Supporting Information

A Bipolar Polymer Cathode for Sodium-ion Batteries

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Experimental Section

Synthesis: A two-neck round bottom flask was fitted with an addition funnel. 236 mg (0.500 mmol) of N,N,N',N'-Tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPDA) was dissolved in 25 mL of THF in the flask. The assembly was purged with nitrogen for 30 minutes before being placed in an ice bath to cool to under 10 °C, and purging continued for another 30 minutes. To the addition funnel was added 307 mg (1.00 mmol) of azobenzene-4,4'-dicarbonyl dichloride (ABDC) dissolved into 10 mL of THF, which was then added dropwise to the flask over 10 minutes under rapid stirring with the temperature maintained under 10 °C. After complete addition, 2 mL of triethylamine was added slowly, and the solution was brought to room temperature and stirred for

an additional 12 hours. The solvent was removed under vacuum, and the solid was dispersed and stirred in 50 mL of ethanol before being filtered and rinsed with an additional 20 mL of ethanol. The solid was then suspended in DME and stirred overnight. The solid was collected by filtration and dried at 80 °C for 4 hours, and then under vacuum at 100 °C overnight. The product, TPDA-ABDC, was a reddish-brown powder with a yield of 88.5%. The synthesis of NTK-TCl followed the same procedure, using terephthaloyl chloride in place of ABDC also in a 2:1 ratio with TPDA. The NTK-TCl product was a yellow powder with a yield of 92.7%.

Material Characterization: XRD pattern was recorded by a Rigaku MiniFlex 600 system using CuKα radiation; Raman measurements were performed on a Horiba XploRA PLUS Raman Microscope; FTIR was recorded by an Agilent Cary 630 FTIR instrument; SEM images were taken by a JEOL JSM-IT500HR. BET porosity was recorded on a Micromeritics ASAP 2020 PLUS.

Electrochemical Measurements: High mass loading electrodes were prepared by mixing the polymer with graphene, Super P, and PTFE in a 6:2:1:1 ratio. The mixture was wetted into a slurry with ethanol to evenly mix and disperse, then dried under vacuum. The composite was rolled flat and cut into small squares with an average mass of 2.5 mg and pressed into 400 count steel mesh current collectors with a diameter of 1.11 cm^2. The electrodes were soaked in electrolyte for 24 hours before being assembled in a half-cell using sodium metal as the counter-electrode and glass fiber separators. Electrochemical performance tests were conducted on an LBT20084 Arbin battery test station. Cyclic voltammograms and impedance tests were conducted on a Gamry Interface 1010 E Potentiostat/Galvanostat/ZRA. Galvanostatic Intermittent Titration Technique (GITT) was conducted by discharging the cell to 1.0 V, then charging to 3.7 V at a current density of 50 mA g^{-1}. During cycling, the cell was discharged/charged for 30 minutes, then rested for three hours, allowing the cell to reach equilibrium potentials.

The theoretical capacity for each polymer was calculated using the formula

$C = [n * F]/M$

where n is the number of electrons transferred, F is Faraday's constant, and M is the mass of the repeating unit (considered as two azobenzene linking units to one N,N,N',N'-Tetrakis(4-aminophenyl)-1,4-phenylenediamine). TPDA-ABDC has a repeating unit mass of 940 g mol^{-1} and transfers 6 electrons per repeating unit, giving a theoretical capacity of 171 mAh g^{-1}. The theoretical capacity for TPDA-TCl is 73 mAh g^{-1} based on a 2-electron transfer and repeating unit mass of 733 g mol^{-1}.

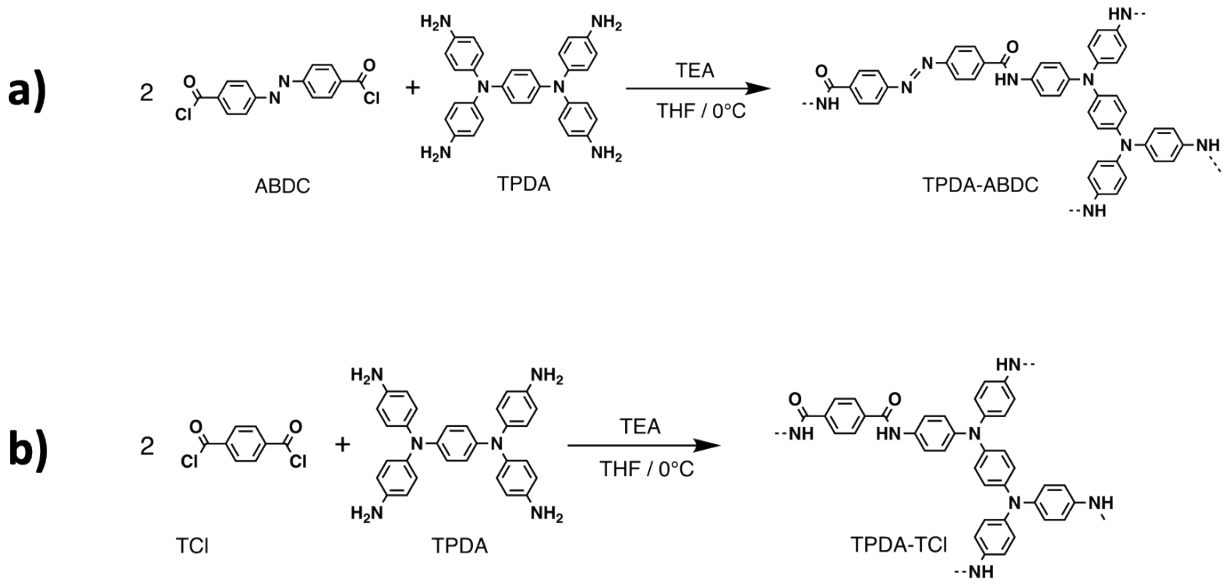


Figure S1: Synthetic Schemes for a) TPDA-ABDC, and b) TPDA-TCl.

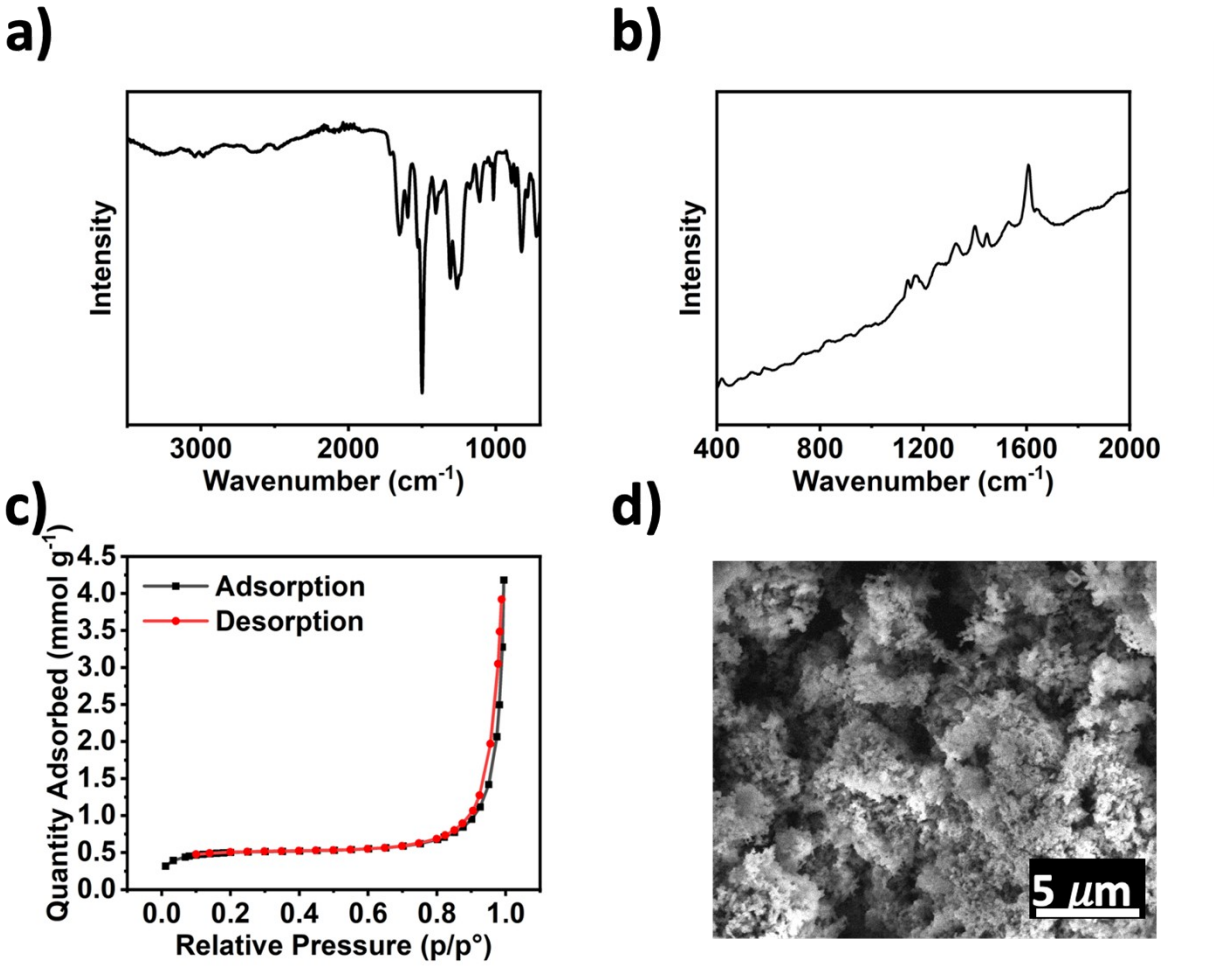


Figure S2: Characterization of TPDA-TCl, a) IR spectrum, b) RAMAN spectrum, c) N_2 adsorption/desorption curves, d) SEM image.

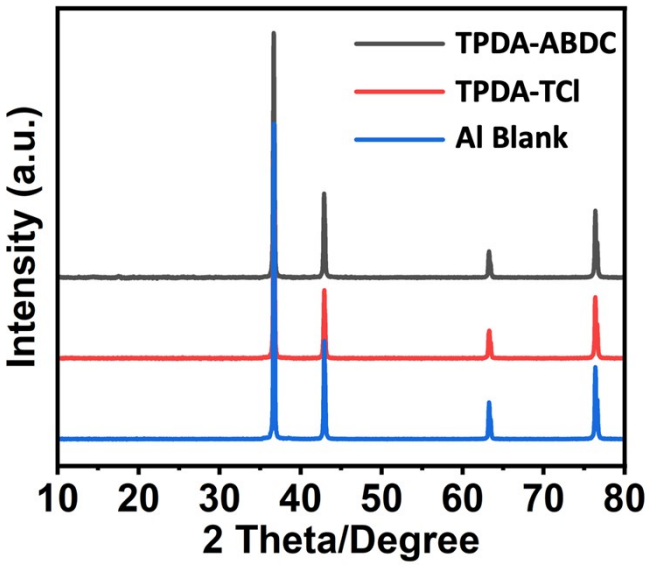


Figure S3: Powdered X-ray diffraction of both polymers and the blank sampling tray. The lack of peaks shows an amorphous structure in both polymers.

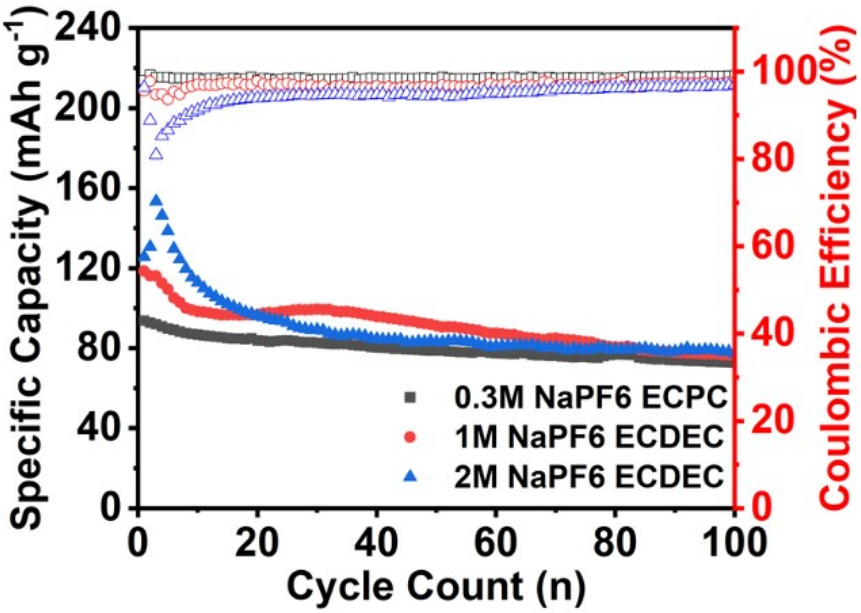


Figure S4: Cycling performance of TPDA-ABDC with different electrolyte systems. Coulombic efficiency never exceeded 99% with either EC:DEC solvent systems.

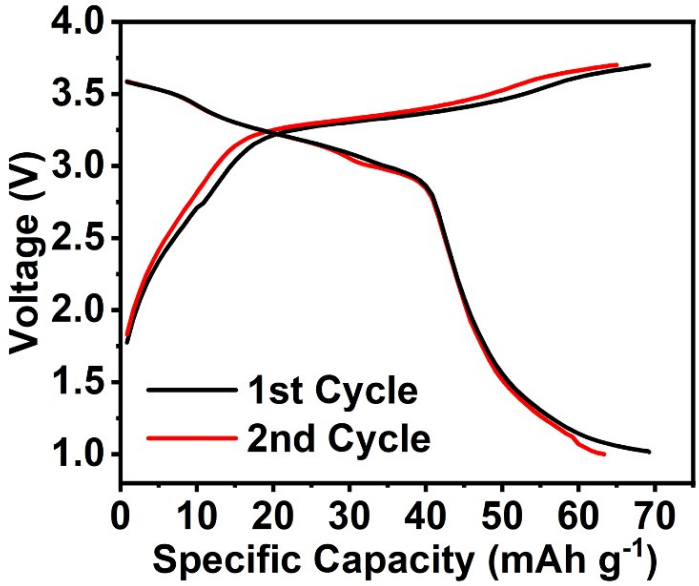


Figure S5: Galvanostatic charge and discharge curve of the first and second cycle of TPDA-TCl.

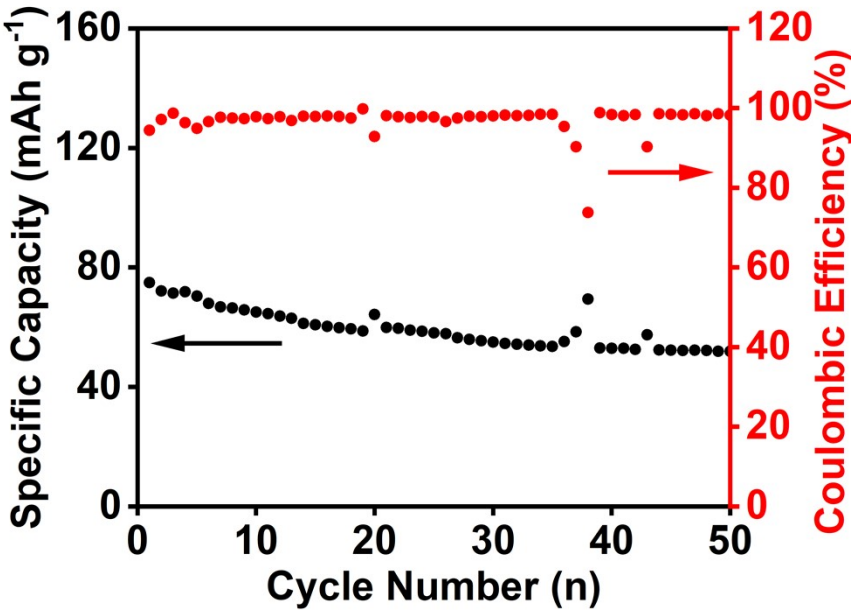


Figure S6: Cycling performance of TPDA-TCl at a current density of 50 mA g^{-1}.

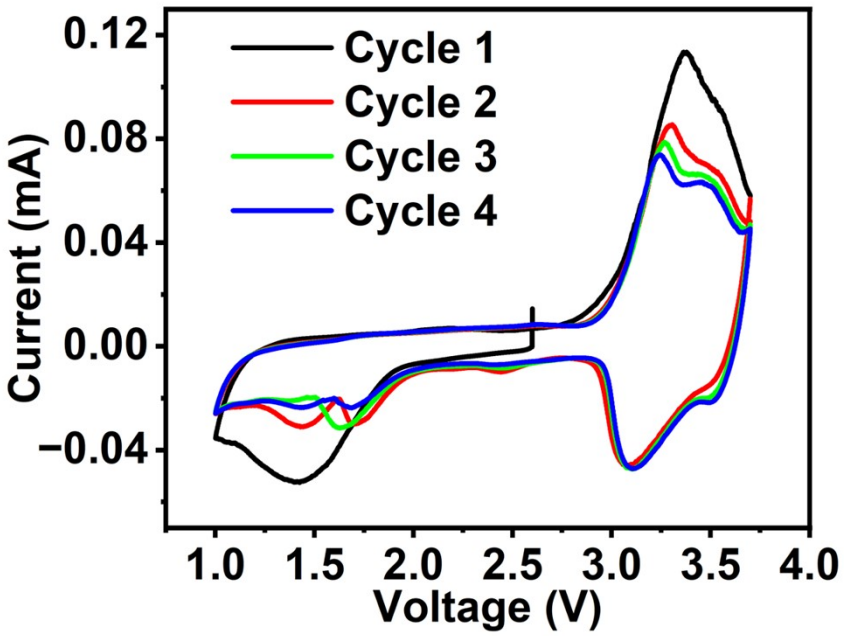


Figure S7: Cyclic Voltammetry initial scans of TPDA-ABDC at a scan rate of 0.1 mV s^{-1}

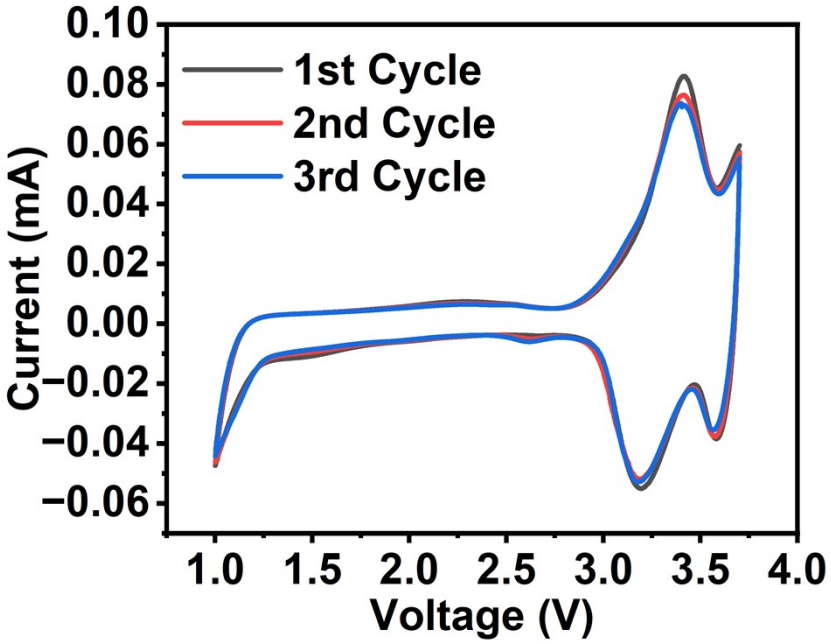


Figure S8: Cyclic Voltammetry initial scans of TPDA-TCl at a scan rate of 0.1 mV s^{-1}

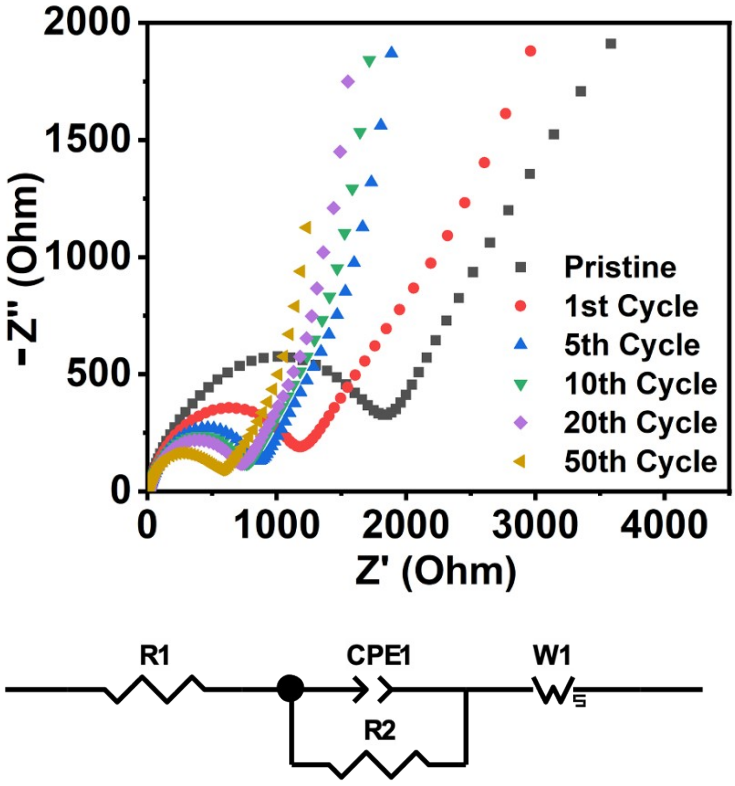
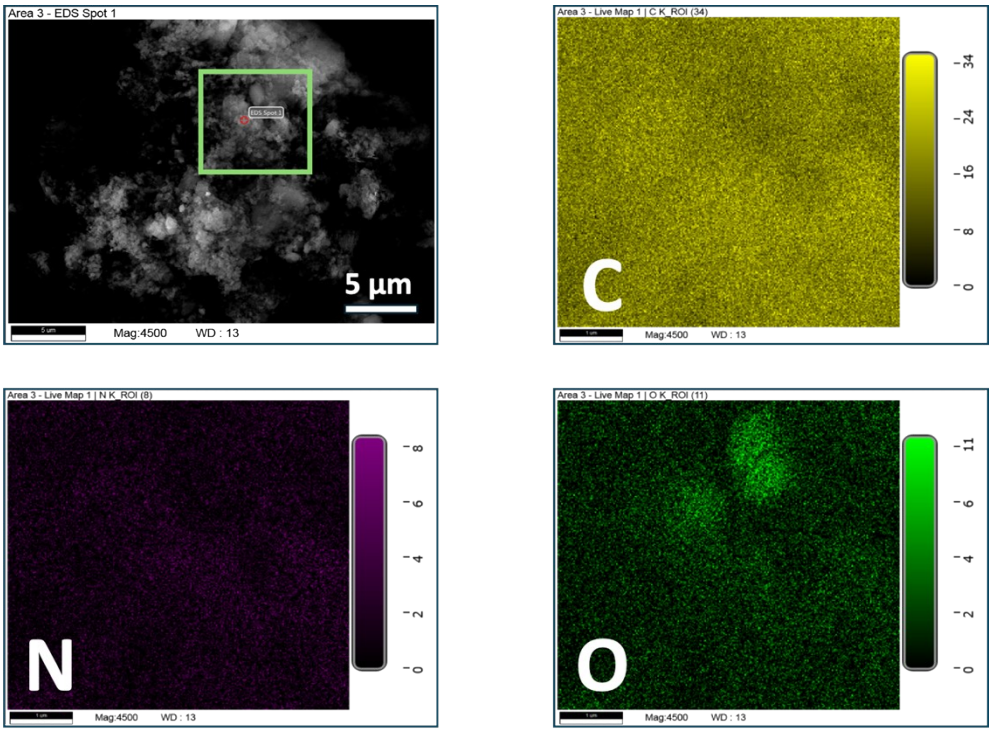
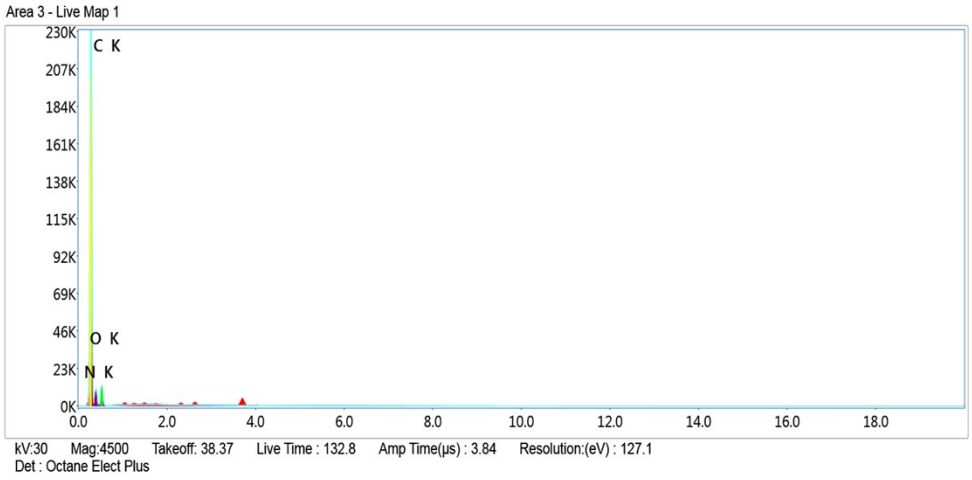


Figure S9: Electrochemical impedance spectroscopy (EIS) of a TPDA-ABDC cell before and after cycling, and the equivalent circuit model.





Element	Weight %	Atomic %
C K	78.80	81.92
N K	13.90	12.38
O K	7.30	5.70

Figure S10: SEM EDX mapping of TPDA-ABDC.

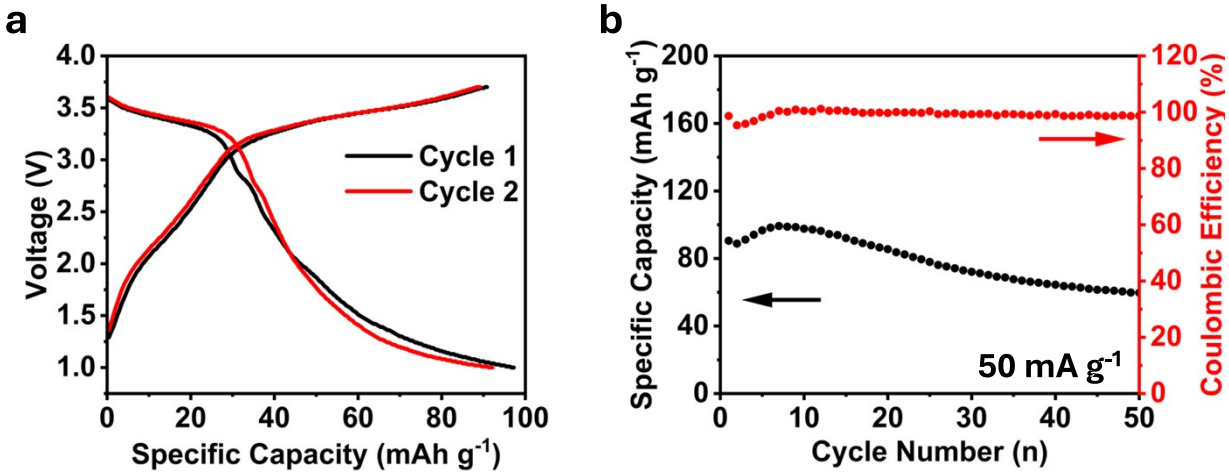


Figure S11: a) Galvanostatic charge and discharge curves, and b) Cycling Performance of TPDA-ABDC in 1M $LiPF_6$ in EC:DEC electrolyte with lithium metal as the counter electrode.

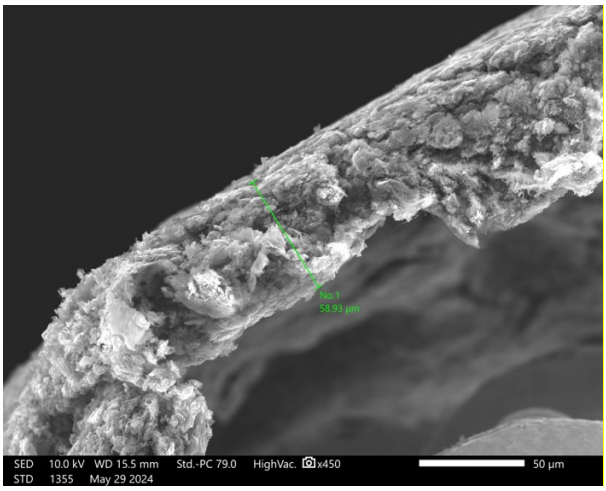


Figure S12: SEM image of TPDA-ABDC electrode composite thickness.

The diffusion coefficient, D, was obtained from GITT measurements and SEM, using Fick's Second Law equation[1]

$$D = \frac{4}{\pi * \tau}\left(\frac{m_b * V_m}{M_B * S}\right)^2\left(\frac{\Delta Es}{\Delta Et}\right)^2\left(\tau \ll \frac{L^2}{D}\right)$$

where τ is the pulse time, V_M is the molar volume of the active material, m_b is the mass of the electrode material, M_B is the molar mass of the active material, S is the contact area, and L is the average thickness of the electrode. The molar mass of TPDA-ABDC is unable to be determined due to its three-dimensional structure and insolubility, so the molar mass of the repeating unit (RU) was used (941.02 g/mol). The mass of the electrode used was 0.8 mg, and the average thickness of the electrode was 58.9 um, determined by SEM imaging above. The composite radius was 10 mm, giving an electrode volume of $4.63*10^{-3}$ cm^3. TPDA-ABDC comprised 60% of the electrode mass, so $4.8*10^{-4}$ g, with the molar mass of the RU giving a molar volume of $5.44*10^3$ cm^3/mol. The contact area of the electrode was 0.785 cm^2. The pulse time was 30 minutes (1800 s). Lastly, both ΔE_S and ΔE_τ are 0.43 V about the redox potential of the azo sodiation, taken from the GITT

(Figure 3f). Based on the measured and calculated values, the diffusion coefficient, D, of TPDA-ABDC is $2.46*10^{-8}$ cm^2 s^{-1}.

References

1 J. Huang, K. I. E. Callender, K. Qin, M. Girgis, M. Paige, Z. Yang, A. Z. Clayborne, C. Luo, *ACS Appl. Mater. Interfaces*, 2022, **14**, 40784-40792.