

Supporting Information

Tuning the electrochemical performances of anthraquinone organic cathode materials for Li-ion batteries through the sulfonic sodium functional group

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Experiment section

Materials preparation

C₁₄H₈O₂ (AQ), NaC₁₄H₇O₅S (AQS), Na₂C₁₄H₆O₈S₂ (AQDS) were bought from Tokyo Chemical Industry Co., Ltd with a purity over 98.0%. They are milling for half an hour, and keep in oven at 70 °C with vacuum. GO was prepared from expanded graphite powder by a modified Hummers method. Typically, 2 g graphite, 1 g NaNO₃ and 50 ml concentrated sulfuric acid were mixed together and stirred at room temperature for 24 h. The mixture solution was put into ice bath under vigorous stirring, followed by drop addition of 6 g KMnO₄. Subsequently, the solution was transferred to a water bath at 35–40 °C and kept for 30 min. After that, 90 ml distilled water was gradually added for three times; each time the solution was stirred for 15 min. The obtained solution was diluted with 280 ml water and treated with 20 ml H₂O₂ (30%). The color turned from dark brown to bright yellow. The warm solution was filtered, and washed successively with 5% HCl solution and water. A resultant GO gel was attained by centrifugation at 20,000 rpm.

Graphene paper was prepared by frozen drying of GO, and then heated at 800 °C for 4 h under 5% H₂/Ar atmosphere. The obtained graphene paper was cut into circular disks with a diameter of 12 mm. AQDS was dissolved into a mixture of distilled water and ethanol (v: v=2: 1), and kept at 80 °C for 30 min with string (15 mg mL⁻¹). Then, we drop the AQDS solution on the grapheme paper and dried at 90 °C, and repeated for three times.

Materials characterization

Thermal stability of the composites was determined by thermogravimetric analysis (Mettler Toledo) with a heating rate of 5 °C min⁻¹ under N₂ atmosphere. The morphology and microstructure of AQ, AQS, AQDS and their electrodes with different cycles were observed by field-emission scanning electron microscope (SEM, S4800, Hitachi) The UV absorption spectra (Perkin Elmer, Lambda35) of the three materials were taken from wavelength of 300 nm to 700 nm with a scan rate of 120 nm min⁻¹. The chemical transformation of the AQDS during charge and discharge processes was investigated by Fourier transform infrared spectroscopy (FTIR, Bruker VECTOR22). The composite was collected from the electrode at different charge and discharge voltage and using KBr to make pellets. XRD patterns were collected at beamline X14A of the National Synchrotron Light Source (NSLS) at Brookhaven national laboratory by a linear position sensitive silicon detector. The wavelength used was 0.07788 nm.

Electrochemical measurements

The electrochemical properties of the composites were evaluated by coin cells with lithium metal as anode and Celgard 2400 film as separator. The cathode was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 in N-methylpyrrolidone to form homogeneous slurry. The slurry was uniformly spread onto pure aluminium foil with a doctor blade cast, and dried at 120 °C for 12 h in vacuum. The electrode was punched into circular disks with diameter of 12 mm with active-material loading of about 2 mg cm⁻². CR2032 coin cells were assembled in an argon-filled glove box (Master 100 Lab, Braun, Germany). 1 mol L⁻¹ LiPF₆/DMC was used as electrolyte. Cells were galvanostatically charged and discharged between 1.5 and 4 V versus Li⁺/Li on a Land CT2001A battery tester. Electrochemical impedance spectroscopy (EIS) and Cyclic Voltammetry (CV) were performed on the coin cell by electrochemical workstation (Autolab PG302N, Netherlands) with an applied sinusoidal excitation voltage of 5 mV in the frequency range from 100 kHz to 0.01 Hz. Cyclic Voltammetry (CV) was performed on the coin cell with an electrochemical workstation (Autolab PG302N, Netherlands) at a scan rate of 0.05 mV s⁻¹ in the range 1.5 to 4 V (1.5 to 3.6 V) versus Li⁺/Li.

Sample name	Relative molecular mass	Theoretical capacity (mAh g ⁻¹)	Average discharge potential (V vs. Li ⁺ /Li)	Decomposition temperature (°C under N ₂)
AQDS	412.3	130	2.41	525
AQS	310.3	173	2.26	440
AQ	208.2	257	2.07	257

Table. S1 General properties of AQ, AQS and AQDS

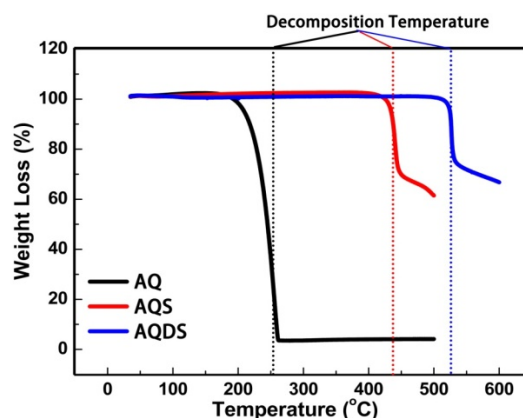


Fig. S1 Thermogravimetric curves of AQ, AQS and AQDS at a heating rate of 5 °C min⁻¹ under N₂ flow.

XRD patterns

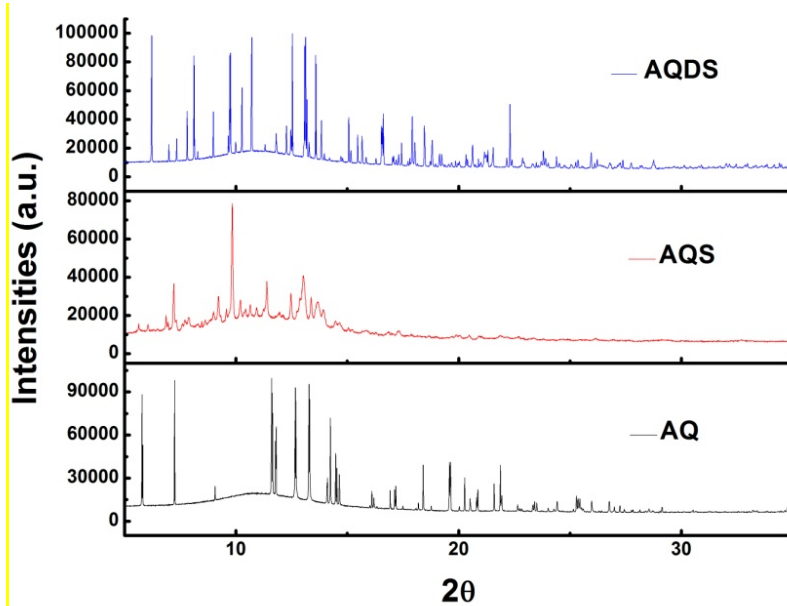


Fig. S2 XRD patterns of AQ, AQS and AQDS

CV curves

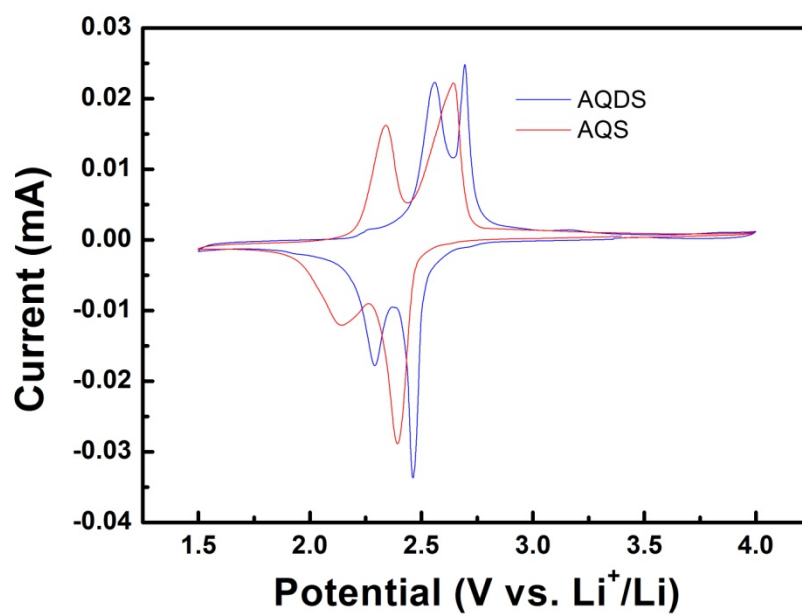


Fig. S3 CV curves of AQ, AQS and AQDS

UV spectrum

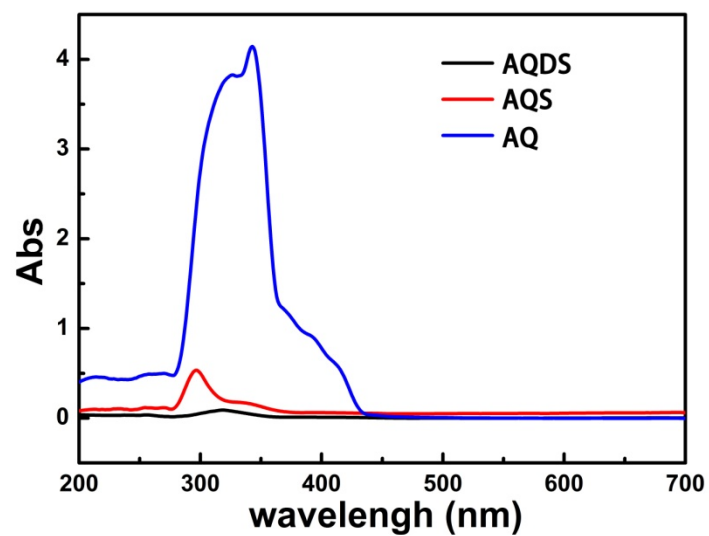


Fig. S4 UV spectra of AQ, AQS and AQDS

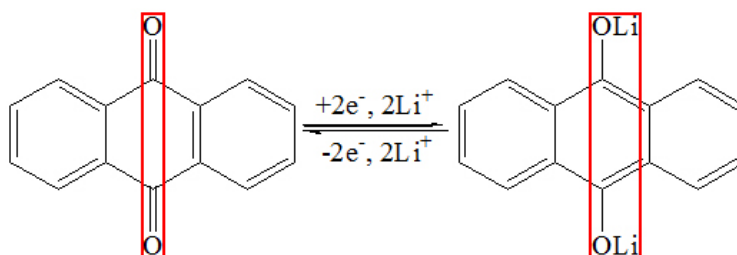


Fig. S5 Reaction equation of anthraquinone.

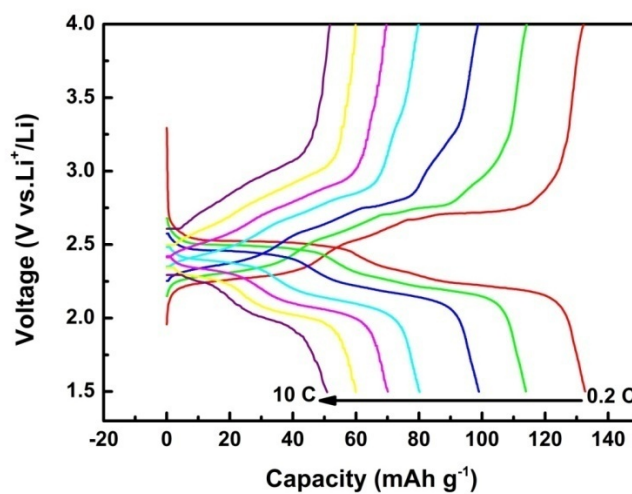


Fig. S6 Discharge and charge curve of AQDS/G paper at different rates.

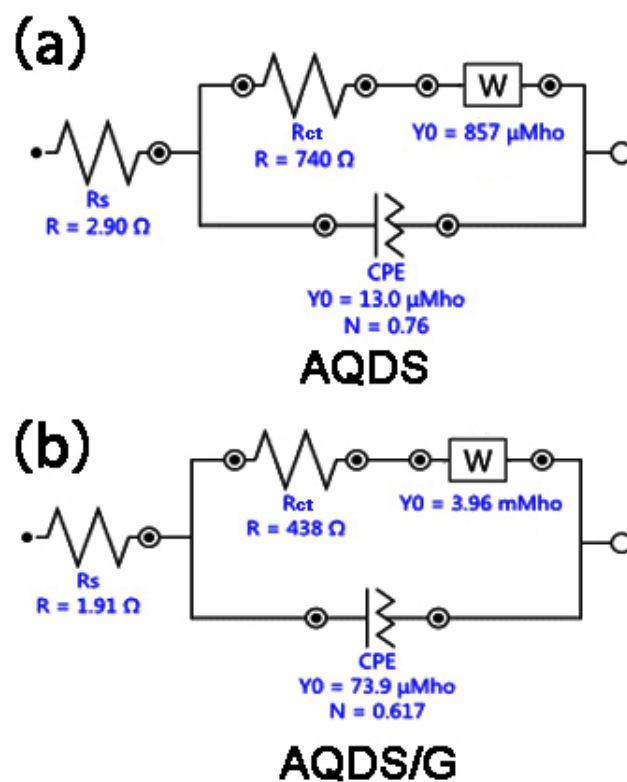


Fig. S7 Equivalent circuit model corresponding to the Nyquist plots of AQDS (a) and AQDS/G paper (b).