

High-rate Aqueous Zinc-ion Batteries Enabled by A Polymer/graphene Composite Cathode Involving Reversible Electrolyte Anion Doping/dedoping

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Experimental section

1.1. The synthesis of POLA

3 mmol (324 mg) of p-benzoquinone (Sigma Aldrich, 98%) was dissolved in 25 ml of ethanol (EtOH, Scharlau, 96%). 1 mmol (108 mg) of p-phenylenediamine (Sigma Aldrich, 98%) previously dissolved in 25 ml of EtOH, was added to the solution dropwise for 15 min. After the addition, the reaction mixture was stirred at room temperature for another 48h. On completion of the reaction, the product was removed from the reaction solution by centrifugation at 10000 rpm for 15 minutes. The black solid (214 mg) was obtained after dried at 60 °C under vacuum.¹

1.2. The synthesis of POLA/G

First of all, the graphene oxide (GO) was prepared by the modified Hummers

method, then a certain amount (60 mg) of POLA was dispersed in 60 mL of GO aqueous solution (2 mg mL⁻¹) under continuous sonication for 30 min. The obtained mixture was then sealed in a 100 mL Teflon-lined autoclave and heated at 180 °C for 24 h. After cooling down to R.T. naturally, the obtained hydrogel was taken out and gently washed with deionized water for three times then crushed subsequently. Finally, the obtained composites were dried at 60 °C for 24 h, and were called POLA/G.^{2,3} The graphene hydrogel was prepared through the same experimental process but without the addition of POLA.

1.3. Characterization

The crystal structures of prepared composites were determined by using an X-ray powder diffractometer (Bruker D8 ADVANCE, Cu K α -radiation λ = 0.15405 nm, 40 kV, 40 mA). The morphologies of the cathode samples were recorded by scanning electron microscopy (SEM, Tescan MAIA3 XMH, 15 kV) and transmission electron microscopy (JEOL JEM-2100 LaB6 TEM). The cathode composites were analyzed in different states by an X-ray photoelectron spectrometer (XPS, PHI 5000 with Mg/Al radiation as the excitation source, calibrate with a carbon peak at 284.8 eV as a reference, and all samples were Ar etched before characterization). The functional groups of the cathode composites were collected with a Fourier transform infrared spectrometer (FTIR, Nicolet IS 10, USA, in a range of 400 to 4000 cm⁻¹). Thermal gravimetric analysis (TGA) was used to test the thermal stability of cathode samples (TGA, NETZSCH STA 449 F3 from 40 to 900 °C) under a pure N₂ atmosphere. The Raman spectra were characterized by a WITec CRM200 with a 532 nm wavelength

laser.

1.4. *Electrochemical measurements*

Coin-type cells (CR2032) which were used to perform the electrochemical measurements were assembled in air. The working electrode was prepared by mixing POLA/G composites, Super P carbon, and Poly tetra fluoroethylene (PTFE) in a mass ratio of 7:2:1 with *N*-methyl-2-pyrrolidone (NMP), and the obtained slurry was coated onto a titanium foil and then dried at 80 °C in a vacuum oven over night. Finally, the weight of the active materials was loaded at about 1.5 mg cm⁻². The cells were mainly made by sandwiching a glass fiber separator between the metallic zinc plate anode and the POLA/G electrode plate cathode which was filled with 3 M Zn(CF₃SO₃)₂ solution as the electrolyte. Galvanostatic test were conducted in the potential range of 0.1-1.6 V (vs. Zn²⁺/Zn) using a multichannel battery testing system (Land CT 2001A). Electrochemical impedance spectra (EIS) were determined using a Metrohm Autolab PGSTAT302N electrochemical workstation. CV curves at different scan rates (0.1-1.6 V vs. Zn²⁺/Zn) were obtained on a CHI660e electrochemical workstation.

1.5. *Specific energy and pow density calculation*

The detailed calculations about the specific energy density and power density of the aqueous Zn//POLA/G cell are as follows:

The specific energy density is calculated in accordance with Equation 1.

$$Espe = C \times V/m \quad (\text{Eq. 1})$$

where Espe is the specific energy density (Wh kg⁻¹); C is the discharge capacity (Ah);

V is the average discharge voltage (V), and m is the total mass (Kg) of POLA/G

cathode.

The specific power density is calculated using Equation 2.

$$P_{spe} = i \times V / m \quad (\text{Eq. 2})$$

where P_{spe} is the specific power density (W kg^{-1}); i is the applied current (A); V is the average discharge voltage (V); and m is the total mass (Kg) of the POLA/G cathode.

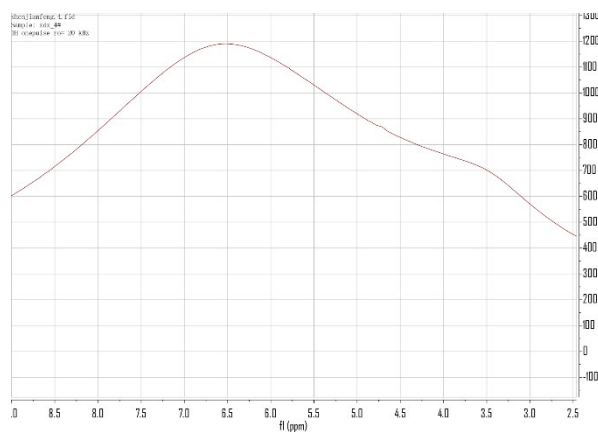


Figure S1. ^1H SSNMR of POLA.

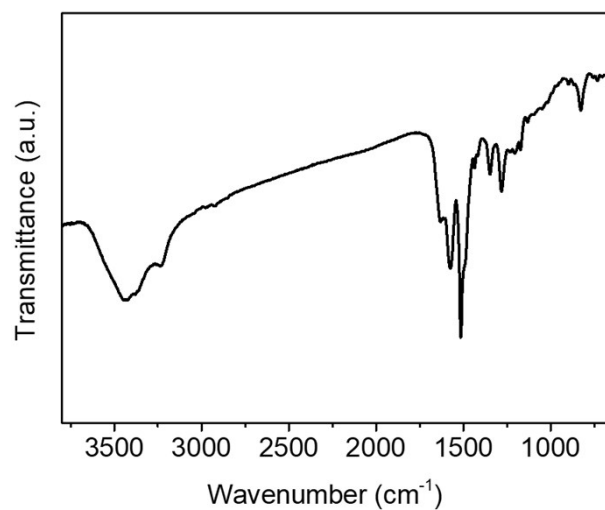


Figure S2. FTIR of POLA.

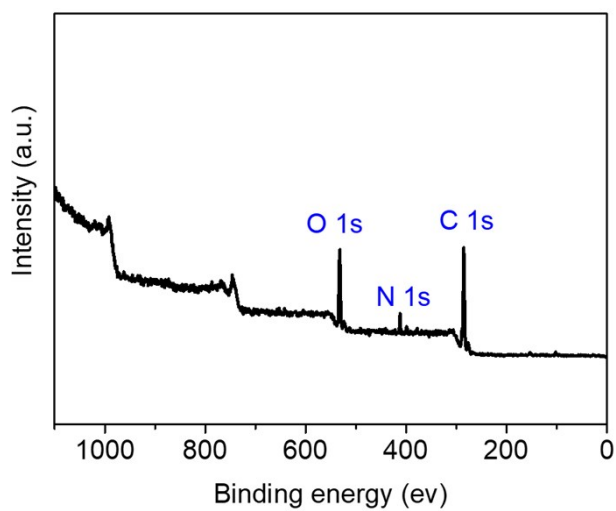


Figure S3. XPS of POLA.

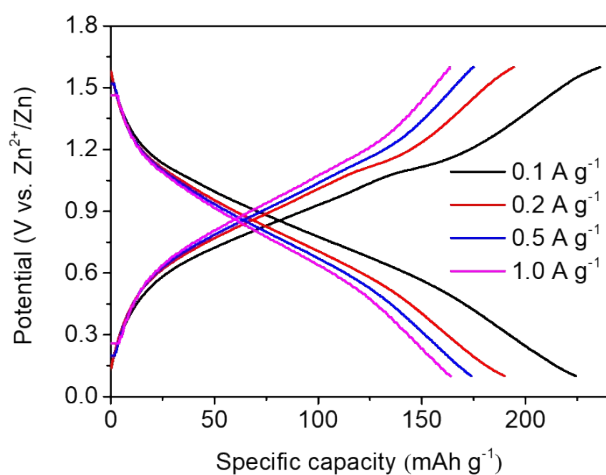


Figure S4 Galvanostatic discharge/charge voltage profiles at 0.1, 0.2, 0.5 and 1.0 A g⁻¹.

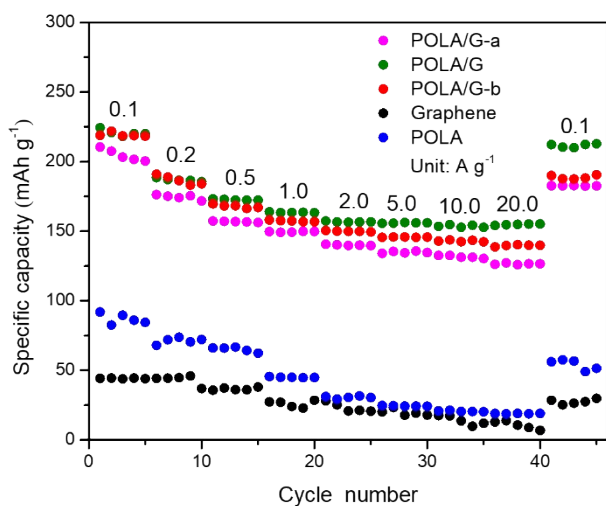


Figure S5. Rate performance of five cathode samples.

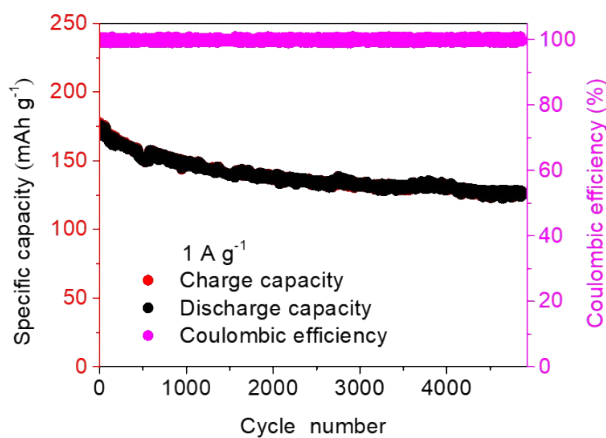


Figure S6. Long term cyclic stability of a POLA/G composite cathode at 1.0 A g⁻¹.

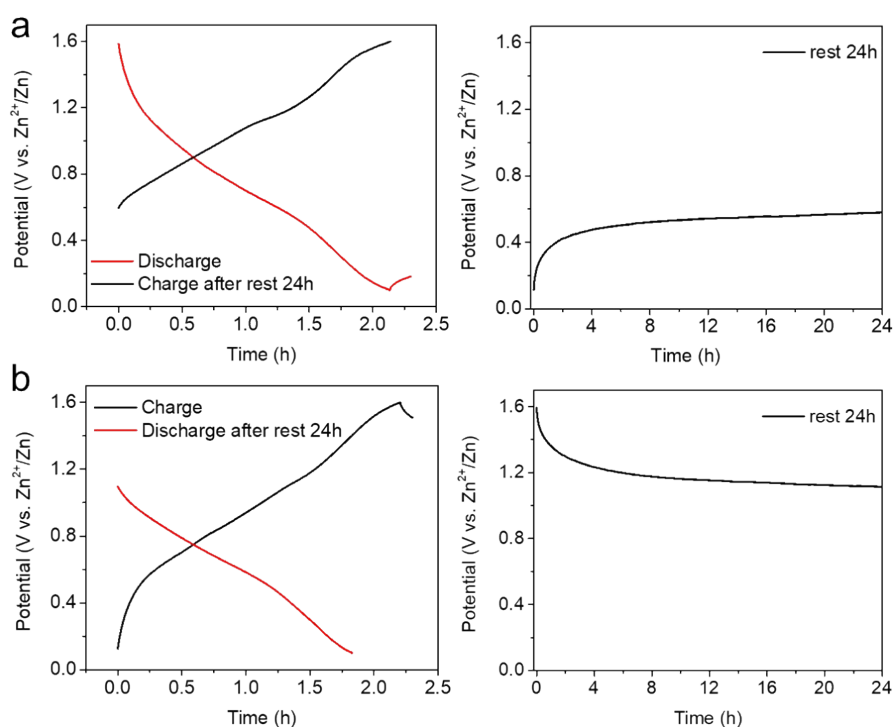


Figure S7. a) When first discharged to 0.1 V, and then charged to 1.6 V after standing for 24 hours, and b) when first charged to 1.6 V, and then discharged to 0.1 V after standing for 24 hours.

We also compared our work with various reported organic cathode materials including polymers/carbon composites (PANI/CFs,⁴ poly(1,5-NAPD)/AC,⁵ PC/G²), polymers (PANMTh,⁶ poly(Ani-co-5-ASA),⁷ PPy⁸), small organic compounds (C4Q,⁹ PTO¹⁰) and COF (HqTp¹¹). This work displays better long cycle life and rate performance than that of most the organic cathodes (Table S1).

Table S1. Comparison of this work and various reported organic cathode materials

Cathode	Specific capacity (mAh g ⁻¹)	Rate capacity: percentage of initial specific capacity	Cyclability: capacity (mAh g ⁻¹)/ cycles	Ref.
PANI/CFs	200.0 (0.05 A g ⁻¹)	47.5% (5.0 A g ⁻¹)	82.0 /3000 /5.0 A g ⁻¹	4
poly(1,5-NAPD)/AC	315.0 (0.19 A g ⁻¹)	46.0% (14.8 A g ⁻¹)	150.0 /10000 /10.0 A g ⁻¹	5
PC/G	281.0 (0.1 A g ⁻¹)	60.8% (5.0 A g ⁻¹)	212.0 /3000 /1.0 A g ⁻¹	2
PANMTh	146.3 (1 mA cm ⁻²)	69.4% (5 mA cm ⁻²)	130.3 /150 / 2 mA cm ⁻²	6
poly(Ani-co-5-ASA)	140.6 (1 mA cm ⁻²)	88.3% (5 mA cm ⁻²)	138.0 /200/ 1 mA cm ⁻²	7
PPy	123.0 (1.9 A g ⁻¹)	29.2% (44.7 A g ⁻¹)	60.0 /200/ 4.4 A g ⁻¹	8
C4Q	273.0 (0.1 A g ⁻¹)	63.3% (1.0 A g ⁻¹)	150.0 /1000/ 0.5 A g ⁻¹	9
PTO	300.0 (0.1 A g ⁻¹)	54.0% (5.0 A g ⁻¹)	145.0 /1000/ 3.0 A g ⁻¹	10
HqTp	276.0 (0.125 A g ⁻¹)	30.8% (3.75 A g ⁻¹)	98.0 /1000/ 3.75 A g ⁻¹	11
POLA/G	224.3 (0.1 A g⁻¹)	70.0% (20.0 A g⁻¹)	145.5 /3000/ 10.0 A g⁻¹	This work

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