Uniformizing Electric Field Distribution and Ion Migration during

Zinc Plating/Stripping via Binary Polymer Blend Artificial

Interphase

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Fig. S1. DSC of pure polymer blend and the polymer containing stoichiometric amount of electrolyte as in the hybrid capacitor. a) heating thermogram of pure PAM/PVP blend. b) heating thermograms of PAM/PVP containing Zn(CF₃SO₃)₂.



Fig. S2. Rheological test of a PAM/PVP gel.

A gel sample of PAM/PVP was prepared for rheology study. The sample shows typical viscoelastic behavior with varying rotational speed of the inner cylinder at 25 °C, where it behaves like a solid at a wide range of shear rate, as can be seen from the relatively higher storage modulus from about 0.2 to 200 rad/s.



Fig. S3. a) Nyquist plots of symmetrical batteries consisting of Bare Zn and PAM/PVP coated Zn. b) Equivalent circuit used for EIS fitting. R_{Ω} , Rct, CPE represent Ohmic resistances, charge transfer resistances and capacitance.

Nyquist plots of symmetrical Zn batteries reveal the influence of PAM/PVP coating on the Zn^{2+} conductivity in the batteries (Fig. S3). Compared to large transfer resistances of about 1050 Ω for bare Zn symmetrical cell, the PAM/PVP coated Zn symmetrical cell exhibited low resistance (927 Ω). Hence, the PAM/PVP coated layer obviously demonstrate the lower charge transfer and ion transport capability along with polar groups.



Fig. S4. The battery volume expansion of Zn symmetric cells after galvanostatic cycling at a current density of 0.2 mA cm⁻² for 300 cycles. a, b, c) Bare Zn anode and d, e, f) PAM/PVP coated Zn symmetric cells.

Fig. S4a, b and c are the images showing the apparent battery volume expansion of Bare Zn symmetric cells after galvanostatic cycling at a current density of 0.2 mA cm⁻² for 300 cycles. The thickness of Bare Zn cell is 3.187 mm before test (Fig. S4a). After galvanostatic charge/discharge at a current density of 0.2 mA cm⁻² for 300 h, the thickness increased to 5.045 mm (Fig. S4b), as can be seen in Fig. S4c where the cells after running cycles show obvious volume expansion. Whereas, for the PAM/PVP coated Zn symmetric cells, after 300 h of galvanostatic plating/stripping at a current density of 0.2 mA cm⁻², only a slight thickness increase from 3.203 mm to 3.314 mm (Fig. S4d, e) was observed, as demonstrated in Fig. S4f the comparison of the cells before and after running cycles.



Fig. S5. a) Voltage profiles of Zn symmetric cells with Bare Zn and PAM/PVP coated Zn at a current density of 1.0 mA cm⁻² with a capacity of 0.5 mAh cm⁻². b, c, d) Magnified views of different cycles in a.

Fig. S5 shows the voltage profiles of Zn anode with Bare Zn and the PAM/PVP coated Zn at a current density of 1 mA cm⁻² with a capacity of 0.5 mAh cm⁻². In the galvanostatic charge and discharge process with a current density of 1 mA cm⁻², the PAM/PVP coated Zn symmetric cell shows a stable electrochemical stability over 600 h (Fig. S5a, d). However, a dramatic voltage fluctuation to 1.2 V after cycling for 220 h (Fig. S5a) and an irregular voltage curve after 14 h of stripping/plating (Fig. S5c) are detected in the Bare Zn symmetric cell. From this perspective, the cycle life of the PAM/PVP coated Zn anodes is 30 times more than that of the Bare Zn. The cell failure of Bare Zn cell results from the side reactions occurred at the interface between Zn electrode and aqueous electrolyte. The long-term stable cycle life of the PAM/PVP coated Zn is benefited from the PAM/PVP blend as a protective layer to avoid direct contact between Zn and aqueous electrolyte.



Fig. S6. a) Voltage profiles of Zn symmetric cells with Bare Zn and PAM/PVP coated Zn at a current density of 5.0 mA cm⁻² with a capacity of 0.25 mAh cm⁻². b, c, d) Magnified views of different cycles in a.

Fig. S6 displays a typical galvanostatic plating/stripping voltage curves of the Bare Zn and the PAM/PVP coated Zn anodes at a current density of 5 mA cm⁻² with a capacity of 0.25 mAh cm⁻². The PAM/PVP coated Zn symmetric cell exhibits a steady electrochemical plating/stripping over 240 h (Fig. S6a). Whereas, a voltage fluctuation at early stage and slightly obvious irregular voltage curve after 14 h of stripping/plating are observed in the Bare Zn symmetric cell (Fig. S6c). The good cycling stability of the PAM/PVP coated Zn is ascribed to the electric field-balancing effect of the PAM/PVP artificial interphase.



Fig. S7. a, c) Voltage profiles of Zn symmetric cells with PAM/PVP coated Zn and Bare Zn at a current density of 8 mA cm⁻² with a capacity of 8 mAh cm⁻², respectively. b, d) Magnified view of different cycles in a, c, respectively.

To detect the adaptability of Zn anode in different working environment, Bare Zn and the PAM/PVP coated Zn symmetric cells were investigated by galvanostatic plating/stripping at a current density of 8 mA cm⁻² with a capacity of 8 mAh cm⁻². The cell with the PAM/PVP coated Zn shows a stable cycling stability over 147 h (Fig. S7a, b), whereas an erratic voltage change at the initial stage is observed for the Bare Zn cell (Fig. 74c, d). This shows that the PAM/PVP coated Zn can withstand more severe working environment and plating/stripping current densities.



Fig. S8. a, c) Voltage profiles of Zn symmetric cells with PAM/PVP coated Zn and Bare Zn at a current density of 10 mA cm⁻² with a capacity of 10 mAh cm⁻². respectively. b, d) Magnified view of different cycles in a, c, respectively.

Under a galvanostatic plating/stripping at a current density of 10 mA cm⁻² and a capacity of 10 mAh cm⁻², the Zn symmetric cell with the PAM/PVP layer can run for 80 h (Fig. S8a, b). In comparison, the cell with Bare Zn failed at the beginning (Fig. S8c, d). This shows that the PAM/PVP coating can act as an artificial interlayer to prevent the corrosion of O_2 and free water. As a result, the cell remains highly reversible with steady voltage signals at a high theoretical depth of discharge.



Fig. S9. a, d, g) Columbic efficiency (CE) of Zn plating/stripping in Bare Zn-Ti cell and PAM/PVP coated Zn-Ti cell at a current density of 1 mA cm⁻², 5 mA cm⁻², 20 mA cm⁻², respectively. b, e, h) Voltage profiles of Bare Zn at a current density of 0.2 mA cm⁻², 5 mA cm⁻², 20 mA cm⁻², respectively. c, f, l) Voltage profiles of PAM/PVP coated Zn in Zn-Ti cell at a current density of 0.2 mA cm⁻², 20 mA cm⁻², 5 mA cm⁻², 20 mA cm⁻², 5 mA cm⁻², 20 mA cm⁻², 7 mA cm⁻², 8 mA cm⁻², 9 mA cm⁻²

Fig. S9a, b, c are the CE of Zn plating/stripping and voltage profiles of Bare Zn and the PAM/PVP coated Zn in Zn-Ti cell at a current density of 0.2 mA cm⁻², 5 mA cm⁻², 20 mA cm⁻², respectively. As can be seen from Fig. S9a, Bare Zn maintains a close-to 100% CE in the first 300 cycles, and experiences significant fluctuations from 300 to 400 cycles. On the contrary, CE of the PAM/PVP coated Zn increases at first 100 cycles, and remains stable at an average of 91.47%. Corresponding to CE in Fig. S9a, the voltage fluctuation of Bare Zn starts to move up and down after 300 cycles, meanwhile, the PAM/PVP coated Zn keeps stable in the whole process (Fig. S9b, c). Fig. S9d, e, f also show similar results to Fig. S9a, b, c. As shown in Fig. S9d, the CE of Bare Zn decreases rapidly after 100 cycles at a current density of 5 mA cm⁻², while the CE of PAM/PVP coated Zn remains steady with little fluctuation. And in accordance with Fig. S9d, voltage fluctuation of Bare Zn starts to jump after 200 cycles (Fig. S9e), whereas the PAM/PVP coated Zn keeps stable at all time (Fig. S9f). When the plating/stripping current density increases to 20 mA cm⁻², the CE of Bare Zn exhibits a huge pulse after 400 cycles, while the CE of the PAM/PVP coated Zn keeps at 100% all the time (Fig. S9g). The respective voltage curve of Bare Zn and the PAM/PVP coated Zn fluctuates continuously and remains steady. Conclusively, (i) with the increase of current density of plating/stripping, the CE of the PAM/PVP coated Zn-Ti cell also increases correspondingly; (ii) the PAM/PVP coated Zn has better corrosion resistance than the Bare Zn.



Fig. S10. a, b) Capacitance-voltage curves of Zn-AC hybrid capacitor with Bare Zn and PAM/PVP coated Zn at a current density of 1 A g⁻¹, respectively.

Fig. S10a, b show the capacitance-voltage curves of Zn-AC hybrid capacitors with Bare Zn and the PAM/PVP coated Zn at a current density of 1 A g⁻¹, respectively. The Bare Zn-AC hybrid capacitor reaches a dead state after only 10 cycles, whereas the hybrid capacitor with the PAM/PVP coated Zn keeps a good cycling performance. The result demonstrates that the PAM/PVP interfacial layer can extend the service life of Zn-AC hybrid capacitors by suppressing the zinc dendrites and side reactions.



Fig. S11. The capacitance-voltage of Zn-AC hybrid capacitor with PAM/PVP coated Zn at current densities of 0.5, 1, 2, 5, 8, 10, 15, 20, 25, 30 A g^{-1} .

Fig. S11 shows the rate performances of Zn-AC hybrid capacitor with the PAM/PVP coated Zn at current densities of 0.5, 1, 2, 5, 8, 10, 15, 20, 25 and 30 A g⁻¹. The capacitance-voltage curves are symmetrical and linear in shape, and the Zn-AC hybrid capacitor with the PAM/PVP coated Zn shows a specific capacitance of 336, 292, 264, 232, 220, 195, 190, 175 and 165 F g⁻¹ at a current density of 0.5, 1, 2, 5, 8, 10, 15, 20, 25 and 30 A g⁻¹.



Fig. S12. Specific power versus specific energy curve.

The specific power versus specific energy curve is shown in Fig. S10. The Zn-AC hybrid capacitors with the PAM/PVP coated Zn shows an energy density of 118.8, 103.8, 95.2, 84.6, 80.5, 75.3, 70.1, 64.8, 59.5 and 56.9 Wh kg⁻¹ at a power density of 318.2, 640.4, 1298.6, 3275.1, 5270.5, 6457.4, 9713.6, 12291.1, 15311.2 and 17097.3 W kg⁻¹.



Fig. S13. a, b) Capacitance-voltage and energy density comparison of Zn-AC hybrid capacitors.

A hybrid supercapacitor is designed to compensate for the low energy density of electric double layer capacitors and the short cycle life of battery. As shown in Fig. S11a, b, this work gives rise to a high energy density of 118.8 Wh kg⁻¹ and a wide working voltage range of 0-2.0 V, which are superior to those of the Zn//AC hybrid ion supercapacitors. The detailed data are shown in Table S1.

Anode//electrolyte//cathode	Operating	Capacitances	Energy	Capacity retention,	ref
	voltage	(current	density	Cycle,	
	(V)	density)	(Wh kg ⁻¹)	(current density)	
			(current		
			density)		
Zn//2 M ZnSO4 (aq)//AC	0.2-1.8	272.25	84.0	91%,	1
		(0.1 A g ⁻¹)	(0.1 A g ⁻¹)	10000,	
				(1 A g ⁻¹)	
Zn//1 M Zn(CF ₃ SO ₃) ₂ (DOL-DME)//AC	0-1.8	144	44.9	Not given	2
		(0.1 A g^{-1})	(0.5 A g ⁻¹)		
Zn//1M Zn(CF ₃ SO ₃) ₂ (AN)//AC	0-1.8	170	52.7	91%,	2
		(1 A g ⁻¹)	(2 A g ⁻¹)	20000,	
				2 A g ⁻¹	
Zn//2 M ZnSO ₄ (aq)//AC	0.5-1.5	259	36.0	100%,	3
		(0.05 A g ⁻¹)	(0.05 A g ⁻¹)	10000,	
				1.56 mA cm ⁻²	
Zn//3M Zn(CF ₃ SO ₃) ₂ (aq)//aMEGO	0-1.9	166	83.2	93%,	4
		(0.5 A g ⁻¹)	(0.5 A g ⁻¹)	80000,	
				5 A g ⁻¹	
Zn//3M Zn(CF ₃ SO ₃) ₂ (aq)//AC	0-2.0	335	118.8	100%,	This
		(0.5 A g^{-1})	(0.5 A g ⁻¹)	6000,	work
				15 A g ⁻¹	

Table S1. Comparison of Zn-based Zn//aqueous electrolyte//AC



Figure S14. Images of interphase surface adhesion at different ratios of PAM/PVP. a) 0.01 g PAM + 1.0 g PVP in 1.5 g deionized H₂O; b) 0.01 g PAM + 1.5 g PVP in 1.5 g deionized H₂O; c) 0.01 g PAM + 2.0 g PVP in 1.5 g deionized H₂O; d) 0.01 g PAM + 2.5 g PVP in 1.5 g deionized H₂O.

As can be seen from the pictures, the adhesion ability and film stability between Zn foil and PAM/PVP interphase with 0.01 g of PAM + 2.0 g of PVP in 1.5 mL of deionized H₂O is the best among all the ratios. When using a tweezers to scratch the surface of as prepared interphase, other three samples are easy to split or peel off the surface of zinc anode.



Fig. S15. Cross-sectional SEM images of the PAM/PVP layer coated on Zn foil.

Fig. S14 shows the thickness of Zn foil with Bare Zn and the PAM/PVP coated Zn. The thickness of the PAM/PVP layer was measured to be about 14.74 μ m.

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