# Ternary chloride-free electrolyte design for highly efficient aqueous Zinc–iodine batteries with four-electron conversion

Wei Han, Jinghao Zhao, Xin Li *.

State Key Laboratory of Space Power-Sources, MOE Engineering Research Center for Electrochemical Energy Storage and Carbon Neutrality in Cold Regions, School of Chemistry and Chemical Engineering, State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001, China.* Corresponding author.

E-mail address: lixin@hit.edu.cn (X. Li).

**Materials:**

Iodine, $ZnSO_4$ $7H_2O$, Betaine, Nicotinamide were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. and used as received without any further purification. Active carbon was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. KI was purchased from Shanghai Yindian Chemical Technology Co., Ltd.

**Synthesis of Iodine/Carbon Composite Materials:**

Firstly, the preparation of activated carbon/iodine composite material involves mixing 200 mg of iodine with an equal weight of ball-milled activated carbon powder. This mixture is thoroughly ground in a mortar until uniform. Subsequently, the mixture is encapsulated in a high-pressure reactor and heated at 150°C for 6 hours. After natural cooling, the mixture is transferred to an open crucible and heated again at 60°C for 2 hours to remove residual iodine on the surface, resulting in pure activated carbon/iodine composite material. To determine the iodine loading, a separate 20-mg sample of this composite material is heated in air at 150°C for 2 hours. The mass of the remaining activated carbon is then measured, and the iodine loading is calculated by subtracting the mass difference.

**Preparation of Activated Carbon/Iodine Composite Cathode:**

The previously prepared activated carbon/iodine composite material is mixed with acetylene black and PVDF in a mass ratio of 8:1:1. This mixture is thoroughly ground in a mortar until uniform. Subsequently, an appropriate amount of NMP (in this case, a ratio of 70 milligrams of PVDF corresponding to 2 milliliters of NMP) is added to the mixture, and it is stirred to form a uniform slurry. Using a 200-micrometer scraper, the slurry is uniformly coated onto carbon paper and then dried in a vacuum at 50°C for over 8 hours. Finally, the dried material is cut into disks with a diameter of 12 mm, ready to be used as an electrode.

## Characterization of Properties:

The Raman spectra were conducted on Renishaw Invia Raman microscope using a laser (wavelength of 532 nm). UV-vis absorption spectroscopy was conducted on LabTech UV blue star 300513.

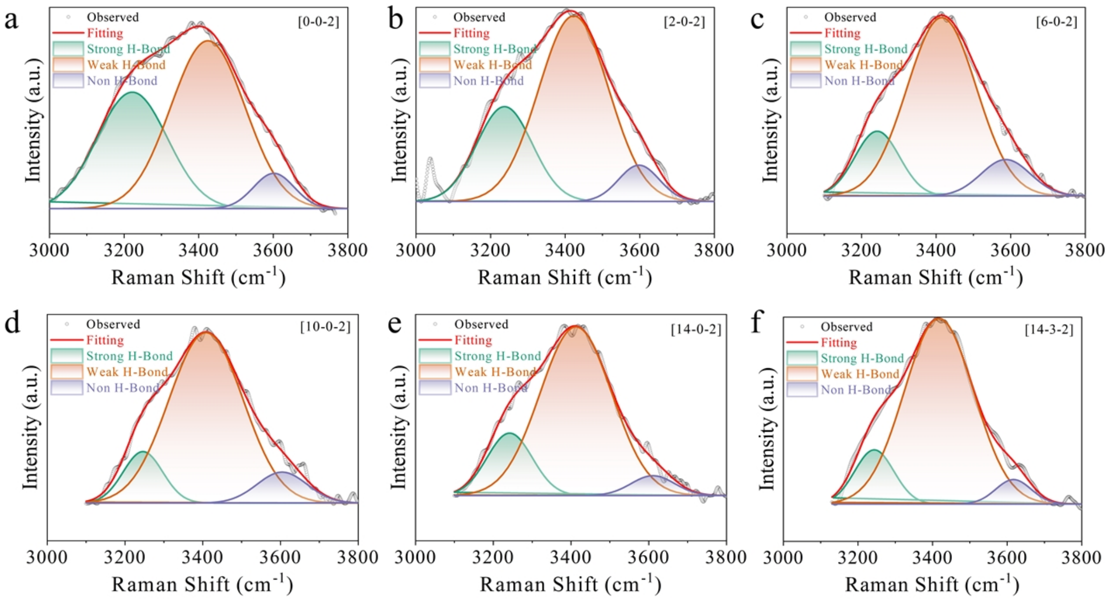


**Figure S1.** The fitted peaks of Raman spectroscopy representing the O−H stretching vibration of water molecules in different electrolyte, respectively.

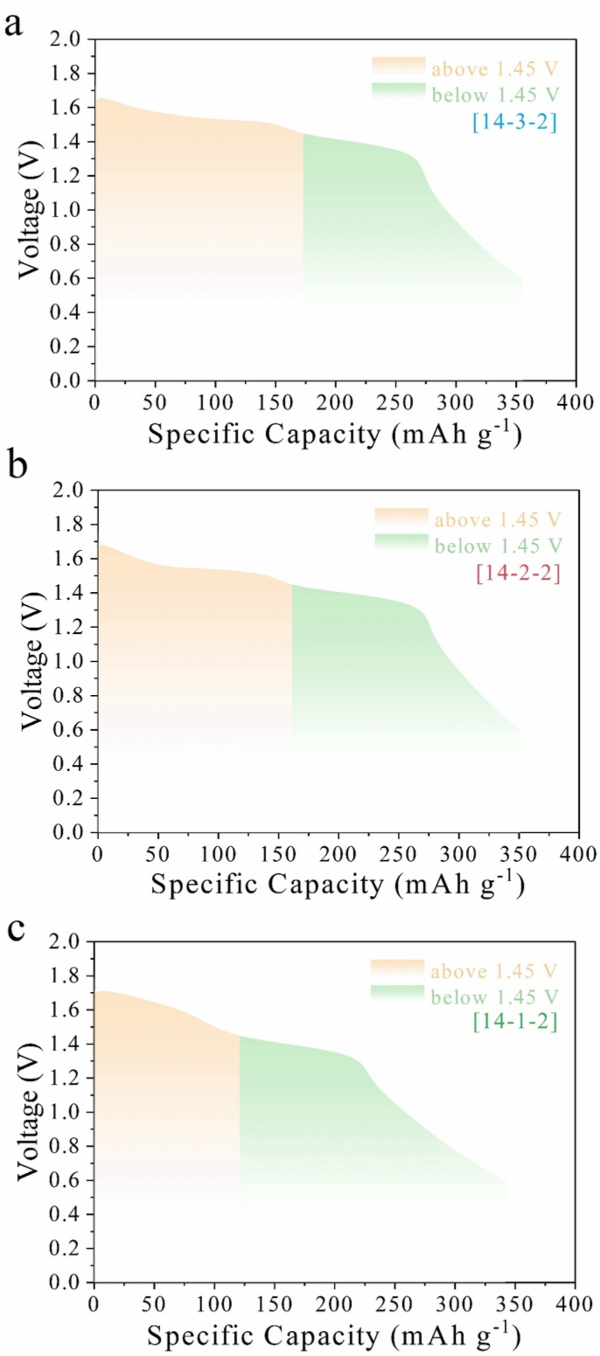


**Figure S2.** Electrochemical performance of the batteries with different electrolytes on discharge profiles. Analysis on plateau divided at the voltage of 1.45 V. Discharge profile with the electrolyte of (a) [14-3-2], (b) [14-2-2] and (c) [14-1-2].

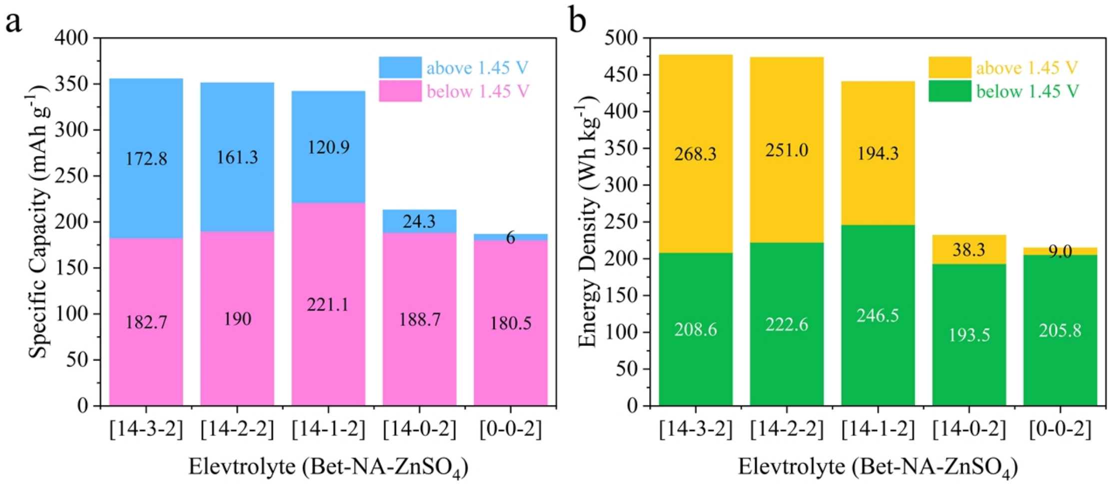


**Figure S3.** Electrochemical performance of the batteries with different electrolytes on discharge specific capacity and energy density. Analysis on plateau divided at the voltage of 1.45 V. a) Discharge specific capacity at two plateaus above and below 1.45 V. b) Specific capacity ratio for the both plateaus. c) Discharge specific energy at two plateaus above and below 1.45 V. d) Specific energy ratio for the both plateaus.

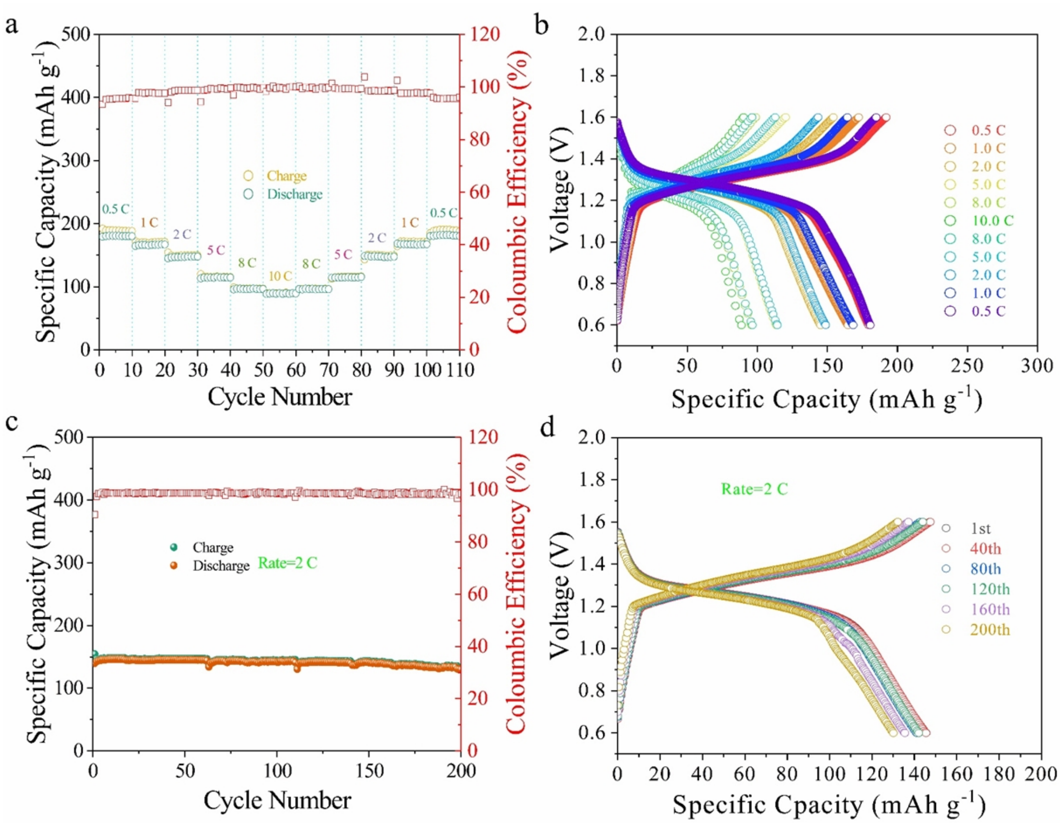


**Figure S4.** The electrochemical performance of Zn-$I_2$ batteries with the ternary mixed aqueous electrolyte. a) Rate performance of Zn-$I_2$ batteries with the electrolyte of [0-0-2]. b) The corresponding charge/discharge profiles for the rate performance. c) Cycling performance with current rate: 2 C. d) The corresponding charge/discharge profiles at current rate of 2 C.

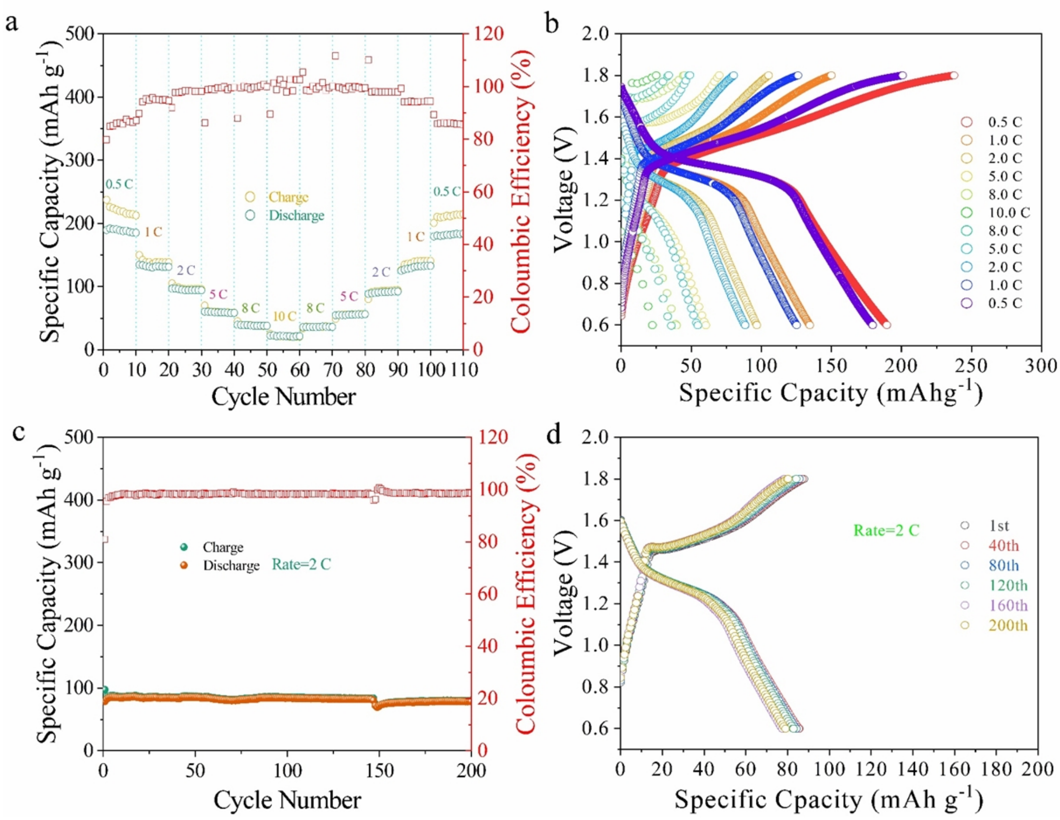


**Figure S5.** The electrochemical performance of Zn-$I_2$ batteries with the ternary mixed aqueous electrolyte. a) Rate performance of Zn-$I_2$ batteries with the electrolyte of [14-0-2]. b) The corresponding charge/discharge profiles for the rate performance. c) Cycling performance with current rate: 2 C. d) The corresponding charge/discharge profiles at current rate of 2 C.

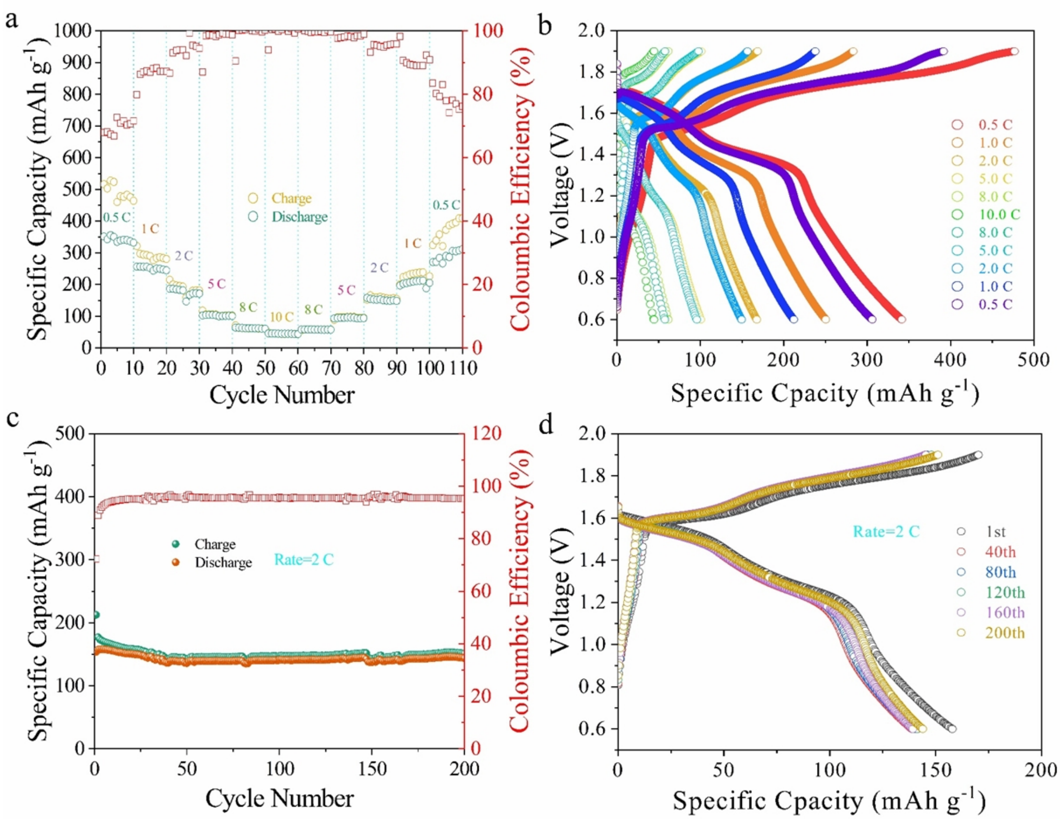


**Figure S6** The electrochemical performance of Zn-$I_2$ batteries with the ternary mixed aqueous electrolyte. a) Rate performance of Zn-$I_2$ batteries with the electrolyte of [14-1-2]. b) The corresponding charge/discharge profiles for the rate performance. c) Cycling performance with current rate: 2 C. d) The corresponding charge/discharge profiles at current rate of 2 C.

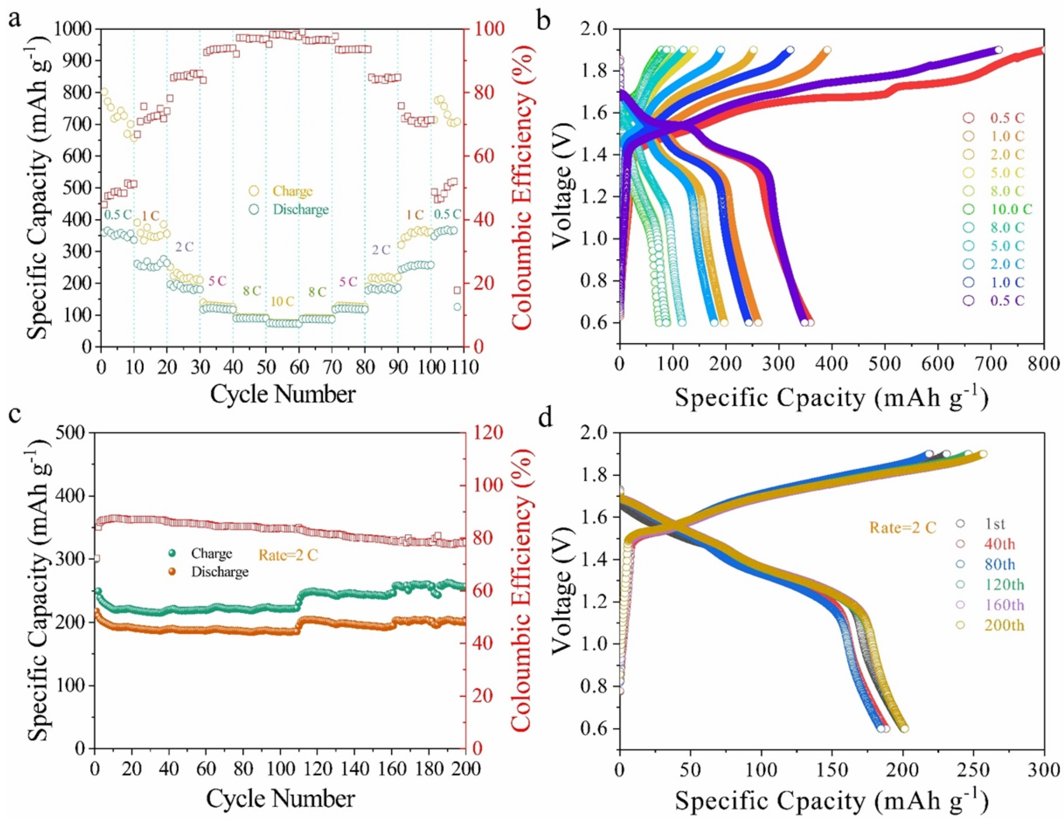


**Figure S7.** The electrochemical performance of Zn-$I_2$ batteries with the ternary mixed aqueous electrolyte. a) Rate performance of Zn-$I_2$ batteries with the electrolyte of [14-2-2]. b) The corresponding charge/discharge profiles for the rate performance. c) Cycling performance with current rate: 2 C. d) The corresponding charge/discharge profiles at current rate of 2 C.

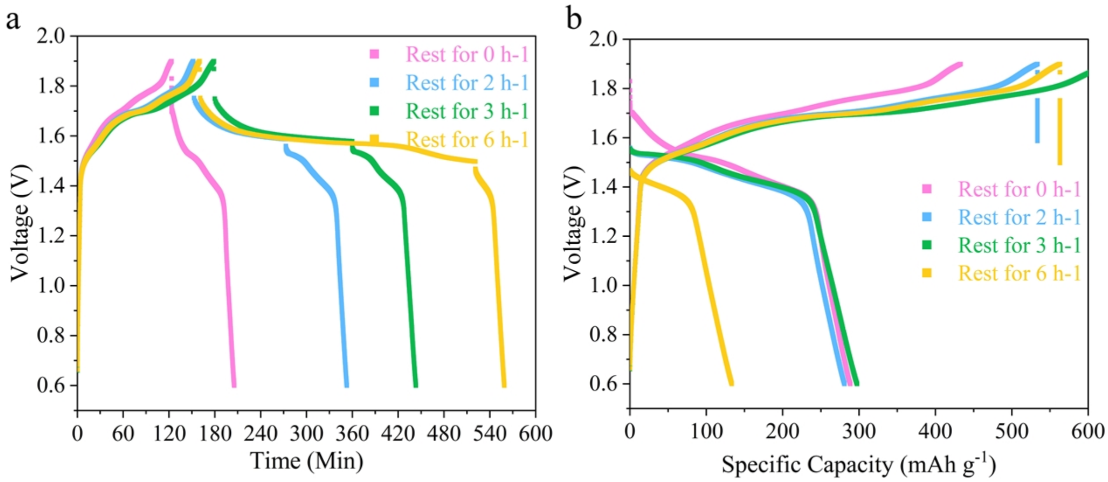


**Figure S8.** Self-discharge experiments on the battery with the ternary hybrid aqueous electrolyte of [14-3-2], rest time ranges from 0-6 h. a) Voltage changes along the charge/discharge profiles depending on time. b) charge/discharge profiles compared for specific capacity.