

Supporting Information

Protonating Imine Sites of Polyaniline for Aqueous Zinc Batteries

Han Yan^{‡a}, Xinjian Mu^{‡a}, Yu Song^{*a}, Zengming Qin^{*a}, Di Guo^a, Xiaoqi Sun^a and Xiao-Xia Liu^{*a}

^a Department of Chemistry, Northeastern University, Shenyang, 110819, China.

[‡] These authors contributed equally.

Corresponding authors:

Yu Song: songyu@mail.neu.edu.cn

Zengming Qin: qinzengming95@foxmail.com

Xiao-Xia Liu: xxliu@mail.neu.edu.cn

Experimental Section

Materials: All the chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received, except aniline which was used after reduced pressure distillation. Graphite foil was purchased from SGL Carbon GmbH, Germany.

Electrochemical exfoliation of graphite foil (EG): The graphite substrate was fabricated using a modified electrochemical exfoliation method reported before.¹ Briefly, the electrochemical exfoliation was conducted in a three-electrode cell using a piece of graphite foil as the working electrode [working area: 0.8 cm (L) × 0.8 cm (W) × 0.25 mm (H)], saturated calomel electrode (SCE) and a piece of platinum flake as the reference and counter electrodes, respectively. The graphite foil was firstly exfoliated in 1 M KOH aqueous electrolyte using a cyclic voltammetry (CV) method scanning from 0.5 to 1.7 V at the scan rate of 20 mV s⁻¹ for 6 cycles. The fabricated electrode was further exfoliated in 1.0 M KNO₃ electrolyte by using an advanced cyclic voltammetry method, scanning from -1.2 to 1.8 V vs. SCE (holding the potential of -1.2 V and 1.8 V for 10 s, respectively) at the scan rate of 20 mV s⁻¹ for 10 cycles. The obtained electrode was washed by deionized water (denoted as EG).

Electrochemical deposition of Polyaniline (PANI): Electrochemical deposition of PANI on EG was carried out by a CV method in a three-electrode cell, scanning from -0.3 to 0.8 V vs. SCE at the scan rate of 50 mV s⁻¹ for 20 cycles. EG was used as the working electrode, a piece of Pt plate and SCE were used as the counter and reference electrodes, respectively. The plating electrolyte contains 0.1 M aniline and 1 M H₂SO₄ (15 mL). The mass loading of the materials on the electrode was measured through the weight difference of the electrode before and after electrochemical deposition using a semi-micro balance (BT 25S, Sartorius, Germany)

with a sensitivity of 0.01 mg. The mass loading of the electrodes was controlled at about ~ 2.23 mg cm⁻².

Activation of PANI (A-PANI): The activation of PANI was conducted by immersing the PANI electrode into the 9 M ZnCl₂ aqueous solution for 12 h. The obtained electrode (denoted as A-PANI) was washed by deionized water.

Materials characterization: The morphologies the samples were studied by scanning electron microscope (SEM, SU 8010, HITACHI, Japan). X-ray photoelectron spectroscopy (XPS) was conducted by an XPS spectrometer (ESCALAB 250Xi, Thermo Scientific, USA) with Al K α radiation as the excitation source ($\lambda=8.34$ Å). The XPS data were calibrated using the C1s peak at 284.8 eV as the reference. Fourier transform infrared spectroscopy was conducted by a Fourier transform infrared spectrometer (FT-IR, Bruker, VERTEX70, Germany). Raman spectra were collected by a confocal laser micro-Raman spectrometer (XPLORA, HORIBA Scientific, France) with an excitation wavelength of 532 nm.

Electrochemical measurements: The electrochemical performance of PANI and A-PANI electrodes were investigated in Swagelok type cells with titanium rods as the current collectors, Zn plate as the anode, using 9 M ZnCl₂ as aqueous electrolyte (100 μ L). The electrochemical impedance spectroscopy (EIS) of PANI and A-PANI electrodes were studied in a three-electrode system (Zn plate and SCE as counter and reference electrodes, respectively) at the open-circuit potential in a frequency range from 0.01 Hz to 100 kHz with a perturbation of 10 mV on a CHI 660E electrochemical workstation (CH Instruments Inc.).

Calculation of energy density and power density: The energy density (E , Wh kg⁻¹) and power density (P , kW kg⁻¹) of the cell were calculated by Eq. S1 and S2:

$$E = \frac{\int_0^t I \times \Delta U(t) dt}{3.6 \times m} \quad (\text{Eq. S1})$$

$$P = \frac{3.6 \times E}{t} \quad (\text{Eq. S2})$$

where I is the discharge current (mA), ΔU is the discharge voltage (V), t is the discharge time (s), dt is the time differential and m is the active mass of the electrode (mg).

Supplementary Figures

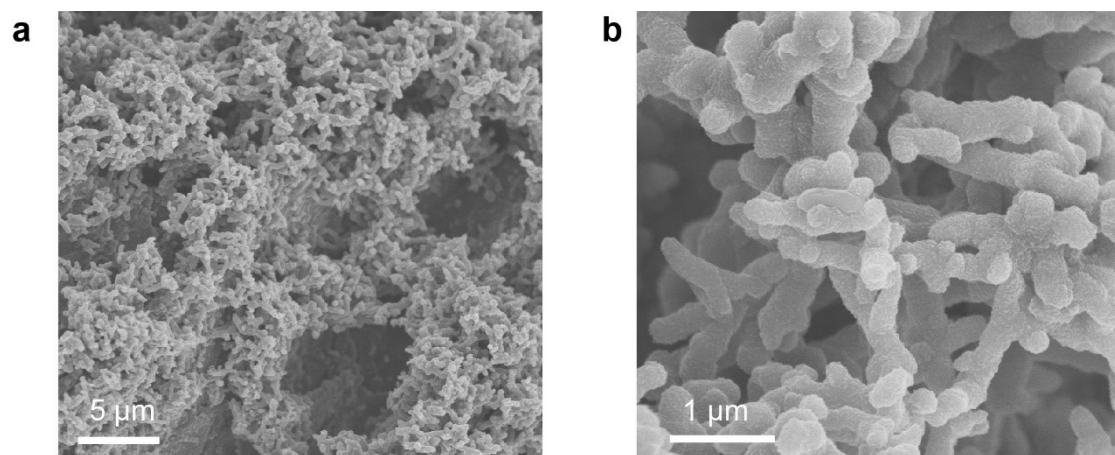


Fig. S1. SEM images of the as-prepared PANI electrode.

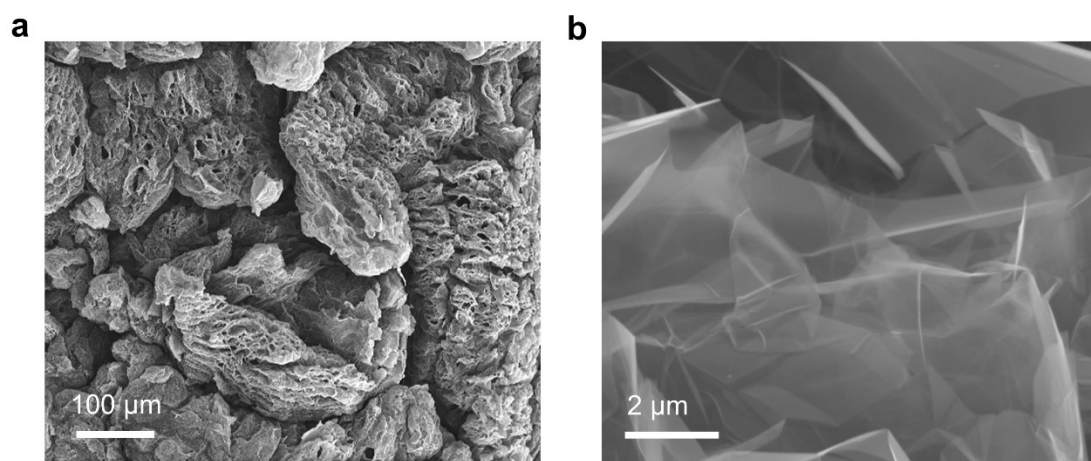


Fig. S2. SEM image for the 3D exfoliated graphite foil substrate.

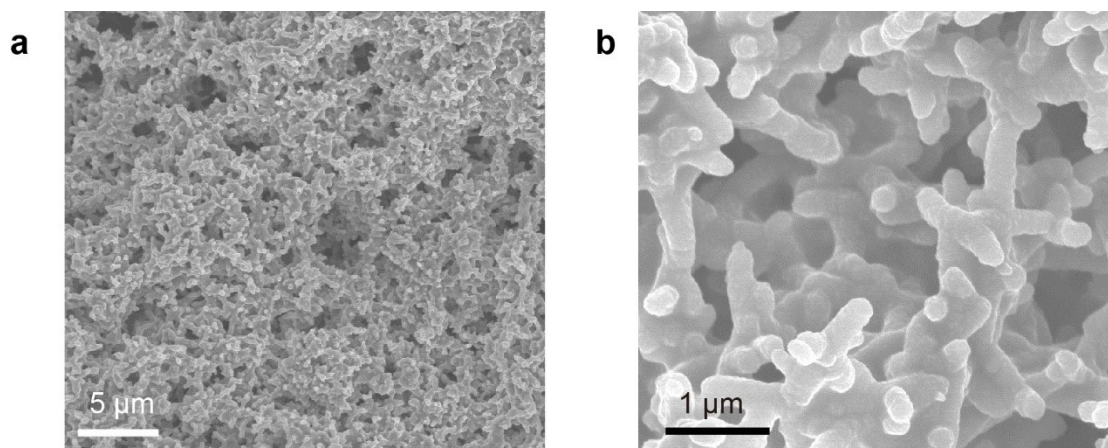


Fig. S3. SEM images for A-PANI.

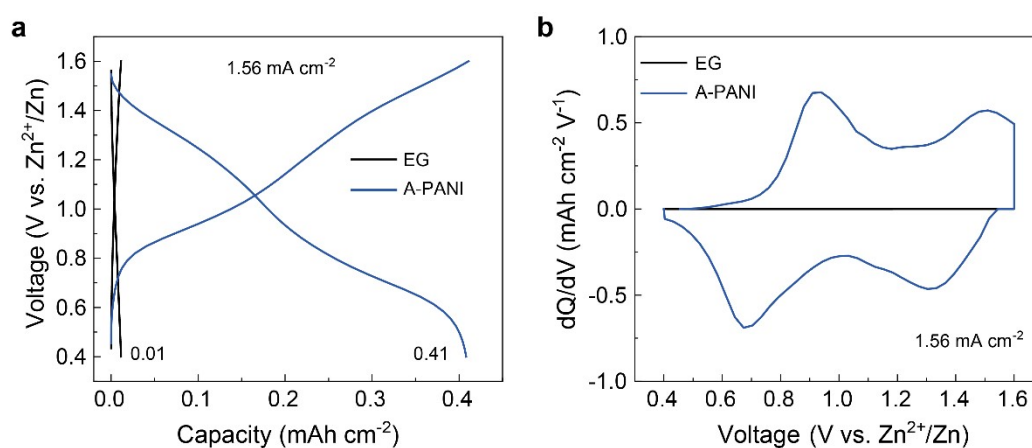


Fig. S4. (a) GCD curves and (b) the corresponding differential capacity curves of EG and A-PANI electrodes obtained at 1.56 mA cm^{-2} .

To evaluate the capacity contribution of EG substrate, we conducted galvanostatic charge-discharge (GCD) tests for the bare EG electrode. As shown in Fig. S4, the EG electrode only displayed an areal capacity of 0.01 mAh cm^{-2} at the current density of 1.56 mA cm^{-2} , while the A-PANI electrode exhibited a capacity of 0.41 mAh cm^{-2} . The active material on the EG substrate still exhibited a high capacity of 179 mAh g^{-1} after subtracting the capacity contribution from EG. The EG substrate only delivers 2.4 % of the overall capacity of the A-

PANI electrode. The actual capacity contribution of EG is much lower considering that the surface of EG is covered by A-PANI material. Therefore, the A-PANI material contributes to the major electrochemical capacity of the electrode.

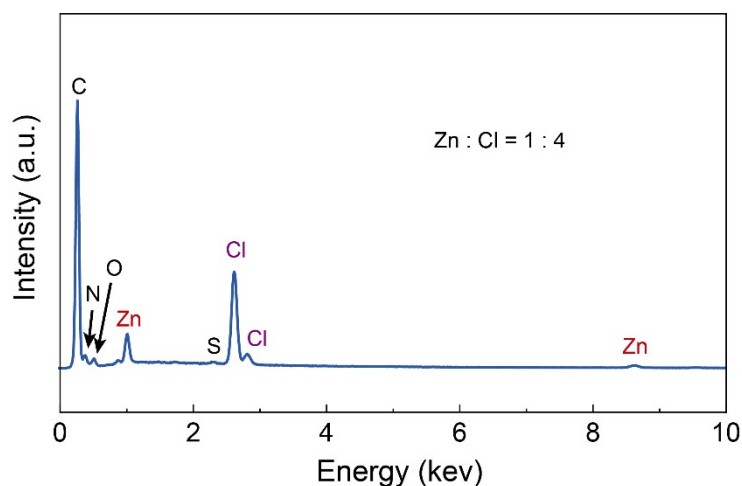


Fig. S5. The EDS results of the A-PANI electrode.

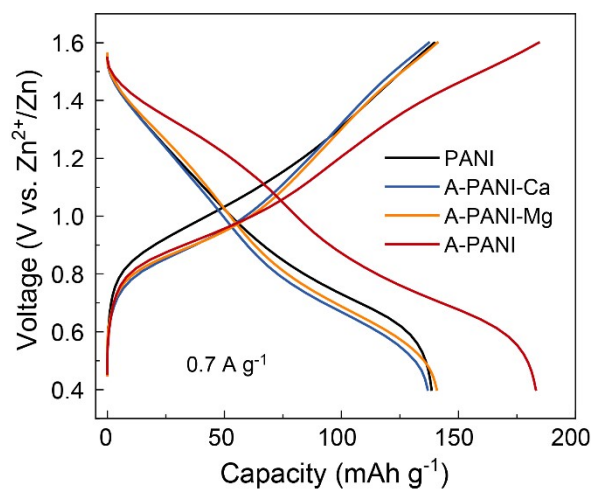


Fig. S6. The GCD curves of the different PANI electrodes.

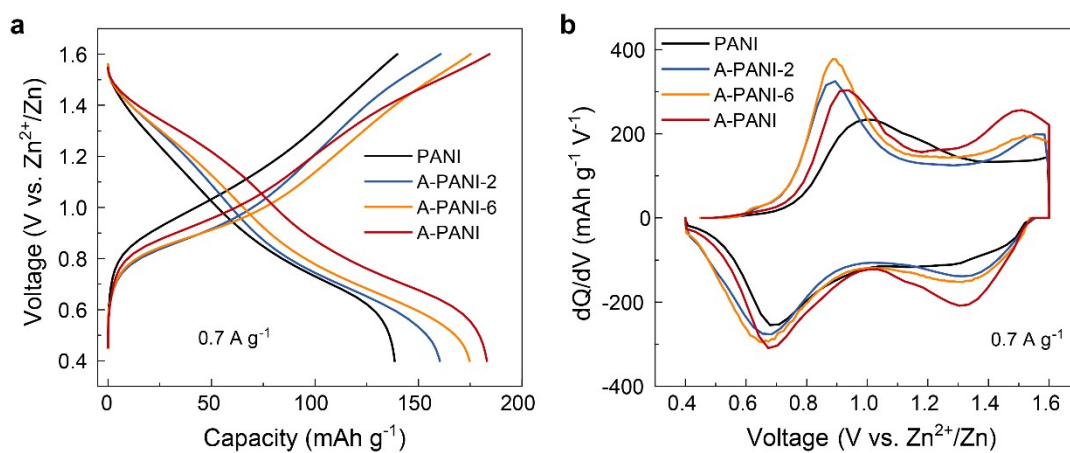


Fig. S7. (a) GCD curves and (b) the corresponding dQ/dV profiles of the PANI electrodes activated in the ZnCl_2 electrolytes with different concentrations.

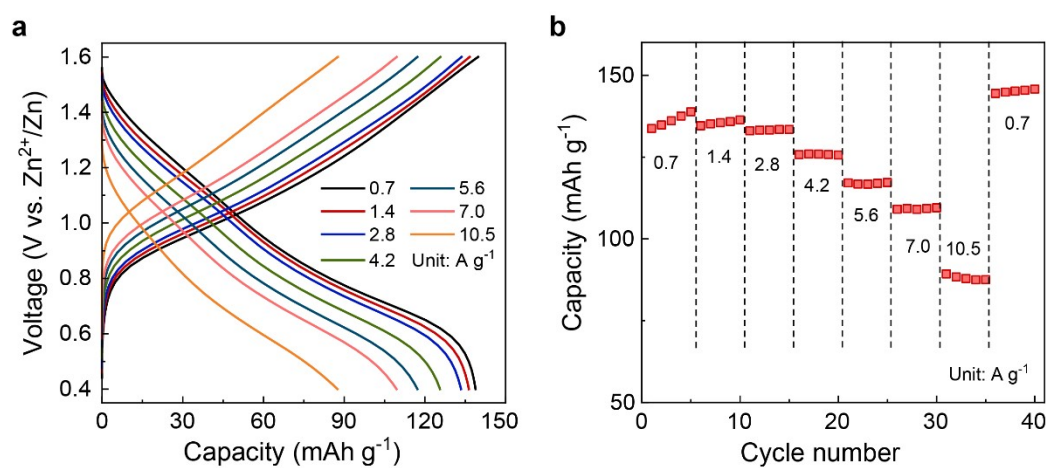


Fig. S8. Charge/discharge curves and rate capability of the PANI electrode.

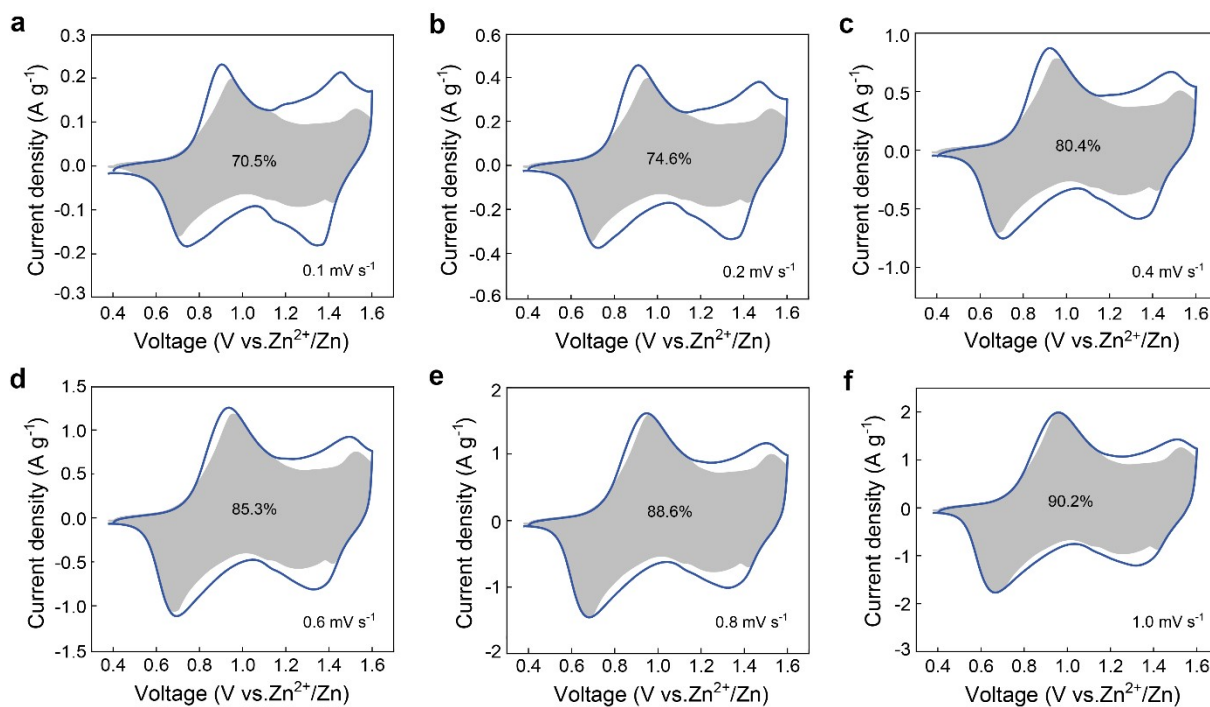


Fig. S9. CV profiles with the capacity contribution of A-PANI at different scan rates.

The capacitive contribution was calculated using the equation:²

$$i(V) = k_1v + k_2v^{1/2}$$

where the total current $i(V)$ is a combination of the capacitive current contribution (k_1v) and the diffusion-controlled current contribution ($k_2v^{1/2}$).

Table S1. The peak assignment of the Raman spectra³⁻⁴ in Fig. 1f

Raman shift (cm ⁻¹)	Assignment
285.8	Zn(H ₂ O) ₂ Cl ₄ ²⁻
418/526/583	Ring deformation
1166	C-H in-plane deformation vibration
1218	C-N stretching vibration in emeraldine
1336	C-N ⁺ stretching vibration of the protonated structure in PANI
1467	C=N stretching vibration of quinone ring
1587	C=C stretching vibration
1630	C-C stretching vibration

Notes and references

- 1 H. Lv, Q. Pan, Y. Song, X.-X. Liu and T. Liu, *Nano-micro Lett.*, 2020, **12**, 118.
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3. Q. Zhang, Y. Ma, Y. Lu, L. Li, F. Wan, K. Zhang and J. Chen, *Nat Commun.*, 2020, **11**, 4463.
4. R. Mažeikienė, G. Niaura and A. Malinauskas, *J. Solid State Electr.*, 2019, **23**, 1631-1640.