Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Subtly manipulating Zn^{2+} coordinated configurations with complexing agent to boost the reversibility of zinc metal anode

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Experimental section

Preparation of L_0, L_1, L_2, and L_3 electrolytes: 50 mL 1 M $ZnSO_4$ containing 0, 2.12, 3 and 4.6 mL ethylenediamine was denoted as L_0, L_1, L_2, and L_3, respectively. The pH values of all the electrolytes were adjusted to ~4.5 with concentrated sulfuric acid.

Preparation of NiHCF cathode material: Solution A was prepared by dissolving 3 mmol $Na_4Fe(CN)_6 \cdot 10H_2O$, 0.24 mol NaCl and 12 mmol sodium citrate in 100 mL deionized water under magnetic stirring. Solution B was formed by dissolving 6 mmol $NiSO_4 \cdot 4H_2O$ in 100 mL deionized water under magnetic stirring. Solution A was kept at a constant temperature of 90 °C through an oil bath under N_2 flow, while solution B was added dropwise to solution A at a rate of 1 mL min^{-1} through a peristaltic pump. Then white precipitate was collected by centrifugation, washed thoroughly with deionized water and ethanol, then dried in a vacuum drying oven at 110 °C for 24 h to obtain NiHCF. As for cathode electrode: NiHCF, Ketjen black and polyvinylidene fluoride (PVDF) were mixed with a mass ratio of 7:2:1. The N-methyl pyrrolidinone (NMP) was added into the mixture, the slurry was then casted onto Ti foil.

Material characterization: The phase structures of zinc foil and by-products were assessed by the X-ray diffraction analyzer (XRD, Bruker D8 diffractometer). The surface structure of zinc foil was characterized by scanning electron microscopy (SEM, Hitachi S-4800).

Electrochemical test: The electrochemical performance of Zn/NiHCF batteries were tested by using CR2025 coin-type cell, which contains a cathode electrode, a piece of Zn foil as anode electrode and Whatman glass fiber as separator. L_0, L_1, L_2, and L_3 were employed as electrolytes. The galvanostatic cycling tests were performed by Neware BTS-5 battery test system. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on the CHI604E electrochemical station.

Table S1 The distribution of different Zn^{2+}-En coordinated configurations of in various electrolytes.

Electrolytes	Zn^{2+}	$Zn(En)^{2+}$	$Zn(En)_2^{2+}$	$Zn(En)_3^{2+}$
L_0	1	0	0	0
L_1	0.455	0.455	0.089	2.87×10^{-4}
L_2	0.290	0.524	0.185	1.08×10^{-3}
L_3	0.088	0.451	0.451	7.49×10^{-3}

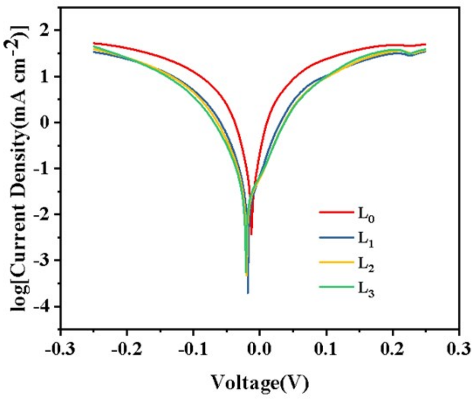

Fig. S1 Tafel curves for the Zn foil in L_0~L_3 electrolytes.

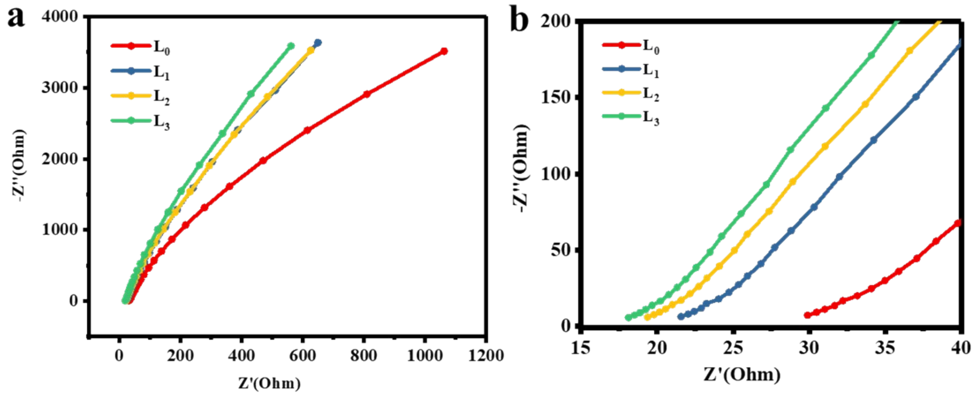

Fig. S2 The EIS plots (a) and the corresponding enlarged view at high-frequency region (b) in different electrolytes for estimation of ionic conductivities.

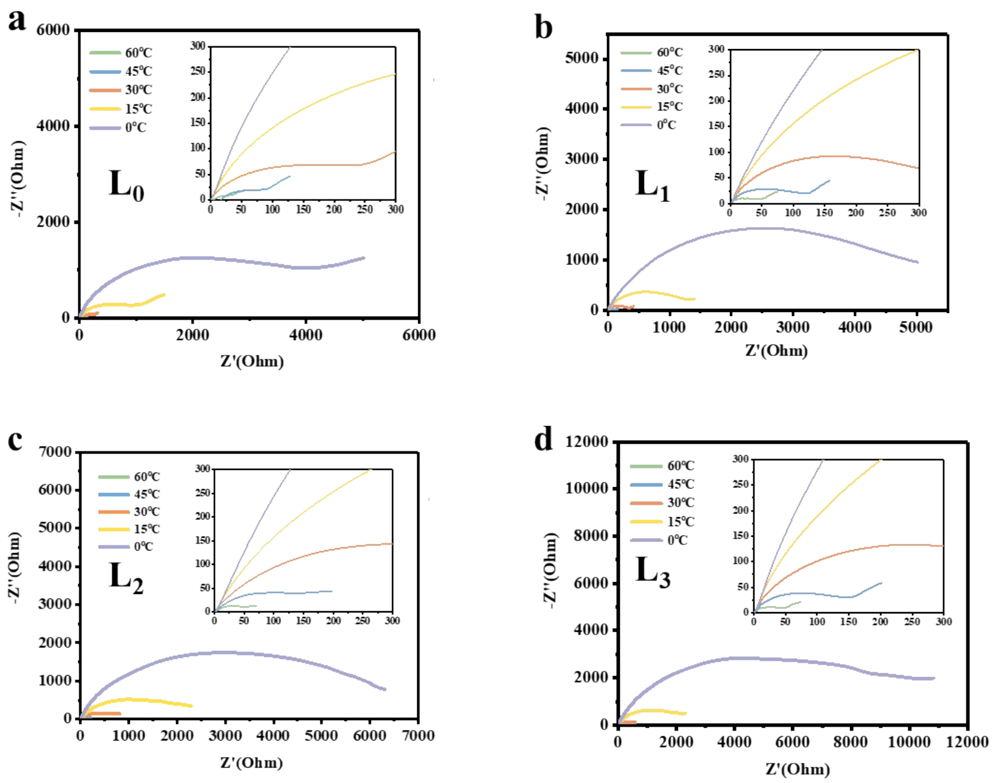

Fig. S3 The EIS plots of Zn/Zn symmetric batteries with various electrolytes at different temperatures

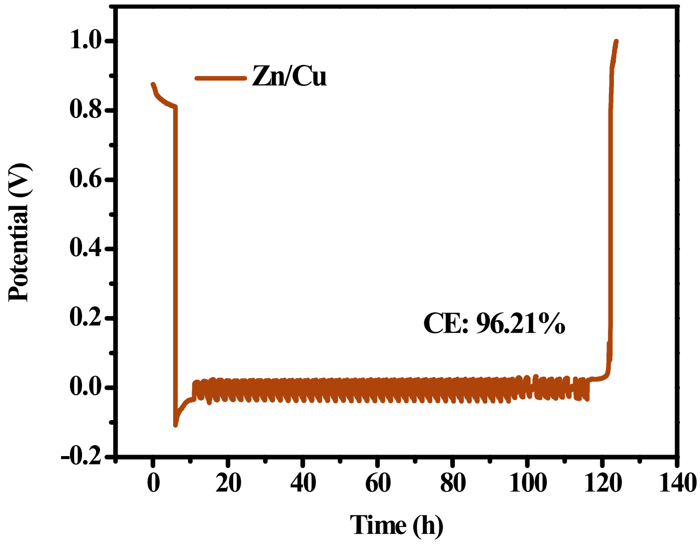

Fig. S4 Coulombic efficiency tested of Zn/Cu cell in L_3 electrolyte.

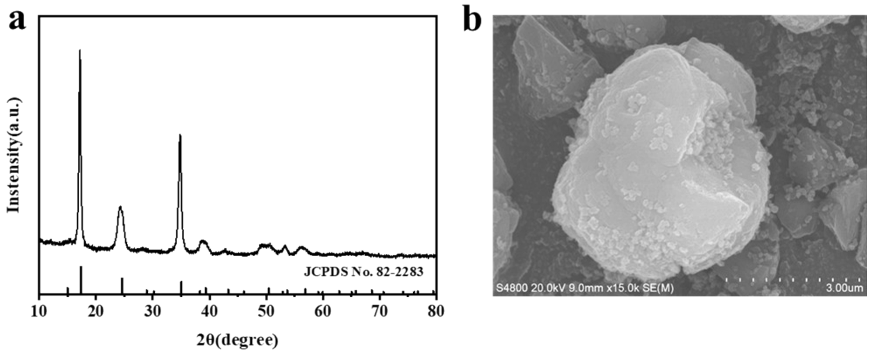

Fig. S5 (a) XRD patterns and (b) SEM image of synthesized NiHCF.

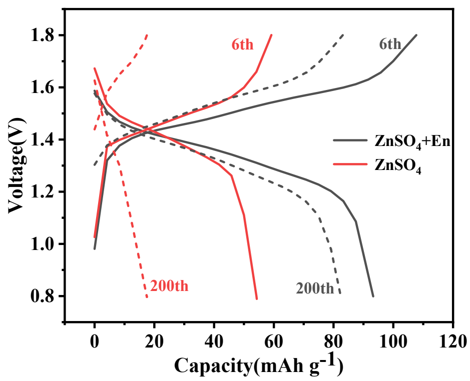

Fig. S6 Galvanostatic charge-discharge profiles of Zn/$ZnSO_4$/NiHCF and Zn/$ZnSO_4$+En/NiHCF batteries at 6 th and 200 th, respectively.