

Supporting Information

Linkage Effects of Phenanthrene-based Polymeric Anodes for Lithium-Ion Batteries

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Supplementary Note 1. Li-ion Battery Cell Preparation and Electrochemical Measurements

The **PQ-polyamides** series polymers were evaluated as anode materials for lithium-ion batteries using a slurry-casting method. The electrode slurry was prepared by thoroughly mixing 40 wt% active polymer material, 50 wt% conductive carbon, and 10 wt% poly(vinylidene fluoride) (PVDF) binder. *N*-Methyl-2-pyrrolidone (NMP) was added as the solvent to obtain a homogeneous slurry. The resulting slurry was uniformly coated onto a copper current collector and initially dried on a hot plate at 60 °C for 12 h, followed by further drying in a vacuum oven at 80 °C for 8 h to ensure complete solvent removal. The dried electrodes were punched into circular disks with a diameter of 12 mm, yielding average active material loadings of approximately 0.17, 0.15, and 0.12 mg cm⁻². All electrodes were transferred into an argon-filled glovebox (Vigor, Vigor Tech USA), where the concentrations of oxygen and moisture were maintained below 0.5 ppm. Coin-type half-cells were assembled using the prepared polymer electrodes as the working electrode, lithium metal foil as the counter/reference electrode, and Celgard 2325 as the separator. A total of 40 μL of electrolyte consisting of 1 M LiPF₆ dissolved in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 v/v) was added to each cell.

Electrochemical measurements were carried out using a MultiPalmSens4 electrochemical analyzer (PalmSens BV, Houten, Netherlands) for cyclic voltammetry (CV) tests within a voltage window of 0.02–3.0 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy (EIS) measurements were performed at various cycling stages using an electrochemical workstation (Model 7061E, CH Instruments, Inc., Texas, USA) with an applied alternating current (AC) amplitude of 10 mV over a frequency range from 10 mHz to 1 MHz. Galvanostatic charge-discharge cycling was conducted using a programmable battery tester (AcuTech Systems Co. Ltd.) under constant-current mode within the same voltage range of 0.02–3.0 V (vs. Li/Li⁺). For each sample, electrochemical measurements were conducted using more than five independent cells ($n > 5$) to ensure the reliability and reproducibility of the data.

Supplementary Note 2. Sweep Rate Voltammetry and Charge-Storage Characteristics

In lithium-ion battery systems, multiple electrochemical processes can occur concurrently within the electrode during cycling. Sweep rate-dependent cyclic voltammetry is a powerful technique for probing these processes and distinguishing their contributions to the overall charge-storage behavior. The total stored charge observed in a CV response can generally be divided into three components^{1, 2}:

- (i) faradaic charge associated with lithium-ion insertion (diffusion-controlled process),
- (ii) faradaic charge arising from surface or near-surface redox reactions (pseudocapacitance), and
- (iii) non-faradaic charge related to electric double-layer capacitance.

In polymer-based electrodes, the contributions from pseudocapacitive and double-layer processes can be significant due to the high surface accessibility and amorphous nature of the electrode materials. The relative contributions of diffusion-controlled and capacitive processes can be evaluated using CV data collected at various scan rates (**Figure S2**). The relationship between the peak current (i) and scan rate (v) follows the empirical power-law equation:

$$i = av^b$$

where a and b are adjustable constants. The b value is obtained from the slope of the linear fit of $\log i$ versus $\log v$ (**Figure 3c**). A b value close to **0.5** indicates a semi-infinite diffusion-controlled process, whereas a value approaching **1.0** suggests a predominantly surface-controlled (capacitive) charge-storage mechanism³⁻⁵. Since the measured current contains contributions from both diffusion-controlled and capacitive processes, a more detailed separation of these components can be achieved using the following relationship^{4, 6, 7}:

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

where the term k_1v represents the surface-controlled (capacitive) contribution and $k_2v^{1/2}$ corresponds to the diffusion-controlled contribution. The values of k_1 and k_2 can be determined by plotting $i/v^{1/2}$ as a function of $v^{1/2}$, allowing quantitative evaluation of the capacitive and diffusion-controlled charge-storage contributions at different scan rates (**Figure 4**).

Table S1. Molecular and Thermal Characteristics of Polyamides (PQ-a to PQ-f).

Polymer	Inherent Viscosity (dL/g)	Tg (°C)	Td @10% (°C, N₂)	Td @10% (°C, Air)	Structural Notes
PQ-a	0.80	232	454	473	Aliphatic diacid, flexible chain
PQ-b	0.54	254	474	466	Cycloaliphatic structure
PQ-c	0.28	338	497	491	Aromatic rigid backbone
PQ-d	0.96	250	538	523	Ether-containing aromatic
PQ-e	0.65	281	536	524	Sulfone-containing aromatic
PQ-f	0.62	293	531	494	CF ₃ -containing rigid backbone

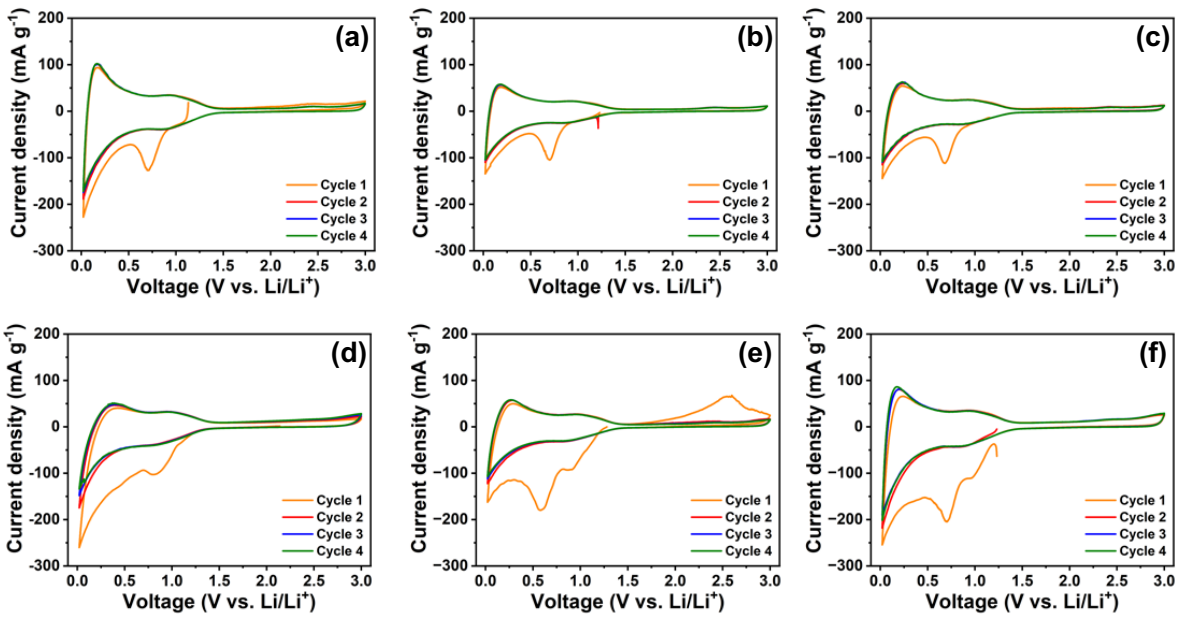


Figure S1. Cyclic voltammograms of (a) PQ-a, (b) PQ-b, (c) PQ-c, (d) PQ-d, (e) PQ-e, and (f) PQ-f recorded over the first four cycles at a scan rate of 0.1 mV s^{-1} in the voltage window of 0.02-3.0 V (vs. Li/Li⁺), illustrating the evolution of redox behavior and stabilization of the lithiation-delithiation process upon initial cycling.

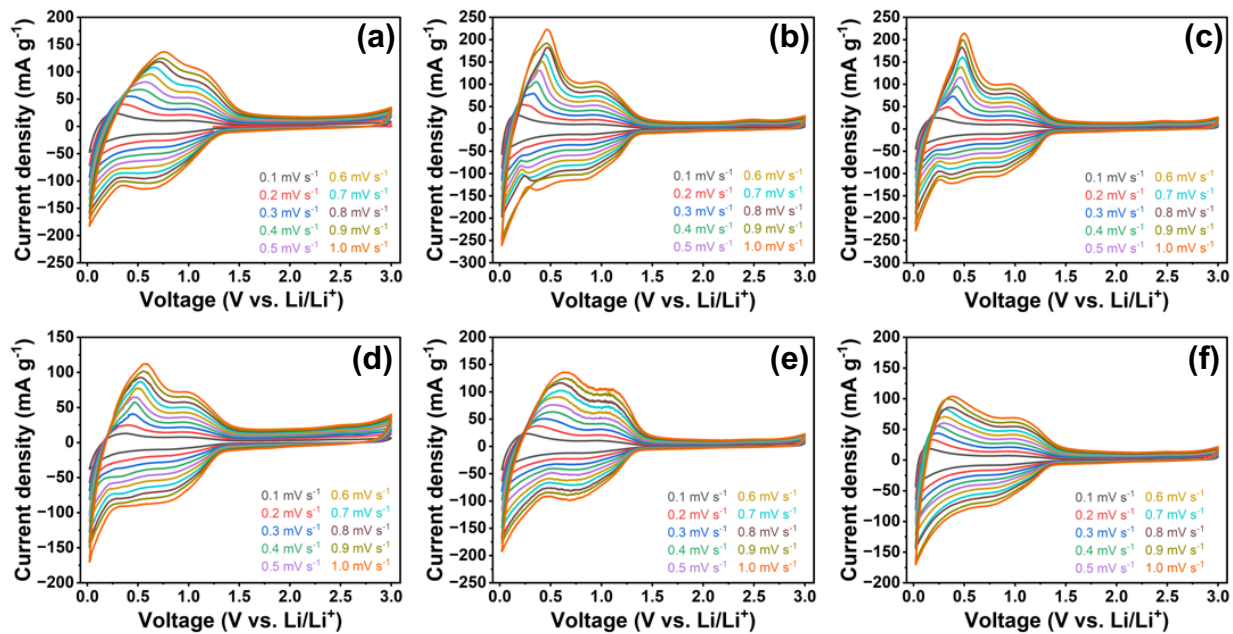


Figure S2. Cyclic voltammograms of a) PQ-a, (b) PQ-b, (c) PQ-c, (d) PQ-d, (e) PQ-e, and (f) PQ-f recorded at various scan rates ranging from 0.1 to 1.0 mV s⁻¹ in the voltage window of 0.02-3.0 V (vs. Li/Li⁺), illustrating the scan-rate-dependent redox behavior and kinetic characteristics of the polymer electrodes.

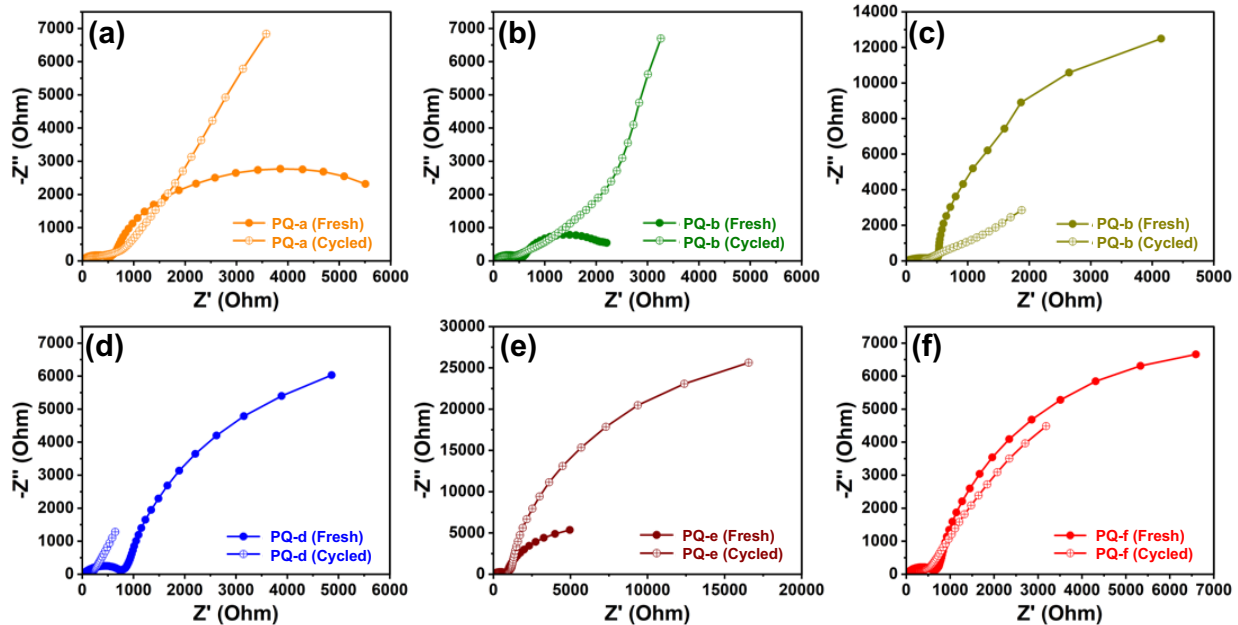


Figure S3. Nyquist plots of **PQ-polyamide** electrodes obtained from electrochemical impedance spectroscopy measurements (a) before cycling and (b) after cycling, showing the evolution of interfacial charge-transfer resistance and ion-transport behavior.

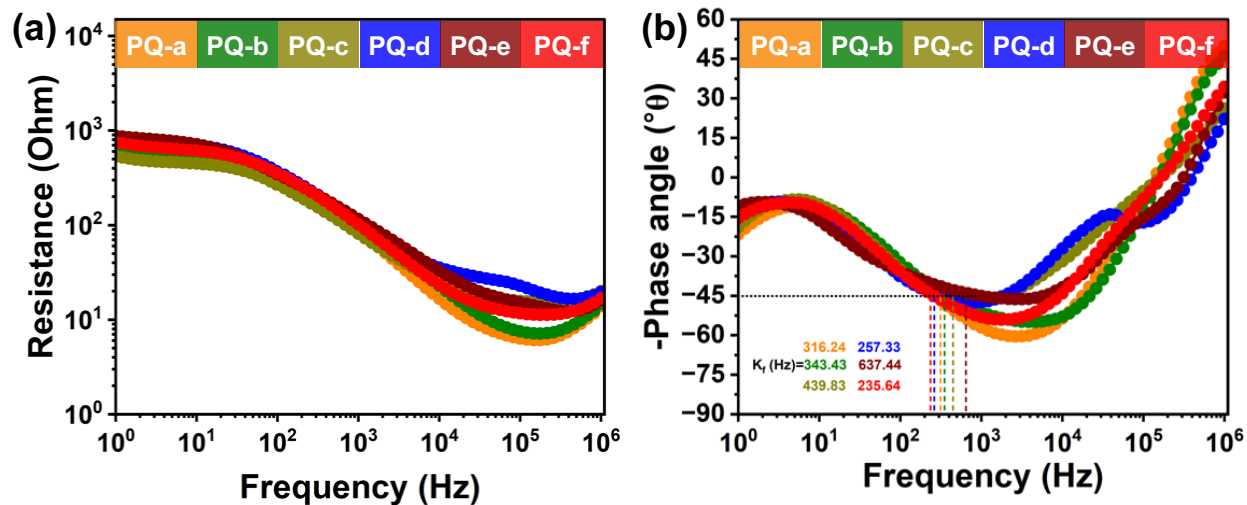


Figure S4. (a) Bode magnitude plots and (b) Bode phase plots derived from EIS spectra of **PQ-polyamide** electrodes. The knee frequency (f_k) and corresponding relaxation time constants (τ) extracted from the phase-angle minima are used to evaluate substituent-dependent electrochemical relaxation kinetics.

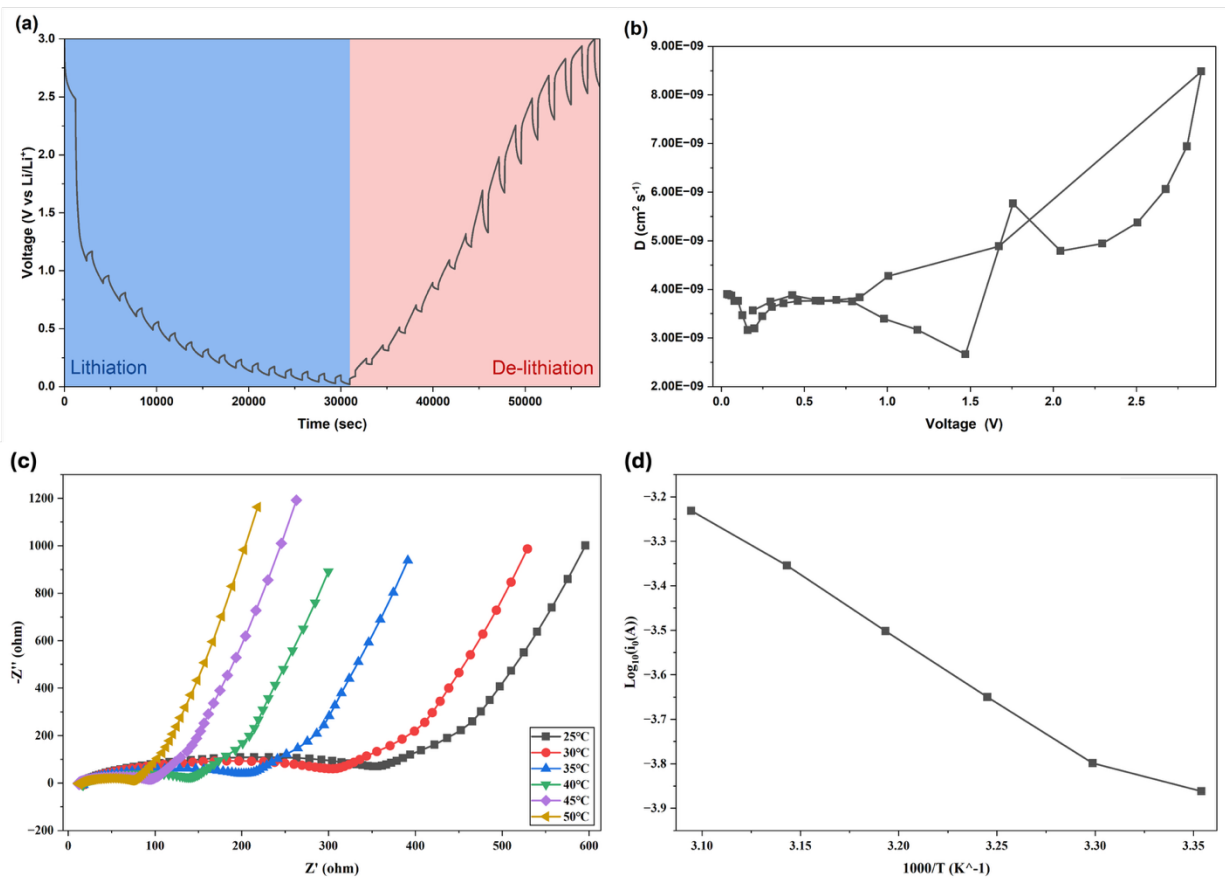


Figure S5. (a) GITT profile of PQ-c during lithiation and delithiation. (b) Lithium-ion diffusion coefficient (D_{Li^+}) as a function of voltage derived from GITT. (c) Nyquist plots at different temperatures (25–50 °C). (d) Arrhenius plot of $\log_{10}(i_0)$ vs. $1000/T$ with an activation energy of 48.75 kJ mol^{-1} .

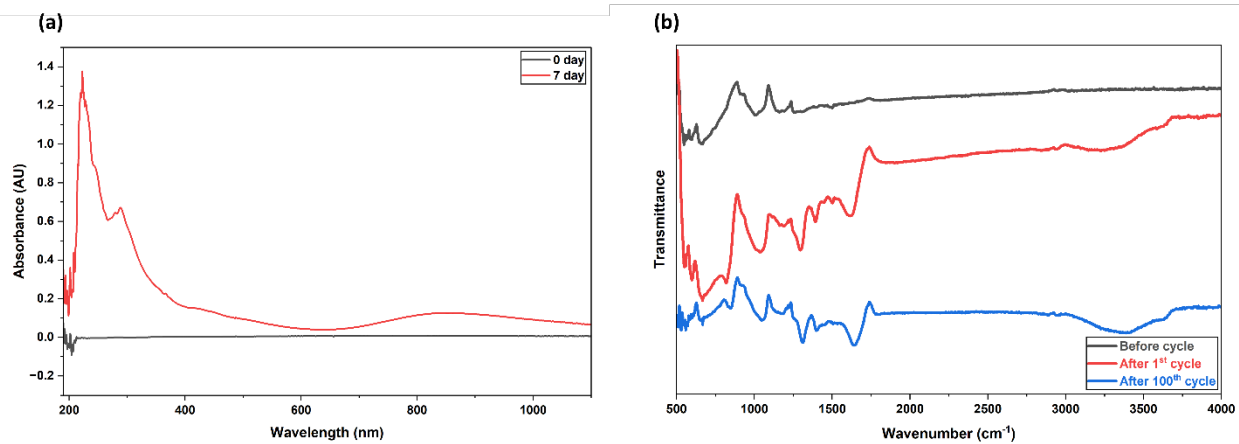


Figure S6. (a) Solubility tests, soaking **PQ-c** in 1 M LiPF₆ in EC:DEC (1:1 v/v) for 7 days, showing an increased absorbance after prolonged soaking, and (b) the ex-situ FTIR at three different statuses of **PQ-c** electrode.

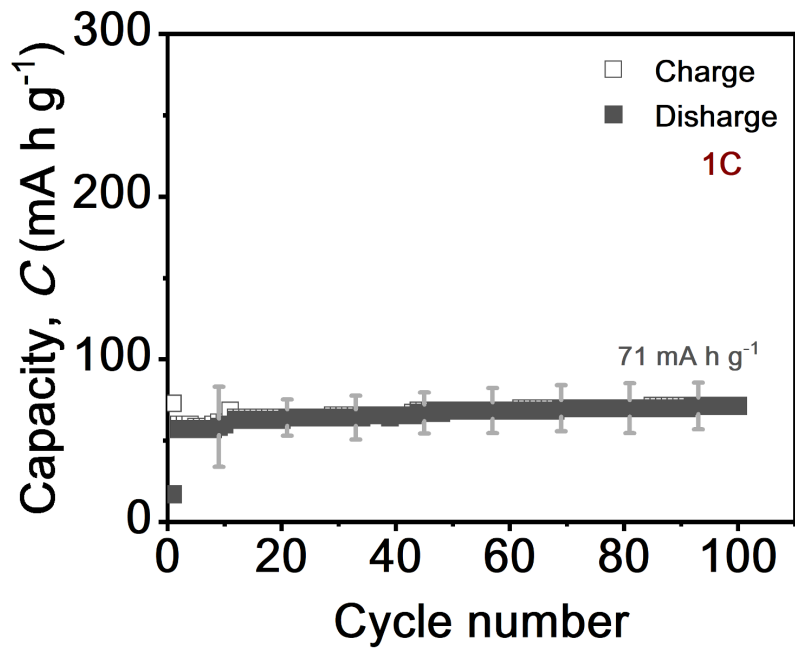


Figure S7. The electrochemical performance of a control electrode consisting of 90 wt.% Super P and 10 wt.% PVDF binder at 1C rate.

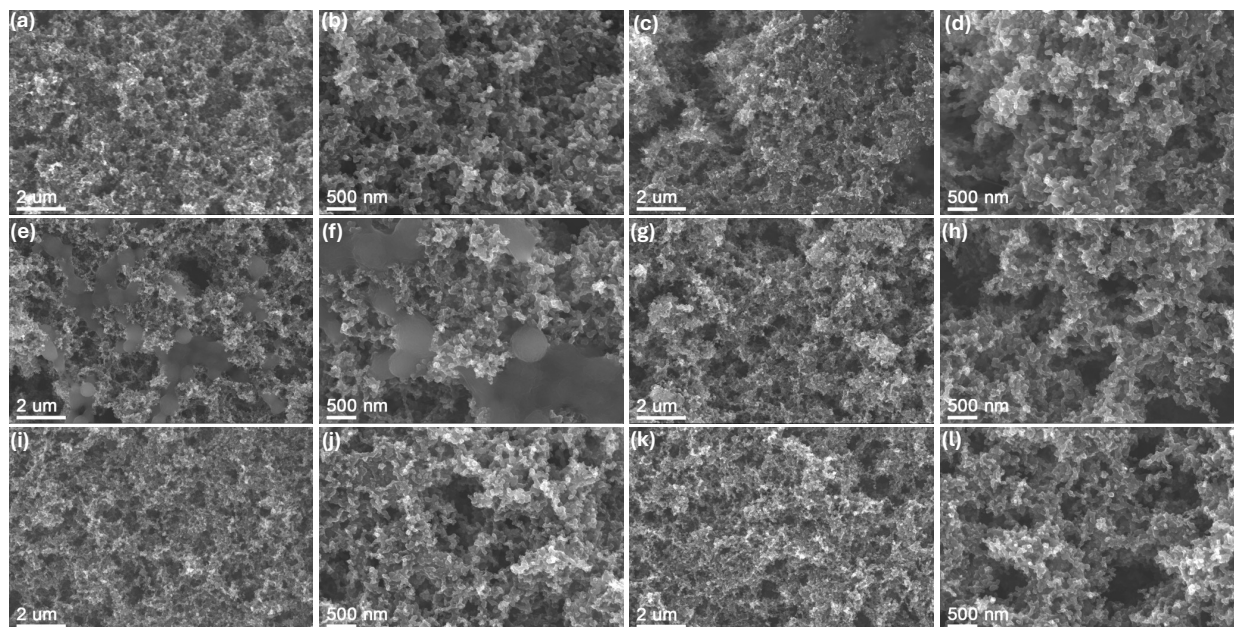


Figure S8. SEM images of **PQ-polyamides** at different magnifications (30k and 70k): (a–b) **PQ-a**, (c–d) **PQ-b**, (e–f) **PQ-c**, (g–h) **PQ-d**, (i–j) **PQ-e**, and (k–l) **PQ-f**.

Table S2. Summary of polymer based anodes for LIBs.

No.	Polymer	Voltage (V vs Li/Li ⁺)	Current density (mA g ⁻¹)	Performance (Specific capacity(mAh g ⁻¹)/ cycle)	Ref.
1	Polydiaminophenylsulfone-triazine	0.0-3.0	100 1000	565/100 375/100	8
2	SNW-1/CNTs	0.01-3.0	500	203/1000	9
3	PI	0.001-3.0	100	578/50	10
4	PMAQ	0.01-3.0	500	465/150	11
5	N-CPIMs	0.0-3.0	10	500/5	12
6	PDCzBT	0.0-3.0	100 200	404/100 312/400	13
7	P(C-TDPP-TA) P(F-TDPP-TA) P(C-TDPP-H) P(F-TDPP-H)	0.01-3.0	100	357/500 298 /500 327 /500 278 /500	14
8	P3-AQT	0.0-3.5	50 100	380/100 400/100	15
9	PTp-COOH	0.01-3.0	500	147/100	16
10	Poly(imine-anthraquinone) (PIAQ)	0.01-3.5	200	486/1000	17
11	Polyanthraquinone-triazine (PAT)	0.01-3.0	200	1770/400	18
12	Multi-carbonyl polyimide (PMTA)	0.01-3.0	100	698/50	19
13	BIAN-based porous organic polymer (PBM)	0.01-3.0	400 750 1000	850/3000 740/2000 300/1100	20
14	TTD-PDA TTD-EDA GA-PDA Schiff-base polymer	0.01-3.0	100	651/240 492/400 416/300	21
15	MA-VA-PcNi polymer	0.01-3.0	200	507/400	22
16	Itaconic acid-graphite composite anode	0.01-3.0	25 100	571/200 693/200	23
17	Tea-polyphenol-Ni chelate (TP-Ni) organic anode		100	454/500	24
18	PQ-a PQ-b PQ-c PQ-d PQ-e PQ-f	0.02-3.0	100	222/100 191/100 293/100 470/100 211/100 153/100	This work

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