Supplementary Information

Network-Reinforcing HACC-co-PAM Hydrogel Electrolytes for Suppressed Zinc Dendrite Growth and High-Performance Zinc-Ion Batteries

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Experimental section

Materials

Acrylamide (AM, AR, Shanghai Titan Technology), quaternary chitosan (HACC, 99%, Shanghai McLean Biochemical Technology), N,N'-methylenebisacrylamide (MBAA, AR, Shanghai Titan Technology), 1-[4-(2-hydroxyethoxy)phenyl]-1-propanone (Irgacure2959, AR, Shanghai Titan Technology), heptahydrated zinc sulfate ($ZnSO_4·7H_2O$, 99.5%, Shanghai McLean Biochemical Technology), zinc foil (80 μm). All reagents were not further purified.

Experimental Methods

Preparation of HACC-co-PAM hydrogel electrolyte: First, 0.2 g of 99% pure chitosan quaternary ammonium salt (HACC) was weighed using an electronic balance and poured into a glass vial, and then 4.37 ml of ultrapure water was added to the vial using a pipette gun and put on a magnetic stirring stage until complete dissolution. Then 1 g of acrylamide (AM) was added to the obtained quaternary chitosan solution, and continued to be stirred on the magnetic stirring table, and a homogeneous solution of quaternary chitosan and acrylamide was obtained, 1.4378 g of $ZnSO_4·7H_2O$ was added, and continued to be stirred after sealing with a sealing film, and after complete dissolution, 0.01 g of the photoinitiator Irgacure2959 was added in sequence, 0.001 g of crosslinking agent MBAA, stirring for about 1h, oxygen extraction, oxygen extraction is completed and injected into the mold, into the photopolymerization box in the photopolymerization of 3 h, can be obtained HACC-co-PAM hydrogel electrolyte.

Preparation of electrolyte: 1.4378 g of $ZnSO_4·7H_2O$ was dissolved in 4.37 ml of ultrapure water and put on the magnetic stirring table for stirring to obtain the electrolyte used in this experiment.

Preparation of pure PAM hydrogel electrolyte: Weigh 1 g of acrylamide with an electronic balance, put it into a glass bottle, add 4.37 ml of ultrapure water, put it on the magnetic stirring table and stir until it is completely dissolved, then add 1.4378 g of $ZnSO_4·7H_2O$, and then continue to stir after sealing with a sealing film. After complete dissolution, add 0.01 g of photoinitiator Irgacure2959 and 0.001 g of crosslinking agent MBAA in turn, stir for about 1h, then carry out the oxygen extraction, after the oxygen extraction is completed, inject it into the mold, and then put it into the photopolymerization box for 3 h, so as to obtain the pure PAM hydrogel electrolyte.

Material characterization and testing

Material characterization: The micro morphology of zinc flakes in Zn-Zn symmetric batteries after charge/discharge cycles was analyzed by SEM, and the functional groups of different electrolytes were analyzed by Fourier transform infrared spectroscopy (FTIR) to investigate the mechanism of the HACC-co-PAM hydrogel electrolyte's effect on suppressing the side reactions of zinc-ion batteries and enhancing the stability of the batteries.

Mechanical Properties: The prepared 1mm thick square hydrogel sheet was cut into long strips. The thickness, width and length of the long strips of hydrogel were measured using a spiral micrometer, and the measured samples were clamped on an electronic universal testing machine. A load was applied to the prepared gel electrolyte at a constant tensile rate, and the values of stress and strain at each point on the displacement-load curve were calculated from the displacement versus load curves plotted from the experimental data.

Ionic conductivity: The HACC-co-PAM hydrogel electrolyte prepared in this experiment had a thickness of 0.5 mm and a diameter of 16mm. Assembled Zn-Zn symmetric cells that were not sealed by a button cell sealer were clamped with a test fixture on the electrochemical workstation, and the impedance R of the HACC-co-PAM hydrogel electrolyte was measured using electrochemical impedance spectroscopy, and then the ionic conductivity was calculated by $\sigma=L/(R\times S)$, where L is the thickness (cm), A is the electrode contact area (cm^2) and R is the volume resistance (Ω) of the gel.

Linear Scanning Voltammetric Curve Test (LSV): The Zn-Zn symmetric cell was clamped with the test clip on the electrochemical workstation, the scanning range was set to 0-3V, and the scanning rate was 0.005mV/s. The peak of the current in the observed curve appeared in the position of the electrochemical stabilization window of the composite hydrogel electrolyte prepared in this experiment.

Tafel: Hydrogen precipitation potentials and oxidation potentials of Zn-Zn symmetric cells assembled and sealed with a button cell sealing machine were tested by an electrochemical workstation using the HACC-co-PAM hydrogel electrolyte and 1M $ZnSO_4$ electrolyte prepared in this experiment, respectively, in the voltage range of -0.2-0.2 V at a 0.005 mV/s rate was scanned.

Electrochemical impedance spectroscopy (EIS): The electrochemical impedance spectroscopy (EIS) was performed on Zn-Zn symmetric batteries assembled and sealed with a button cell sealing machine by an electrochemical workstation using the HACC-co-PAM hydrogel electrolyte and 1M $ZnSO_4$ electrolyte prepared in this experiment, and the frequency range of the test was 0.1-10^6 Hz.

Constant current charge/discharge test: Constant current charge/discharge test was carried out on Zn-Zn symmetric cells and Zn-MnO_2 full cells assembled and sealed with a button cell sealing machine by electrochemical workstation, and the batteries tested were the HACC-co-PAM hydrogel electrolyte and the 1M $ZnSO_4$ electrolyte, respectively, prepared in this experiment, and the current density of the test was 1mA/cm^2.

Deposition dissolution performance: Deposition dissolution performance: the Zn-Cu batteries assembled and sealed using a button cell sealer were tested in charge/discharge cycles, and a constant current density of 1mA/cm^2 was set to pay attention to the changes in the Coulombic efficiency of the batteries during each cycle.