Supplementary Material

**Using redox electrolytes to extend the charge storage capacity in an aqueous hybrid ion battery**

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**S1. Chemicals and materials**

In this work, all the reagents or chemicals that were used as received without any pre-purification or pre-treatment and modification. Ni(NO3)2⋅H2O, Na2SO4, ZnSO4,Zn-foil from Alfa Aesar. Na4Fe(CN)6⋅10H2O, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL or 4-HO-TEMPO), N-methyl-2-pyrrolidone (NMP), poly (vinylidene) fluoride (PVDF) from Sigma-Aldrich. SuperP carbon (SPC) from TIMCAL. To prepare the electrolytes, deionized water used with the conductivity of 18.2 MΩ/cm. NASICON (Na3Zr2Si2PO12)with ionic conductivity of ∼3×10−4 S/cm and coin cell components were purchased from 4toONE Corporation (South Korea).

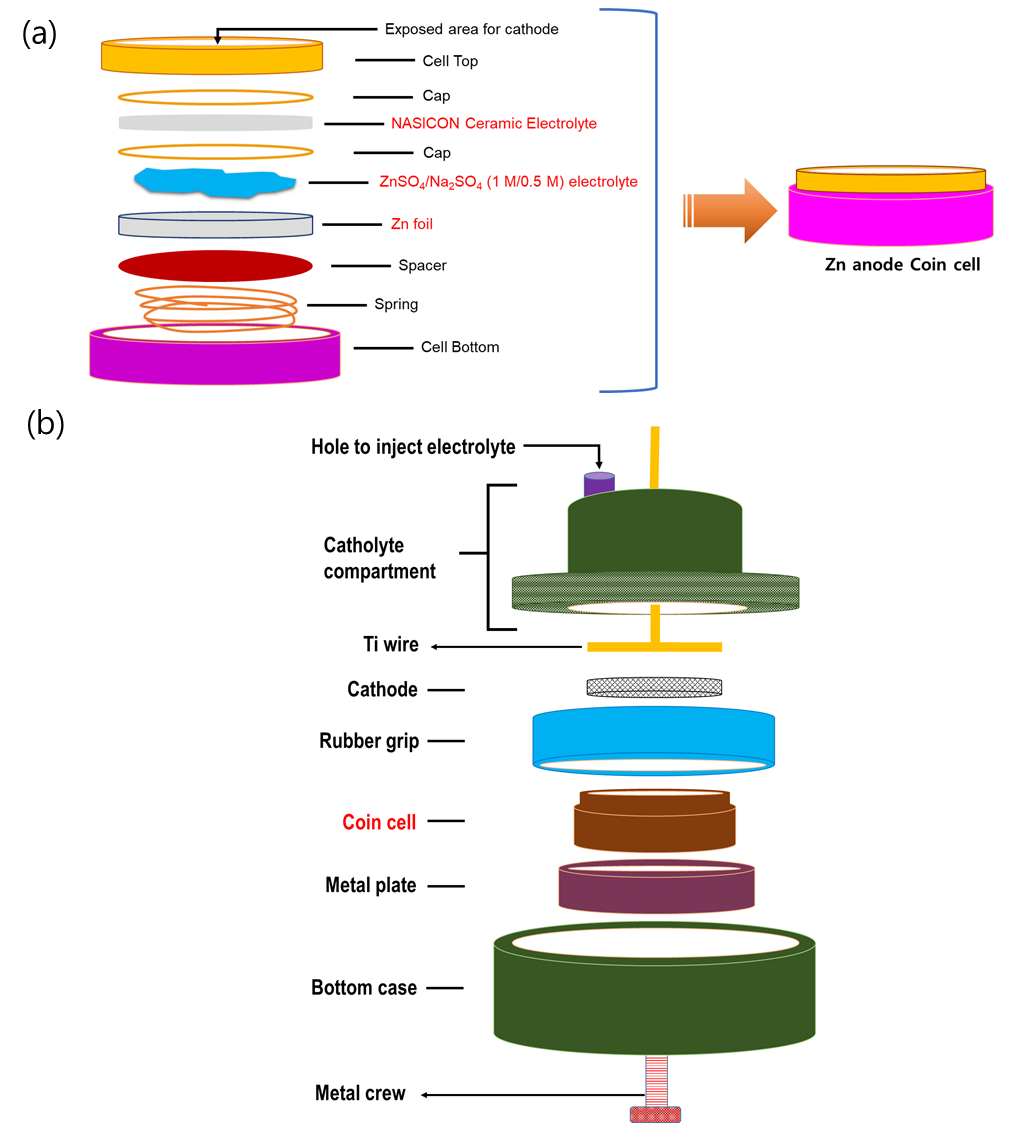
**S2. Preparation of Na-NiHCF coated glassy carbon electrode**

The Na-NiHCF coated GCE was prepared using the ink of Na-NiHCF. The ink was prepared by mixing Na-NiHCF (27 mg), carbon block (3 mg) and 5 wt% Nafion solution (100 µL) in sonication for 3 hours. Then the prepared ink was used coated on GCE (0.07 cm2) and dried at room temperature before to use for CV measurement.

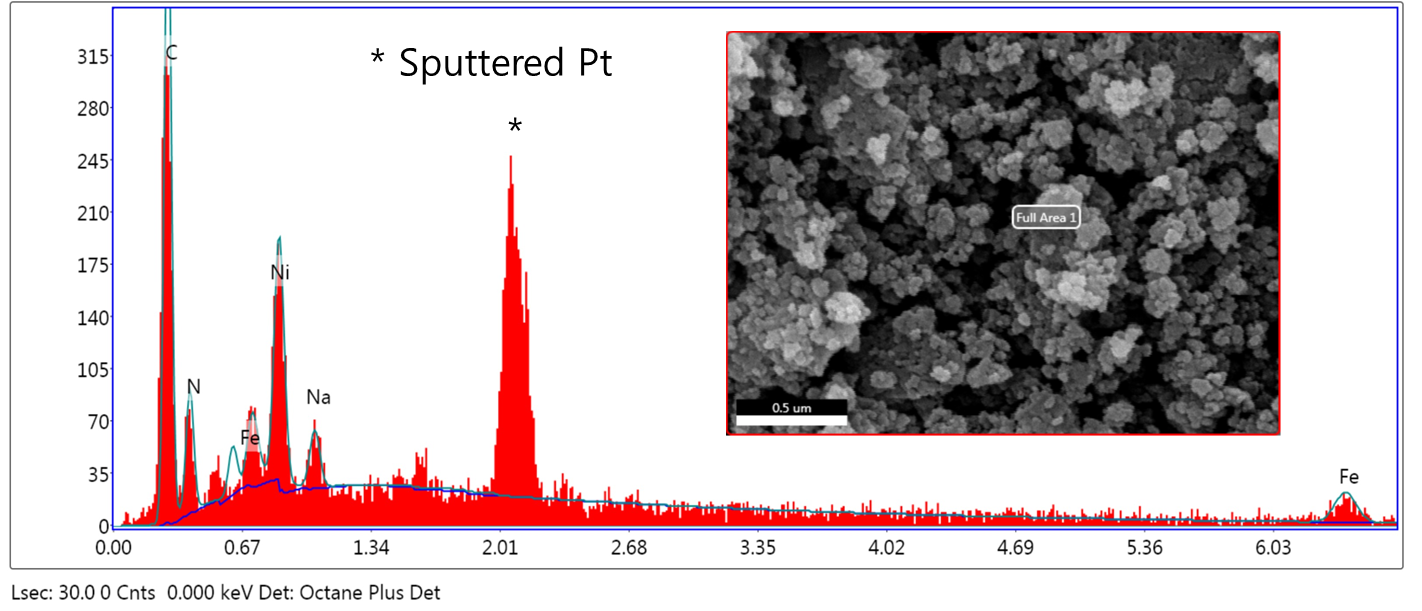
**S3. Physico-chemical Characterization**

The X-ray diffraction (XRD) pattern was collected using Bruker D8 Advance X-ray diffractometer with a source of Cu Kα x-ray radiation between 10° to 80° (2θ). The collected XRD result was evaluated using X΄Pert highscore plus software. Cold field-emission scanning electron microscopy at an accelerating voltage of 10 kV (SU-8220, Hitachi) was used for Scanning electron microscopy (SEM) images. Fourier-transform infrared (FTIR) spectroscopy result was collected form Nicolete 6700 from Thermo Scientific.

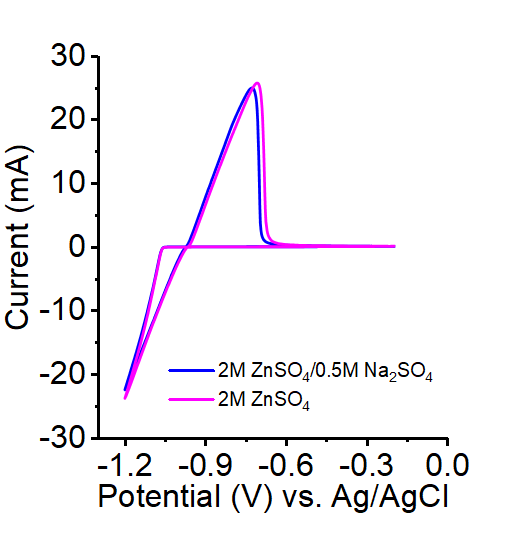
**S4. Supporting Results**



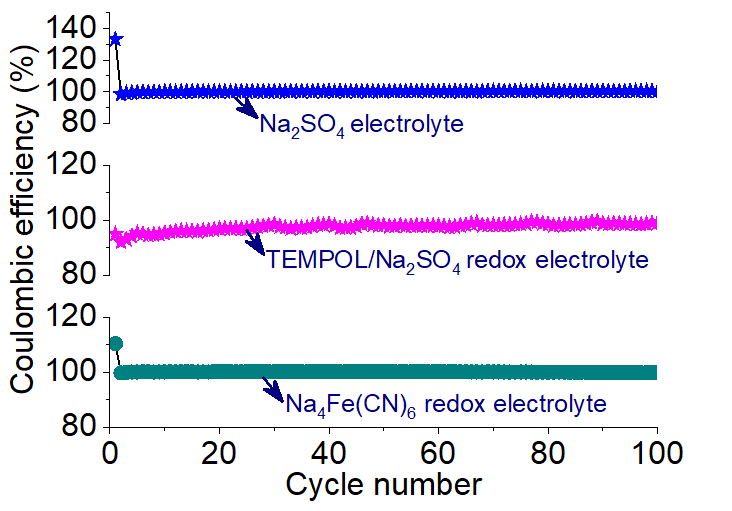
**Figure S1.** (a)Zn anode coin cell assembly and (b) Assembly of redox electrolyte-based hybrid Zn/Na-ion battery.

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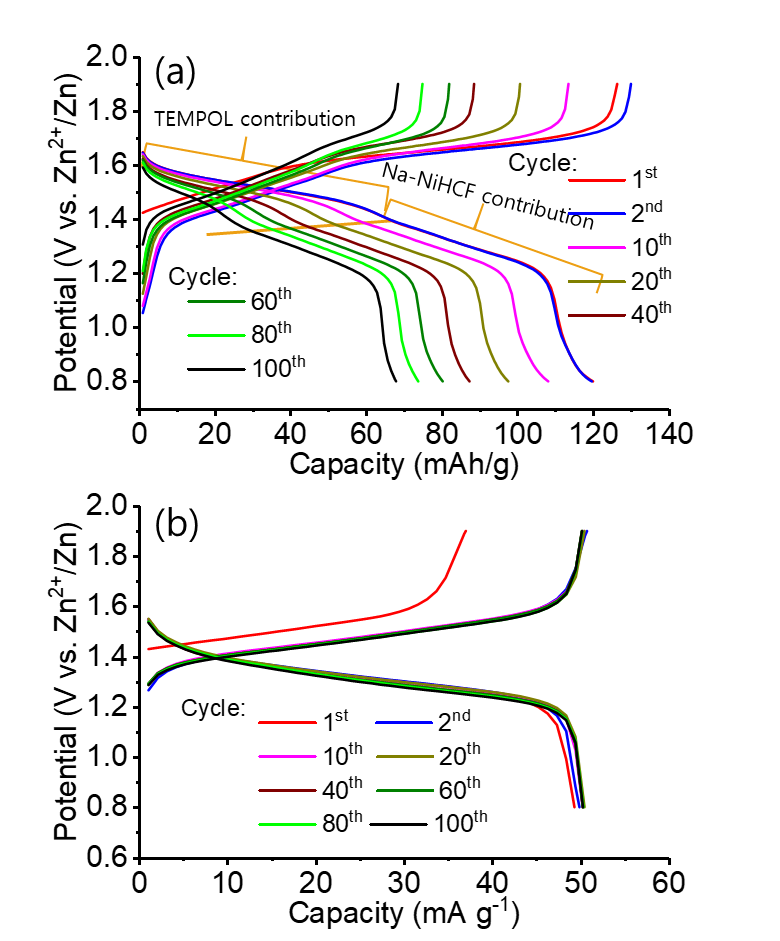
**Figure S2.** EDAX spectra and SEM images (insets) of as-prepared Na-NiHCF.



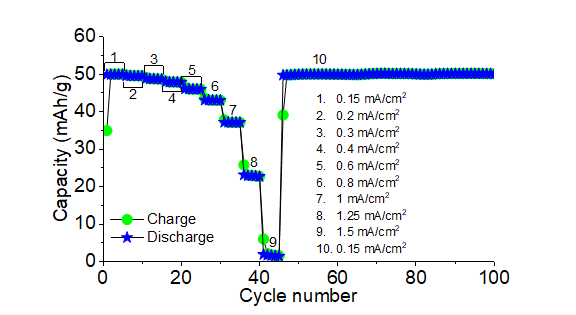
**Figure S3.** CV curve comparion of Zn anode in ZnSO4/Na2SO4 (2/0.5 M) electrolyte and ZnSO4 (2 M) electrolyte (at 10 mV/s).

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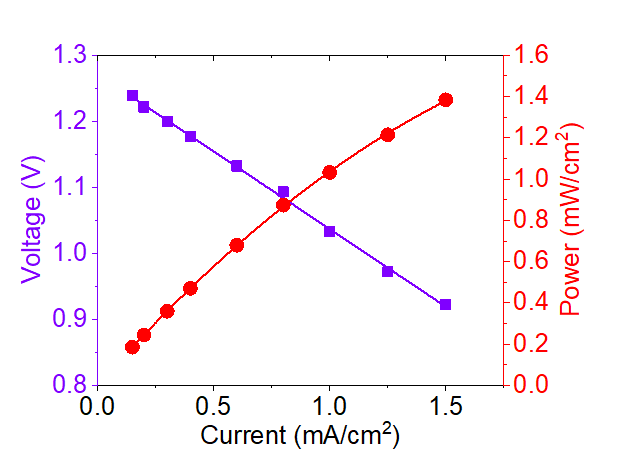
**Figure S4.** Coulombic efficiency performance (concerning cycle number) of the TEMPOL/Na2SO4 (0.1 M/0.5 M) electrolyte-based AHZSIB and the Na4[Fe(CN)6] (0.1 M) electrolyte-based AHZSIB and their comparison with the Na2SO4 (1 M) electrolyte-based AHZSIB (at 0.15 mA/cm2). The provided coulombic efficiency is obtained based on the discharge capacity and charge capacity that displayed in Figure 4d.



**Figure S5.** 1st, 2nd, 10th, 20th, 50th and 100th charge-discharge curves of TMPOL/Na2SO4 (0.1 M/=0.5 M) electrolyte (a) used AHZSIB at 0.15 mA/cm2 and Na2SO4 (1 M) electrolyte used AHZSIB (b) used AHZSIB at 0.15 mA/cm2.



**Figure S6.** Rate performance of Na2SO4 (1 M) electrolyte used AHZSIB.



**Figure S7.** Current, Voltage and Power relation of Na4[Fe(CN)6] (0.1 M) electrolyte used AHZSIB.

The power density was calculated using the relation, ; Where V is discharge voltage, and I is applied current density for discharge.