In-situ electropolymerized bipolar organic cathode for stable and high-rate lithium-ion batteries

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ABSTRACT To address the dissolution issue and enhance the electrochemical performance of organic electrode materials, herein, a bipolar organic cathode was prepared by *in-situ* electropolymerization of amino-phenyl carbazole naphthalene diimide (APCNDI). APCNDI is composed of n-type 1,4,5,8-naphthalene tetracarboxylic diimide that stores Li cations and p-type carbazole groups which react with anions and serve as polymerization sites. Electropolymerization completely eliminated the dissolution problem of APCNDI, and the electropolymerized cathode demonstrated a bipolar reaction with excellent electrochemical performance, stable cycling performance with a capacity retention of 92 mA h g⁻¹ after 1000 cycles, and a superior rate performance of 72 mA h g⁻¹ at 10 A g⁻¹. The bipolar feature and reactions of APCNDI were systematically investigated and verified by multiple characterization techniques. Our findings provide a novel strategy for the design and fabrication of electrodes for high-performance organic batteries.

Keywords: lithium-ion battery, bipolar organic cathode, *in-situ* electropolymerization, polyimide, carbazole

INTRODUCTION

Redox-active organics have attracted significant research interest as promising electrode materials for lithium-ion batteries (LIBs) owing to their several merits including abundant resources of raw materials and structural versatility, which afford considerable potential for the development of sustainable batteries [1–3]. Unlike inorganic electrode materials that are prepared using limited mineral resources, redox-active organic materials are mainly fabricated employing unlimited resources such as C, H, N, and O [2,4–7]. Moreover, some organic compounds can be directly obtained from natural biomass *via* environmentally benign production methods [8]. From the viewpoint of molecular structure design, organic com-

pounds have diverse structures and can be functionalized with various groups. Therefore, organic compounds are promising candidates for electrode materials with high electrochemical performance including high specific capacity and high rate capability [2]. Additionally, organic materials have flexible structures and generally contain multiple active sites in one unit, which enable versatile storage reactions, particularly for beyond LIBs chemistries [2,9]. Clearly, organic materials offer a platform to realize novel battery technologies that may replace LIBs.

Organic electrode materials are mainly categorized into three types based on the redox reaction mechanism: n-type, p-type, and bipolar [10–13]. The n-type materials react with Li⁺ cations, and the positive charges are compensated by the uptake of the same number of electrons, leading to a reduction reaction. This n-type reaction generally results in high specific capacity at a low voltage (<3 V), which is not favorable for high-energy-density batteries [2]. Representative n-type materials are carbonyl organics [14,15], which are the most investigated organic electrode materials. For example, *p*-benzoquinone has a theoretical specific capacity of 496 mA h g⁻¹ [16], and Lu *et al.* [17] reported a cyclohexanhexone cathode material that exhibits a high capacity of 902 mA h g⁻¹. However, these organic molecules are highly soluble in organic liquid electrolytes, causing a fast capacity decay [16,17]. In contrast, p-type materials can accept anions and transform from neutral to positively charged states [18,19]. A p-type reaction typically occurs at a high voltage of >3 V and has fast reaction kinetics owing to the lack of desolvation that commonly takes place on the anode side. However, it often delivers a low capacity, which needs to be addressed for future applications of p-type materials. Contrarily, bipolar molecules contain both n- and p-type parts and can react with both cations and anions [20–23], which may exhibit the combined merits (namely, high

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capacity, high voltage, and fast kinetics) of both n- and p-type parts. They can be used as both cathode and anode depending on the potential level. Based on this concept, all-organic symmetric batteries have been developed using bipolar compounds [21]. However, the specific capacity of these batteries is low because only a single type of reaction occurs on each side, leading to limited energy density [21]. Recently, bipolar compounds were employed as cathode materials to achieve high energy density. Enhanced specific capacities were obtained with insufficient cycling stability [22,23].

Dissolution and insulating problems are intrinsic drawbacks of redox-active organic compounds [1,2,24]. Although many efforts have been made to overcome these issues, these problems still persist. Among the reported strategies, the use of polymers [25–29] is the most effective approach to address the dissolution issue; nevertheless, polymers suffer from severe aggregation during electrode preparation, thereby resulting in poor kinetics, incomplete reaction, and inferior electrochemical performance [19,27,28]. Completely utilizing the advantages of organic electrode materials is still a significant challenge. Recently, a novel preparation method, namely, *in-situ* electropolymerization has been reported for the fabrication of polymer electrodes [30,31]. Traditional methods of polymer electrode fabrication require pre-synthesized polymer materials, and it is difficult to realize uniform distribution of these materials and conductive agents. However, electropolymerization involves the use of small molecules, which can improve the dispersion of organic molecules in conductive agents [32–36]. Polymerization of organic molecules and charging of the battery occurred simultaneously, the dissolution problem was completely solved, and the battery exhibited exceptional performance with stable cycling ability and fast rate capability. This shows that *in-situ* electropolymerization is a quite promising method for the construction of high-performance Li-organic batteries.

Herein, a bipolar polymer cathode was fabricated by *in-situ* electropolymerization. Amino-phenyl carbazole naphthalene diimide (APCNDI) comprising p-type carbazole units and n-type 1,4,5,8-naphthalene tetracarboxylic diimide (NTCDI) units was employed as a small molecule precursor. The n-type units offer a high theoretical capacity of approximately 200 mA h g^{-1} , and the p-type units function as not only high-voltage reaction sites, but also polymerization agents to produce a polymer structure. *In-situ* electropolymerization of polymer cathode completely solved the dissolution problem, and the electropolymerized cathode demonstrates ex-

ceptional cycling stability and suitable reaction kinetics, thus delivering a high reversible capacity of 141 mA h g^{-1} at a current density of 0.1 A g^{-1} , an excellent rate performance of 72 mA h g^{-1} at a high rate of 10 A g^{-1} , and stable cycling performance over 1000 cycles with a capacity retention of 92 mA h g^{-1} . Results reveal that the p-type reaction enables the electropolymerization of the organic cathode, while severe dissolution problem persists when only the n-type reaction occurs.

EXPERIMENTAL SECTION

Materials

Carbazole (99%), Pd (containing 10 wt% charcoal, denoted as Pd/C, 99%), 4-fluoronitrobenzene (98%), and anhydrous potassium carbonate (K_2CO_3 , 99%) were purchased from Innochem Co., Ltd. 1,4,5,8-Naphthalene tetracarboxylic acid dianhydride (NTCDA, 99%), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98%), anhydrous ethanol (EtOH, 99.7%), anhydrous dimethyl sulfoxide (DMSO, 99.5%), and anhydrous *N,N*-dimethylformamide (DMF, 99.5%) were obtained from Energy Co., Ltd. Anhydrous methanol (MeOH, AR) was procured from Tianjin Komiou Chemical Reagent Co., Ltd. Graphene was purchased from Changzhou Sixth Element Technology Co., Ltd.

Synthesis

Synthesis of 9-(4-nitrophenyl)-9H-carbazole

Carbazole (1.67 g, 10 mmol), anhydrous K_2CO_3 (2.76 g, 20 mmol), and 4-fluoronitrobenzene (1.55 g, 11 mmol) were added to a 50-mL round-bottom flask. Then, 15 mL of anhydrous DMSO was added to the abovementioned solution followed by stirring for 20 min. Subsequently, the temperature was raised to 160°C . The reaction was performed under an inert atmosphere for 10 h, and then, the reaction mixture was cooled to room temperature and poured into 200 mL of ice water followed by stirring for 20 min. The crude product was washed with anhydrous MeOH and then filtered through membranes. The reaction yield was 96%. The obtained product was a yellowish crude powder. ^1H nuclear magnetic resonance (NMR) (400 MHz, CDCl_3 , 298 K) δ : 8.50 (t, 1 H), 8.48 (t, 1 H), 8.16 (t, 1 H), 8.14 (t, 1 H), 7.82 (t, 1 H), 7.81 (t, 1 H), 7.51–7.43 (m, 4 H), 7.37–7.33 (m, 2 H).

Synthesis of 4-(9H-carbazol-9-yl)aniline

Under an inert atmosphere, 9-(4-nitrophenyl)-9H-carbazole (0.72 g, 2.5 mmol) and 10% Pd/C (21 mg) were

added to a 50-mL round-bottom flask followed by the introduction of absolute ethanol (15 mL) and thorough stirring. Then, the reaction temperature was raised to 90°C. After the solvent was refluxed, 0.6 mL of anhydrous hydrazine hydrate was added to the reaction mixture to reduce the nitro group to the amino group. The reaction mixture was refluxed for 9 h and the hot reaction solution was filtered to remove Pd/C. Finally, the filtrate was subjected to rotary evaporation to remove the solvent. Consequently, a brown viscous liquid was acquired. The reaction yield was 94%. ^1H NMR (400 MHz, $\text{d}^6\text{-DMSO}$, 298 K) δ : 8.21 (d, 2 H), 7.40 (t, 2 H), 7.27–7.22 (m, 4 H), 7.19 (d, 2 H), 6.81 (d, 2 H), 5.43 (s, 2 H).

Synthesis of APCNDI

The abovementioned brown viscous liquid (0.61 g, 2.35 mmol) and excess NTCDA (0.29 g, 1.07 mmol) were added to a 50-mL round-bottom flask, followed by the introduction of 15 mL of DMF. The reaction temperature was raised to 160°C, and the mixture was refluxed for 16 h under an inert atmosphere. After the reaction mixture was cooled to room temperature, the acquired precipitate was washed with DMF, and suction filtration was conducted to obtain red powders. The reaction yield was 70%.

Characterization

Solid-state ^{13}C NMR spectra were recorded using a Bruker NMR spectrometer. Chemical shifts were reported in ppm relative to the internal standard tetramethylsilane for ^{13}C NMR. ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature. Chemical shifts for protons in all the spectra were referred to as the residual proton resonance of $\text{d}^6\text{-DMSO}$ (δ : 2.54 ppm) and deuterated chloroform (CDCl_3 , δ : 7.26 ppm). Morphologies and structures of the cathodes were investigated by scanning electron microscopy (SEM, S-4800 instrument). X-ray diffraction (XRD) patterns were acquired *via* Rigaku Ultima IV using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA). Fourier transform infrared (FTIR) spectra were recorded in the attenuated total reflectance mode in the range of 4000–400 cm^{-1} using a Bruker Alpha II FTIR spectrometer. Ultraviolet-visible spectroscopy (UV-vis, Shimadzu UV-3600 plus, Japan) and X-ray photoelectron spectroscopy (XPS, K-Alpha, UK) were conducted to analyze the chemical compositions of the pristine and cycled cathodes. The cycled cathodes used for characterization were washed with diethyl carbonate (DEC) and dried. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (STA

449F3 Instruments, Germany) at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere. Gaussian 09W program was used to conduct density functional theory (DFT) calculations. Geometric optimization was performed based on the theoretical level of B3LYP by standard gradient techniques, which employ 6-31+G(d) as the basic set.

Electrochemical measurements

APCNDI, graphene, and polyvinylidene fluoride binder were mixed at a weight ratio of 6:3:1, followed by the addition of a certain amount of *N*-methyl pyrrolidone solvent to form a slurry; subsequently, this slurry was coated on a carbon-coated aluminum foil. The resulting cathodes were dried in vacuum at 100°C for 12 h with a loading of 0.6–0.8 mg cm^{-2} . Coin-type cells were assembled in a vacuum glove box (O_2 and H_2O levels < 0.1 ppm) using lithium metal foil as the counter electrode, a polypropylene (PP) separator (Celgard 2500, LLC Corp., USA), and 1 mol L^{-1} lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and DEC as the electrolyte. Galvanostatic charging and discharging tests were conducted at voltage ranges of 1.5–4.4, 1.5–3.0, and 3.0–4.4 V using a Neware battery test system. Cyclic voltammetry (CV) measurements were performed employing Solartron Analytical 1400 (AMETEK, USA) at the scan rates of 0.05 and 0.1 mV s^{-1} . Rate performance was examined at different current densities ranging from 0.1 to 10 A g^{-1} . Electrochemical impedance spectroscopy (EIS) spectra were recorded using a frequency response analyzer (Solartron Analytical, 1400) coupled with an electrochemical interface (Solartron Analytical, 1470) at an amplitude of 5 mV and in the frequency range of 0.1–100,000 Hz.

RESULTS AND DISCUSSION

The procedure for the synthesis of APCNDI is illustrated in Schemes S1–S3 [37,38]. Herein, 9-(4-nitrophenyl)-9H-carbazole was generated by the Ullmann condensation reaction of carbazole and 4-fluoronitrobenzene. Then, 9-(4-nitrophenyl)-9H-carbazole was reduced to 4-(9H-carbazol-9-yl)aniline by hydrazine hydrate. Finally, APCNDI molecules were synthesized in an acceptable yield *via* a dehydration condensation reaction of 4-(9H-carbazol-9-yl)aniline and NTCDA. A single APCNDI molecule comprises four n-type carbonyl groups, which can reversibly store alkali metal cations and a couple of p-type carbazole groups that can adsorb anions (Fig. 1a). The chemical structure of APCNDI was confirmed by FTIR and solid-state ^{13}C NMR spectroscopies (Fig. S1).

Figure 1 (a) Molecular structure, (b) HOMO and LUMO energy levels, and (c) n-type and p-type reactions of APCNDI.

The characteristic peaks located at 1714 and 1670 cm^{-1} are ascribed to asymmetric and symmetric stretching vibration peaks of the carbonyl groups in NTCDI, respectively. The peak of the $-\text{C}-\text{N}$ bond in NTCDI appears at 1335 cm^{-1} , and the absorption peak at 1242 cm^{-1} is attributed to the stretching vibration of the $-\text{C}-\text{N}$ bond in the carbazole groups [38]. These characteristic peaks confirm the co-existence of carbonyl groups and two types of $\text{C}-\text{N}$ bonds in APCNDI. The ^{13}C NMR spectrum shows characteristic chemical shifts at 162 and 141 ppm corresponding to the C atoms in the carbonyl groups of NTCDI and in the $\text{C}-\text{N}$ bonds of the carbazole groups [39]. The absorption peaks in the UV-vis spectra are consistent with the results reported in the Ref. [38] (Fig. S2). The abovementioned results demonstrate the successful synthesis of APCNDI for electropolymerization. TGA was conducted to evaluate the stability of APCNDI. Results indicate that APCNDI is very stable at ambient temperature (Fig. S3). Morphology of APCNDI was examined by SEM, showing a flaky structure with randomly distributed sizes (Fig. S4a). XRD reveals a suitable crystalline structure of APCNDI (Fig. S4b).

Distributions of the highest occupied molecular orbital

(HOMO) and lowest unoccupied molecular orbital (LUMO) of APCNDI were evaluated by DFT calculations (Fig. 1b). The LUMO of APCNDI is mainly concentrated on the NTCDI part, and the HOMO is distributed on the carbazole groups, highlighting the bipolar feature of APCNDI. The completely separate distribution of HOMO and LUMO avoids their interference with each other during the n- and p-type reactions, ensuring high reactivity. The n- and p-type reactions have average voltages of approximately 2.4 and 4.0 V vs. Li^+/Li , respectively (Fig. 1c), implying that APCNDI would exhibit two voltage plateaus and a theoretical capacity of 143 mA h g^{-1} [40,41].

Solubility of APCNDI in the electrolyte was examined by immersing APCNDI in 1 mol L^{-1} LiPF_6 in a mixed solvent of EC and DEC with a volume ratio of 1:1 for six days. The soaked electrolyte was analyzed by FTIR and ^1H NMR (Fig. S5). No significant difference was observed between the pristine and soaked electrolytes, and no signal of APCNDI was detected in the FTIR and ^1H NMR spectra. These results show that APCNDI has poor solubility in the electrolyte, which can be attributed to the large molecular conjugated system and rigid molecular

structure of APCNDI. Organic electrode materials with poor solubility are preferred to achieve a stable cycling performance of the battery.

Electrochemical performance of APCNDI was investigated in coin-type cells. Initially, the cycling performance of APCNDI was examined in the 1.5–3.0 and 3.0–4.4 V voltage ranges, which correspond to single n-type and p-type reactions (Fig. 2), respectively. In the low-voltage range of 1.5–3.0 V, the galvanostatic charge/discharge curves show typical voltage plateaus at 2.6/2.2 V, respectively, which are consistent with the CV curves (Fig. S6a) and similar to those of the NTCDI electrodes (Fig. 2a) [40]. These results are associated with the reversible transformation between enol and carbonyl structures upon the insertion/extraction of lithium ions. The initial reversible capacity of APCNDI is approximately 70 mA h g^{-1} , close to half of the theoretical capacity (Fig. 2b), suggesting high activity of NTCDI in APCNDI. In the higher cycling voltage range of 3.0–4.4 V, a long charging plateau was obtained for the first cycle, which was attributed to the electropolymerization of APCNDI molecules under an electric field. For the second cycle, a sloping voltage plateau

centered at 4.0 V was acquired, which resulted from the p-type reaction based on the insertion/extraction of anions into/out of the carbazole groups, respectively (Fig. 2c, d) [41]. These results are also reflected in the CV curves (Fig. S6b) and show that APCNDI has bipolar electrochemical activity as a cathode material for LIBs. It is noted that low-voltage cycling suffers a fast capacity decay, and only 37 mA h g^{-1} capacity was retained after 500 cycles (Fig. 2b) due to the dissolution of lithiated APCNDI molecules (Fig. 2e, f) [42]. In contrast, the capacity of APCNDI gradually increased to a stable level at 3.0–4.4 V, indicating that no dissolution occurred owing to electropolymerization (Fig. 2d). Therefore, electropolymerization plays a key role in the cycling performance of APCNDI (Fig. 2g).

Dissolution behaviors of the APCNDI cathodes, separators, and electrolytes cycled at different voltages were also explored. The cells were first cycled at 1.5–3.0 and 1.5–4.4 V for 500 cycles, and then disassembled upon being charged/discharged to 3.0 V to retrieve the cycled samples. Fig. 3a, b show the images of the cycled separators. When the separator was cycled at 1.5–3.0 V, it turned dark green, implying that lithiated APCNDI se-

Figure 2 (a, c) Galvanostatic charge/discharge profiles of APCNDI cathode under different potential ranges at 1 A g^{-1} , and (b, d) cycling performance of APCNDI cathode under different potential ranges of (a, b) 1.5–3.0 V and (c, d) 3.0–4.4 V at 1 A g^{-1} . Schematic illustrations of the APCNDI cathode cycling in (e) 1.5–3.0 V, (f) 3.0–4.4 V, and (g) electrochemical polymerization reaction.

Figure 3 (a) Digital images of PP separators and (b) electrolytes soaked with APCNDI electrodes after 500 cycles at 1 A g^{-1} under different voltage windows. (c) UV-vis spectra, (d) FTIR spectra, and (e) SEM images of pristine and cycled APCNDI cathodes in different voltage ranges of 1.5–3.0 and 1.5–4.4 V. (f) Reaction of *in-situ* electropolymerization.

verely dissolved in the electrolyte. However, the separator cycled in the wider voltage range did not show any apparent change, suggesting no considerable dissolution of lithiated APCNDI. Furthermore, the cycled APCNDI cathodes were immersed in 2 mL of electrolyte for three days. The electrolyte soaked with the low-voltage cycled cathode turned pale pink, whereas the high-voltage cycled cathode remained colorless. Considering the red color of pristine APCNDI, the color variation of the separators shows that soluble products were generated during low-voltage cycling, whereas no such products were produced during high-voltage cycling. To eliminate the interference from the ester group, the cathodes cycled at 1.5–3.0 V were soaked in 2 mL of pure dimethoxyethane electrolyte. FTIR spectra of the soaking solution also indicated the dissolution of the discharge products (Fig. S7). The same phenomenon was revealed by the UV-vis spectra of the soaking electrolytes (Fig. 3c). In the spectrum of the low-voltage cycled electrolyte, characteristic absorption peaks for the π - π^* transition of aromatic amine, n - π^* transition of carbonyl groups, and the large conjugated system of the entire molecule were obtained at 238, 290, and 300–400 nm, respectively [38]. However, no absorption

peak was observed in the UV-vis spectrum of the high-voltage cycled electrolyte. These results manifest that high-voltage cycling can effectively avoid the dissolution of organic electrode materials because of the electropolymerization.

FTIR spectra of the pristine and cycled cathodes at different voltage ranges prove the occurrence of electropolymerization during high-voltage cycling (Fig. 3d). A peak at 745 cm^{-1} was observed in the FTIR spectra of the pristine and low-voltage-cycled cathodes, which corresponds to the out-of-plane C-H bending vibration of bis-substituted benzene [39]. Nevertheless, it is absent for the high-voltage cycled cathodes, showing that the benzene rings in the carbazole groups varied from bis-substituted to tri-substituted, confirming the occurrence of electropolymerization at high voltages. Stability of the APCNDI cathode was also verified by comparing the morphologies of the pristine and cycled cathodes *via* SEM (Fig. 3e and Fig. S8). The pristine and high-voltage cycled cathodes demonstrated similar morphologies, and APCNDI particles were clearly observed, indicative of improved stability of the APCNDI cathode. However, no active material apparently presented in the case of the

low-voltage cycled cathode because of the dissolution of the lithiated APCNDI molecules in the electrolyte. A schematic of the *in-situ* electropolymerization of APCNDI is shown in Fig. 3f. A cross-linked structure of APCNDI was formed during electropolymerization.

Kinetic evolution of the APCNDI cathode during cycling at different voltages was investigated by EIS. Fig. S9 shows the Nyquist plots of the APCNDI cathodes after different cycles and the fitting equivalent circuits, where R_s , R_f and R_{ct} represent the bulk resistance of the electrolyte, the electrode/electrolyte interphase resistance, and the charge transfer resistance, respectively. The fitted values are summarized in Tables S1 and S2. Similar impedances were observed during the initial 10 cycles; nevertheless, substantially smaller impedances were noticed after 100 cycles in the voltage range of 1.5–4.4 V compared with those in the voltage range of 1.5–3.0 V, indicating that the cathodes were effectively stabilized by electropolymerization.

Influences of the charge cut-off voltage on the electrochemical performance of APCNDI were investigated (Fig. S10). The discharge capacity gradually increased from 82 to 141 mA h g⁻¹ as the cut-off voltage raised from 4.0 to 4.7 V (Fig. S10a). With the variation of the charge cut-off voltage, no significant change was observed in the low-voltage plateau corresponding to the n-type reaction, whereas the capacity contribution by the high-voltage p-type reaction showed a gradual increase (Fig. S10b). These findings indicate that the n-type reaction is independent of the charge cut-off voltage, whereas a more complete p-type reaction occurs at a higher cut-off voltage (Fig. S10c, d). Coulombic efficiency of the APCNDI cathode significantly decreased as the cutoff voltage increased (Fig. S11a–d), which should be caused by the more severe decomposition of electrolyte at high voltages and led to poor cycling stability. SEM images of the cathodes cycled at different high cut-off voltages showed that the increase in the high cut-off voltage intensified the decomposition of the electrolyte (Fig. S11e, f).

Therefore, a mediate cut-off voltage of 4.4 V was used for the cycling performance test (Fig. 4). CV curves were acquired at a scan rate of 0.05 mV s⁻¹ (Fig. 4a). During the first cycle, an extremely strong and sharp anodic peak near 4.4 V and two small sharp peaks at 2.6 and 2.1 V for charge and discharge were observed, respectively. The strong sharp peak was attributed to the electropolymerization of APCNDI. All the abovementioned peaks disappeared during the second cycle, implying that they were associated with electropolymerization. After the first cycle, two redox bands were obtained at approxi-

mately 2.4 and 4.0 V, corresponding to the n- and p-type reactions. This finding is in appropriate agreement with the bipolar structural feature of APCNDI. Electropolymerization is also indicated by the presence of a long flat charge voltage plateau above 4.2 V in the charge/discharge profiles (Fig. 4b). From the second cycle onwards, no change was observed in the voltage profiles, suggesting suitable cycling stability of APCNDI. APCNDI delivered an initial reversible capacity of 118 mA h g⁻¹, which increased to 141 mA h g⁻¹ after 100 cycles due to the electropolymerization of APCNDI (Fig. 4c).

Rate performance of the electropolymerized cathode was examined at different current densities ranging from 0.1 to 10 A g⁻¹ after precycling at 0.1 A g⁻¹ (Fig. 4d). The electropolymerized cathode demonstrated an exceptional rate performance. Its initial discharge capacity was 139 mA h g⁻¹ with a coulombic efficiency of approximately 96% at 0.1 A g⁻¹. As the current density increased from 0.1 to 1 A g⁻¹, the discharge capacity slightly varied from 139 to 123 mA h g⁻¹. When the current density was up to 10 A g⁻¹, the capacity remained at 72 mA h g⁻¹. When the current density returned to 0.1 A g⁻¹, the specific discharge capacity recovered to 141 mA h g⁻¹, which demonstrated the electropolymerized cathode exhibited a better rate performance in the high-voltage range than that in the low-voltage range (Fig. S12). At all current densities, two plateaus were clearly observed, which agreed well with the bipolar feature of APCNDI (Fig. S13). At 5 A g⁻¹, a reversible capacity of 103 mA h g⁻¹ was achieved, and a capacity of 92 mA h g⁻¹ was retained after 1000 cycles with a high coulombic efficiency of approximately 100%. Moreover, the charge/discharge curves remained almost unchanged after 1000 cycles (Fig. 4e and Fig. S14), which indicates that APCNDI has outstanding cycling stability at high current densities. Additionally, APCNDI exhibited excellent rate capability and cycle life when compared with those of other bipolar electrode materials for LIBs (Fig. S15 and Table S3).

Reaction mechanism was investigated by *ex-situ* FTIR and XPS spectroscopies at different charge/discharge states (Fig. 5a–c). APCNDI and the conductive agent graphene showed distinct signals from 800 to 850 cm⁻¹ (Fig. S16), which overlapped with the characteristic peak of PF₆⁻ at 830 cm⁻¹ (Fig. S17a) [30,43]. To avoid the interference of graphene, lithium tetrafluoroborate (LiBF₄) was employed in the FTIR spectroscopy because of its characteristic infrared peak (766 cm⁻¹) and similar physicochemical properties as a charger carrier in different electrolytes (Fig. S17b). Strong characteristic peak of BF₄⁻

Figure 4 Electrochemical performance of APCNDI cathodes: (a) CV curves at 0.05 mV s^{-1} , (b) selected charge/discharge profiles, (c) cycling performance in the voltage range from 1.5–4.4 V at 0.1 A g^{-1} , (d) rate performance, and (e) long-term cycling performance at 5 A g^{-1} .

anions located at 766 cm^{-1} was clearly acquired at 4.4 V, but it became weaker at lower voltages and disappeared below 2.5 V, demonstrating the reversible p-type reaction of carbazole groups. Similarly, the peaks of the carbonyl groups at 770, 1714, and 1670 cm^{-1} and the peak of C–O–Li at 1380 cm^{-1} underwent a reversible variation during charge/discharge [44], indicative of the n-type reaction of the carbonyl groups (Fig. 5b). In the full survey XPS spectrum of the pristine APCNDI cathode, four peaks were obtained at 284, 400, 532, and 687 eV, corresponding to C 1s, N 1s, O 1s, and F 1s (Fig. S18). When the cathode was charged to 4.4 V, a new peak appeared at 400.5 eV in the N 1s spectrum, which was attributed to PF_6^- ; it became weaker at 3.0 V and disappeared at 1.5 V [30]. The F 1s spectra at different states also confirmed the adsorption of PF_6^- at high voltages (Fig. S19). This was accompanied by the appearance of the C–O–Li peak and the increase in the intensity of the carbonyl group peaks in the O 1s XPS spectra (Fig. 5c). These results are

well consistent with the FTIR results. Fig. 5d shows that a low platform originates from the reduction reaction of the n-type carbonyl groups, whereas a high platform derives from the oxidation reaction of the p-type carbazole groups, proving the bipolar electrochemical activity of APCNDI molecules. The electrochemical performance of APCNDI was investigated using different lithium salts, namely LiBF_4 , lithium perchlorate (LiClO_4), and lithium bis(fluorosulfonyl)imide (LiFSI). Results showed that LiPF_6 delivered the best performance (Fig. S20).

CONCLUSIONS

In summary, a bipolar organic cathode was constructed by *in-situ* electropolymerization using APCNDI, which is composed of an n-type NTCDI part that stores Li^+ and p-type carbazole groups which react with anions and serve as polymerization sites. Electropolymerization completely solved the dissolution issue of APCNDI, and the electropolymerized cathode demonstrated excellent electro-

Figure 5 (a) Galvanostatic charge/discharge profiles with marked points for FTIR and XPS tests. (b) FTIR spectra and (c) high-resolution N 1s and O 1s spectra of APCNDI cathode at different charge/discharge states marked in (a). (d) Mechanism illustration of the n- and p-type reactions of APCNDI.

chemical performance, with cycling stability of 1000 cycles and a superior rate performance of 72 mA h g^{-1} at 10 A g^{-1} . The bipolar feature and reactions of APCNDI were systematically investigated and verified by multiple analytical techniques. Our findings offer a new strategy for the design and fabrication of electrodes for high-performance organic batteries.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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原位电化学聚合方法制备稳定且高倍率的锂离子电池双极性有机正极材料

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摘要 为了解决有机电极材料的溶解问题并提高电化学性能, 本文通过原位电化学聚合的方法制备了双极性对氨基苯基咪唑萘二酞亚胺(APCNDI)有机正极材料. 该正极由能够储存锂离子的n型1,4,5,8-萘四甲酰基二酞亚胺基团和吸附阴离子的p型的咪唑基团组成, 其中咪唑基团同时可以充当电化学聚合反应位点. 由原位电化学聚合方法制备的该正极材料有效解决了有机材料在电解质中的溶解问题, 表现出双极性特征的氧化还原反应, 并具有出色的倍率性能和稳定的循环性能. 该有机正极材料循环1000次后的容量仍能保持为 92 mA h g^{-1} , 在 10 A g^{-1} 的大电流密度下比容量剩余 72 mA h g^{-1} . 同时, 通过多种表征手段对APCNDI正极材料的双极性特征和反应机理进行了系统的研究和验证. 该发现为发展高性能的有机电极材料提供了一种新颖的设计思路和制备方法.