Electronic Supplementary Information:

Towards the practical application of Zn metal anodes for mild aqueous rechargeable Zn batteries

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Table S1. The description of modification methods, CE values, current density and areal capacity of the reference in Figure 1g. (M: mol L^{-1}, m: mol kg^{-1})

Ref	Electrolyte composition	CE (%)	Note	Current / capacity
[1]	2 M $ZnSO_4$ + 2 mM SeO_2	99.6	average CE	2 mA cm^{-2}, 2 mAh cm^{-2}
[2]	2 M $ZnSO_4$ + 0.5 g L^{-1} TMBAC	99.2	average CE	1 mA cm^{-2}, 1 mAh cm^{-2}
[3]	2 M $ZnSO_4$ + 5 mg mL^{-1} silk peptide	99.7	average CE	1 mA cm^{-2}, 1 mAh cm^{-2}
[4]	1 M $ZnSO_4$ + 0.2 wt% PAM	99.65	after 170 cycles	2 mA cm^{-2}, 2 mAh cm^{-2}
[5]	1 m $Zn(TFSI)_2$ + 20 m LiTFSI	99.7	after ~30 cycles	1 mA cm^{-2}, ~0.17 mAh cm^{-2}
[6]	$Zn(TFSI)_2$-TEEP@MOF-H_2O	99.9	after 300 cycles	1 mA cm^{-2}, 0.5 mAh cm^{-2}
[7]	$Zn(TFSI)_2$/Ace eutectic solution	99.7	average CE	CV: 1 mV s^{-1}, ~0.61 mAh cm^{-2}
[8]	2 M $Zn(TfO)_2$ + 40% vol DME	99.7	after 800 cycles	1 mA cm^{-2}, 1 mAh cm^{-2}
[9]	4 m $Zn(TfO)_2$ + 0.5 m $Me_3EtNOTF$	99.9	after 100 cycles	0.5 mA cm^{-2}, 0.5 mAh cm^{-2}
[10]	1 M $Zn(TfO)_2$ in H_2O:ACN =3:1	99.3	average CE	1 mA cm^{-2}, 1 mAh cm^{-2}
[11]	4 m $Zn(TfO)_2$ + 2 m $LiClO_4$	99.43	average CE	1 mA cm^{-2}, 1 mAh cm^{-2}
[12]	2 m $Zn(TfO)_2$ in H_2O:DMC=4:1	99.8	average CE	5 mA cm^{-2}, 2.5 mAh cm^{-2}

Table S2. The description of modification methods, cycle life, CE values, current density and areal capacity in Zn-based half cells of the reference in Figure 2a. (M: mol L^{-1}, m: mol kg^{-1})

Ref	Electrolyte composition	Cycle life (h)	CE (%)	Current / capacity	DODs
[4]	1 M $ZnSO_4$ + 0.2 wt% PAM	2200	99.65	1 mA cm^{-2}, 1 mAh cm^{-2}	5.7%
[13]	1 M $ZnSO_4$ in H_2O:AN (volume ratio 90:10)	2640	99.65	1 mA cm^{-2}, 2 mAh cm^{-2}	\
[14]	1 M $ZnSO_4$ + 0.5 wt% PEO	3000	>99.5	1 mA cm^{-2}, 1 mAh cm^{-2}	0.7%
[6]	$Zn(TFSI)_2$-TEEP@MOF-H_2O	350	99.9	1 mA cm^{-2}, 0.5 mAh cm^{-2}	\
[15]	1 M $ZnTFSI_2$ + 0.2 wt% PEO	700	98.7	1 mA cm^{-2}, 1 mAh cm^{-2}	5.7%
[8]	2 M $Zn(TfO)_2$ +40% vol DME	1600	99.7	1 mA cm^{-2}, 1 mAh cm^{-2}	3.4%
[16]	0.5 M $Zn(TfO)_2$+ 5 mM $Cu(OAc)_2$ in DMF	1700	99.6	0.5 mA cm^{-2}, 0.5 mAh cm^{-2}	0.4%
[9]	4 m $Zn(TfO)_2$ + 0.5 m $Me_3EtNOTF$	2000	99.9	0.5 mA cm^{-2}, 0.5 mAh cm^{-2}	\

Table S3. The description of modification methods, cycle life, current density and areal capacity in Zn||Zn symmetric cells of the reference in Figure 2a. (M: mol L^{-1}, m: mol kg^{-1})

Ref	Electrolyte composition	Cycle life (h)	Current / capacity	DODs
[17]	1 M $ZnSO_4$ + 10 mM glucose	2000	1 mA cm^{-2}, 1 mAh cm^{-2}	1.7%
[3]	2 M $ZnSO_4$ + 5 mg mL^{-1} silk peptide	3000	1 mA cm^{-2}, 1 mAh cm^{-2}	1.7%
[18]	zeolite-modified 2 M $ZnSO_4$	4756	0.8 mA cm^{-2}, 0.8 mAh cm^{-2}	1.4%
[6]	$Zn(TFSI)_2$-TEEP@MOF-H_2O	700	0.5 mA cm^{-2}, 0.5 mAh cm^{-2}	\
[7]	$Zn(TFSI)_2$/Ace eutectic solution	1000	0.1 mA cm^{-2}, 0.05 mAh cm^{-2}	\
[19]	~30 mol% H_2O in urea/LiTFSI/$Zn(TFSI)_2$	2400	0.1 mA cm^{-2}, 0.74 mAh cm^{-2}	6.6%
[20]	3 M $Zn(TfO)_2$ aqueous electrolyte at 0 ℃	2500	1 mA cm^{-2}, 1 mAh cm^{-2}	0.9%
[8]	2 M $Zn(TfO)_2$ +40% vol DME	5000	2 mA cm^{-2}, 1 mAh cm^{-2}	3.4%
[9]	4 m $Zn(TfO)_2$ + 0.5 m $Me_3EtNOTF$	6000	0.5 mA cm^{-2}, 0.25 mAh cm^{-2}	\

Table S4. The average Coulombic efficiency and cycle life values of Zn anodes calculated from 2-4 parallel cells in the aqueous electrolytes with different salt concentrations of Zn||Cu (Ti or SS) and Zn||Zn cells in Figure 1g and 2a. (1 mA cm^{-2} and 1 mAh cm^{-2}).

	0.5 M $ZnSO_4$	1 M $ZnSO_4$	2 M $ZnSO_4$	4 M $ZnSO_4$
the 20th CE (%)	99.02	99.25	99.24	99.36
cycle life of Zn||Cu cells (h)	147	147	200	227
cycle life of Zn||Zn cells (h)	\	799	521	\
	0.5 M $Zn(TFSI)_2$	1 M $Zn(TFSI)_2$	2 M $Zn(TFSI)_2$	4 M $Zn(TFSI)_2$
the 20th CE (%)	90.2	71.1	86.4	82.6
cycle life of Zn||Cu cells (h)	81	91	123	59
cycle life of Zn||Zn cells (h)	\	149	203	\
	0.5 M $Zn(TfO)_2$	1 M $Zn(TfO)_2$	2 M $Zn(TfO)_2$	4 M $Zn(TfO)_2$
the 20th CE (%)	86.9	85.4	68.7	90.6
cycle life of Zn||Cu cells (h)	120	151	79	84
cycle life of Zn||Zn cells (h)	\	212	198	\

Table S5. The average Coulombic efficiency and cycle life values of Zn anodes calculated from 2-4 parallel Zn||Cu (Ti, or SS) cells under different test conditions (1 M $ZnSO_4$ aqueous electrolyte).

	1 mA cm^{-2} 0.5 mAh cm^{-2}	**1 mA cm^{-2} 1 mAh cm^{-2}**	**1 mA cm^{-2} 2 mAh cm^{-2}**	**1 mA cm^{-2} 5 mAh cm^{-2}**	**1 mA cm^{-2} 8 mAh cm^{-2}**	**1 mA cm^{-2} 10 mAh cm^{-2}**
the 1st CE (%)	85	88.15	88	91.57	92.2	92.14
the 20th CE (%)	98.85	99.25	99.43	\	\	\
cycle life (h)	193	137	230	166	110	76
	2 mA cm^{-2} 1 mAh cm^{-2}	**2 mA cm^{-2} 2 mAh cm^{-2}**	**2 mA cm^{-2} 5 mAh cm^{-2}**	**2 mA cm^{-2} 8 mAh cm^{-2}**	**2 mA cm^{-2} 10 mAh cm^{-2}**	
Cycle life (h)	172	137	173	105	74	
	1 mA cm^{-2} 1 mAh cm^{-2}	**2 mA cm^{-2} 1 mAh cm^{-2}**	**5 mA cm^{-2} 1 mAh cm^{-2}**	**8 mA cm^{-2} 1 mAh cm^{-2}**	**10 mA cm^{-2} 1 mAh cm^{-2}**	
the 20th CE (%)	99.25	99.54	99.64	99.69	99.76	
	Cu foil	**Ti foil**	**SS**			
the 20th CE (%)	99.25	98.53	55.41			

Table S6. The average cycle life values of Zn anodes calculated from 2-4 parallel Zn||Zn symmetric cells under different test conditions (1 M $ZnSO_4$ aqueous electrolyte).

	1 mA cm^{-2}, 1 mAh cm^{-2}	**1 mA cm^{-2}, 2 mAh cm^{-2}**	**1 mA cm^{-2}, 5 mAh cm^{-2}**	**1 mA cm^{-2}, 10 mAh cm^{-2}**
cycle life (h)	799	518	367	68
	2 mA cm^{-2}, 1 mAh cm^{-2}	**2 mA cm^{-2}, 2 mAh cm^{-2}**	**2 mA cm^{-2}, 5 mAh cm^{-2}**	**2 mA cm^{-2}, 10 mAh cm^{-2}**
Cycle life (h)	1260	533	292	113
	5 mA cm^{-2}, 1 mAh cm^{-2}	**5 mA cm^{-2}, 2 mAh cm^{-2}**	**5 mA cm^{-2}, 5 mAh cm^{-2}**	**5 mA cm^{-2}, 10 mAh cm^{-2}**
Cycle life (h)	1440	748	253	54
	10 mA cm^{-2}, 1 mAh cm^{-2}	**10 mA cm^{-2}, 2 mAh cm^{-2}**	**10 mA cm^{-2}, 5 mAh cm^{-2}**	**10 mA cm^{-2}, 10 mAh cm^{-2}**
Cycle life (h)	558	249	190	87

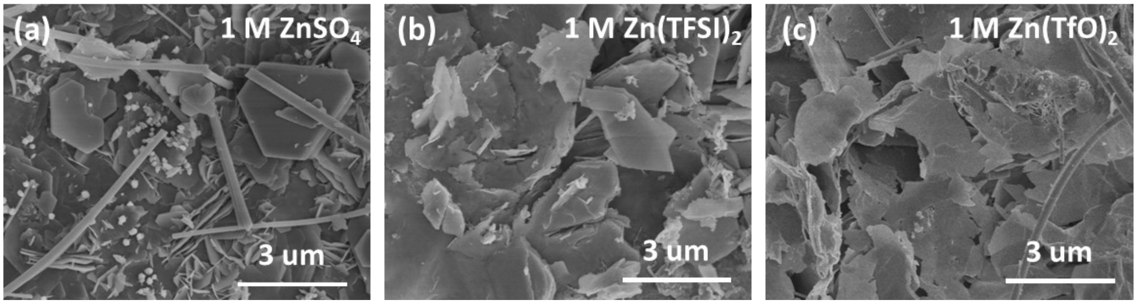

Fig. S1 SEM images of Zn deposition in (a) 1 M $ZnSO_4$, (b) 1 M $Zn(TFSI)_2$ and (c) 1 M $Zn(TfO)_2$ electrolytes (1 mA cm^{-2}, 1 mAh cm^{-2}).

Figure S1 shows that the morphology of deposited Zn cycled in 1 M $Zn(TFSI)_2$ and 1 M $Zn(TfO)_2$ aqueous electrolytes show large, irregular flaky structures, which are different from the dense and platelet-like morphology observed in 1 M $ZnSO_4$ aqueous electrolyte.

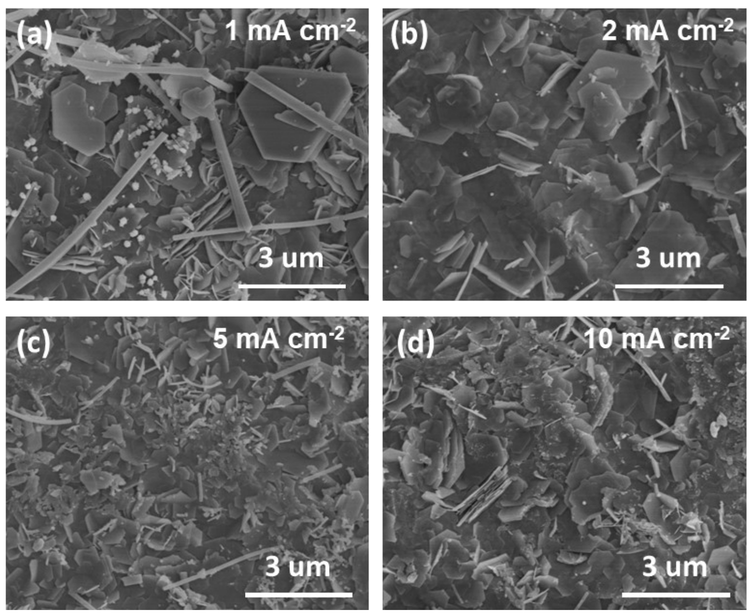

Fig. S2 SEM images of Zn deposition under different current densities in 1 M $ZnSO_4$ electrolytes. (a) 1 mA cm^{-2}, (b) 2 mA cm^{-2}, (c) 5 mA cm^{-2} and (d) 10 mA cm^{-2} for 1 mAh cm^{-2} capacity.

Figure S2 reveals that small current densities favor the growth of large Zn deposition morphology with reduced surface area, while large current densities benefit smaller and more uniform Zn deposition morphology due to high overpotential in 1 M $ZnSO_4$ electrolytes.

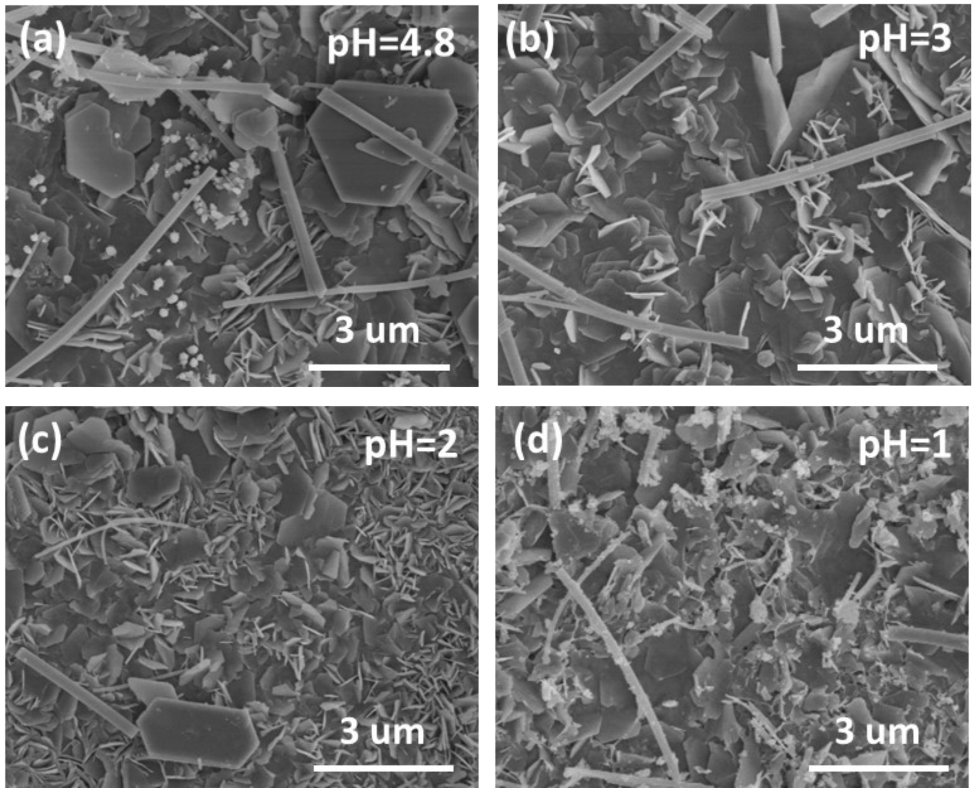

Fig. S3 SEM images of Zn deposition in 1 M $ZnSO_4$ electrolyte with different pH values. (a) pH=4.8, (b) pH=3, (c) pH=2 and (d) pH=1. (1 mA cm^{-2}, 1 mAh cm^{-2}, the pH values of 1 M $ZnSO_4$ electrolytes are controlled by adding a trace of H_2SO_4 solution with different concentrations)

Figure S3 shows that the deposited Zn platelets turn to be smaller size and grow vertically along with the decrease of pH values in 1 M $ZnSO_4$ electrolytes.

The detailed calculation process for the relevant estimation of the gravimetric energy density for aqueous Zn batteries:

1) The energy density of aqueous Zn batteries based on the total mass of the cell is according to the following equation S1[21] (E: the estimated gravimetric energy density, U: the average voltage of the cell, C_+: the specific capacity of cathode material, m_+: the mass of cathode material, m_{total}: the mass of the whole cell):

$$E = \frac{U \cdot C_+ \cdot m_+}{m_{total}} \tag{S1}$$

2) N/P ratio (R) corresponds to the following equation S2 (C_-: the specific capacity of Zn anode, m_-: the mass of Zn anode):

$$R = \frac{m_- \cdot C_-}{m_+ \cdot C_+} \tag{S2}$$

3) k presents the mass fraction of active cathode and anode materials in the total mass of the whole cell, which is calculated according to the equation S3:

$$k = \frac{m_+ + m_-}{m_{total}} \tag{S3}$$

4) By applying equations S2 and S3 in equation S1, the gravimetric energy density based on the k value and N/P ratio (R) can be obtained as shown in equation S4:

$$E = k\frac{U}{\frac{1}{C_+} + \frac{R}{C_-}} \tag{S4}$$

Taking examples of published aqueous Zn batteries, we calculate the achievable energy density of the batteries according to equation 1:

***Example 1*: Self-Healing SeO_2 Additives Enable Zinc Metal Reversibility in Aqueous $ZnSO_4$ Electrolytes (Advanced Functional Materials, 2022, 32, 2112091)[1]**

Reported specific capacity of MnO_2 cathode (C_+): 403 mAh g^{-1}

Specific capacity of Zn anode (C_-): 819 mAh g^{-1}

Reported N/P ratio of Zn||MnO_2 full cell (R): 4.2

Reported average voltage of Zn||MnO_2 full cell (U): 1.3 V

k value: 0.6

According to the equation 1, the calculated achievable energy density of Zn||MnO_2 full cell could be 102 Wh kg^{-1} when k of 0.6 is used as the mass fraction of active materials in the cell.

***Example 2*: Advanced Buffering Acidic Aqueous Electrolytes for Ultra-Long Life Aqueous Zinc-Ion Batteries (Small, 2022, 18, 2200742)[22]**

Reported specific capacity of V_2O_5 cathode (C_+): 291 mAh g^{-1} at 0.1 C

Specific capacity of Zn anode (C_-): 819 mAh g^{-1}

Reported N/P ratio of Zn||V_2O_5 full cell (R): 2.2

Reported average voltage of Zn||V_2O_5 full cell (U): 0.9 V

k value: 0.6

According to the equation 1, the calculated achievable energy density of Zn||V_2O_5 full cell could be 88 Wh kg^{-1} when k of 0.6 is used as the mass fraction of active materials in the cell.

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