batteries

MDPI

Supplementary Information

Prototype System of Rocking-Chair Zn-Ion Battery adopting Zinc Chevrel Phase Anode and Rhombohedral Zinc Hexacyanoferrate Cathode

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Abbreviations

Zinc-ion battery	ZIB
Energy storage system	ESS
Lithium-ion battery	LIB
$K_x(H_2O)_{0.22}Zn_3[Fe(CN)_6]_2$	ZPB
N-methyl-2-pyrrolidone	NMP
X-ray diffraction	XRD
zinc-inserted ZPB phase	$Zn_{0.72}$ZPB
cyclic voltammogram	CV
The just wetted phase	Zn_0ZPB
Negative to positive	N/P

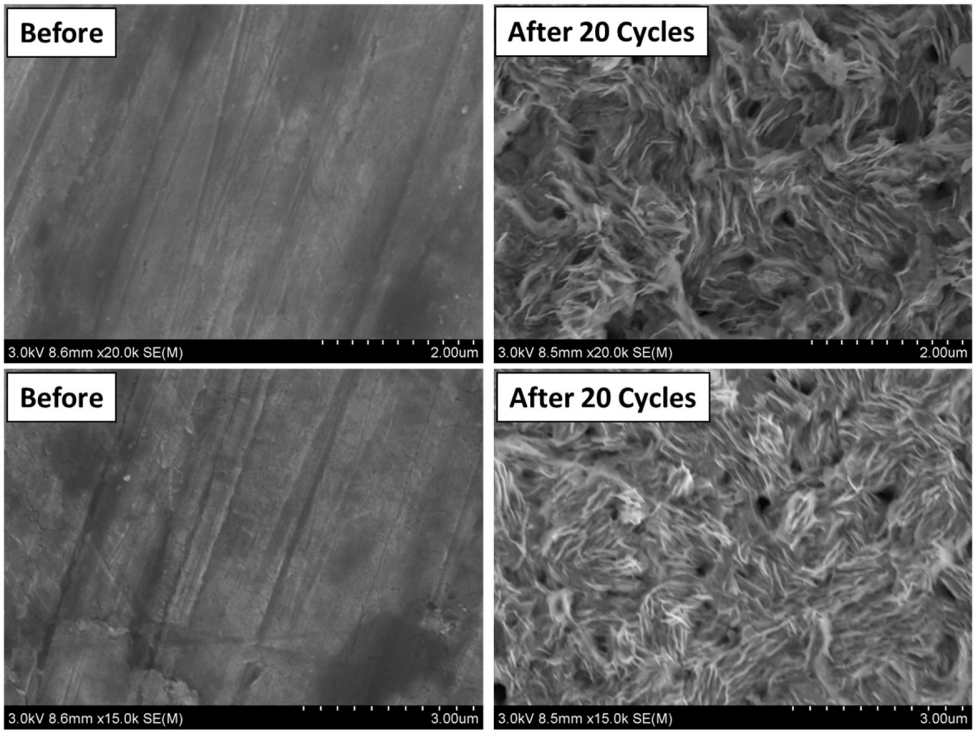

Figure S1. SEM images of the zinc anode before and after 20 cycles.

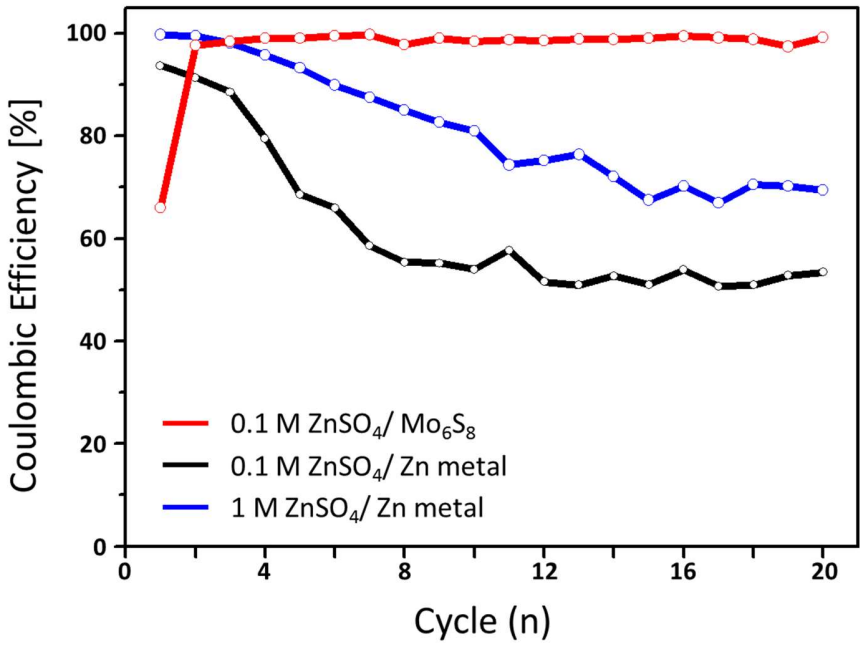

Figure S2. Coulombic efficiencies for zinc metal and Mo_6S_8 in 0.1M $ZnSO_4$ or 1M $ZnSO_4$ aqueous electrolytes.

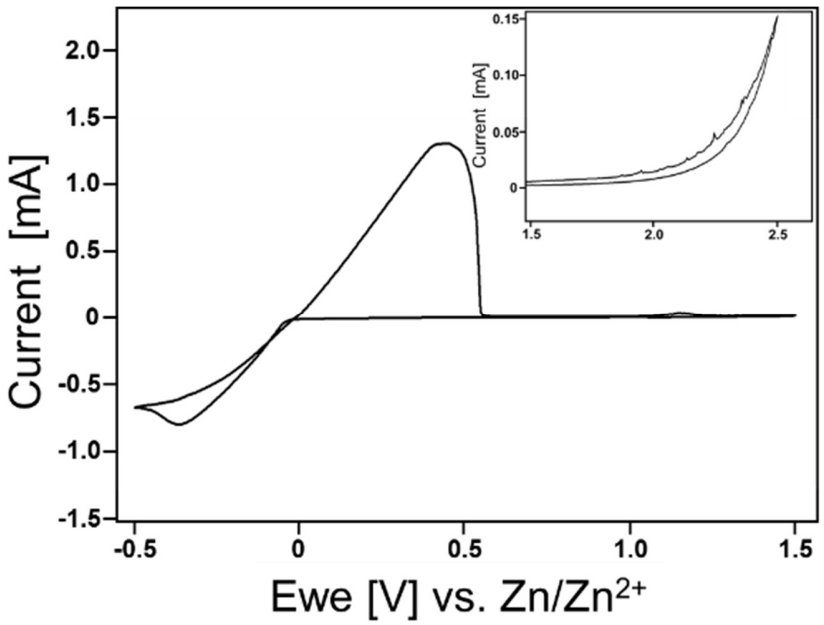

Figure S3. Cyclic voltammogram of 0.1M $ZnSO_4$ aqueous electrolyte. Pt was used as the working electrode at 25 °C and a scan rate of 20 mV s^{-1}.

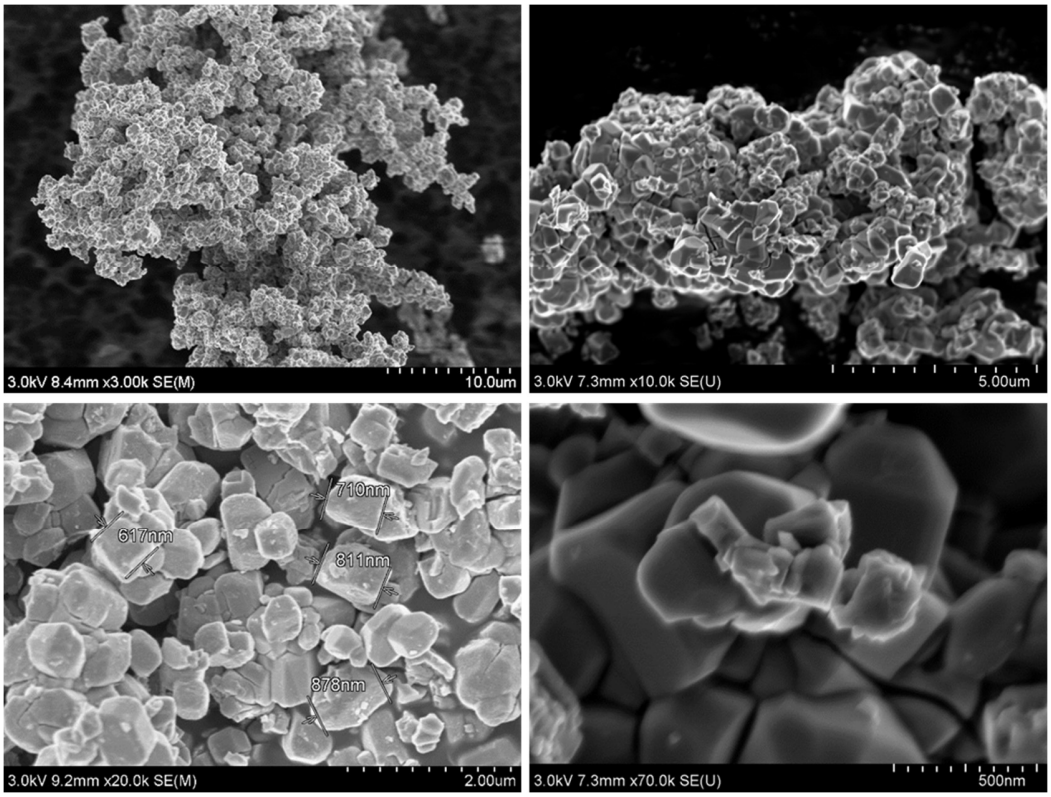

Figure S4. SEM images of synthesized Mo_6S_8 powder.

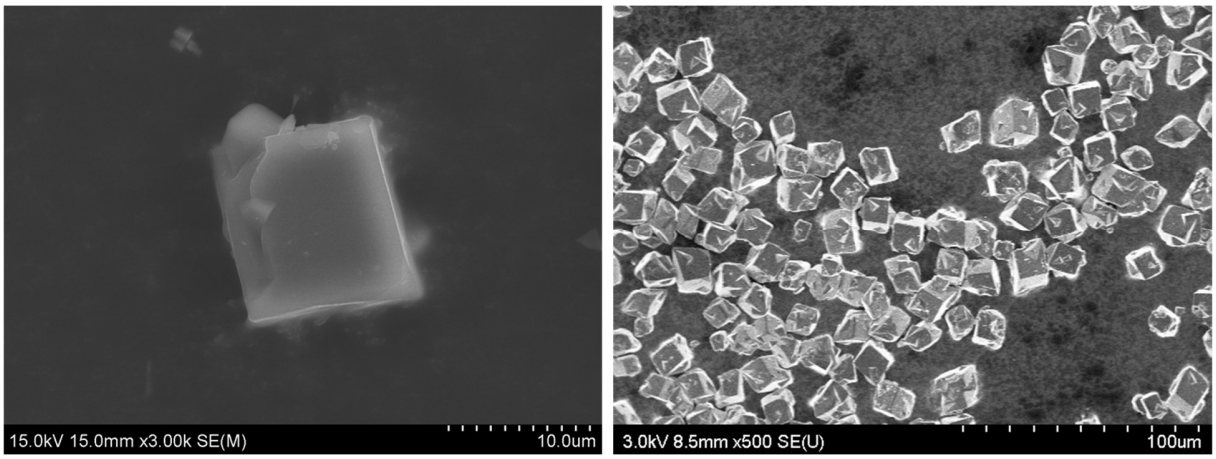

Figure S5. SEM images of the synthesized zinc hexacyanoferrate (ZPB) particles.

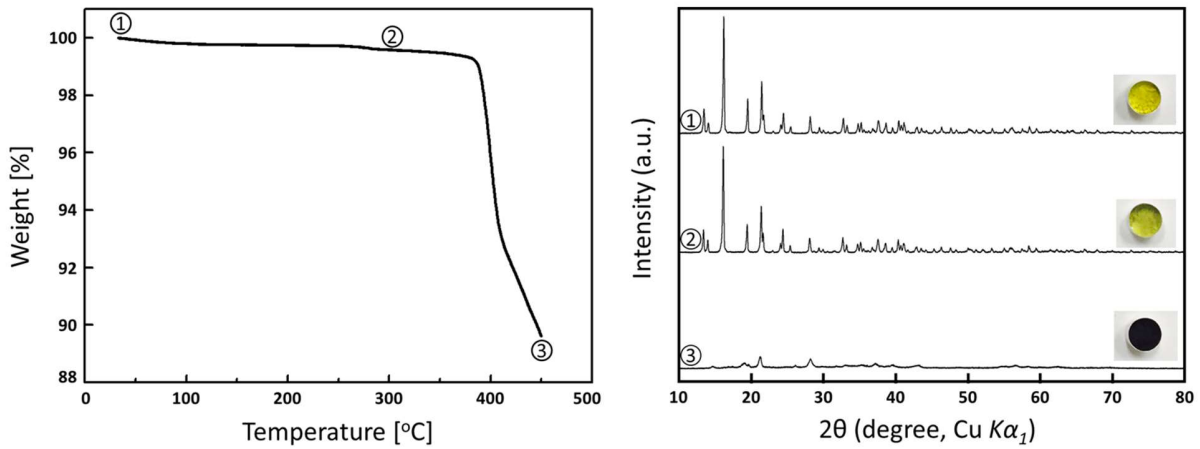

Figure S6. Thermogravimetric analysis for $K_{0.02}(H_2O)_{0.22}Zn_{2.94}[Fe(CN)_6]_2$ (ZPB) under nitrogen flowing atmosphere and XRD patterns to check structural stability (rate = 10 °C/min).

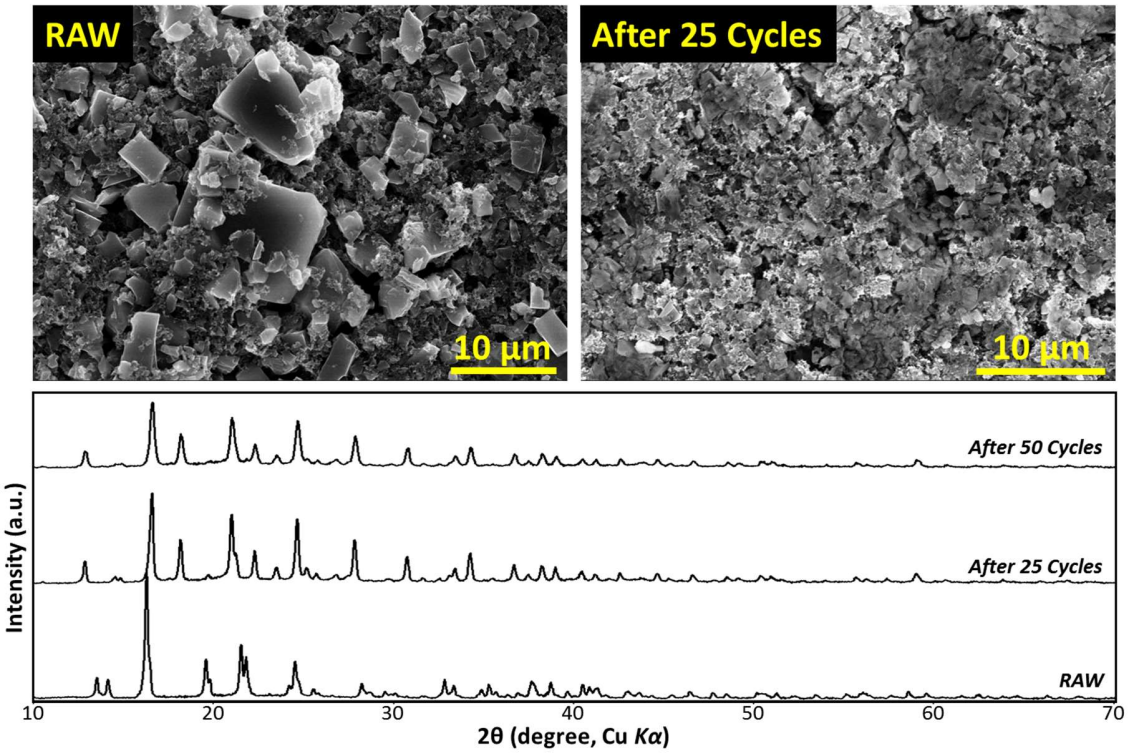

Figure S7. SEM images of XRD patterns of ZPB electrodes before and after 25cycles.

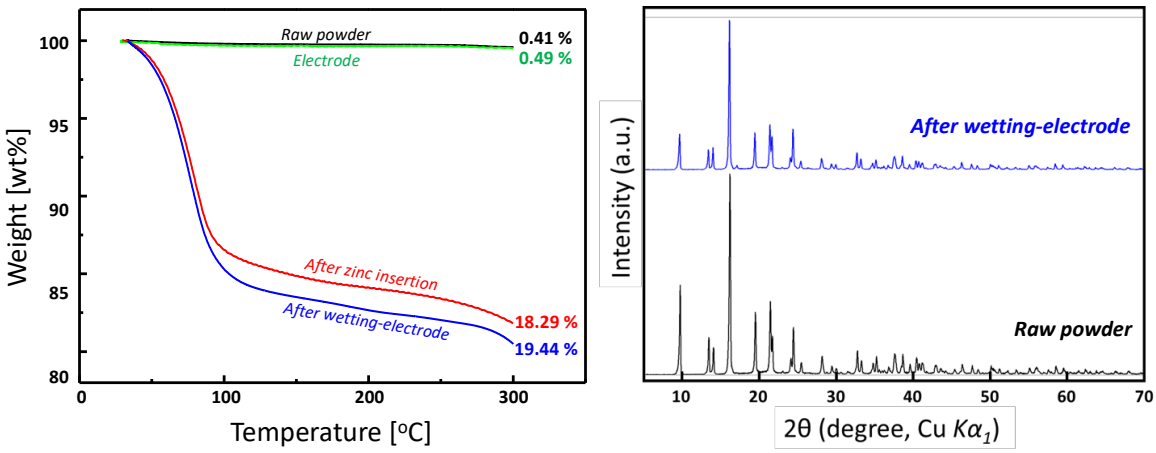

Figure S8. (Left) Thermogravimetric analysis for $K_{0.02}(H_2O)_{0.22}Zn_{2.94}[Fe(CN)_6]_2$ (ZPB) and $Zn_xK_{0.02}(H_2O)_{8.3}Zn_{2.94}$ $[Fe(CN)_6]_2$ (Zn_xZPB) (x = 0, 0.72)phases under nitrogen flowing atmosphere. (Right) XRD patterns of raw (ZPB) and its wetted phase (Zn_0ZPB).

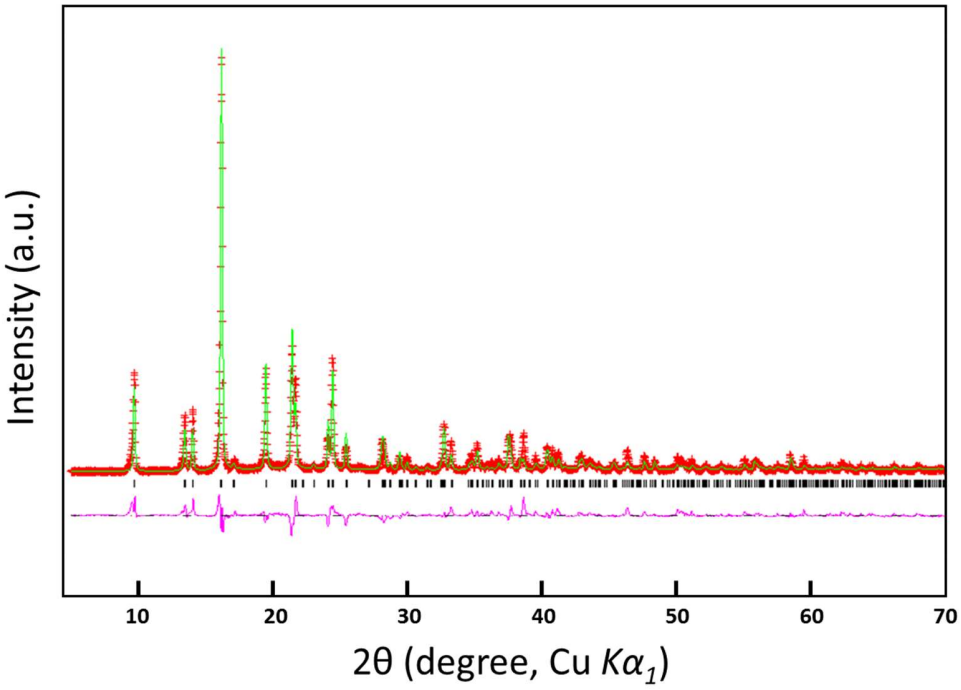

Figure S9. Powder XRD Rietveld refinement profile for the wetted ZPB phase, $K_{0.02}(H_2O)_{8.3}Zn_{2.94}[Fe(CN)_6]_2$ (= Zn_0ZPB) at room temperature.

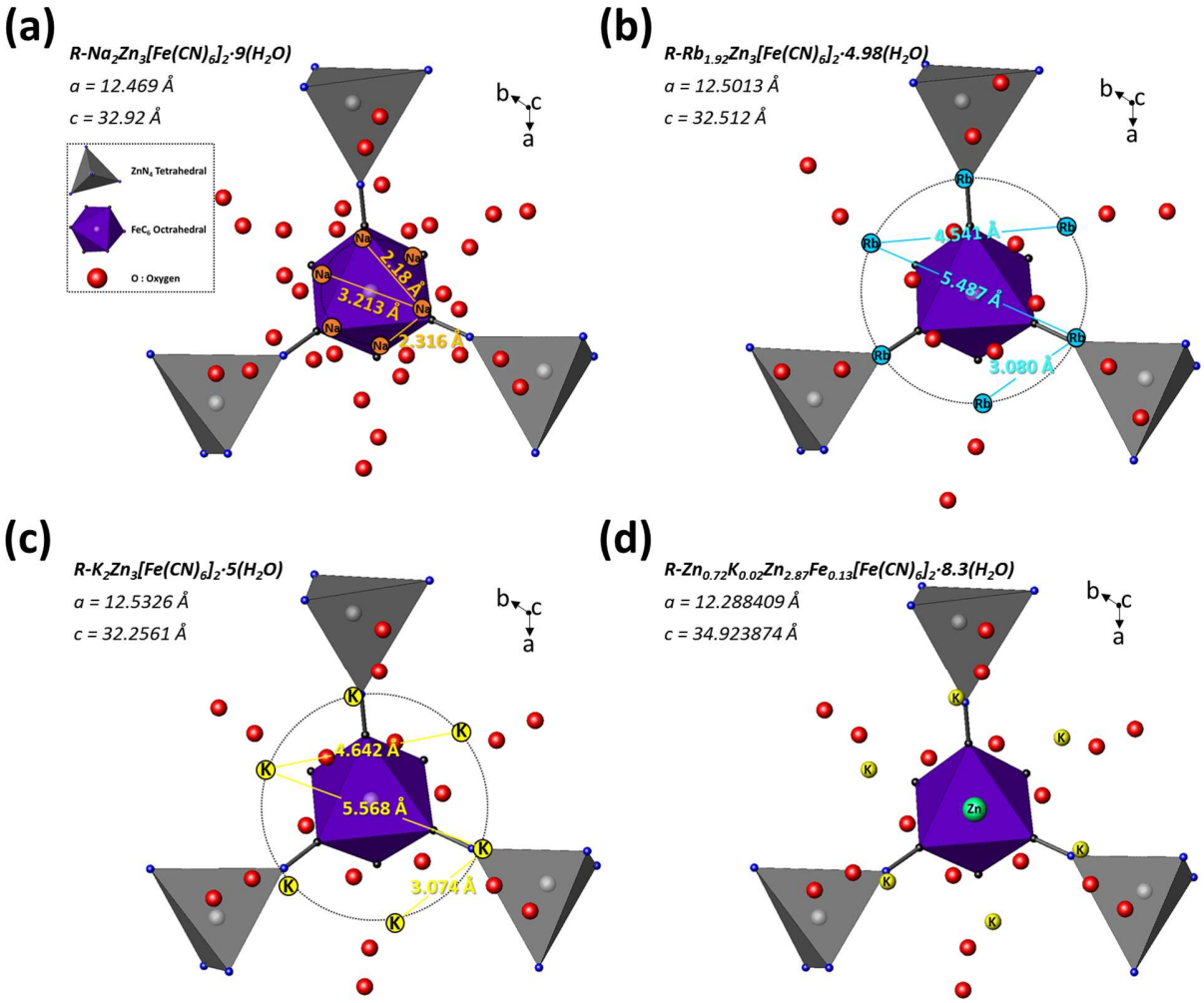

Figure S10. Structural illustration for intercalation position of various gest ions (a) Na^+, (b) Rb^+, (c) K^+, (d) Zn^{2+}).

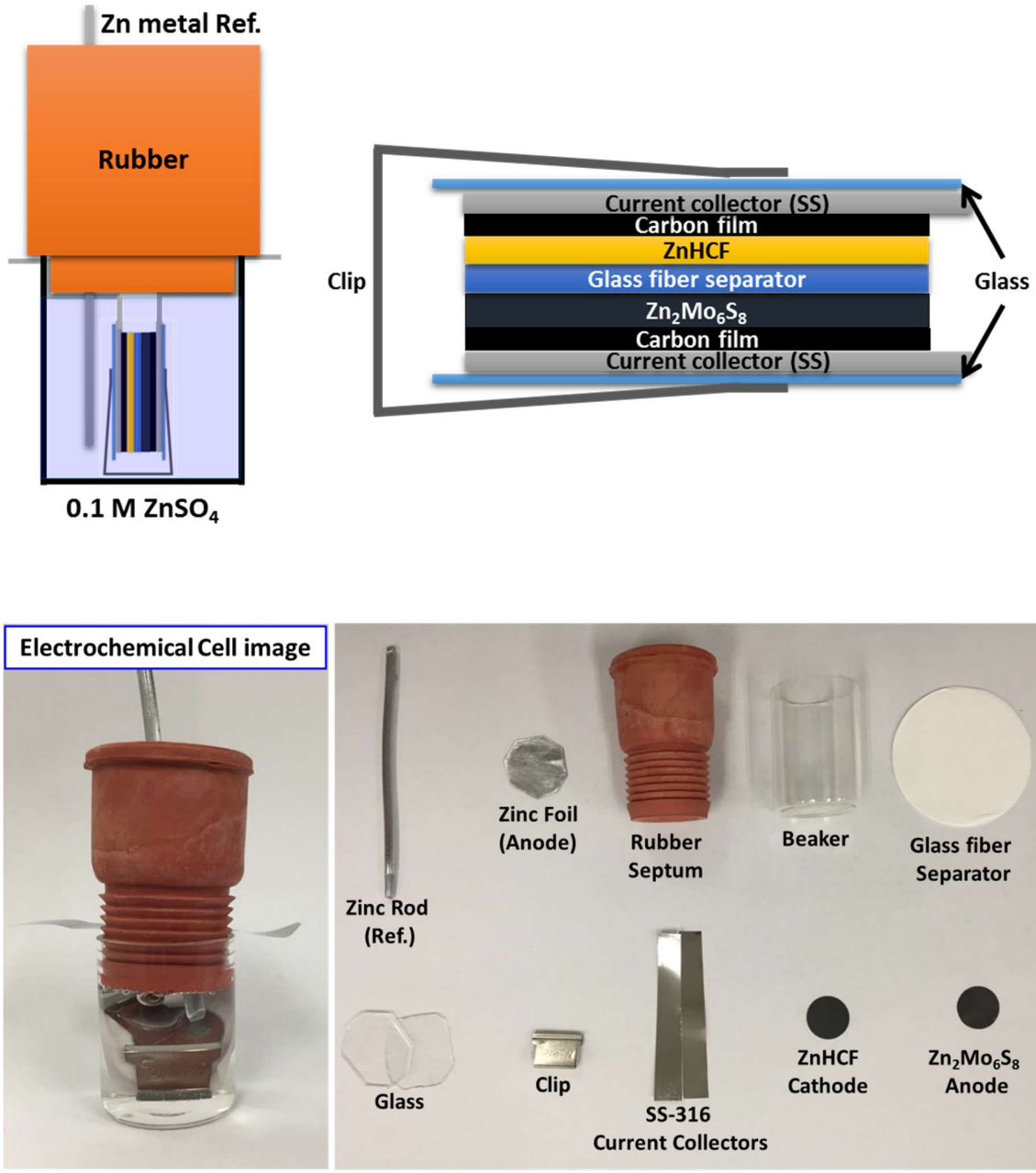

Figure S11. The schematic design of $Zn_2Mo_6S_8$/ZnPB full cell system, and the photographic images of the beaker-type cell and its components used in this work.

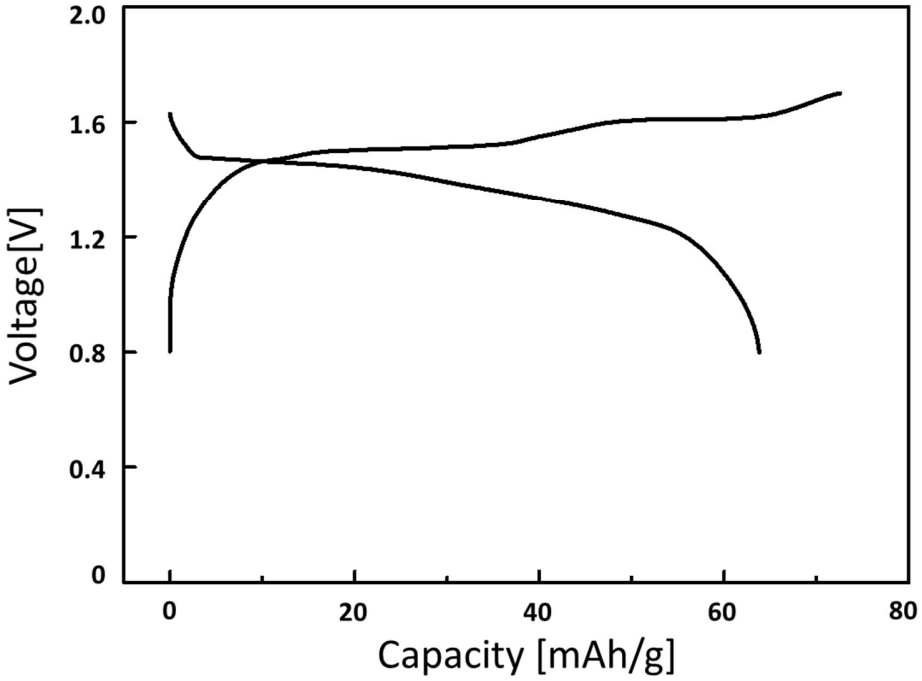

Figure S12. Galvanostatic curves of the $Zn_2Mo_6S_8$/ZnPB full cell at 0.5C-rate. Note that the voltage is the cell voltage (the difference between the cathode and anode).

Table S1. Crystallographic data and Rietveld refinement results of Mo_6S_8 powder: atomic coordinates, site occupancies, isotropic displacement parameters and reliability factors at room temperature.

Crystal System			Trigonal			
Space Group			R $\bar{3}$ (no. 148)			
Lattice Parameter			a = 9.1952(1) Å, c = 10.8825(3) Å, V = 796.86(2) Å^3, Z = 3			
Atoms	x	y	Z	Wyckoff	Occupancy	U_{iso}
Mo	0.8234(2)	0.8381(2)	0.3876(1)	18f	1.0000	0.0089(2)
S1	0.9630(4)	0.6736(4)	0.4175(3)	18f	1.0000	0.008(1)
S2	0.0000	0.0000	0.2107(5)	6c	1.0000	0.003(2)

*R_p = 0.102, R_{wp} = 0.135, R_{exp} = 0.062, $R(F^2)$ = 0.186, χ^2 = 4.71

Table S2. Selected interatomic distances (Å) in the crystal structure of Mo_6S_8 at room temperature.

Mo1-Mo1	2.702(2) Å * 2	Mo1-S2	2.534(4) Å
Mo1-Mo1	2.903(2) Å * 2	Mo1-S2	2.481(4) Å
Mo1-S1	2.478(5) Å	Mo1-S2	2.411(4) Å
Mo1-S2	2.446(4) Å		

Table S3. Crystallographic data and powder XRD Rietveld refinement results for $K_{0.02}(H_2O)_{0.22}Zn_{2.94}[Fe(CN)_6]_2$ (ZPB) powder: atomic coordinates, site occupancies, isotropic displacement parameters and reliability factors at room temperature.

Crystal System			Trigonal			
Space Group			R $\bar{3}$ c (no. 167)			
Lattice Parameter			a = 12.6006 (3) Å, c = 32.9652 (12) Å, V = 4532.81 (3) Å^3, Z = 12			
Atoms	x	y	z	Wyckoff	Occupancy	U_{iso}
Zn1	0.2905(2)	0.0000	0.2500	18e	0.9800	0.0118(5)
Fe1	0.0000	0.0000	0.1466(1)	12c	1.0000	0.0118(5)
C1	0.016(13)	0.1333(9)	0.1804(3)	36f	1.0000	0.0222(24)
C2	0.1255(9)	0.1138(10)	0.1111(3)	36f	1.0000	0.0222(24)
N1	0.0293(9)	0.2134(6)	0.2023(2)	36f	1.0000	0.0222(24)
N2	0.2162(6)	0.1863(7)	0.0962(3)	36f	1.0000	0.0222(24)
K1	0.04667	0.2333	0.0233	36f	0.0033	0.0118(5)
O1	0.34667	0.01333	0.05333	36f	0.0122	0.0222(24)
O2	0.14667	0.04333	0.00333	36f	0.0122	0.0222(24)
O3	0.26333	0.00667	0.03667	36f	0.0122	0.0222(24)

** R_p = 0.153, R_{wp} = 0.205, R_{exp} = 0.072, $R(F^2)$ = 0.135, χ^2 = 8.18*

Table S4. Selected interatomic distances (Å) in the structure of $K_{0.02}(H_2O)_{0.22}Zn_{2.94}[Fe(CN)_6]_2$ (ZPB) at room temperature.

Zn1-N1	1.976 (6) Å * 2	K1-C2	3.623 (13) Å
Zn1-N2	1.986 (4) Å * 2	K1-N1	3.092 (5) Å
Fe1-C1	1.939 (5) Å * 2	K1-N2	3.458 (11) Å
Fe1-C2	1.913 (4) Å * 2	K1-O1	2.02248 (4) Å
C1-N1	1.185 (5) Å	K1-O2	3.28191 (7) Å
C2-N2	1.156 (5) Å	K1-O3	0.96391 (2) Å
K1-C1	3.504 (11) Å	O2-O3	2.06427 (4) Å

Table S5. Elemental ratios estimated from ICP (Inductively coupled plasma) analysis for $K_{0.02}(H_2O)_{0.22}Zn_{2.94}[Fe(CN)_6]_2$ (ZPB) powder.

	Mass ratio (%)			**Relative atomic ratio**		
	K	Zn	Fe	**K**	**Zn**	**Fe**
Sample						

ZnPB	0.004	63.055	36.610	**0.02**	**1.47**	**1.00**

Table S6. Quantitative HR FE-SEM EDX data from which the (Zn/Fe) atomic ratios were estimated for each electrode sample of $Zn_xK_{0.02}(H_2O)_{8.3}Zn_{2.94}[Fe(CN)_6]_2$ (Zn_xZPB) (x = 0, 0.25, 0.50, 0.72) during discharge/charge cycle.

Point #	**Atomic%**		**Atomic ratio**	
	Zn	Fe	Zn/Fe	ΔZn
ZnPB				
Sample 1	60.22	39.78	1.51	0.03
Sample 2	58.67	41.33	1.42	-0.16
Sample 3	60.97	39.03	1.56	0.12
		Average	**1.50**	**0.00**
$Zn_{0.25}$ZnPB				
Sample 1	62.21	37.79	1.64	0.29
Sample 2	62.79	37.21	1.68	0.38
Sample 3	62.48	37.52	1.66	0.33
		Average	**1.67**	**0.33**
$Zn_{0.5}$ZnPB				
Sample 1	64.06	35.94	1.78	0.56
Sample 2	62.90	37.10	1.70	0.39
Sample 3	64.30	35.70	1.80	0.60
		Average	**1.76**	**0.52**
$Zn_{0.72}$ZnPB				
Sample 1	64.72	35.28	1.83	0.67
Sample 2	64.39	34.91	1.86	0.73
Sample 3	64.18	34.98	1.86	0.72
		Average	**1.85**	**0.71**
$Zn_{0.5}$ZnPB				
Sample 1	63.21	36.79	1.72	0.44
Sample 2	64.39	35.61	1.81	0.62
Sample 3	64.18	35.82	1.79	0.58
		Average	**1.77**	**0.54**
$Zn_{0.25}$ZnPB				
Sample 1	63.21	36.79	1.72	0.43
Sample 2	61.87	38.13	1.62	0.24
Sample 3	62.40	37.60	1.66	0.31
		Average	**1.67**	**0.33**
ZnPB				
Sample 1	58.89	41.11	1.43	-0.13
Sample 2	59.78	40.22	1.49	-0.03
Sample 3	61.31	38.69	1.58	0.16

	Average	**1.50**	**0.00**

Table S7. Elemental ratios estimated from ICP (Inductively coupled plasma) analysis for $K_{0.02}(H_2O)_{0.22}Zn_{2.94}$ $[Fe(CN)_6]_2$ (ZPB), $Zn_xK_{0.02}(H_2O)_{8.3}Zn_{2.94}[Fe(CN)_6]_2$ (Zn_xZPB) samples (x = 0.72 and 0).

	Mass ratio (%)		**Relative atomic ratio**	
	Zn	Fe	**Zn**	**Fe**
Sample				
ZnPB **(raw)**	63.25	36.75	**1.470**	**1.000**
$Zn_{0.72}$ZnPB **(discharged)**	68.16	31.83	**1.829**	**1.000**
ZnPB **(charged)**	63.59	36.41	**1.491**	**1.000**

Table S8. XRD powder diffraction and Rietveld refinement results for the wetted ZPB phase, $K_{0.02}(H_2O)_{8.3}Zn_{2.94}[Fe(CN)_6]_2$ (= Zn_0ZPB): atomic coordinates, unit-cell parameters, site occupancies, isotropic displacement parameters and reliability factors from the Rietveld refinement.

Crystal System			Trigonal			
Space Group			R $\bar{3}$ c (no. 167)			
Lattice Parameter			a = 12.596 (1) Å, c = 32.954 (4) Å, V = 4528.2 (4) Å^3, Z = 12			
Atoms	x	y	z	Wyckoff	Occupancy	U_{iso}
Zn1	0.2879(7)	0.0000	0.2500	18e	0.9800	0.072(2)
Fe1	0.0000	0.0000	0.1458(4)	12c	1.0000	0.072(2)
C1	0.006(4)	0.1121(23)	0.1881(5)	36f	1.0000	0.072(2)
C2	0.1191(16)	0.1053(32)	0.1057(5)	36f	1.0000	0.072(2)
N1	0.0194(24)	0.2072(14)	0.2000(5)	36f	1.0000	0.072(2)
N2	0.2200(12)	0.1826(18)	0.0982(7)	36f	1.0000	0.072(2)
K1	0.0467	0.2333	0.0233	36f	0.0033	0.072(2)
O1	0.3467	0.0133	0.0533	36f	0.4610	0.072(2)
O2	0.1467	0.0433	0.0033	36f	0.4610	0.072(2)
O3	0.2633	0.0067	0.0367	36f	0.4610	0.072(2)

* R_p = 0.204, R_{wp} = 0.259, R_{exp} = 0.101, $R(F^2)$ = 0.315, χ^2 = 6.61

Table S9. Selected interatomic distances (Å) for the wetted ZPB phase, $K_{0.02}(H_2O)_{8.3}Zn_{2.94}[Fe(CN)_6]_2$ (Zn_0ZPB) at room temperature.

Zn1-N1	2.014 (14) Å * 2	K1-C2	3.66 (4) Å
Zn1-N2	2.012 (7) Å * 2	K1-N1	3.099 (10) Å
Fe1-C1	1.959 (7) Å * 2	K1-N2	3.558 (24) Å
Fe1-C2	1.941 (7) Å * 2	K1-O1	2.0225 (1) Å
C1-N1	1.188 (7) Å	K1-O2	3.2802 (2) Å
C2-N2	1.178 (7) Å	K1-O3	0.96428 (5) Å
K1-C1	3.504 (31) Å	O2-O3	2.06357 (11) Å

Table S10. XRD powder diffraction and Rietveld refinement results for $Zn_{0.72}ZPB$ sample: atomic coordinates, unit-cell parameters, site occupancies, isotropic displacement parameters and reliability factors from the Rietveld Refinement.

Crystal System			Trigonal			
Space Group			R $\bar{3}$ c (no. 167)			
Lattice Parameter			a = 12.2884 (2) Å, c = 34.9239 (12) Å, V = 4567.14 (12) Å^3, Z = 12			
Atoms	x	y	z	Wyckoff	Occupancy	U_{iso}
Zn1	0.2942(3)	0.0000	0.2500	18e	0.9800	0.036(1)
Fe1	0.0000	0.0000	0.1526(2)	12c	1.0000	0.036(1)
C1	0.0210	0.1340	0.1820	36f	1.0000	0.036(1)
C2	0.1350	0.1150	0.1190	36	1.0000	0.036(1)
N1	0.0370	0.2127	0.2050	36	1.0000	0.036(1)
N2	0.2152	0.1891	0.0980	36	1.0000	0.036(1)
K1	0.0467	0.2333	0.0233	36	0.0033	0.036(1)
O1	0.3467	0.0133	0.0533	36	0.4456	0.036(1)
O2	0.1467	0.0433	0.0033	36	0.4456	0.036(1)
O3	0.2433	0.0087	0.0367	36	0.4456	0.036(1)
O4	0.0000	0.0000	0.0000	6	0.2800	0.036(1)
Zn2	0.0000	0.0000	0.0000	6	0.7200	0.036(1)

*R_p = 0.041, R_{wp} = 0.055, R_{exp} = 0.045, $R(F^2)$ = 0.246, χ^2 = 1.46

Table S11. Selected interatomic distances (Å) in $Zn_{0.72}ZPB$ at room temperature.

Zn1-N1	2.034 (2) Å * 2	K1-Zn2	2.75062 (4) Å
Zn1-N2	1.926 (2) Å * 2	K1-N1	3.18551 (6) Å
Fe1-C1	1.846 (4) Å * 2	K1-N2	3.53777 (7) Å
Fe1-C2	1.945 (5) Å * 2	K1-O1	3.58447 (9) Å
C1-N1	1.19550 (2) Å	K1-O2	3.21164 (5) Å
C2-N2	1.20024 (2) Å	K1-O3	0.96391 (2) Å
K1-C1	3.47233 (5) Å	O2-O3	1.85847 (3) Å