Supplementary Information

Acidic-Neutral Decoupled Biphasic Electrolytes Enhance Deposition-Dissolution Chemistry in Zn–Mn Batteries

Yidan Cui,[a] Qingyun Dou,*[b] Jiewen Yang,[c] Jingke Yang,[c] Xiaoxi Zhao,[d] Guosheng Li,[b] Pengwei Jing,[b] Qingyue Yin,[a] Caihong Tao*[a] and Xingbin Yan[b]

* Corresponding authors

[a] School of Chemistry and Chemical Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P. R. China. E-mail: taoch@mail.lzjtu.cn

[b] School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: douqy3@mail.sysu.edu.cn

[c] South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510275. China.

[d] Research Center of Resource Chemistry and Energy Materials, State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

The interfacial conductivity of the biphasic electrolyte was characterized via electrochemical impedance spectroscopy (EIS). The experiment was as follows: two titanium foils (1 cm × 1 cm) served as electrodes, each immersed in the aqueous phase and organic phase. The distance between the two electrodes was 1 cm. EIS measurements were performed using an electrochemical workstation. Interfacial resistivity (ρ) and conductivity (σ) were calculated using:

$$\rho = RS/L \tag{1}$$

$$\sigma = 1/\rho \tag{2}$$

where ρ denotes resistivity (Ω m), R represents resistance (Ω), S is the cross-sectional area (m^2), L is the distance between electrodes (m), and σ corresponds to conductivity (S m^{-1}).

The H^+ concentration in the organic phase was quantified by acid-base titration. Five organic phases (BE-T/P(0:1), BE-T/P(1:4), BE-T/P(1:2), BE-T/P(2:3) and BE-T/P(3:2)) were mixed with the aqueous phase and then allowed to stratify. 1 mL of each organic phase was measured with the addition of 20 µL methyl orange indicator. 0.1 M KOH standard solution was slowly dripped into the five organic phases until a sudden color change from orange-red to yellow. The consumed KOH volume was recorded.

Table 1. Acid-base titration experiments of five electrolytes.

Electrolytes	T/P(0:1)	T/P(1:4)	T/P(1:2)	T/P(2:3)	T/P(3:2)
Volume of KOH consumed (µL)	600	400	350	320	300

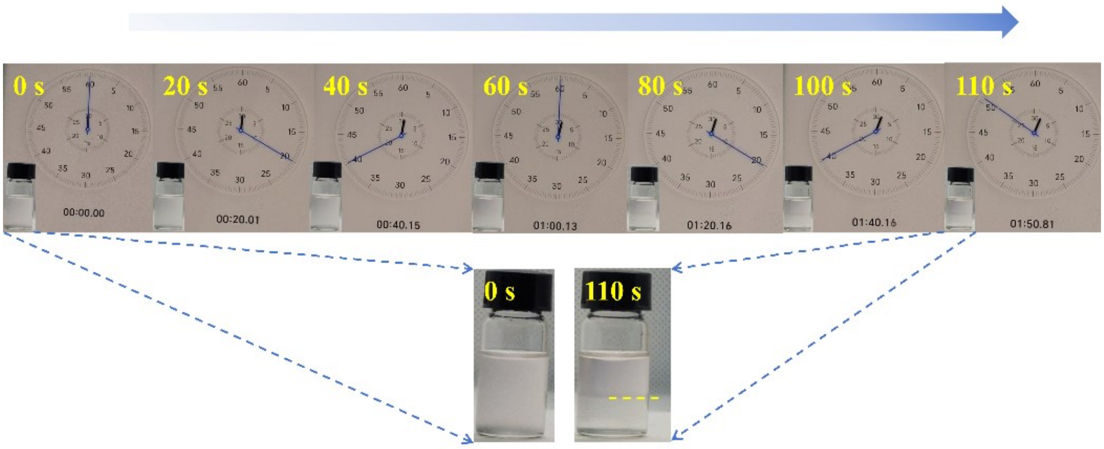

Fig. S1. Photographs showing the phase separation behavior after shaking for the BE-T/P(2:3).

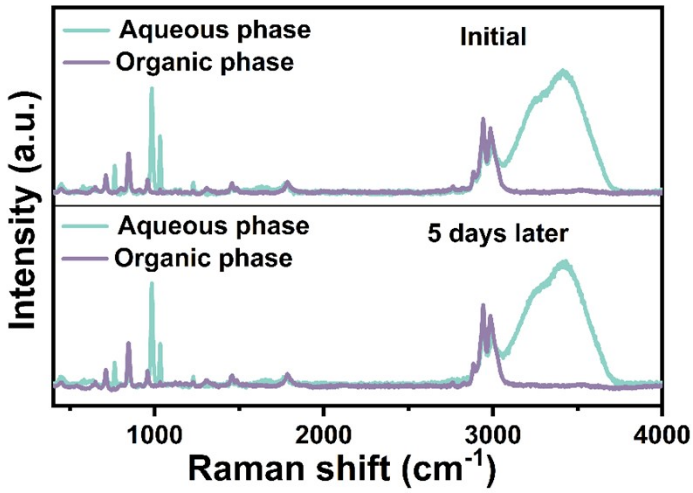

Fig. S2. Raman spectra of the organic phase and aqueous phase for the BE-T/P(2:3) in its initial condition and after 5 days of storage.

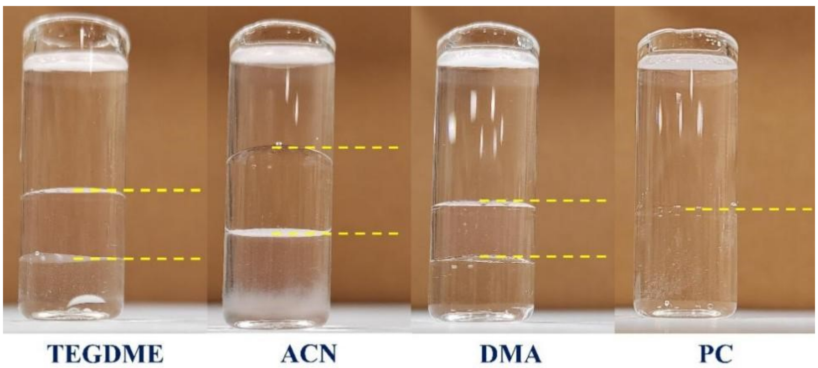

Fig. S3. Photographs showing the phase separation of the electrolyte systems with different organic solvents and TFEP mixed with water.

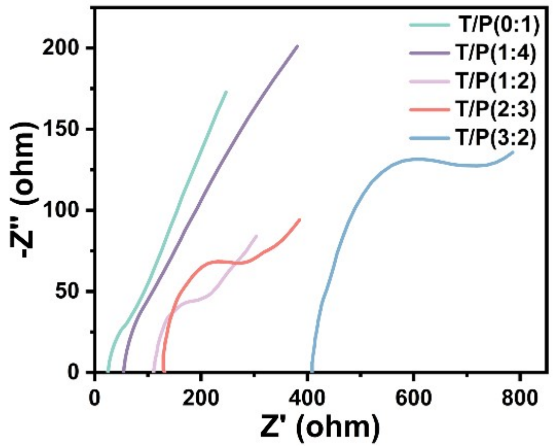

Fig. S4. EIS plots of five biphasic electrolytes for characterizing interfacial conductivity.

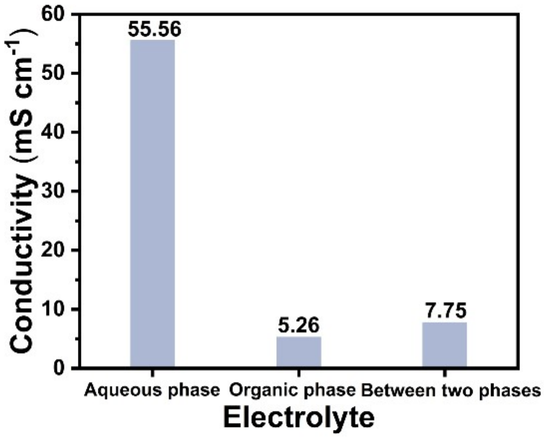

Fig. S5. Conductivity of aqueous phase, organic phase, and between two phases for the BE-T/P(2:3).

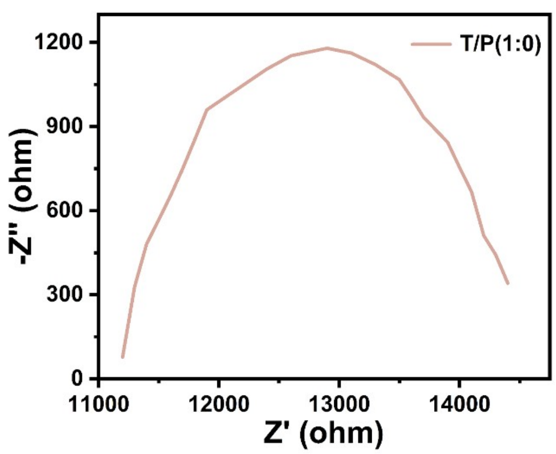

Fig. S6. EIS plots of BE-T/P(1:0) for characterizing interfacial conductivity.

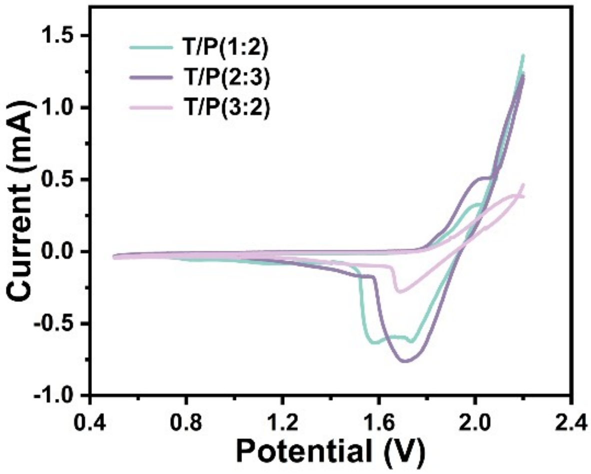

Fig. S7. CV curves of three batteries using BE-T/P(1:2), BE-T/P(2:3), and BE-T/P(3:2).

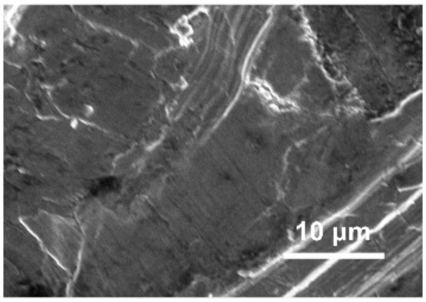

Fig. S8. SEM images of polished pure Zn foil.

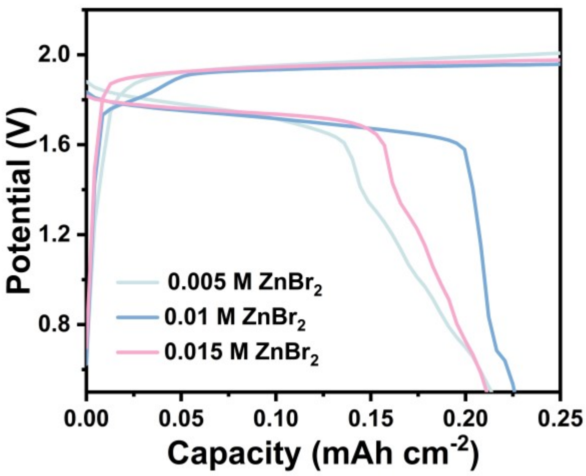

Fig. S9. GCD curves of batteries with different concentrations of $ZnBr_2$.

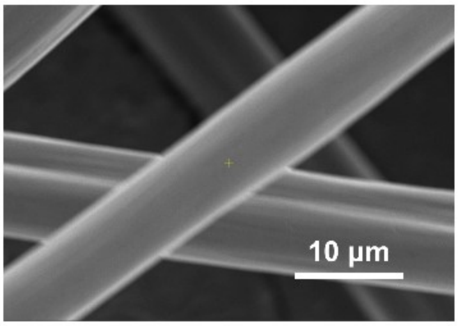

Fig. S10. SEM images of pristine carbon felt.

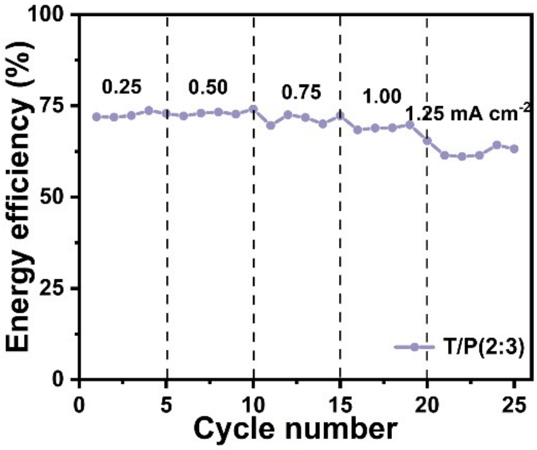

Fig. S11. Coulombic efficiency of the battery using BE-T/P(2:3) at current densities of 0.25, 0.50, 0.75, 1.00, and 1.25 mA cm^{-2}.