discharge profiles at charge rate of 2 C and discharge rate of 1C; (c, f, and i) 1D XRD patterns.

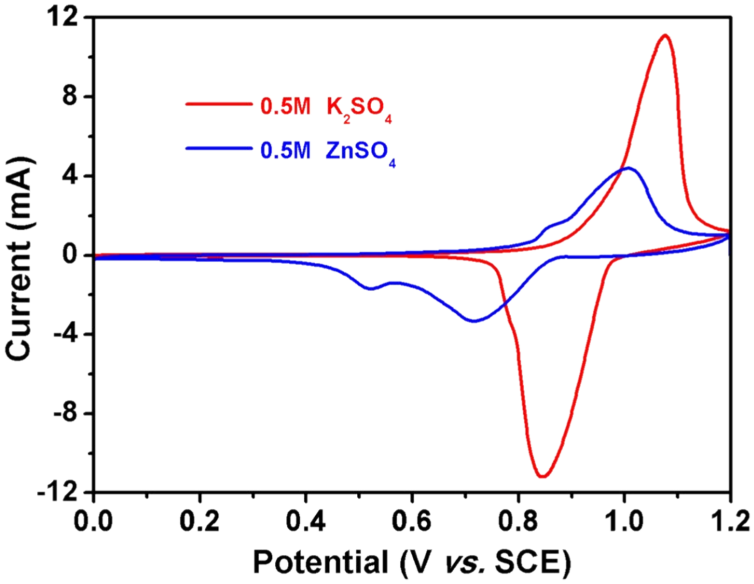

Fig. S12. Cyclic voltammetry of same ZnHCF sample was tested in 0.5 M K_2SO_4 electrolyte (red curve) and 0.5 M $ZnSO_4$ electrolyte (blue curve) at 5 mV s^{-1}.

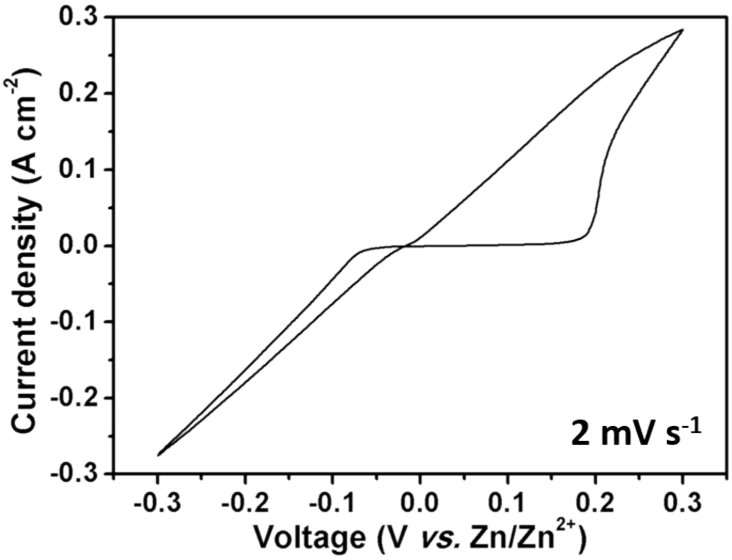

Fig. S13. Cyclic voltammetry curves of Zn at 0.5 M ZnSO4+0.25 M K_2SO_4 electrolyte using a three-electrode cell setup (Zn plates were employed as reference and counter electrodes).

References

1 T. Brezesinski, J. Wang, S.H. Tolbert and B. Dunn, *Nat. Mater.,* 2010, **9,** 146-151.
2 V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.L. Taberna, S.H. Tolbert, H.D. Abruna, P. Simon and B. Dunn, *Nat. Mater.,* 2013, **12,** 518-522.
3. L. Zhang, L. Chen, X. Zhou and Z. Liu, *Adv. Energy Mater.,* 2015, **5,** 1400930.
4. Z. Liu, G. Pulletikurthi and F. Endres, *ACS appl. mater. Inter.,* 2016, **8,** 12158-12164.
5. W. Li, K. Wang, S. Cheng and K. Jiang, *Energy Storage Mater.,* 2018, **15,** 14-21.
6. W. Ren, X. Chen and C. Zhao, *Adv. Energy Mater.,* 2018, **8,** 1801413.