Supplementary Information

A High Capacity Small Molecule Quinone Cathode for Rechargeable Aqueous Zinc-Organic Batteries

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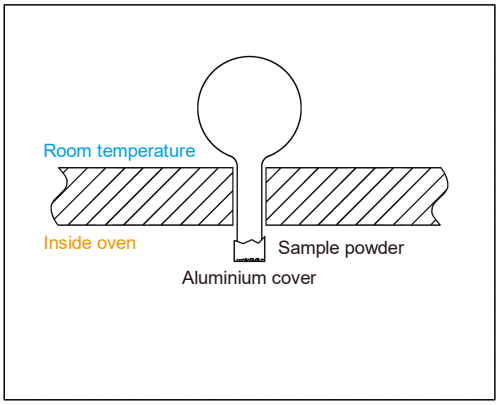
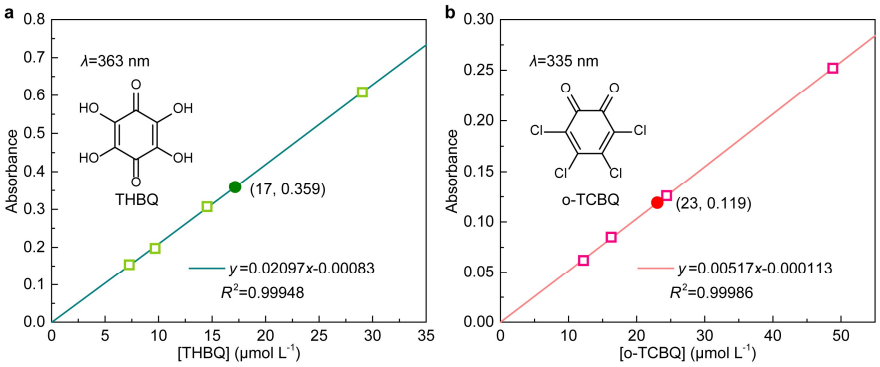
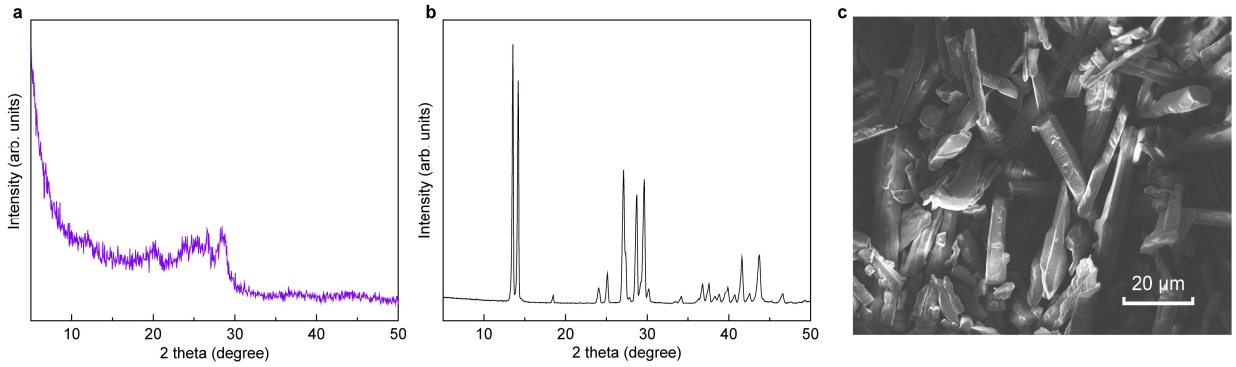
Supplementary Figures and Table



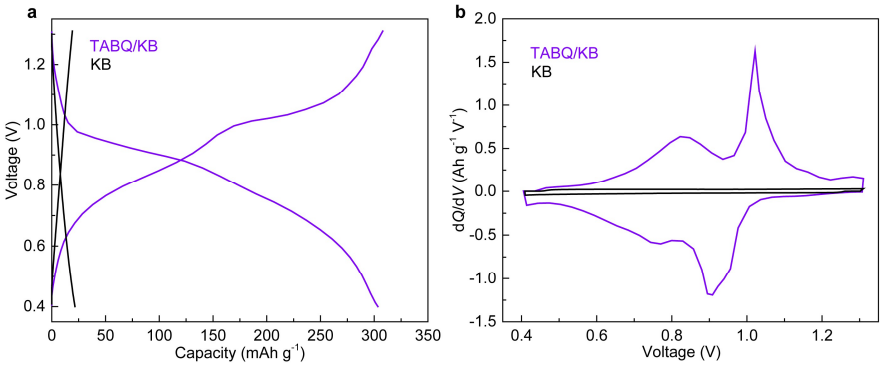
Supplementary Figure 1. Schematic illustration for the setup for sublimation behavior studies.



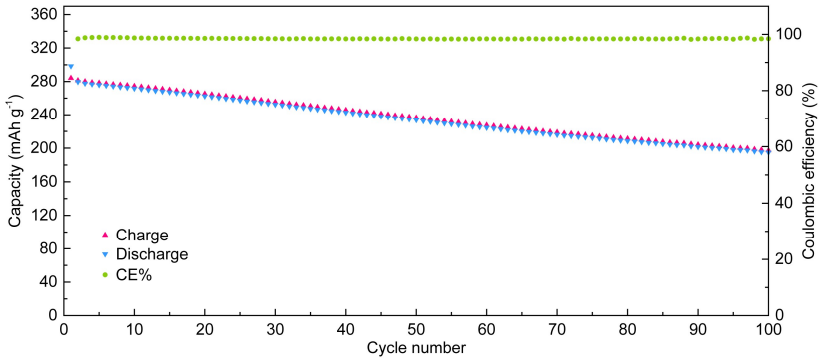
Supplementary Figure 2. UV-vis analysis to calculate the solubility of quinone materials: calibration curves of **a** THBQ and **b** o-TCBQ in 1 M $ZnSO_4$.



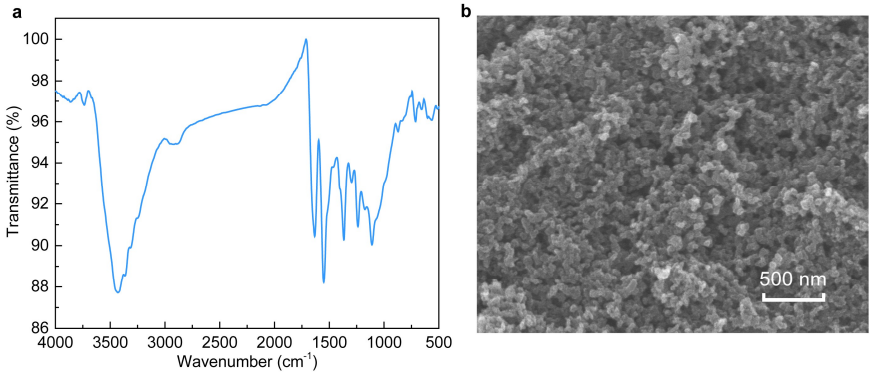
Supplementary Figure 3. a XRD of the TABQ electrode. **b** XRD and **c** SEM image of the as-prepared TABQ.



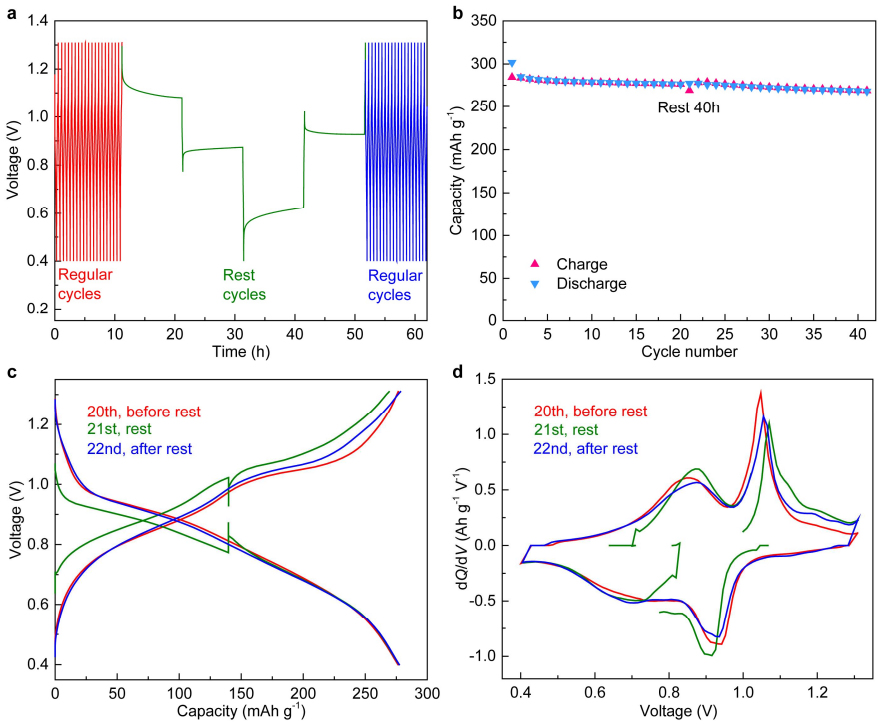
Supplementary Figure 4. Electrochemical performance of TABQ/KB and KB electrodes in 1 M $ZnSO_4$: **a** charge/discharge curves and **b** differential capacity curves.



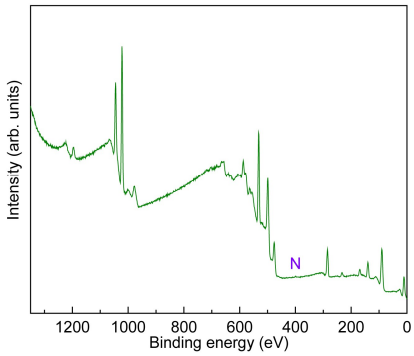
Supplementary Figure 5. Capacity and coulombic efficiency evolution of TABQ at 0.16 A g^{-1} for 100 cycles.



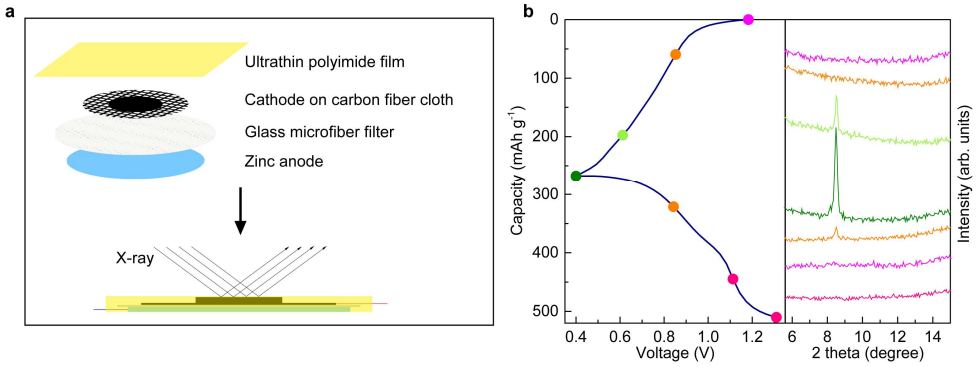
Supplementary Figure 6. Characterizations of the TABQ electrode after 1000 cycles: **a** FT-IR spectrum. **b** SEM image.



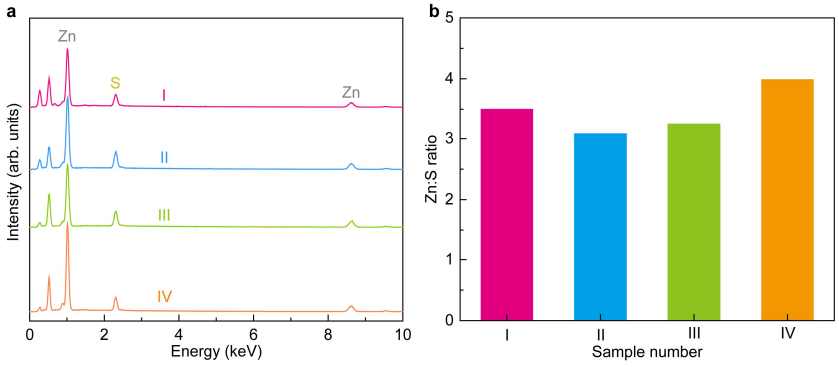
Supplementary Figure 7. Electrochemical performance of the TABQ cathode during rest test: **a** voltage evolution over time; **b** capacity evolution of TABQ; **c** charge/discharge curves and **d** differential capacity curves before, during and after the cycle with rest.



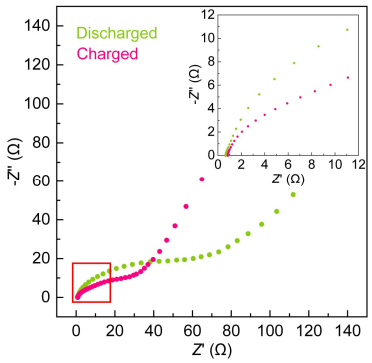
Supplementary Figure 8. XPS of the Zn anode after 10 cycles at 0.1 A g^{-1} in the cell with TABQ cathode and the electrolyte of 1 M $ZnSO_4$ containing saturated TABQ.



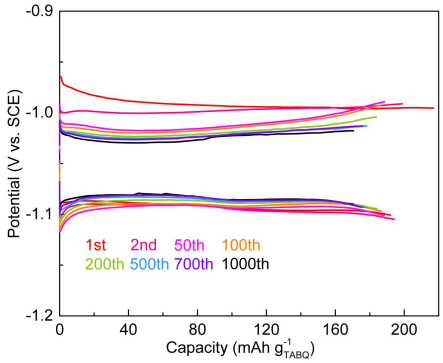
Supplementary Figure 9. In-situ XRD of TABQ: **a** schematic diagram of the in-situ XRD analysis; **b** XRD peak evolution along discharge and charge.



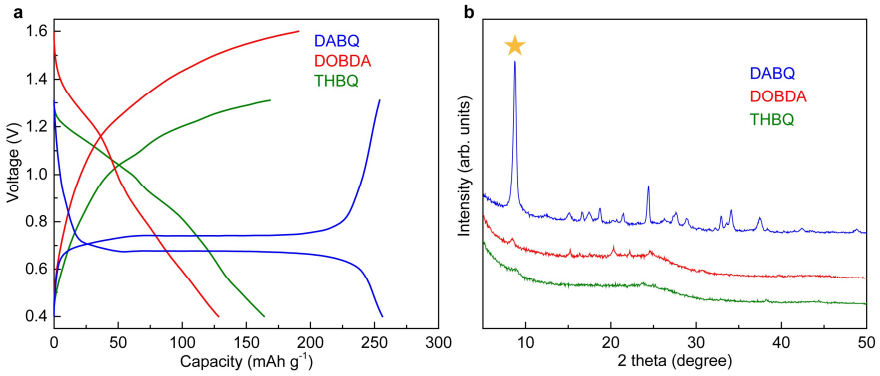
Supplementary Figure 10. EDS analysis of discharged TABQ: **a** EDS spectra and **b** the corresponding Zn:S molar ratios from four parallel measurements.



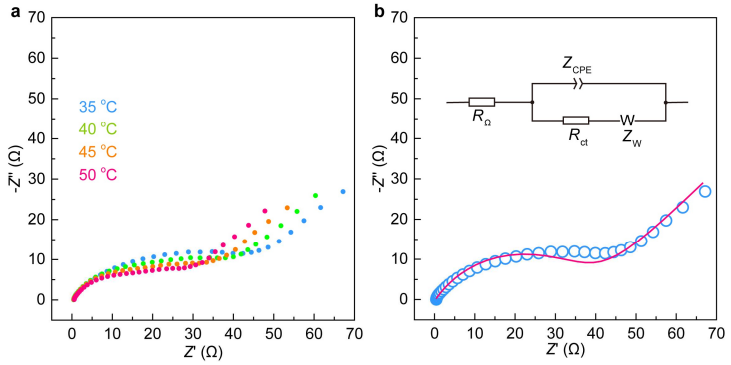
Supplementary Figure 11. The Nyquist plots of TABQ at the end of discharge and charge.



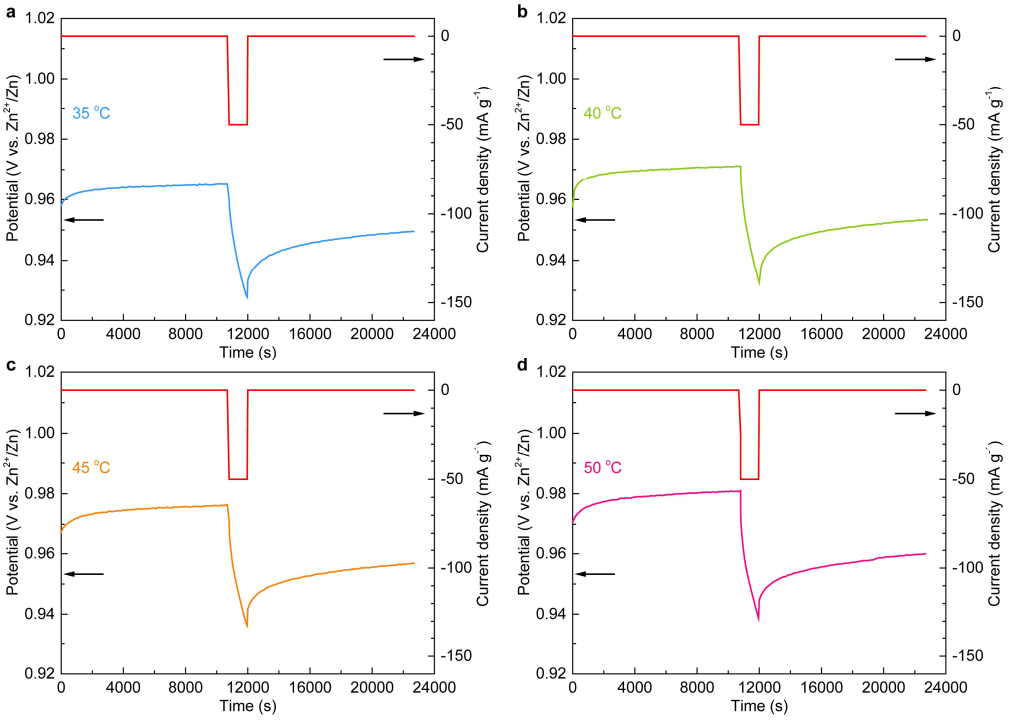
Supplementary Figure 12. Charge/discharge curves of Zn electrode during long-term cycling test.



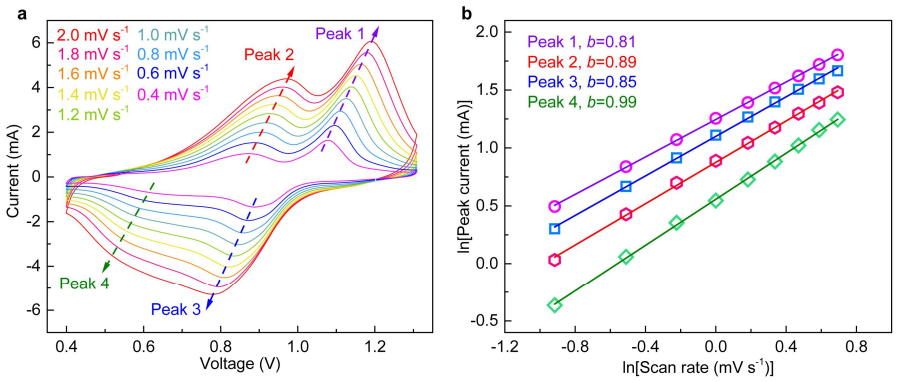
Supplementary Figure 13. Electrochemical performance of DOBDA, THBQ and DABQ in aqueous zinc cells: **a** charge/discharge curves and **b** XRD patterns of the discharged electrodes.



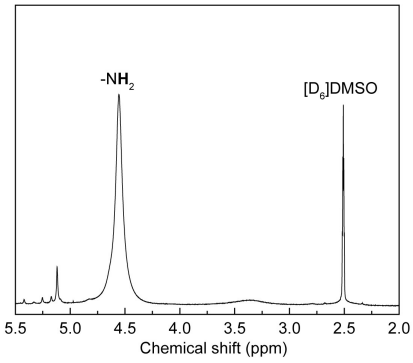
Supplementary Figure 14. EIS analysis of TABQ: **a** Nyquist plots at various temperatures and **b** the representative fitting of the 35 ºC plot with a typical equivalent circuit (inset).



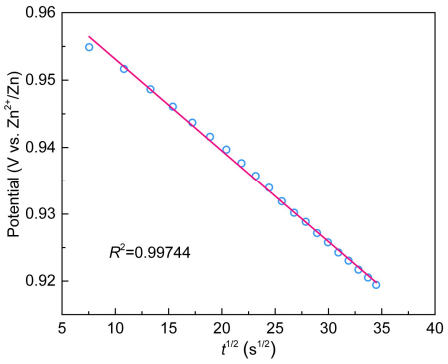
Supplementary Figure 15. GITT curves of TABQ at various temperatures.



Supplementary Figure 16. Kinetics studies of TABQ: **a** CV curves at various scan rates; **b** the linear fits of $\ln(i)$ vs. $\ln(v)$ plots to calculate b values according to the equation of $i = av^b$.



Supplementary Figure 17. ^{1}H NMR of the as-prepared TABQ.



Supplementary Figure 18. The linear relationship between voltage and $t^{1/2}$ during GITT pulse.

Supplementary Table 1. Calculated R_{ct} of TABQ at various temperatures.

Temperature (°C)	R_{ct} (Ω)	Relative standard errors (%)
35	40.00	6.2
40	32.94	6.2
45	27.85	6.1
50	24.21	5.5

Supplementary Discussions.

Quantitative calculation of proton vs. Zn^{2+} storage in TABQ

In the discharged cathode, zinc exists in $Zn_4SO_4(OH)_6{\cdot}4H_2O$ as well as Zn^{2+} inserted TABQ, and SO_4^{2-} exists in $Zn_4SO_4(OH)_6{\cdot}4H_2O$.The weight percentage of zinc was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The SO_4^{2-} was extracted from the discharged cathode with dilute hydrochloric acid, and the amount was measured by ion chromatography (IC). The ICP-OES and IC analysis resulted in Zn and SO_4^{2-} weight percentages of 17.34% and 5.76% in the discharged cathode, respectively.

The discharged cathode contains the mixture of: (1) proton inserted TABQ (2H-TABQ), (2) Zn^{2+} inserted TABQ (Zn-TABQ), (3) $Zn_4SO_4(OH)_6{\cdot}4H_2O$ and (4) KB and PVDF. Their weight percentages obey the following equations:

$$\text{2H-TABQ wt\% + Zn-TABQ wt\% + } Zn_4SO_4(OH)_6{\cdot}4H_2O \text{ wt\% + [KB + PVDF] wt\% = 100\%} \quad \text{(S1)}$$

$$SO_4^{2-} \text{ wt\% = } Zn_4SO_4(OH)_6{\cdot}4H_2O \text{ wt\% } \times \omega[SO_4^{2-} \text{ in } Zn_4SO_4(OH)_6{\cdot}4H_2O] = 5.76\% \quad \text{(S2)}$$

$$\text{Zn wt\% = Zn-TABQ wt\% } \times \omega[\text{Zn in Zn-TABQ}] + Zn_4SO_4(OH)_6{\cdot}4H_2O \text{ wt\% } \times \omega[\text{Zn in } Zn_4SO_4(OH)_6{\cdot}4H_2O] = 17.34\% \quad \text{(S3)}$$

$$\text{TABQ wt\% = 2H-TABQ wt\% } \times M_w[\text{TABQ}]/M_w[\text{2H-TABQ}] + \text{Zn-TABQ wt\% } \times M_w[\text{TABQ}]/M_w[\text{Zn-TABQ}] = \text{[KB + PVDF] wt\%} \quad \text{(S4)}$$

The meaning of the symbols in the above equations are as below:

2H-TABQ wt%: weight percentage of proton inserted TABQ in the discharged cathode;

Zn-TABQ wt%: weight percentage of Zn^{2+} inserted TABQ in the discharged cathode;

$Zn_4SO_4(OH)_6{\cdot}4H_2O$ wt%: weight percentage of $Zn_4SO_4(OH)_6{\cdot}4H_2O$ in the discharged cathode;

[KB + PVDF] wt%: weight percentage of KB and PVDF in the discharged cathode;

$\omega[SO_4^{2-} \text{ in } Zn_4SO_4(OH)_6{\cdot}4H_2O]$: mass fraction of SO_4^{2-} in $Zn_4SO_4(OH)_6{\cdot}4H_2O$, which is 18.07%;

$\omega[\text{Zn in } Zn_4SO_4(OH)_6{\cdot}4H_2O]$: mass fraction of Zn in $Zn_4SO_4(OH)_6{\cdot}4H_2O$, which is 49.19%;

ω[Zn in Zn-TABQ]: mass fraction of Zn in Zn^{2+} inserted TABQ, which is 28.00%;

M_w[TABQ]: molecular weight of TABQ, which is 168.15 g mol^{-1};

M_w[2H-TABQ]: molecular weight of proton inserted TABQ, which is 170.17 g mol^{-1};

M_w[Zn-TABQ]: molecular weight of Zn^{2+} inserted TABQ, which is 233.54 g mol^{-1}.

The above equations result in 2H-TABQ wt% and Zn-TABQ wt% of 29.14% and 5.93%, respectively. Therefore, the mole of inserted proton is 13.5 times of Zn^{2+}. It confirms the domination of proton storage in TABQ during the redox processes.

Discussion of pH influence on TABQ redox potential

The potential difference between pH~0 and pH~4 electrolytes can be explained by Nernst shift as discussed below. The redox reaction on TABQ is written as:

$$\text{TABQ} + 2H^+ + 2e^- \rightleftharpoons \text{2H-TABQ} \quad \text{(S5)}$$

The potential (E) is calculated according to the Nernst equation:

$$E = E^\circ + (0.0592/2)\lg(a_{\text{TABQ}} \times a_{\text{proton}}^2 / a_{\text{2H-TABQ}}) \quad \text{(S6)}$$

With both TABQ and 2H-TABQ in the solid state, the equation is rearranged to:

$$E = E^\circ + 0.0592\lg(a_{\text{proton}}) \quad \text{(S7)}$$

The proton activities in pH~4 and pH~0 electrolytes are around 4 and 0, respectively. Therefore,

$$E[\text{pH}\sim4] = E^\circ - 0.0592 \times 4 \quad \text{(S8)}$$

$$E[\text{pH}\sim0] = E^\circ - 0.0592 \times 0 \quad \text{(S9)}$$

The potential difference between the two groups of electrolytes is around:

$$E[\text{pH}\sim0] - E[\text{pH}\sim4] = 0.24\ \text{V} \quad \text{(S10)}$$

The value is close to the potential difference we obtained experimentally, confirming the proton involved redox reaction in TABQ.