Supporting Information

Polyhydroxy starch with abundant hydroxyls and a unique structure enables

uniform Zn deposition

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Experimental

Materials

The used materials including zinc sulfate heptahydrate (ZnSO₄·7H₂O, 99%), starch ((C₆H₁₀O₅)n), N-Methyl-2-pyrrolidone (NMP, C₅H₉NO, 99%), Oxalic acid (H₂C₂O₄, 99%) and Vanadium pentoxide (V₂O₅, 99%) were purchased from Aladdin. The conductive carbon black (Timical) and polyvinylidene fluoride (PVDF, Arkema) were from Saibo Electrochemical Materials Pte Ltd. Glass microfiber filter (Whatman GF/D, Diameter 47mm, 1823-047) serving as separator was obtained from Huidi Pte Ltd. The Zn foils (30 μ m, 99.9%), Cu foil (30 μ m, 99.9%), Titanium mesh and stainless steel were provided by Shengshida Metallic Materials Pte Ltd.

Electrolyte preparation

 $1M ZnSO_4$ aqueous electrolyte serving as the base electrolyte was prepared using $ZnSO_4 \cdot 7H_2O$ and deionized water (denoted as "without starch"). Different amounts of starch were introduced into the $ZnSO_4$ electrolyte, forming the electrolyte containing starch. The electrolyte with 0.2 mg mL⁻¹ starch was signed as "with starch". The electrolyte with 0.1 and 0.4 mg mL⁻¹ starch were denoted as "0.1 starch" and "0.4 starch", respectively.

Fabrication of Zn||Zn and Zn||Cu cell

The Zn plating/stripping behavior were tested with symmetrical Zn||Zn cells, in which two pieces of Zn foil (30 µm) were used as electrodes. Coulombic efficiency (CE) were evaluated by asymmetrical Zn||Cu cells with Zn foil and copper foil as electrodes.

Fabrication of Zn||VO2 full cell

VO₂ was synthesized and used to fabricate the full cell. To obtain VO₂, V₂O₅ (1.2 g) was firstly dispersed in deionized water (40 mL). Then, 1.8 g of H₂C₂O₄ was added. After heating at 80 °C for 1 h, the obtained solution was transformed into a hydrothermal reactor, which was maintained at 180 °C for another 4 h to obtain the VO₂. The cathode in this work was prepared by mixing VO₂, conductive carbon black and PVDF at the weight ratio of 7:2:1 with NMP as the solvent to form homogeneous slurry. The obtained slurry was then spread onto the titanium mesh, and dried in a vacuum oven at 60 °C overnight. The mass loading of active materials on the cathode was about 2.0~4.0 mg cm⁻². Zinc foil was directly used as the anode in the Zn||VO₂ cells.

Electrochemical test

The performances of Zn||Zn, Zn||Cu, and Zn||VO₂ cells were tested on a Neware CT-3008 battery test system. The stability of Zn||Zn cells were tested at 5 mA cm⁻² / 1 mAh cm⁻², 5 mA cm⁻² / 5 mAh cm⁻², 10 mA cm⁻² / 5 mAh cm⁻², and 30 mA cm⁻² / 1 mAh cm⁻² respectively. The rate performance of Zn||Zn cells were tested at 1, 2, 3, 5, 10, 20, 30, 40 and 1 mA cm⁻² with the areal capacity of 1 mAh cm⁻². The Zn||Cu asymmetric cells were carried out at 1 mA cm⁻² / 0.5 mAh cm⁻² to evaluate the reversibility of Zn anode . For the Zn||VO₂ cell, the cycling stability was evaluated in the voltage range of 0.3~1.5 V under 0.5 A g⁻¹, and the rate performance was tested at the current range of 0.1~2 A g⁻¹. The specific capacities were evaluated according to the mass of active materials. The corrosion, diffusion, and hydrogen evolution behaviors of Zn anode were tested on an electrochemical workstation (CHI 660e) with a three-electrode system. The Zn foil, Pt and Ag/AgCl were used as work electrode, counter electrode, and reference electrode, respectively. The Tafel plot was obtained in a potential range of ± 0.3 V versus open-circle potential at 1 mV s⁻¹. The Zn²⁺ diffusion curves were measured by the chronoamperometry method at an overpotential of -150 mV. The hydrogen evolution behaviors was investigated by the linear sweep voltammetry (LSV) with a potential range of $-1\sim-1.6$ V at 1 mV s⁻¹. The cyclic voltammetry (CV) method was employed to test the nucleation overpotential with a voltage rage of $-1.4\sim-0.2$ V (Zn, Ti and Ag/AgCl serving as the counter electrode, work electrode, and reference electrode). The electrochemcial potential window was tested at 1 mV s⁻¹ with the steel-mesh as working electrode and counter electrode, and Ag/AgCl electrode as reference electrode. Electrochemical impedance spectroscopy (EIS) of Zn||Zn cells was carried out within a range of 10^5 to 10^{-2} Hz.

Characterization

The properties of electrolyte were studied by FT-IR (Bruker Alfar) and contact angle meter (Jinhe, JY-PHB). The electrode including Zn foil and prepared VO₂ were characterized by the X-ray diffraction with Cu K α (λ =1.54060 Å) (XRD, Rigaku, Ultima IV). The field-emission scanning electron microscopy (SEM, Hitachi SU8600) was employed to characterize the morphology of materials. The cycled Zn electrode were also characterized by the X-ray photoelectron spectroscopy with Al k α ray (hv=1486.6eV) (XPS, ThermoFischer, ESCALAB 250XI). An optical microscope (Aoweisi, AW33T-4K) was employed to observe the Zn deposition process.

Electrochemical digital holography

A Mach-Zehnder interferometer optical setup was employed for electrochemical digital holography with a charge-coupled device camera to document the dynamic processes. It was performed in the Zn||Zn symmetric cells. 1M ZnSO₄ with and without starch were used as the electrolytes. During the Zn plating/stripping process, the concentration of certain species in the solution can alter, which can be described as follows:

$$\Delta C = k\Delta n = k(\frac{\lambda_0}{2\pi d})\Delta \phi$$

where ΔC is the change in the solution concentration. k and Δn refer to the concentrative refractivity and the change of the solution refractive index, respectively. λ_0 , d and $\Delta \phi$ are the wavelength of the laser light, the path length of the refractive index change and the phase difference, respectively. The solution concentration is correspond with color. If $\Delta \phi > 0$, $\Delta C > 0$, the phase map is yellow or red, indicating the concentration increases. If $\Delta \phi = 0$, $\Delta C = 0$, the phase map is green, meaning the concentration is unchanged; If $\Delta \phi < 0$, $\Delta C < 0$, the phase map is blue, suggesting the concentration decreases.

Calculations

The interaction between $Zn^{2+}-H_2O$, and Zn^{2+} - starch were calculated by the quantum chemistry calculations. It was carried out by using the Gaussian 09 software package. All structures were optimized from the density functional theory-based method using the B3LYP functional and the 6-31G basis set.



Fig. S1 Scheme of starch structure.



Fig. S2 The overall electrochemical stability window.



Fig. S3 Tafel curves in different electrolytes.



Fig. S4 XRD patterns of pristine Zn foil and Zn foil soaked in different electrolytes for 6 h.



Fig. S5 Schematic diagram of different Zn planes.



Fig. S6 EIS profile of Zn||Zn cells in different electrolytes after 10 cycles.



Fig. S7 Contact angles of different electrolytes on the Zn electrode.



Fig. S8 Cycling performance of the Zn||Zn cells at (a) 5 mA cm⁻² and 5 mAh cm⁻²; (b) 10 mA cm⁻² and 5 mAh cm⁻².



Fig. S9 Cycling performance of the Zn||Zn cells in electrolyte with 0.1 mg mL⁻¹ starch at (a) 5 mA cm⁻² / 1 mAh cm⁻²; (b) 10 mA cm⁻² / 5 mAh cm⁻²; (c) 5 mA cm⁻²/5 mAh cm⁻².



Fig. S10 Cycling performance of the Zn||Zn cells in electrolyte with 0.4 mg mL⁻¹ starch at (a) 5 mA cm⁻² / 1 mAh cm⁻²; (b) 10 mA cm⁻² /5 mAh cm⁻²; (c) 5 mA cm⁻²/5 mAh cm⁻².

Electrolyte components	Current density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Lifespan (h)	Refs.
2 M ZnSO ₄ +1.5 wt% penta-sodium	2	1	800	1
diethylene-triaminepentaacetic acid salt	2	1	000	1
2M ZnSO ₄ +10 M zinc dodecyltrimethyl	10	5	500	2
ammonium chlorid				
2 M ZnSO ₄ +100 mM trehalose	5	1	1600	3
2 M ZnSO ₄ +30 mM TiOSO ₄	5	1	1000	4
2 M ZnSO4+40 mM sodium L-tartrate	2	1	1500	5
2 M ZnSO ₄ +1 mM ammonium hydroxide	5	5	250	6
2 M ZnSO ₄ +2 mg mL ⁻¹ Tween-85	5	5	450	7
2 M ZnSO4+1% dioxane	10	3	180	8
2 M ZnSO ₄ +0.2 M sodium hydroxyethyl	4	1	460	9
sulfonate				
1 M ZnSO ₄ +1.0 mM epigallocatechin gallate	5	5	350	10
2 M ZnSO ₄ +1% dioxane	10	3	180	11
2 M ZnSO ₄ +1% fluorophosphate ester	5	1	1050	12
2 M ZnSO_4 +0.25 g L ⁻¹ cellulose	5	1	600	13
2 M ZnSO ₄ +50 mM maltose	5	2.5	800	14
1 M ZnSO_4 +0.2 mg mL ⁻¹ starch	5	5	225	This
				work
$1 \text{ M ZnSO}_4+0.2 \text{ mg mL}^{-1} \text{ starch}$	5	1	1500	This
				work
1 M ZnSO_4 +0.2 mg mL ⁻¹ starch	10	5	350	This
				work

Table S1 Summary of the performance of $Zn \|Zn$ cells in different electrolytes.



Fig. S11 Rate performance of Zn||Zn cells in different electrolytes.



Fig. S12 Cycling performance of Zn||Zn cells in different electrolytes at 30 mA cm⁻² and 1 mAh cm⁻².



Fig. S13 Voltage and capacity of Zn||Cu cells at different cycles in electrolyte with (a) and without starch (b).



Fig. S14 Morphology of zinc deposits at 20 mA cm⁻² and 1 mAh cm⁻² in electrolyte (a) with starch; (b) without starch; Surface morphology of the copper foil after Zn stripping in electrolyte (c) with starch; (d) without starch.



Fig. S15 XPS spectrum of Zn 2p after 50 cycles.



Fig. S16 XRD pattern of prepared VO₂.



Fig. S17 SEM image of prepared VO₂.

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