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Cyclized polyacrylonitrile anode for alkali metal ion batteries

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Abstract: Alkali metal (Li, Na, and K) ion batteries are vital in portable and large-scale stationary energy storage. Recently, organic anodes have attracted increasing attention for alkali metal ion batteries due to their chemical diversity and potential high capacity. In this work, we discovered that cyclized polyacrylonitrile (cPAN) can serve as a superior anode for alkali metal ion batteries. Remarkably, upon activation cycling, as an anode of lithium-ion battery, cPAN exhibits a reversible capacity as high as 1238 mAh g⁻¹ under a current density of 50 mA g⁻¹. Based on electrochemical experiments and first-principles calculations, it is demonstrated that the hexagonal carbon ring, piperidine ring, and pyridine nitrogen in ladder cPAN are the main active sites for lithium-ion storage. In addition, we show that cPAN displays a unique potential-dependent solid electrolyte interphase formation from 0.1 to 0.01 V vs. Li/Li⁺. Furthermore, cPAN displays decent performances as an anodes in SIBs and PIBs. The discovery of cPAN anode could pave the way for the future development of organic anodes for alkali metal ion batteries.

Introduction

The increasing demand for extended-mileage electric vehicles has triggered intensive research activities on high capacity anode materials.^[1–3] Due to the scarcity of lithium resources, sodium-ion batteries (SIBs) and potassium ion batteries (PIBs) are being developed as low-cost alternatives for lithium-ion batteries (LIBs) in future large-scale stationary energy storage.^[4–6] High-capacity alloying anodes have been widely investigated to promote the energy density of alkali metal ion batteries. The main technological barrier for the commercialization of alloying anodes has been their poor stability during cycling, resulting from their high volume change and pulverization.^[7,8] Various alloying and carbonaceous anodes have been investigated and implemented in commercial applications.^[9,10] Recently, organic compounds have attracted increasing attention for the anodes of alkali metal ion batteries.

Organic anodes have the merits of low energy consumption, tunable structures, chemical diversity, and little environmental impact after disposal.^[11] Most importantly, organic anodes could achieve a lithium-storage capacity higher than graphite. Polyacetylene, with a practical capacity of 340 mAh g⁻¹, has been investigated as an anode in the early development of LIB.^[12,13] Various organic anodes, such as simple organic compounds (maleic acid,^[14] conjugated dicarboxylate,^[15] π -conjugated triquinoxalylene^[16]), polymers (polyimides,^[17]

poly(chalcogenoviologen),^[18] hexaazatriphenylene-based polymer,^[19] benzophenone-3,3',4,4'-tetracarboxylimide oligomer (BTO)^[20] and polymeric Schiff bases^[21], and covalent organic frameworks (COF) (graphdiyne,^[22,23] triazine-based,^[24] triazole-triformyl phloroglucinol-based^[25] and other COFs^[26,27]), have been investigated as the organic anodes of LIB. Nevertheless, organic anodes have been facing the issues of low capacity, poor cycling stability, dissolution in aprotic organic electrolytes, and low conductivity. The cycling stability of organic anodes could be improved by the formation of π conjugated structures,^[16] while, the capacity of organic anode could be enhanced by the introduction of multi-functional active sites.^[24] New organic anode family with abundant active sites and facile synthesis strategy is in urgent need to be explored and developed to support the fast-growing LIB, SIB, and PIB technologies.^[11]

Polyacrylonitrile (PAN) has been widely investigated and developed for the preparation of engineering carbon materials,^[28] and carbonaceous anodes for alkali metal ion batteries.^[29,30] The carbonaceous material prepared from annealing PAN at a temperature of 550 °C exhibited a moderate capacity of 550 mAh g⁻¹ as a LIB anode.^[29] Carbonaceous material derived from annealing PAN at 650 °C delivered a capacity of around 230 mAh g⁻¹ for PIBs.^[31] Nevertheless, few research reported the energy storage capabilities of organic derivatives from PAN. Cyclized PAN (cPAN), with a partial π -electron system, has a ladder structure containing both sp³ hybridized C-C (C-N) bonds and sp² hybridized C=C (C=N) bonds.^[32,33] cPAN has been widely applied as an inert coating of electrode materials.^[34,35] However, cPAN has not been investigated as electrode active material. In this work, we demonstrate that cPAN, as a simple organic derivative of PAN, can be used as an anode in LIBs, SIBs, and PIBs. The hexagonal carbon ring, piperidine ring, and pyridine nitrogen are demonstrated as active sites for lithium-ion adsorption. This work opens a new avenue for alkali metal ion storage using cPAN based organic materials.

Results and Discussion

Chemical structure of cPAN

After exothermic condensing cyclization reaction at 280 °C shown by differential scanning calorimetry (DSC) (Figure 1a), linear PAN is transformed into ladder cPAN. cPAN shows brown color (Figure S1a) and block-shaped morphology as observed by scanning electron microscopy (SEM) image (Figure

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S2a). In stark contrast, PAN shows white color (Figure S1b) and sphere-shaped morphology (Figure S2b). High-resolution transmission electron microscopy (HRTEM) image of cPAN showed an amorphous structure with some parallel regions (Figure 1b) which are ascribed to the π - π stacking of the ladder structures in cPAN. The defect-rich structure of cPAN shown in HRTEM image (Figure 1c) indicates the low degree of cross-linking between ladder structures. The cyclization reaction of PAN completed as revealed by Fourier-transform infrared (FTIR)

spectroscopy. PAN showed a typical peak at 2245 cm^{-1} (Figure S3), which is ascribed to the characteristic nitrile group ($\text{C}\equiv\text{N}$).^[36] After cyclization, this peak completely disappeared. Instead, a peak at 1596 cm^{-1} (Figure 1d) appeared, indicating the formation of $\text{C}=\text{N}$ or $\text{C}=\text{C}$ bonds in cPAN. The peak at 1257 cm^{-1} reflects the existence of $\text{C}-\text{N}$ single bonds in cPAN. The peak at 1376 cm^{-1} is due to the bending of $\text{C}-\text{H}$ bonds on the backbone of cPAN. Minor methylene group (CH_2) existed due to the hydrogen radical reactions.

Figure 1 Physicochemical characterization of cPAN. (a) TGA and DSC curves of PAN. The inset schematic illustrates the cyclization of PAN. (b, c) HRTEM images of cPAN. The parallel yellow lines and red dashed circles show the inter-ladder structure of cPAN, while the yellow arrows show the defective structure or isolated ladder structure. (d) FTIR spectra. (e) XRD pattern. (f) Raman spectra. (g) N 1s high-resolution XPS spectra. (h) ^{15}N CP/MAS SS-NMR spectra. (i) Schematic diagram illustrating the structure of cPAN.

The semi-crystalline structure of PAN (Figure S4) evolved into amorphous carbon-like structure of cPAN. The XRD pattern of cPAN had two broad peaks around 18° and 24.5° (Figure 1e), indicating large interlayer spacing between the neighboring ladder structure of cPAN. The broad peak at 18° demonstrates that the interlayer spacing of cPAN is much larger than amorphous carbon obtained by annealing PAN at $>500^\circ\text{C}$.^[37] Typical D (1360 cm^{-1}) and G (1570 cm^{-1}) peaks shown in Raman spectra indicate the co-existence of sp^3 hybridized $\text{C}-\text{C}$ ($\text{C}-\text{N}$) and sp^2 hybridized $\text{C}=\text{C}$ ($\text{C}=\text{N}$) structures (Figure 1f). The precise chemical structure of cPAN was further interpreted by X-ray photoelectron

spectroscopy (XPS), solid-state nuclear magnetic resonance (SS-NMR), and elemental analysis. After cyclization, the binding energy of N 1s decreases from 401.5 eV of the nitrile group (Figure S5) to 399 eV , which reveals the evolution of the chemical environment of nitrogen. The N 1s high-resolution XPS spectra of cPAN was deconvoluted into two major peaks centering at 398 and 399.5 eV (Figure 1g). The peak at 398 eV is attributed to the formation of pyridine nitrogen. The peak around 400 eV is generally the pyrrolic nitrogen^[38] or piperidine nitrogen^[39] in carbonaceous materials, but is regarded as graphitic nitrogen in cPAN by some researchers.^[34,35] Since radical reactions of the scission of $\text{C}-\text{C}$ bond mainly occur above 400°C ,^[40] it is hard to

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have pyrrolic nitrogen in a pentagonal atom ring due to the low heat-treatment temperature of cPAN. So, it is necessary to differentiate the existence of piperidine or graphitic nitrogens in cPAN. To resolve this issue, we performed ^{15}N CP/MAS SS-NMR. A broad peak ranging from 270 to 220 ppm is attributed to the pyridine nitrogen in different hexagonal structures, while a peak with a chemical shift around 120 ppm is the amine (N-H) bond from piperidine units (Figure 1h). A peak at 77 ppm chemical shift is due to the formation of minor primary amines (NH_2). After cyclization, cPAN was not oxidized (Figure S6). The 1D ^1H MAS and 2D ^1H - ^{15}N CP HETCOR SS-NMR (Figure S7) demonstrate the chemical environment of ladder cPAN and the formation of amine bonds. The formation of amine bonds is due to hydrogen transfer reactions (Figure S8).

The C 1s XPS spectra demonstrate the existence of $\text{sp}^2\text{C}=\text{C}$, $\text{sp}^3\text{C}-\text{C}$, $\text{C}=\text{N}$, and $\text{C}-\text{N}$ bonds in cPAN (Figure S9a), while the O 1s XPS spectra suggests the existence of minor oxygen in the form of ketone ($\text{C}=\text{O}$) (Figure S9b). Finally, based on the elemental analysis, we proposed the chemical structure of cPAN ($\text{C}_{24}\text{N}_6\text{H}_{20}$) (Figure 1i). In the chemical structure of cPAN (Figure 1i), sp^3 -hybridized N atom in piperidine provides one extra electron forming N-H bond and an extra pair of p-electrons. Pyridine nitrogen has one lone pair electrons forming sp^2 hybridization and one single electron forming π -electron system. Both the piperidine and pyridine nitrogen could provide an electron-rich environment for adsorbing alkali metal ions. Energy-dispersive X-ray spectroscopy (EDS) and its mapping results confirmed the homogeneous distribution of carbon, nitrogen, and oxygen without phase separation (Figure S10). The narrow linewidth of electron paramagnetic resonance (EPR) (8 Gauss) compared with that of an amorphous carbon^[41] indicates the localized electrons and thus low cross-link degree among ladder cPAN structures (Figure S11).

Electrochemical performances of cPAN

The lithium-ion storage performance of cPAN was first investigated in Li//cPAN half-cell (Figure 2a) by cyclic voltammetry (CV) (Figure 2b). The cPAN electrode with acetylene black (AB) conductive agent showed lithium (de)intercalation peaks around 0.01 V, and redox peaks around 0.95 V which could be caused by reversible redox reactions of cPAN. In the first cycle CV, a broad cathodic peak ranging from 0.95 to 0.25 V appeared resulting from the formation of solid electrolyte interphase (SEI). CV curves recorded at various scan rates showed stable and reversible electrochemical behavior, indicating good rate capability (Figure S12). Based on the power-law relationship ($i = av^b$, ($0.5 < b < 1.0$)) between current response (i) and scan rate (v), we calculated the b value of the cathodic lithium intercalation process, a b value of 1.2 higher than 1.0 was observed (Figure S13a). The current response increases when either the cycle number or the scan rate increases. The abnormal b value is attributed to the current (capacity) increase with a gradual increase of scan number (Figure S13b). Galvanostatic charge-discharge (GCD) was employed to investigate the lithium-ion storage performance of cPAN (Figure 2c). Pure cPAN without AB additive showed a low discharge capacity of 31 mAh g^{-1} and a charge capacity of 19.3 mAh g^{-1} (Figure S14) due to its low conductivity ($3.81 \times 10^{-8} \text{ S cm}^{-1}$). Low specific capacities of pure organic anodes are usually observed in low-conductivity COF materials.^[24,26]

To fully exert the lithium-ion storage capacity of cPAN, cPAN was mechanically mixed with AB and sodium carboxymethyl cellulose (CMC) binder to form a composite electrode. The cPAN electrode with AB additive showed a first cycle discharge capacity of as high as 1210 mAh g^{-1} and a reversible charge capacity of 673 mAh g^{-1} (Figure 2c). The first GCD cycle showed a long tail approaching 0.01 V. The zoom-in of this low potential range displayed an obvious oscillation phenomenon (Figure S15), which indicates that the lithiation occurs in two phases with Li^+ concentration gradient.^[42–44] This may be resulted from the gradient lithium concentration in cPAN composite electrode, or the difference of lithium concentration in AB and cPAN. We further tested the GCD curves at different current densities ranging from 50 to 5000 mA g^{-1} (Figure S16). After the rate test for 70 cycles, from the 71st to 100th cycles, the current density was switched back to 50 mA g^{-1} , at the 100th cycle, cPAN electrode showed higher capacity and lower polarization than the initial cycles at 50 mA g^{-1} (Figure 2d). The initial Coulombic efficiency (ICE) of cPAN electrode was 55.6%. The Coulombic efficiency (CE) quickly increased from 55.6% to 93.9%, and to 98.0% from the first to the second and third cycle. The CEs retained high values around 99.5% afterward (Figure 2d). The capacities were tested stepwise at various current densities. The cPAN electrode displayed capacities of 551, 494, 444, 382, 328, 281, 213 mAh g^{-1} at current densities of 50, 100, 200, 500, 1000, 2000, and 5000 mA g^{-1} . When the current density was switched back to 50 mA g^{-1} , cPAN electrode displayed a capacity of 544 mAh g^{-1} at the 71st cycle, while the capacity increased to 681 mAh g^{-1} at the 100th cycle. The rate capability was then tested again with the same protocol in Figure 2d. During the second-set test (Figure 2e), the cPAN electrode showed reversible capacities of 702, 659, 607, 535, 475, 407 and 316 mAh g^{-1} at current densities of 50, 100, 200, 500, 1000, 2000 and 5000 mA g^{-1} . When the current density was switched back to 50 mA g^{-1} , the capacity recovered to 677 mAh g^{-1} at the 71st cycle and 791 mAh g^{-1} at the 207th cycle. The gradually increased capacities could be ascribed to the activation of the cPAN electrode and the exposure of active sites for lithium-ion intercalation.

We further tested the long-term cycling stability of cPAN electrode for LIB anode at 1 A g^{-1} (Figure 2f). The cPAN electrode showed increasing CEs from 91.8% to 99% in the initial 50 cycles' GCD test (highlighted area in Figure 2f). The lower CE in the initial 50 GCD cycles could be due to the continuous SEI formation in the low potential range during cycling. The cPAN electrode displayed an initial capacity of 216 mAh g^{-1} for the first cycle. The capacity of cPAN electrode increased quickly from the first to the 220th cycles (585 mAh g^{-1}), and gradually increased afterward to the 1000th cycles. From 980th to 1090th cycles, the capacity of cPAN electrode stabilized around 810 mAh g^{-1} (Figure 2f and Figure S17a). The 1000th GCD curve showed a much lower polarization of 54 mV compared with the higher polarization of 173 mV at the 1st cycle (Figure S17b). The decreased polarization of cPAN is due to the enlarged electrochemical active surface area and the decreased charge transfer resistance. After 1000 cycles' GCD cycling, we further tested the capacity at a current density of 50 mA g^{-1} . The cPAN electrode showed a reversible capacity of 1238 mAh g^{-1} with a high CE of 99.3% (Figure S18). It needs to be noted here that the capacity of AB additive (220 mAh g^{-1} at 50 mA g^{-1} , Figure S19) has been excluded. This high capacity corresponds to a high lithium concentration in Li^+ -intercalated cPAN ($\text{Li}_{18}\text{C}_{24}\text{N}_6\text{H}_{20}$).

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Figure 2 Electrochemical performances of cPAN as LIB anode. (a) Schematic diagram of half-cell of cPAN. (b) CV curves of cPAN electrode at a scan rate of 0.1 mV s^{-1} . (c) The GCD curves of cPAN at a current density of 50 mA g^{-1} . (d, e) Rate capabilities of cPAN at different current densities. (f) Dependence of capacities and CEs on cycle number at a current density of 1 A g^{-1} . (g) Relationship between the real impedance and the reciprocal square root of the angular velocity. (h) Dependence of the diffusion coefficients of AB and cPAN on the potential. (i) Capacities of cPAN for LIBs, SIBs, and PIBs.

We tracked the evolution of impedance by electrochemical impedance spectroscopy (EIS) during the GCD cycling process. The EIS spectra showed two semi-circles (resistances of SEI and charge transfer) at high-frequency range and an oblique line (semi-infinite diffusion-controlled process) at the low-frequency range. The cPAN electrode showed decreased impedance upon cycling (Figure S20a and S20b), which is a sign that the charge transfer resistance decreases and the number of active sites increases. As the imaginary impedance decreased significantly with the increase of cycle number, we calculated the gravimetric capacitance at 10 mHz .^[45] cPAN had an initial gravimetric specific capacitance of 5.58 F g^{-1} . After 10 cycles, the specific capacitance increased to 7.11 F g^{-1} , and after 1000 cycles, the capacitance increased to 29.98 F g^{-1} (Figure S20c). The increased surface capacitance reveals the increase of electrochemically active sites for lithiation, which is in line with the decrease of charge transfer resistance. The increase of capacitance of cPAN could be due to the exfoliation of cPAN during repeated GCD cycling, which effectively exposes the active sites. The exfoliation phenomenon of cPAN after long-term cycling was observed by ex situ TEM (Figure S21). Further, we calculated the diffusion coefficient of Li^+ ion based on the Warburg semi-infinite diffusion model using the

low-frequency range of the EIS spectra. The Warburg coefficient (σ) is calculated by the slope of Z_{re} vs $\omega^{-1/2}$. The σ values decreased from $384.1 \text{ } \Omega \text{ s}^{-1/2}$ to $356.8 \text{ } \Omega \text{ s}^{-1/2}$ to finally $40.96 \text{ } \Omega \text{ s}^{-1/2}$, from the 1st cycle to the 10th cycle and finally to the 1000th cycle (Figure 2g). The diffusion coefficient of Li^+ ions (D_{Li^+}) increased from $1.03 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for the 1st cycle, to the $1.19 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for the 10th cycle, and finally to $9.045 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the 1000th cycle (Figure S20d). The increased D_{Li^+} suggests the enhanced diffusion pathways for Li^+ ions. We further performed galvanostatic intermittent titration technique (GITT) for the cPAN to calculate D_{Li^+} (Figure S22). Both AB and cPAN electrodes showed decreasing D_{Li^+} in the lithiation process (Figure 2h). In the lithiation process at 0.5 V , cPAN electrode had a D_{Li^+} of $6.7 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, while AB had a D_{Li^+} of $2.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ which is 38.8 times that of cPAN electrode. The low D_{Li^+} of cPAN may result from its hydrogen-rich skeleton. Furthermore, the D_{Li^+} of cPAN electrode showed a sharp decrease with deep lithiation to 0.01 V , D_{Li^+} decreased to a low value of $1.41 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The above results reflect the lower diffusion coefficient of Li^+ ions in cPAN materials compared with carbonaceous AB materials. Furthermore, we tested the cPAN as an anode for SIB and PIB. For SIB, cPAN anode showed a reversible electrochemical behavior, decent rate capability, and a stabilized capacity of 280

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mAh g⁻¹ comparable to hard carbon anodes (Figure S23).^[4] As a PIB anode, cPAN also showed a reversible behavior, a decent stabilized capacity of 230 mAh g⁻¹ (Figure 2i) and rate capability (Figure S24) comparable to graphitic carbon anodes.^[46] The reversible capacities of cPAN as anodes for SIB and PIB are comparable to some anodes, such as graphitic carbon,^[46] 2D COF materials,^[47] and disodium terephthalates.^[48,49]

Electrode/electrolyte interface of cPAN electrode

We performed ex situ XPS, SEM and TEM to track the evolution of the electrode/electrolyte interface. Pristine cPAN electrode showed comparable N 1s peak intensity compared with cPAN discharged to 0.2 V (Figure 3a). The N 1s peak decreased as cPAN was discharged from 0.2 to 0.1 V. The N 1s peak intensity decreased sharply from 0.1 V to 0.01 V (Figure 3a), which indicates that the SEI on cPAN mainly forms in the potential range from 0.1 to 0.01 V which is much lower than most inorganic

anodes (around 0.6–1.2 V vs. Li/Li⁺).^[30,41,50–53] The intensity of N 1s peak did not recover when cPAN electrode was charged to 3.0 V, which indicates that a robust SEI covers on cPAN. After discharged to 0.2 V, the carbon content decreased from 79.4 at. % to 29.7 at. %, while the carbon content stabilized around 24.0 at. % after discharged to 0.1 V and 0.01 V (Figure 3b). The decreased carbon content of cPAN electrode indicates that the SEI film is oxygen-rich. The oxygen content continued to increase from 0.2 to 0.01 V, which suggests the continuous formation of SEI. The oxygen content remained unchanged after cPAN is charged to 3 V, which indicates the stable chemical composition of SEI on cPAN electrode. Since the SEI forms on carbonaceous materials at a potential around 0.7 V vs. Li/Li⁺, we speculate that the SEI preferentially forms on AB at 0.7 V, and then the SEI forms on cPAN continuously from 0.1 to 0.01 V. The lithiation and continuous SEI formation on cPAN could be the origin of the oscillation phenomenon at low potential.

Figure 3 Evolution of surface chemistry of cPAN electrode. (a) Evolution of N 1s XPS spectra. (b) Evolution of chemical compositions of cPAN electrodes. (c) Relative intensities and their ratios of R-OCO₂Li and C-C. SEM images of cPAN electrode (d) discharged to 0.1 V, (e) discharged to 0.01 V, and (f) charged to 3 V. The rectangular shape with blue dashed line shows the area exposed to the electron beam for 20 s.

In XPS spectra, pristine cPAN electrode did not show a typical peak of lithium alkyl carbonates (R-CH₂-OCO₂Li) in SEI (Figure S25). When cPAN was discharged to 0.2 V, the appearance of R-CH₂-OCO₂Li peak is related to the SEI formation on AB. Since R-CH₂-OCO₂Li is a typical component of SEI,^[54–57] we investigated the peak intensities of R-CH₂-OCO₂Li and C-C (Figure S26) to study the characteristic of SEI on cPAN electrode. We calculated the ratio of R-CH₂-OCO₂Li to C-C (I_R/I_C) (Figure 3c). The intensity of I_R/I_C gradually increased, which indicates the build-up of a SEI layer on cPAN. When cPAN was discharged from 0.2 to 0.1, to 0.01 V, there was a sharp increase of I_R/I_C from 0.93 to 1.36 to 1.95, which is a signal of increased R-CH₂-OCO₂Li component and the SEI formation on cPAN particle. The I_R/I_C ratio remained at 1.91 when cPAN was charged to 3.0 V, which reveals that the SEI on cPAN has a stable composition. The SEM and TEM images of cPAN electrode did not show

obvious SEI formation on cPAN from 0.2 V (Figure S27) to 0.1 V (Figure 3d and Figure S28a). However, manifest SEI film formed on cPAN at 0.01 V (Figure S28b), as this film decomposed when we increased the electron beam exposure time to more than 20 seconds (Figure 3e and 3f). The formation of SEI on cPAN is a slow and gradual process. SEI forms on AB preferentially, and then the SEI forms on cPAN apparently from 0.1 to 0.01 V (Figure S29a). The Li⁺ ion conductive SEI coupled with Li⁺/electron conductive AB could facilitate the lithiation of cPAN (Figure S29b), which enhances the reversible capacity of cPAN. The outer SEI on cPAN is rich in oligomers derived from the decomposition of electrolyte, while the inner SEI is rich in lithium species (Figure S30). Li 1s and F 1s XPS spectra demonstrate that the SEI contains LiF and R-CH₂-OCO₂Li species (Figure S31). cPAN

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exhibits a unique SEI formation behavior at the potential range from 0.1 to 0.01 V.

Figure 4 Mechanism of lithium-ion storage in cPAN. (a) CV curves of cPAN electrode without AB additive recorded at 0.05 mV s⁻¹. (b) FTIR spectra of cPAN. (c) Raman spectra of cPAN electrode. (d) ⁷Li MAS SS-NMR spectra of cPAN electrode discharged to 0.01 V.

The lithium storage mechanism of cPAN

The lithium storage in cPAN was further studied by ex situ XRD, FTIR, Raman, and NMR. To show the (de)lithiation in pure cPAN material, we tested the CV of pure cPAN electrode without AB additives at 0.05 mV s⁻¹. Besides the cathodic lithium intercalation peak around 0.01 V, two pairs of redox peaks (A1, C1; A2, C2) appeared between 0.5 to 2.0 V (Figure 4a). These two pairs of redox peaks are attributed to electron transfer of cPAN, which is similar to a carbonaceous anode obtained by carbonizing PAN at 550 °C.^[29] We further tested the ex situ FTIR of cPAN electrode. cPAN showed a blue-shift of the C=N peak from 1577 to 1592 cm⁻¹ when fully lithiated. The position of C=N peak recovered to 1581 cm⁻¹ after cPAN was delithiated to 3.0 V (Figure 4b). The variation of wavenumber of C=N peak is a direct evidence that pyridine nitrogen is involved in the (de)lithiation process, which is similar to pyridine nitrogen-doped amorphous carbon,^[41] and C=N bonds in some organic polymers.^[58] The bending vibration of C-H bond blue-shifted from 1365 cm⁻¹ to 1396 cm⁻¹ when cPAN was lithiated to 0.01 V, while recovered to 1375 cm⁻¹ when cPAN was delithiated to 3.0 V. The blue shift of peak of C-H bond suggests the lithiation of the hexagonal atom rings, which is similar to the lithiation of hexagonal carbon rings in polyimides.^[17] Both the D and G peaks blue shifted due to the lithiation process (Figure 4c), which could be attributed to electron doping^[59] and the increase of the force constants of the in-plane C-C bonds.^[60] The peak position does not recover to its original position, which suggests that some lithium ions could be irreversibly adsorbed in the cPAN matrix. Ex situ XRD peak shifted to a higher 2θ value and then shifted back upon lithiation

and delithiation (Figure S32), indicating reversible lithiation and delithiation behaviors of cPAN. Ex situ ⁷Li SS-NMR was used to probe the chemical environment of lithium species in lithiated cPAN (Figure 4d). The NMR spectra of lithiated cPAN was fitted into three components (A, B and C). Peak A is ascribed to the lithium ions in ionic state from SEI or electrolyte residue.^[61] Peak B is ascribed to the electrochemically adsorbed lithium ions in cPAN matrix.^[37] A small but visible peak C at a chemical shift of 18 ppm demonstrates the storage of Li⁺ in adjacent ladder structures of cPAN (LiC_x). The above results demonstrate that Li ions are stored on the active sites of pyridine nitrogen, hexagonal atom ring in lithiated cPAN.

First-principles calculations

Furthermore, we performed first-principles calculations to probe the active sites for Li storage and the associated charge reconstruction. First, we tested several possible adsorption sites by calculation of the adsorption energy, $E_a = E_{\text{total}} - E_{\text{cPAN}} - E_{\text{Li}}$, where E_{total} , E_{cPAN} , and E_{Li} are the total energies of Li-adsorbed cPAN, a cPAN molecule, and a Li atom. According to this definition, a more negative E_a denotes a more favorable site. We identified four stable sites for Li adsorption: Adsorption beside a pyridine nitrogen atom yielded the most negative E_a of -2.40 eV (Figure 5a), adsorption above the center of a hexagonal piperidine ring was less favorable ($E_a = -0.66$ eV, Figure S33a) than adsorption above the hexagonal carbon ring ($E_a = -1.00$ eV, Figure 5b), and adsorption beside a piperidine nitrogen atom yielded the least negative E_a of -0.40 eV (Figure 5c). Charge difference isosurfaces for Li adsorption on different sites of cPAN showed electron transfer from Li to cPAN (Figure 5d-i). In

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particular, the pyridine nitrogen atom strongly attracted electrons from the Li atom (Figure 5d, g). The electron transfers calculated by Bader analysis^[62] were 0.79, 0.85, 0.80, and 0.52 |e| for the hexagonal carbon ring, pyridine nitrogen atom, hexagonal piperidine ring, and piperidine nitrogen atom, respectively (Figure 5d-i and S33b-c), which reflects an ionic bond nature between the Li atom and cPAN skeleton. The fact that the pyridine nitrogen atom displays a much more negative E_a than the piperidine nitrogen atom, although they both possess one lone pair of electrons, can be understood as follows: The sp^2 hybridization of

the pyridine nitrogen atom results in formation of a π electron systems with the neighboring carbon atoms (Figure S34), which enables efficient charge transfer during lithiation of cPAN. In the case of the sp^3 -hybridized piperidine nitrogen atom, H atom weakens the ionic bonding with the Li atom. When 18 Li atoms were adsorbed on cPAN, we obtained a rather negative average E_a of -1.25 eV (Figure S35), which reflects high capacity of cPAN as LIB anode. Therefore, the pyridine nitrogen atom, hexagonal piperidine ring, and hexagonal carbon ring are active sites for efficient Li storage.

Figure 5 First-principles calculation results for Li adsorption on different sites of cPAN. (a-c) Optimized structures as well as (d-f) top and (g-i) side views of the charge difference (isovalue = $0.01 \text{ e}/\text{\AA}^3$) are shown for Li absorbed (a, d, and g) beside a pyridine nitrogen atom, (b, e, and f) above the center of the hexagonal carbon ring, and (c, f, and i) beside a piperidine amine group. White, green, black, and red spheres denote H, Li, C, and N atoms, respectively. Yellow and white isosurfaces denote accumulation and depletion of electrons, respectively. The amount of charge transfer obtained by Bader analysis and the adsorption energy are given.

Conclusion

In summary, we discovered that cPAN can be used as an anode in alkali metal-ion batteries. Experimental and computational studies demonstrate that Li^+ ions are reversibly adsorbed in cPAN matrix on the chemical structure of hexagonal carbon ring, piperidine ring, and pyridine nitrogen of the ladder cPAN formed in the cyclization process. After activation cycling, cPAN showed an ultrahigh capacity 1238 mAh g^{-1} , which accounts for a theoretical formula of $\text{Li}_{18}\text{C}_{24}\text{N}_6\text{H}_{20}$ with high lithium concentration. This high capacity outperforms the most well-studied carbonaceous and organic anodes. Furthermore, cPAN could be used as an anode in SIBs and PIBs, in which cPAN showed decent capacity, rate capability, and cycling stability. The discovery of cPAN could pave the way to future development of organic anodes for alkali metal ion batteries.

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Keywords: Lithium-ion battery • anode • polyacrylonitrile • carbon • pyridine • active site

Conflict of interest

The authors declare no conflict of interest.

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