Supporting Information

Enhancing Organic Cathodes of Aqueous Zinc-Ion Batteries via Utilizing Steric Hindrance and Electron Cloud Equalization

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Experimental Section

Material：Aniline (Maclean's，AR analysis pure), 50% phytic acid (Aladdin，AR analysis pure), zinc sulfate heptahydrate (Maclean's，AR analysis pure), zinc phytate (Aladdin，AR analysis pure), ammonium persulfate (Aladdin，AR analysis pure), conductive carbon black (Pioneer Nano，AR analysis pure), sulfuric acid (Aladdin，AR analysis pure), hydrochloric acid (Aladdin，AR analysis pure), deionized water, anhydrous ethanol (Aladdin，AR analysis pure), carbon cloth (Cloride，≥99.9%), electrolytic cell.

Preparation of polyaniline doped with different concentration of phytic acids：The phytic acid-doped polyaniline (PANI-P) was synthesized via an *in situ* polymerization method. Different concentrations of dopant acid, namely 0.03mol, 0.06mol and 0.30mol of phytic acid (PA) added to 2 ml of deionized water. After stirring for 2 minutes, 0.05mol of aniline (An) was added and the mixtures was continuously stirred until complete solubility was achieved. (The An: PA =: 5:3, 5:6, 5:30) Put the above samples into 2℃~8℃ environment and refrigerate for 10 minutes. Dissolve 2.28g of ammonium persulfate ($(NH_4)_2S_2O_8$) in 1ml of deionized water and set it aside. Add 0.845ml of ammonium persulfate solution to the aniline solution, thoroughly mix, and transfer it into a controlled environment at 2℃~8℃ for polymerization over a period of 12h. Subsequently, remove the mixture and subject it to multiple washes with deionized water and alcohol followed centrifugation. Finally, place the sample in a vacuum oven set at 60℃. The PANI-P in the main text represents the molar ratio of An: PA = 5: 3.

Preparation of polyaniline doped with sulfuric acids (PANI-S) and hydrochloride acid (PANI-C) ：The sulfuric acid-doped polyaniline (PANI-S) and hydrochloride acid-doped polyaniline (PANI-C) were synthesized via an *in situ* polymerization method. 0.03mol sulfuric acid and hydrochloric acid were added to 2 ml of deionized water respectively. After stirring for 2 minutes, 0.05mol of aniline (An) was added and the mixtures was continuously stirred until complete solubility was achieved. Put the above samples into 2℃~8℃ environment and refrigerate for 10 minutes. Dissolve 2.28g of ammonium persulfate ($(NH_4)_2S_2O_8$) in 1ml of deionized water and set it aside. Add 0.845ml of ammonium persulfate solution to the aniline solution, thoroughly mix, and transfer it into a controlled environment at 2℃~8℃ for polymerization over a period of 12h. Subsequently, remove the mixture and subject it to multiple washes with deionized water and alcohol followed centrifugation. Finally, place the sample in a vacuum oven set at 60℃.

Preparation of polyaniline cathode doped with different acids：Take 32μl aniline solution and add it dropwise onto 1*2cm^2 carbon cloth, followed by the addition of 8μl ammonium persulfate solution dropwise. Evenly apply this mixture onto a 1*1cm^2 area and put it into 2℃~8℃ environment to polymerize for 12h. The PANI-P electrodes with different ratios, as well as PANI-S and PANI-C electrodes, were prepared using the aforementioned method.

Formulation of different electrolytes： Preparation of 1M zinc sulfate: Take 28.76g of zinc sulfate heptahydrate ($ZnSO_4·H_2O$) and fix the volume to 100ml with deionized water, then stir until it dissolves completely. 1M zinc sulfate with zinc phytate (1%): Take 28.76g of zinc sulfate heptahydrate ($ZnSO_4·H_2O$) and fix the volume to 100ml with deionized water, then stir until it dissolves completely, add 1.04g of zinc phytate ($C_6H_6O_{24}P_6Zn_6$) powder to the solution and stir while adding a small amount of phytate to the solution to dissolve.

Materials Characterization: SEM was carried out by Apero S HiVac. In situ Raman was carried out by DXR2. In situ FTIR was carried out by FTIR 920. UV was carried out by Cary 60. In situ XPS was carried out by ESCALAB-250.

Electrochemical measurements: CV was tested by using in-situ polymerized polyaniline electrode as the positive electrode and zinc foil as the negative electrode with two different electrolytes, and the test machine was VMP3. The OER and HER was measured by using T&H electrochemical workstation.

Calculation:

The electrophilic and nucleophilic sites for the polymer and its monomer were studied via density functional theory (DFT), where they have been optimized by the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) hybrid functional method and def2-SVP basis set with Grimme's DFT-D3(BJ) empirical dispersion correction by Gaussian 09 package. Harmonic vibrational frequency was performed at the same level to guarantee that there is no imaginary frequency in these molecules, i.e. they locate on the minima of the potential energy surface. The molecular electrostatic potential (MEP) was calculated to predict the reactive site whose input files were extracted from formatted checkpoint files gained from Gaussian and plotted by Gauss View.

Supplementary Figures S1-S15

S1

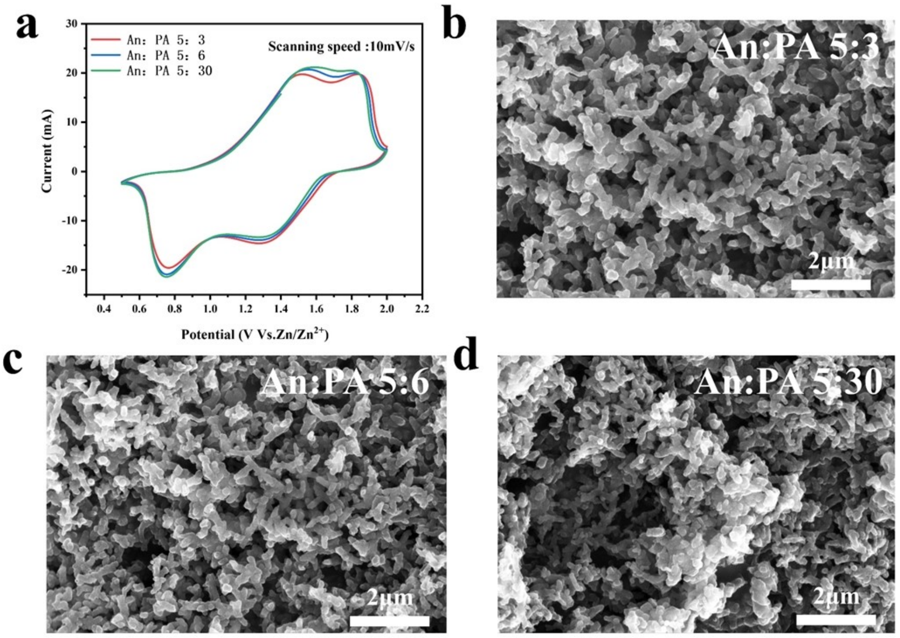

Figure S1. (a) CV curves and (b-d) SEM images of polyaniline with different phytic acid (PA) doping ratio.

S2

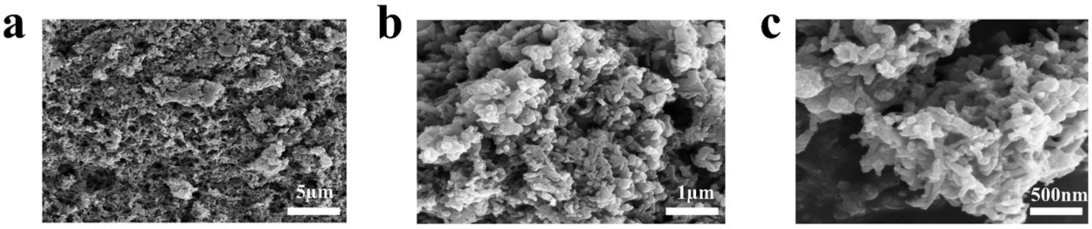

Figure S2. SEM images of hydrochloric acid doped polyaniline (PANI-C).

We compared the morphology of polyaniline doped with three kinds of acids (phytic acid, sulfuric acid, hydrochloric acid) and found that when small molecular acids were doped, polyaniline was more inclined to irregular stacking growth, while when large molecular acids were doped, the large molecular structure of phytic acid molecules would facilitate the dispersion of aniline, and the structure would be more conducive to molecular transport during polymerization.

S3

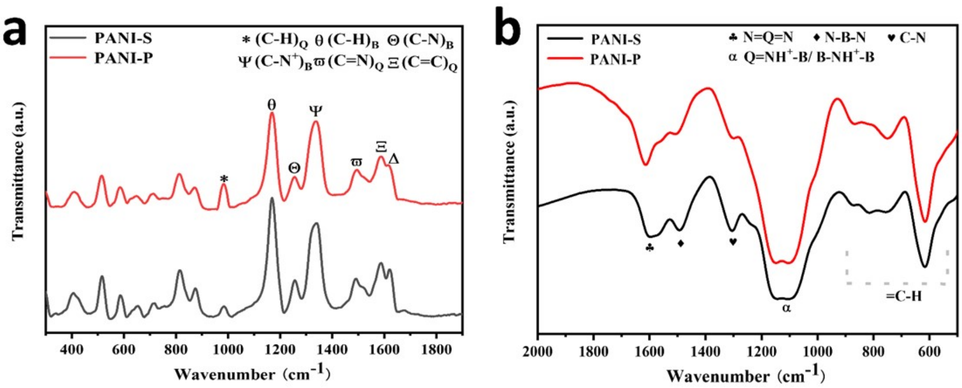

Figure S3. Raman and FTIR spectra of different acids doped with polyaniline.

S4

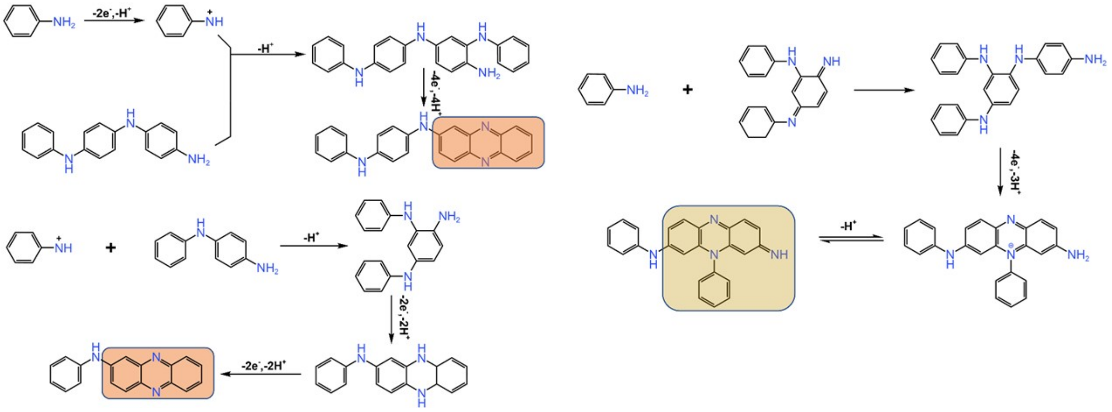

Figure S4. Other fragments appearing during in-situ polymerization of polyaniline.

Different PH values and different temperatures will affect the regularity of aniline polymerization, and inevitably produce other organic fragments, which will have electrochemical activity, such as phenazine and saffranine.

S5

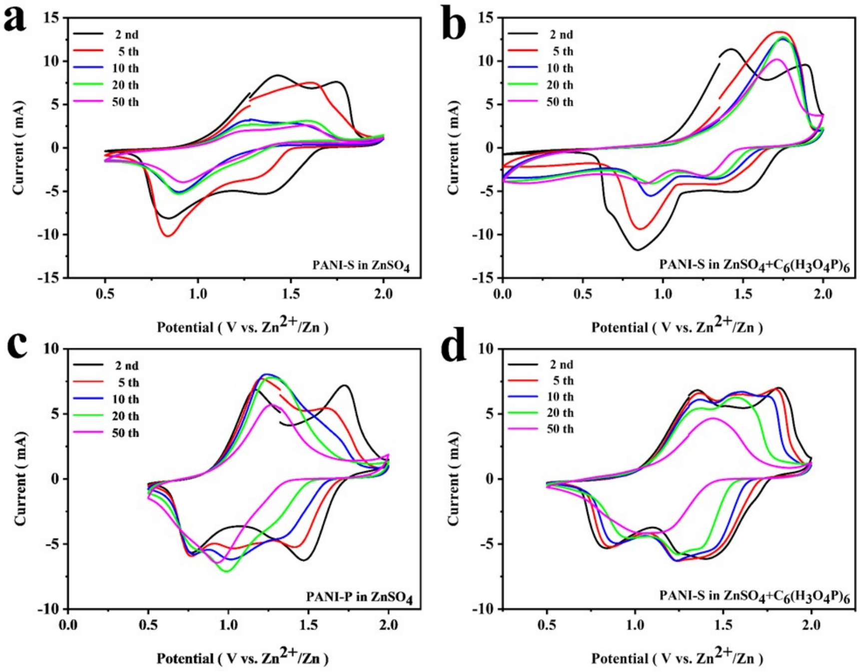

Figure S5. CV curves of polyaniline doped with different acids in different electrolytes: (a) PANI-S in zinc sulfate electrolyte; (b) PANI-S added zinc sulfate electrolyte to zinc phytate (1%); (c) PANI-P in zinc sulfate electrolyte; (d) PANI-P added zinc sulfate electrolyte to zinc phytate (1%).

S6

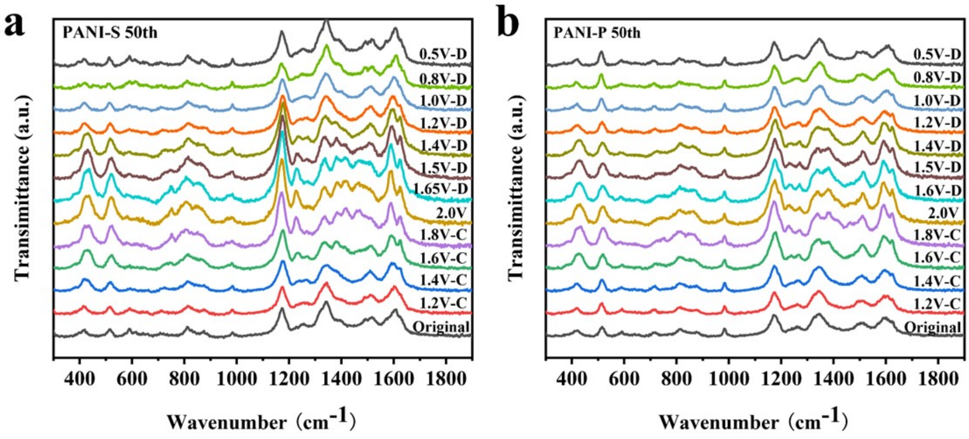

Figure S6. In-situ Raman spectra of PANI-P and PANI-S electrodes in a polyaniline battery at the 50th cycle.

S7

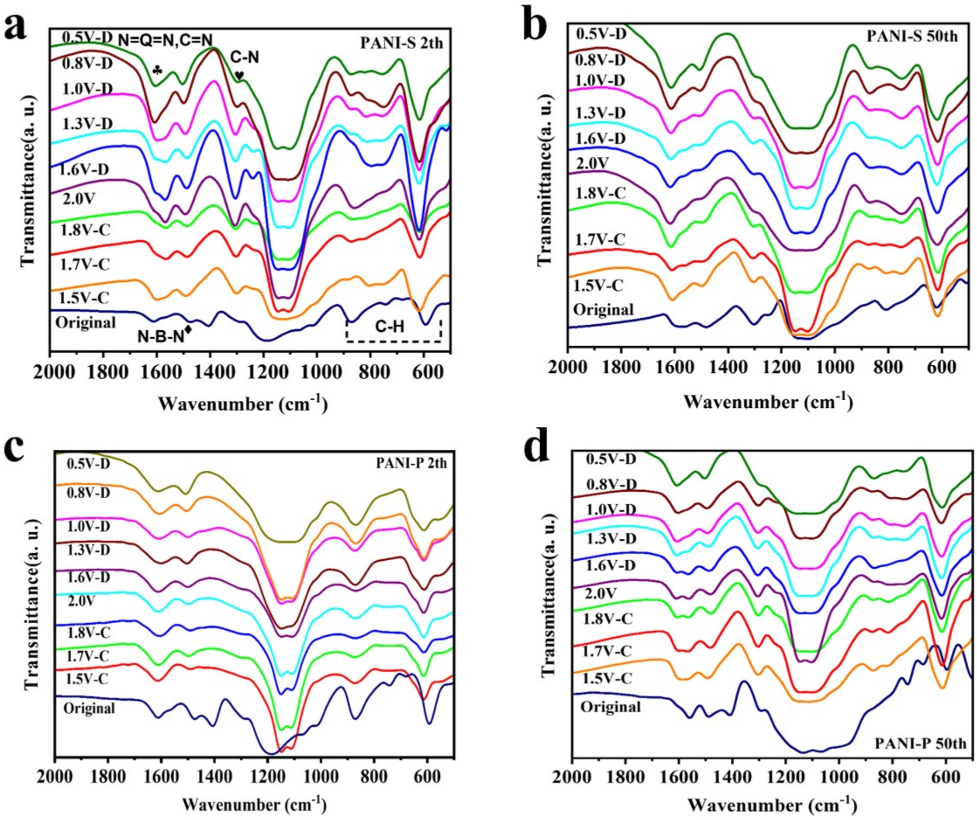

Figure S7. In situ infrared spectra of PANI-P and PANI-S electrodes at different voltages at the second and 50th cycles in a polyaniline cell: (a,b) PANI-S; (c,d) PANI-P.

S8

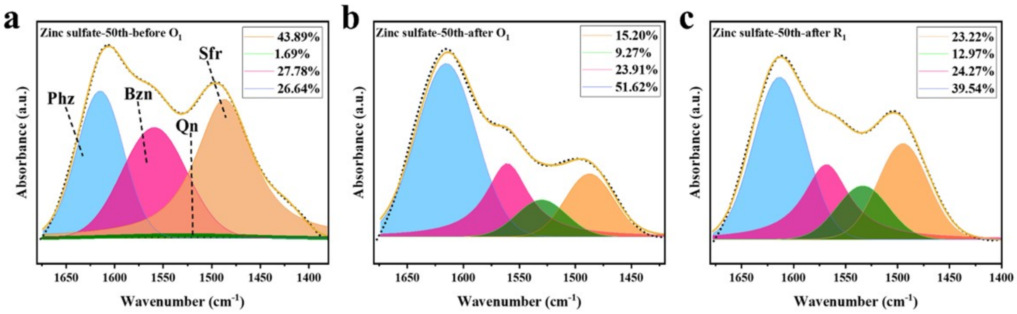

Figure S8. XPS spectra show content changes of phenazine, saffranine, quinone ring and benzene ring fragments at the first oxidation peak and the first reduction peak at the 50th cycle through infrared peak segmentation: (a) before O1; (b) after O1; (c) after R1.

S9

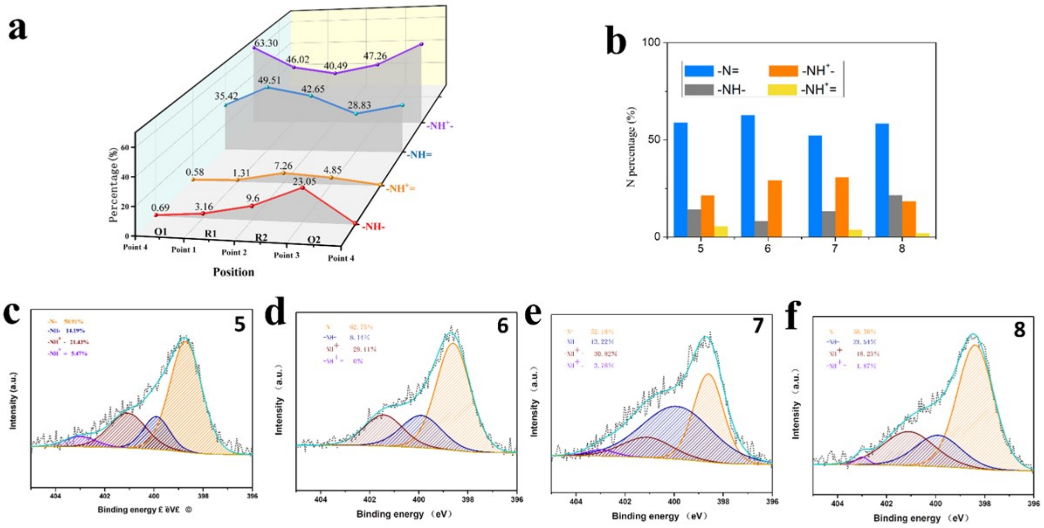

Figure S9. (a) The change of the bonding content of N atoms at the second turn of the in-situ Raman cycle of the polyaniline electrode; (b) The change of N atom bonding content at the 50th turn of in-situ Raman cycle of polyaniline electrode; (c-f) The change of N atom bonding content at each point under different voltages at the 50th turn of in-situ Raman cycle of polyaniline electrode.

S10

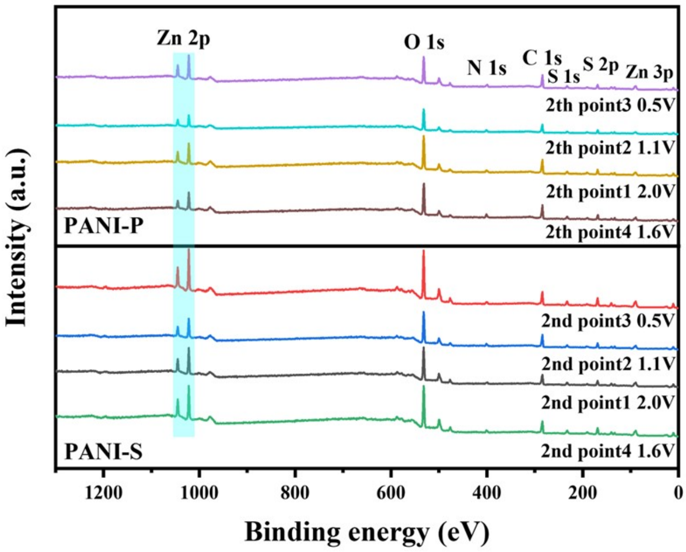

Figure S10. Full spectrum information of XPS in situ at PANI-P and PANI-S electrodes in a polyaniline cell.

S11

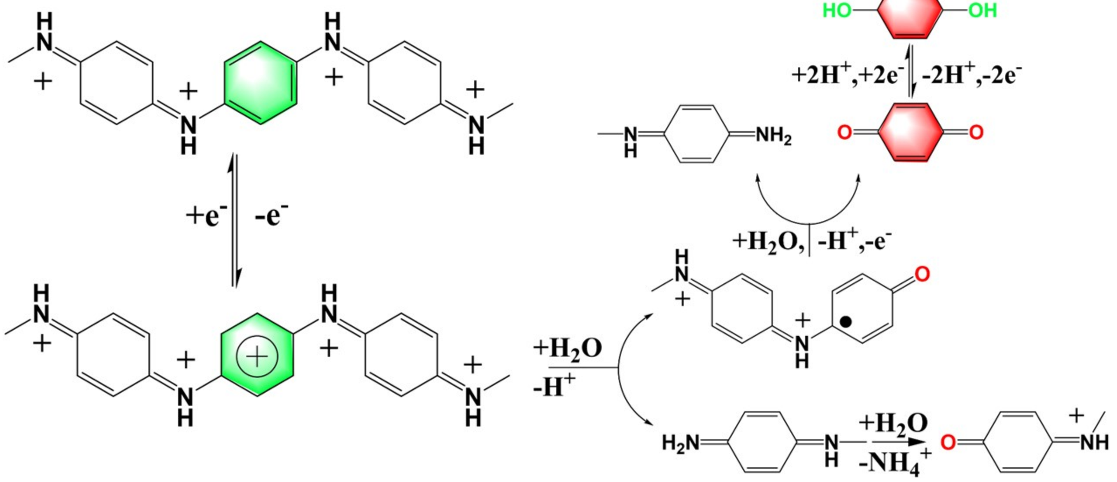

Figure S11. Schematic diagram of PANI degradation in an aqueous environment.

S12

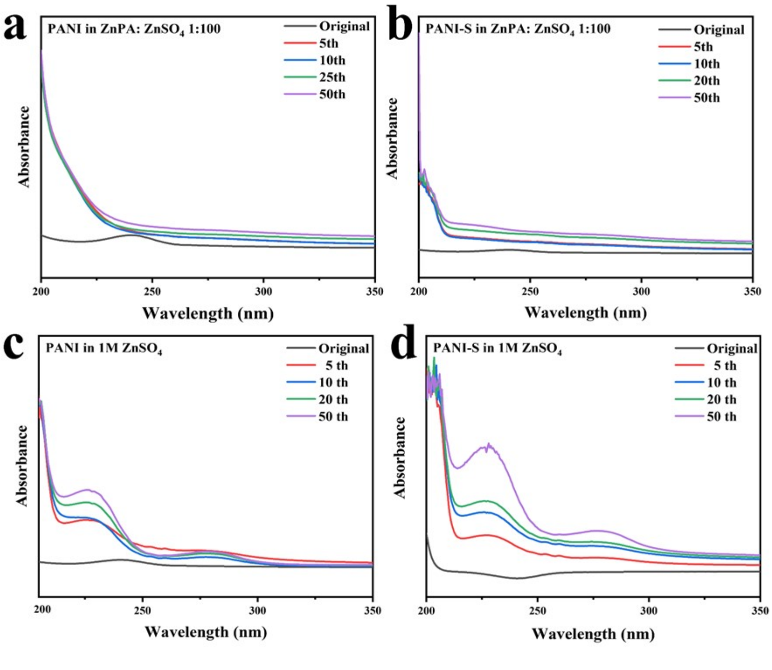

Figure S12. UV spectra of PANI (a, c) and PANI-S (b, d) in zinc phytate (ZnPA): $ZnSO_4$ = 1:100 (a, b) and 1M $ZnSO_4$ (c, d) with a variation of C=O bond content in the 0th and 50th cycles.

S13

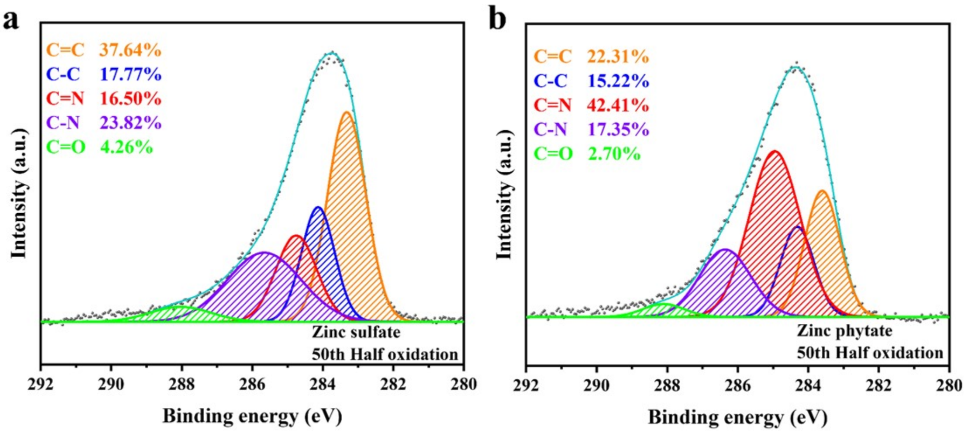

Figure S13. The content changes of various functional groups of PANI-S (a) and PANI-P (b) at the first oxidation peak and the first reduction peak during the cycle to the 50th circle obtained by the O1s sub-peak of XPS.

The content change of C=O bond can be clearly observed through in situ XPS peaking treatment of C1s at various high voltage states, to predict the number of p-benzoquinone produced by PANI-P and PANI-S at high voltage, and judge the degradation degree of polyaniline.

S14

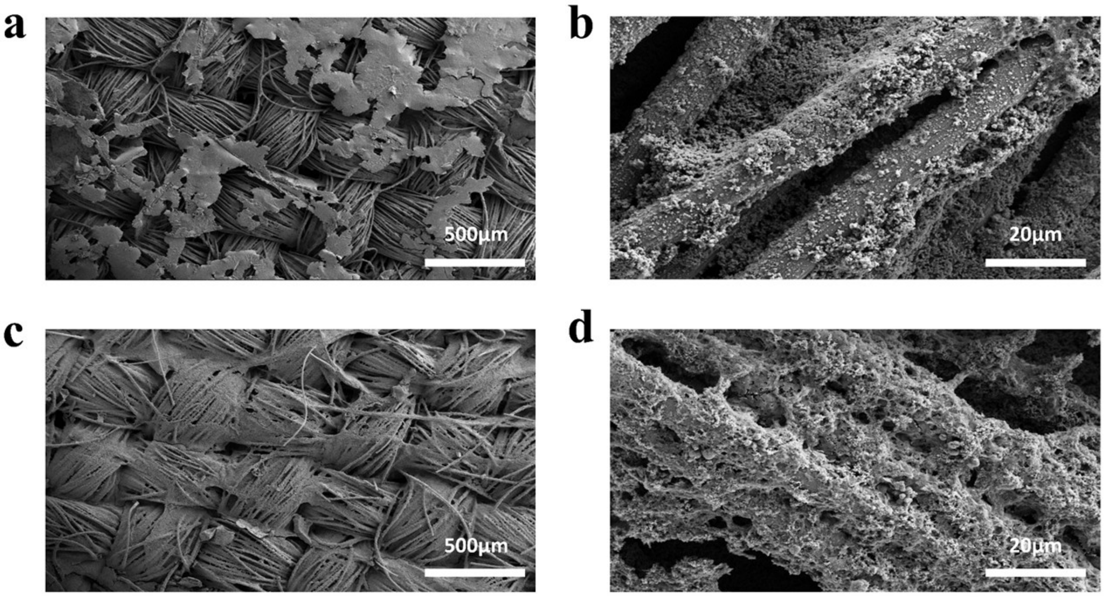

Figure S14. SEM of PANI-S electrode surface after 200 cycles in zinc sulfate electrolyte (a,b) and PANI-P electrode surface after 200 cycles in zinc sulfate electrolyte with zinc phytate (1%)(c,d).

S15

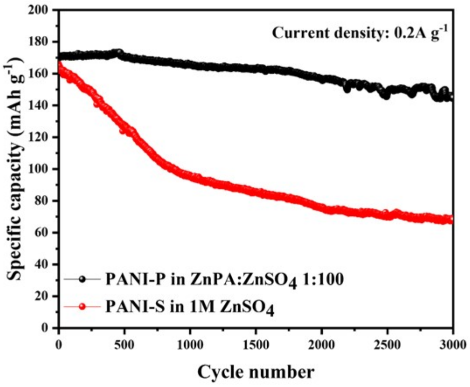

Figure S15. Long-term cycling tests of PANI-S and PANI-P at a low current density (0.2 A g^{-1}) in electrolytes with and without additives.

Supplementary Table S1

Table S1:

Electrolyte type	**Before testing PH**	**After testing PH**
Zine sulfate	**5.60**	**3.36**
Zinc sulfate + Zinc phytate(1%)	**3.56**	**3.83**