Stabilization of zinc metal electrodes by solvation structure modulation of $Zn(NTf_2)_2$ electrolyte additives

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Experimental Section

Raw materials

Metal zinc was purchased from Shengyuan Metal (China). Iodine was purchased from Nanjing Middle East Chemical Glass Instrument Co., LTD. Other chemical reagents were provided by Sinopharm Chemical Reagent Co. Ltd.

Materials characterization

The surface morphology and microstructure of zinc were characterized by thermal emission scanning electron microscopy (SEM, Sigma 300). The zinc anode of the Zn//Zn symmetric cell which cycled for 50 cycles was characterized using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The morphology change and the contact angles of 1 M $ZnSO_4$ electrolyte and 3% $Zn(NTf_2)_2$ electrolyte drops on Zn metal surfaces were confirmed by in-situ microscope camera (Belona, 200X-800X) coupled with Wi-Fi box. The proportion of iodine loss in the preparation process was determined by thermogravimetric (TG, Netzsch TG 209 F3 Tarsus).

Electrochemical Measurement

All cells (CR20332 type) were assembled in normal environment(26 ℃). 1 M $ZnSO_4$ and 3% $Zn(NTf_2)_2$ was employed as electrolyte (about 180 μL per cell). All cells use the nonwovens as the separator. All the electrochemical performances use the LAND battery test system at room temperature (25 ± 2 ℃).The electrochemical impedance spectroscopy (EIS) was carried out in an electrochemical workstation (DH7000, DONGHUA, China).

Preparation of Full cells and Symmetric cells

Solution-adsorption method was used for the preparation of cathodes. 100 mg I_2 were mixed with 100 mg activated carbon (AC), then 200 mL deionized water was added. Then the mixture was stirred, filtered and freeze dried. Finally, the cathode material AC@I_2 was obtained. Zn anode electrode was made from purchased zinc sheets cut into 16mm sodium sheets. The Zn//AC@I_2 full cells were cycled between 0.3-1.7V. Zn//Zn symmetric cells were evaluated with 0.4 $mA \cdot cm^{-2}$.

HOMO-LUMO gap

Based on Kohn-Sham density functional theory, the HOMO and LUMO levels of H_2O and $Zn(NTf_2)_2$ were obtained using Gaussview.

Molecular dynamics simulation

Simulation models of electrolyte with 1 M $ZnSO_4$ as electrolyte, water as solvent and 0%, 1%, 3%, and 5% $Zn(NTf_2)_2$ additives were built respectively by Materials Studio 2020. Then the structure optimization and molecular dynamics simulation were carried out through the Forcite module. Based on dynamic simulations, we obtained mean square displacement (MSD) curves. Analysis of the slope of these curves allowed us to determine the diffusion coefficient of Zn^{2+}.

In-situ optical microscopies

In-situ optical microscopies of the electrolyte–electrode interface during electrodeposition on different electrodes is tested by micro-camera. The micro-camera is consisting of an in-situ microscope camera (Belona, 200X-800X) with a Wi-Fi box and a batteries cell assembled by insulating rubber blocks (electrolyte separate the cathode and anode).

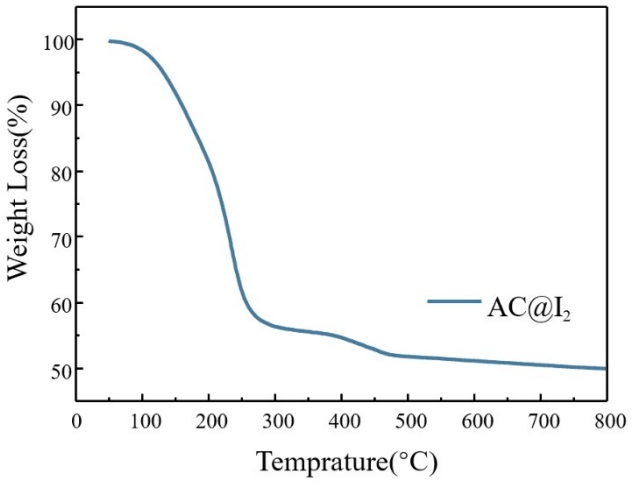


Fig. S1 TG test results of the obtained AC@I_2 sample.

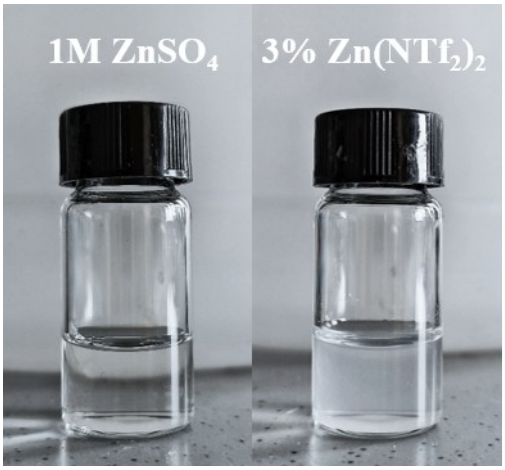


Fig. S2 The optical state of 1 M $ZnSO_4$ and 3% $Zn(NTf_2)_2$ added to 1 M $ZnSO_4$.

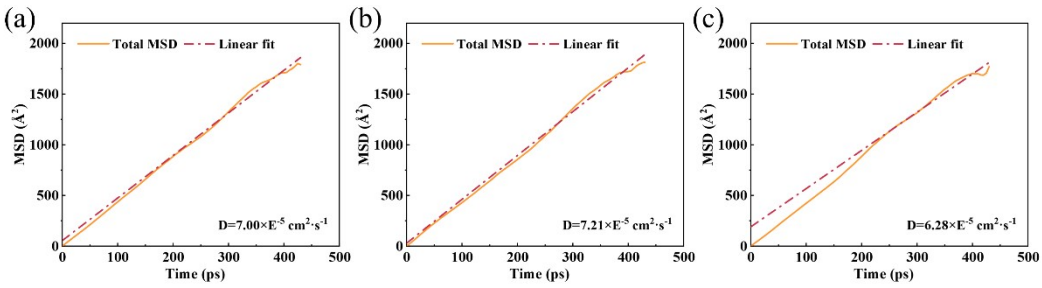
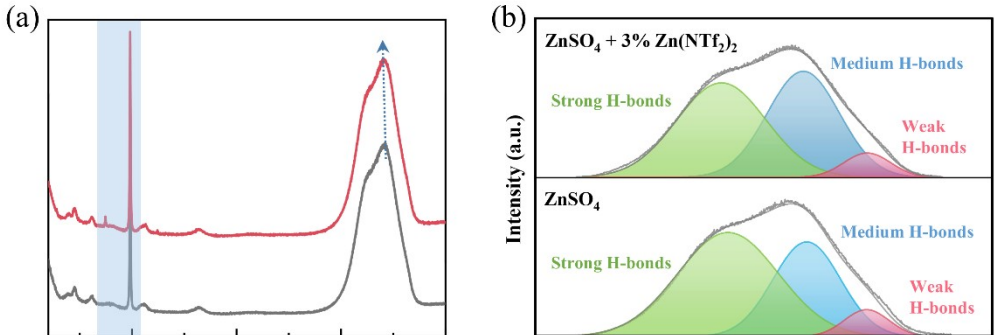


Fig. S3 The MSD results simulated with different concentrations of $Zn(NTf_2)_2$: (a) 1% $Zn(NTf_2)_2$. (b) 3% $Zn(NTf_2)_2$. (c) 5% $Zn(NTf_2)_2$.



Compared to that of the 1 M $ZnSO_4$ electrolyte, the Raman spectrum of the electrolyte with added 3% $Zn(NTf_2)_2$ shows an additional band at ~730cm^{-1}, corresponding to the vibration of the zinc-oxygen bond. The stretching vibration peak of O-H group, which is typically located at 3000-3750 cm^{-1} also reflects the alteration of coordination environment. As shown **in Fig.S4**, the fitted peaks representing strong, medium, and weak hydrogen bonds. After the addition of 3% $Zn(NTf_2)_2$, the proportion of strong hydrogen bonds in the electrolyte environment decreased. This suggests that highly electronegative (NTf_2) groups from $Zn(NTf_2)_2$ form hydrogen bonds with water molecules, thereby breaking the strong hydrogen bonds between free water molecules and inhibiting HER.

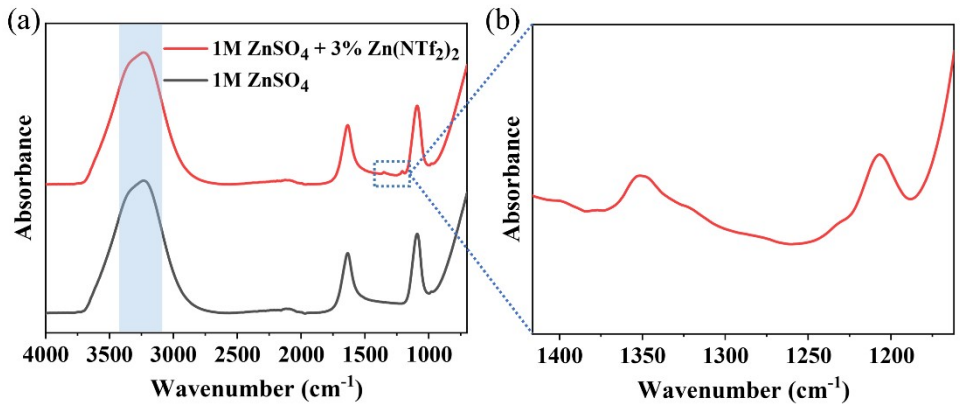


Fig. S5 FTIR spectra comparison of 1M $ZnSO_4$ electrolyte and 1M $ZnSO_4$ electrolyte with 3% $Zn(NTf_2)_2$.

In order to investigate the effect of adding $Zn(NTf_2)_2$ on the solvation structure of Zn^{2+} in electrolyte, Fourier transform infrared (FTIR) analysis was carried out. In Figure S5, a slight blue shift in wave number was observed in the stretching vibration of O-H bonds in water molecules after the addition of 3% $Zn(NTf_2)_2$, indicating that the highly electronegative (NTf_2) groups from $Zn(NTf_2)_2$ destroyed the original hydrogen bond network and reduced the content of surface active water molecules onto Zn. In addition, at 1206 cm^{-1} and 1351 cm^{-1}, the infrared spectra of 3% $Zn(NTf_2)_2$ electrolyte showed two new absorption peaks, which indicated the presence of C-F and C≡N bonds.

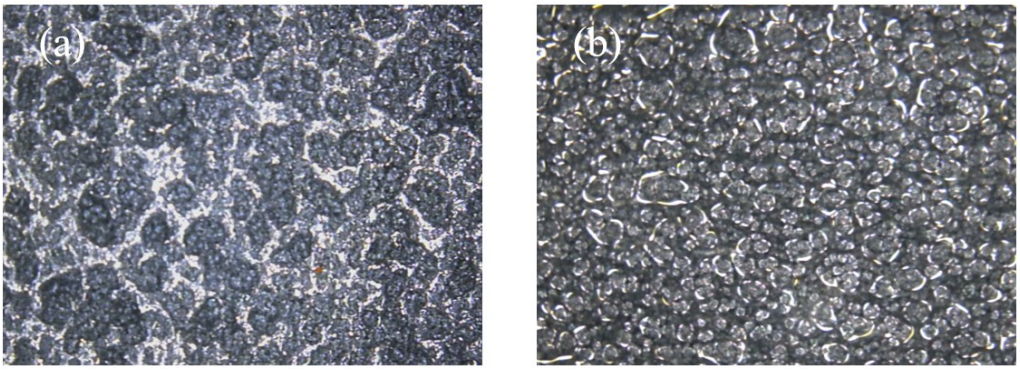


Fig. S6 The electrode deposition morphologies of the symmetric cells assembled with (a) 1 M $ZnSO_4$ and (b) 3% $Zn(NTf_2)_2$.

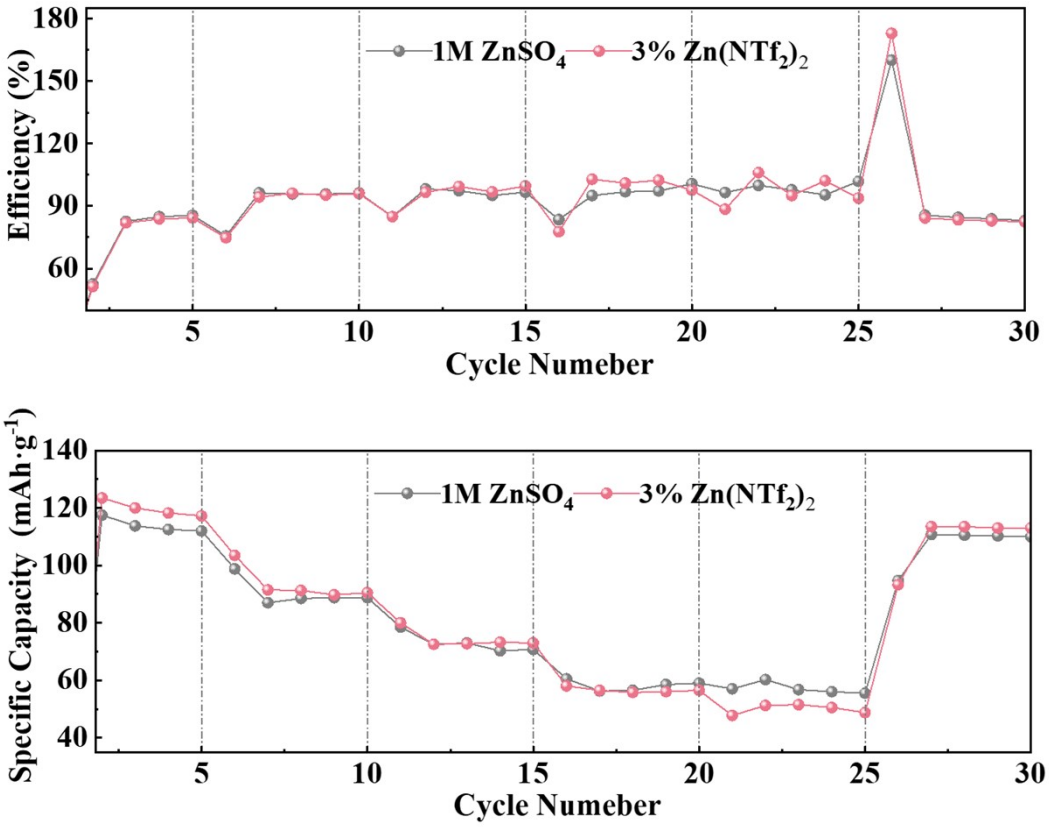
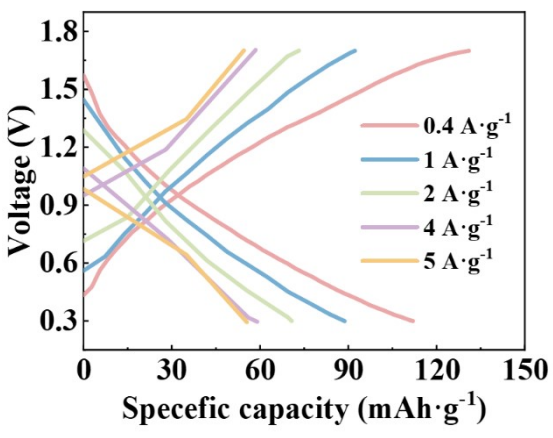


Fig. S7 Rate performance of Zn//AC@I_2 full cells at different current densities of 0.4, 1, 2, 3, 5 and 0.4 $A \cdot g^{-1}$.



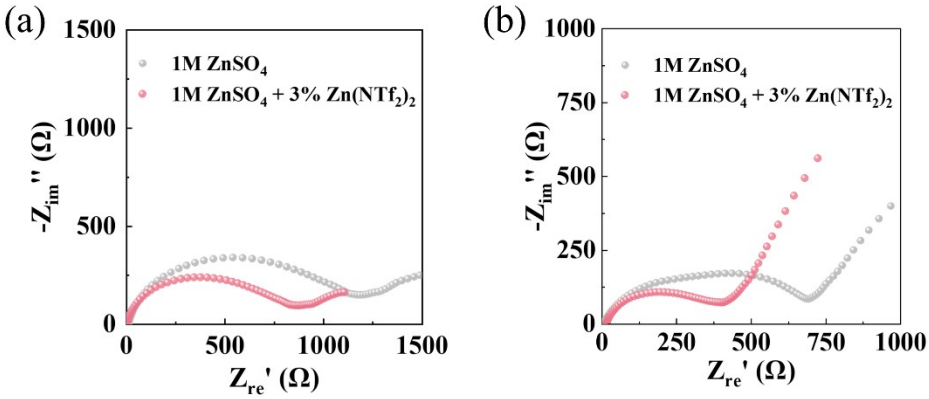


Fig. S9 EIS test plot of (a) Zn symmetric cells and (b) Zn//AC@I_2 full cells with 1 M $ZnSO_4$ and 3% $Zn(NTf_2)_2$.