

A polyimide cathode with superior stability and rate capability for lithium-ion batteries

Jianghui Zhao^{1,2}, Tuo Kang², Yanli Chu^{1,2}, Peng Chen², Feng Jin^{1,2}, Yanbin Shen^{1,2} (云), and Liwei Chen^{2,3} (云)

¹ School of Nano Technology and Nano Bionics, University of Science and Technology of China, Hefei 230026, China

² *i-Lab, CAS Center for Excellence in Nanoscience, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China* ³ *School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China*

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ABSTRACT

Organic-based electrode materials for lithium-ion batteries (LIBs) are promising due to their high theoretical capacity, structure versatility and environmental benignity. However, the poor intrinsic electric conductivity of most polymers results in slow reaction kinetics and hinders their application as electrode materials for LIBs. A binder-free self-supporting organic electrode with excellent redox kinetics is herein demonstrated via *in situ* polymerization of a uniform thin polyimide (PI) layer on a porous and highly conductive carbonized nanofiber (CNF) framework. The PI active material in the porous PI@CNF film has large physical contact area with both the CNF and the electrolyte thus obtains superior electronic and ionic conduction. As a result, the PI@CNF cathode exhibits a discharge capacity of 170 mAh·g⁻¹ at 1 C (175 mA·g⁻¹), remarkable rate-performance (70.5% of 0.5 C capacity can be obtained at a 100 C discharge rate), and superior cycling stability with 81.3% capacity retention after 1,000 cycles at 1 C. Last but not least, a four-electron transfer redox process of the PI polymer was realized for the first time thanks to the excellent redox kinetics of the PI@CNF electrode, showing a discharge capacity exceeding 300 mAh·g⁻¹ at a current of 175 mA·g⁻¹.

KEYWORDS

polyimide, carbonized nanofibers, organic electrode material, rate capability, lithium-ion batteries

1 Introduction

Lithium-ion batteries (LIBs) have played an essential role on energy storage for portable electronic devices in recent decades. However, the ever-growing energy storage demands, especially those driven by electrical vehicles and grid-scale storage of renewable electricity, have generated a great concern not only over the energy density and power density, but also the safety, cost, and sustainability of LIBs [1, 2]. Considering the elaborate preparation process, limited resource and environmental and safety issues of the conventional inorganic battery electrode materials, organic materials are intriguing alternatives for sustainable batteries [3, 4] because of the potentially low-cost, high safety, recyclability, design diversity of molecular structures, and high theoretical capacities due to low formula weight and capability of multiple electron transfer [5–8].

The development of organic compounds as electrode material actually started as early as that of the inorganic materials [9], but the progress is lagging behind due to the tremendous success of inorganic intercalation compounds in the late 1980's [10]. The main problem of most organic materials is their electronic insulating nature. This means that a large amount of conductive carbon (usually more than 30 wt.%) is normally required for the preparation of an organic electrode using the typical slurry coating method [11]. When the mass of the conductive carbon, the polymer binder and the Al current collector is considered, the practical energy density of organic electrodes is quite low [7]. Besides, uniform distribution and good physical contact of organic active materials and the conductive additive in the electrode is often difficult to achieve with the slurry

coating method, resulting in low utilization of the active material and poor rate performance [12].

Polyimide (PI), an important engineering plastic with excellent mechanical strength and outstanding thermal stability, belongs to the category of organic carbonyl compounds, which bear high theoretical capacity for storage of lithium ion [13, 14]. Li ions reversibly that absorb or desorb on oxygen atoms as the carbonyl groups are reduced or oxidized [15]. This process is also known as enolation [15, 16]. Theoretically, PI polymers with 1 mole of repeating units can react to 4 moles of Li ions, resulting in a theoretical capacity of ~ 400 mAh·g⁻¹. However, redox processes beyond two-electron transfer reaction have not been reported for PI electrodes in LIBs. It was predicated that four-electron redox process is nearly impossible to be realized reversibly because deep enolation would damage the molecular structure of PI materials [12, 15]. Furthermore, reaction kinetics of PI electrodes needs to be improved for practical considerations [17].

In this work, a free-standing PI electrode is prepared via *in situ* polymerization of PI on a carbonized nanofiber (CNF) framework. The CNF framework acts as both electronic conductive path and current collector. The resulting core-shell PI@CNF structure shows a uniform PI coating layer on the surface of the highly conductive CNF, and the free-standing film electrode remains porous. The core-shell structure of the three-dimensional (3D) PI@CNF and the porous structure of the electrode ensure that the PI polymer are well contacted with both the electronic and the ionic conductor, which is crucial to the practical application of organic materials. As a result, the PI@CNF cathode exhibits an initial discharge capacity

Address correspondence to Yanbin Shen, ybshen2017@sinano.ac.cn; Liwei Chen, lwchen2008@sinano.ac.cn



of 170 mAh·g⁻¹ and an 81.3% capacity retention after 1,000 cycles at a current density of 1 C. More importantly, the PI@CNF cathode shows remarkable rate-performance (70.5% of 0.5 C capacity can be obtained at a 100 C discharge rate).

2 Experimental

2.1 Synthesis of the poly(amic acid) (PAA) precursor

The PI active material was obtained by thermal imidization of a PAA precursor. To prepare the PAA precursor, firstly, p-phenylenediamine (Adamas) was dissolved in N,N-Dimethyl Formamide (DMF) (Sigma-Aldrich) solvent at a three-necked flask that immersed in an ice-water bath. The dissolution process was under mechanical stirring in nitrogen atmosphere. Afterwards, a stoichiometric amount of pyromellitic dianhydride (Alfa Aesar) was slowly added to the solution. Accompanied by the complete dissolution of the dianhydride, the viscosity of the solution mixture increased and the solution color changed to light green, indicating the formation of the PAA. The solution mixture was further stirred at 0 °C under nitrogen atmosphere for 4 h and the resulting PAA solution was then diluted with DMF to a concentration of 5 wt.% and refrigerated for future use.

2.2 Fabrication of CNF films

The CNF films were prepared via carbonization of a polyacrylonitrile (PAN) film that was made by electrospinning technique [18]. Firstly, 2 g of PAN (Sigma-Aldrich) were dissolved in 18 g of anhydrous DMF solvent under intensive stirring. Subsequently, the solution was loaded into a 10 mL syringe for electrospinning with an applied voltage of 10 kV, a receiving distance of 6 cm, and a flow rate of 0.6 mL·h⁻¹. The electrospun PAN films were first heated at 260 °C in air for 0.5 h for pre-oxidation, then further carbonized at 700, 800, 900, 1,000 or 1,100 °C for 3 h under N₂ atmosphere to obtain CNF films.

2.3 Fabrication of the PI@CNF electrodes

To obtain the PI@CNF electrodes, the CNF films were soaked into a 5 wt.% PAA/DMF solution for 6 min before taken out to obtain a PAA/DMF@CNF film. Then one side of the CNF film surfaces was wiped with a clean paper to secure electronic contact. The CNF films absorbed with PAA/DMF solution were dried under infrared radiation for 2 min to remove DMF, resulting in PAA@CNF films. For thermal imidization, PAA@CNF films were first dried at 100 °C for 30 min, and then heated at 300 °C for imidization under argon gas for 1 h. The free-standing PI@CNF electrode was thus obtained and the PI mass content is \sim 42 wt.%. The PI mass content can be increased by repeating the PAA soaking and thermal imidization process.

2.4 Cell assembly and testing

Coin-type cells (CR2025) were assembled using as-prepared PI@CNF films as the cathode. The mass loading of active material for the PI@CNF electrode that contains 42 wt.% PI was approximately 1 mg·cm⁻². The recipe for preparing a PI electrode by traditional slurry coating method is PI:acetylene black: PVDF = 42 wt.%:48 wt.%:10 wt.%. A porous polypropylene membrane (Celgard) was used as separator and lithium metal foil (China energy lithium Co., Ltd) was used as anode. 1 M LiTFSI in a solvent mixture of DOL/DME (1:1 v/v) was used as the electrolyte. All of the coin cells were assembled in an argon-filled glove box. Galvanostatic charge–discharge measurements were conducted on a battery test system (NEWARE, NEWARE technology Ltd. Shenzhen). The electrochemical impedance spectroscopy (EIS) measurements were conducted using a VMP300 electrochemical workstation (Bio-Logic) in a frequency range of 500 kHz to 50 mHz with an amplitude of 5 mV.

2.5 Characterization

The electrical conductivities of CNF film were measured using a 4-Point Probes Resistivity Measurement System (PROBES TECH RTS-5). Raman spectra were measured using a confocal micro-Raman system (Jobin-Yvon LabRam HR 800). The wettability of CNFs was measured using an optical contact angle meter (Dataphysics OCA20, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 spectrometer. Thermogravimetric (TG) test was performed from 20 to 800 °C using a Seiko TG/DTA 6300 instrument under N₂ protection at a heating rate of 5 °C·min⁻¹. The morphology of the CNF films and PI@CNF electrodes were characterized using a scanning electron microscope (SEM) (Hitachi S-4800) operated at 5 kV. Transmission electron microscopy (TEM) observations were carried out using a Tecnai G2 F20 S-TWIN at 200 kV.

3 Results and discussion

Figure 1(a) illustrates the preparation of PI@CNF electrodes. A porous CNF film was prepared by carbonization of an electrospun PAN nanofiber film. Then a PAA/DMF solution was added to the porous CNF film for adsorption of PAA on the CNFs. Note that the PAA/DMF solution on the back side of the CNF film was removed



Figure 1 (a) Schematic illustration of the preparation process for the PI@CNF electrode. (b) The D/G peak intensity ratio in Raman spectra and the electronic conductivity of CNF films carbonized at different temperatures. (c) Optical photographs of contact angle measurements showing a 1.5μ L DMF droplet absorbed by the CNF film. (d) FTIR spectra of PAA, PI and the PI@CNF electrode.

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to expose the surface for electronic conduction in coin cell assembly. The PAA in the CNF film was then thermally imidizated to PI by heating at 300 °C for 1 h, resulting in a porous PI@CNF electrode composed of core-shell nanofibers with a CNF core and a uniform PI shell layer. Chemical reactions involved during the preparation of PI was shown in Scheme S1 in the Electronic Supplementary Material (ESM). The electronic conductivity of the CNF film was important since CNFs acted as both the current collector and the electronic conduction path of the PI@CNF electrode. It was found that the electrical conductivity of the CNF films increased with the carbonization temperature, and the conductivity of the CNF film carbonized at 1,000 °C was as large as 10 S·cm⁻¹ (Fig. 1(b)). Raman spectroscopy was employed to reveal the structure of the CNFs and its correlation with the electrical conductivity [19]. As shown in Fig. S1 in the ESM, all Raman spectra showed two characteristic peaks at about 1,360 and 1,580 cm⁻¹, which are generally known as D and G peaks, respectively [20, 21]. The intensity of the D peak is related to the amount of the sp³ defects, and the G peak is a characteristic peak of highly ordered macroscopic graphite crystals and is associated with in-plane atomic displacement and had E_{2g} -symmetry [22]. As shown in Fig. 1(b), the intensity ratio of the D peak and G peak (I_D/I_G) of the CNF samples was found to decrease with the increase of the carbonization temperature $(I_D/I_G$ of the CNF films prepared at 700, 800, 900 and 1,000 °C are 1.23, 1.08, 1.00 and 0.97, respectively). This indicates that the degree of graphitization and thus the sp² conjugated carbon structure of the CNFs increases with the temperature. Thus the electrical conductivity of the CNF film is proportional to the degree of graphitization. The electrical conductivity of the CNF film carbonized at 1,100 °C was measured to be similar (8 S·cm⁻¹) to that at 1,000 °C (10 S·cm⁻¹). Therefore, CNF film carbonized at 1,000 °C was used for preparation of PI@CNF hereafter.

The solvent wettability of the CNF current collector is also important for the fabrication of the PI@CNF electrode, since it determines the loading and the uniformity of PI on the CNFs. As shown in Fig. 1(c), the wettability of a dense CNF film towards DMF solvent was measured and compared to that of a carbon nanotube (CNT) membrane made by vacuum filtration process. When a droplet of 1.5 μ L DMF contacted with the surface of the CNF film, the DMF was immediately absorbed by the CNF film. In contrast, an apparent contact angle of 22° was observed for the DMF droplet on the surface of the CNT membrane at the same measured condition (Fig. S2 in the ESM). More information about the wettability measurement is shown in Video ESM1. Apparently, the wettability of CNF film was superior to that of the CNT membrane and this was the reason that the CNF films was chosen as current collector instead of CNT membranes.

The transformation of the PAA to PI during thermal imidization was characterized by TG measurements and IR spectroscopy. Figure S3 in the ESM presented the mass loss of the PAA precursor when heated to 800 at a rate of 10 °C·min⁻¹. The PAA sample experienced a slow weight loss of 8 wt.% before 150 °C, which should be related to residual solvent evaporation. A sudden mass loss of 16 wt.% occurred at ~ 200 °C, indicating the dehydration cyclization of PAA to form PI [23]. Then the sample mass kept stable until 650 °C where the PI started to decompose, indicating outstanding thermal stability of the PI polymer [24]. The IR spectra of the PAA precursor, the PI powder imidizated from PAA, and the prepared PI@CNF film were shown in Fig. 1(d). Almost all of the characteristic peaks of the imide group (1,774 cm⁻¹ for C=O asymmetric stretching, 1,710 cm⁻¹ for C=O symmetric stretching, 1,348 cm⁻¹ for C-N asymmetric stretching and 718 cm⁻¹ for C=O bending) were found in the PI powder and the PI@CNF samples, while characteristic peaks of the PAA (3,320 cm⁻¹ for symmetric N-H stretching, and 1,653 cm⁻¹ for symmetric C=O stretching)

were not present in PI spectra, suggesting that the PAA absorbed on the CNF film had been completely converted to PI [25].

The morphologies of the CNF film carbonized at 1,000 °C and the corresponding PI@CNF electrode were inspected by SEM and TEM. As shown in Figs. 2(a) and 2(b), the CNF film is composed of large amounts of nanofibers with uniform diameters of around 250 nm, resulting in a 3D nanofiber network with large specific surface area [26]. Figures 2(d) and 2(f) showed that the 3D fiber network structure was maintained in the PI@CNF electrode, and the PI material uniformly wrapped around the CNF, resulting in a core-shell structure with a highly conductive CNF core and a uniform PI shell. The thickness of the PI coating layer is around 80-100 nm (Fig. 2(e)), corresponding to a weight content of 42% PI in the PI@CNF electrode and a mass loading of ~ 1 mg·cm⁻². Figures 2(c)and 2(f) showed that the addition of 1 mg·cm⁻² of PI led to no change in film thickness (the thickness of both of the CNF and the PI@C NF film are $\sim 45 \,\mu$ m), confirming that the PI is coated on the CNFs. Figures S4(a) and S4(b) in the ESM showed that further increase in PI content would lead to extra PI in the space amid the CNFs. The extra PI was not in direct contact with the CNF conductor network, and thus would not be utilized. Therefore, the sample with 42 wt.% of PI was used for further characterization.

The electrochemical performance of the PI@CNF electrode with 42 wt.% PI was measured using CR-2025-type coin cells in etherbased electrolyte with lithium metal foil as the anode. As shown in Fig. 3(a), the galvanostatic charge–discharge curves of the cell exhibit an average discharge voltage of ~ 2.10 V and charge voltage of ~ 2.34 V at a current density of 175 mA·g⁻¹. While the discharge/charge voltage profile exhibits a continuous slope without obvious plateau, the corresponding dQ/dV-V plots in Fig. 3(b) clearly show two pairs of redox peaks between 1.5–3.0 V. Two redox pairs appear at 1.95 V/2.11 V and 2.27 V/2.36 V (vs Li⁺/Li), respectively, indicating that the reversible redox process involves two steps that correspond to transfer of two electrons [15].

As shown in Scheme S2 in the ESM, the storage of Li⁺ in the PI is based on the reversible lithium enolation of carbonyl groups (C=O). Each repeating unit in PI has four C=O groups, therefore, one mole of PI repeating units can theoretically absorb four moles of Li⁺, resulting in a capacity of 370 mAh·g⁻¹ [12]. However, it is believed that only two carbonyl groups of the PI polymer can be lithium enolated, corresponding to a two-electron transfer process when the discharge voltage is cut off at 1.5 V (vs. Li⁺/Li) [27].

The theoretical capacity corresponding to the two-electron transfer of PI shall be approximately 185 mAh·g⁻¹. However, as shown in Fig. 3(a), the PI@CNF electrode showed a capacity of only 100 mAh·g⁻¹ at the initial cycle when discharged a current density of 175 mA·g⁻¹. Interestingly, the capacity kept increasing in the following cycles and arrived at ~ 170 mAh·g⁻¹ at the 40th cycle, which is closed to the theoretical capacity considering the relatively large discharge current



Figure 2 SEM and TEM images showing the morphology and cross section of the CNF film ((a), (b), (c)), and the morphology and cross section of the PI@CNF electrode with 42 wt.% PI polymer ((d),(e), (f)).



Figure 3 (a) The voltage profiles of the Li||PI@CNF cell at the 1st, 10th, 20th, 30th, 40th and 45th galvanostatic charge–discharge cycles at 1 C-rate in an etherbased electrolyte. (b) The corresponding dQ/dV-V plot at the 1st, 10th, 20th, 30th and 40th galvanostatic charge–discharge cycles from (a). (c) The long-term cycling performance of the Li||PI@CNF cell at 1 C-rate. The inset image shows the reversible lithium enolation process of the PI polymer based on a two-electron transfer process.

density. Moreover, the polarization between the charge and discharge profiles gradually decreased with cycling and stabilized at the 40th cycle, indicating improvements in reaction kinetics in the first 40 cycles (Fig. 3(a)). Therefore, we take the first 40 cycles as an activation process of the PI@CNF electrode, which will be analyzed in the next section.

After the activation process, the PI@CNF electrode exhibited impressive long-term cycling stability. As shown in Fig. 3(c), take the largest capacity of 170 mAh·g⁻¹ at the 40th cycle as the initial capacity, the PI@CNF electrode has a capacity retention of 81.3% and 62% after 1,000 and 2,500 cycles at 1 C, respectively. The evolution of the voltage profile during cycling can be found in Fig. S5 in the ESM. A control Li||CNF cell was also assembled and discharged/charged at the same condition to measure the capacity of the CNFs. As shown in Fig. S6 in the ESM, the capacity contributed by CNFs is negligible.

As shown in Fig. 4(a), the PI coating layer on the conductive CNF looks dense and smooth before cycling, indicating that only the surface layer of the PI has direct contact with the electrolyte. This means that although the PI layer is around 80–100 nm thick, only the surface part of the PI polymer is involved in the lithium enolation process. Therefore, the specific capacity is relatively small and the polarization is large at the initial cycle. As the cycling goes on, the morphology of the PI layer changes from dense and smooth (Fig. 4(a)) to wrinkled and rough (Figs. 4(b) and 4(c)), resulting in larger PI polymer surface area. Since the newly formed PI surface area for Li⁺ to participate in the redox process thus the PI material utilization and the reaction kinetic are improved in the activation process.

As shown in Fig. 3(a), the discharge capacity at the 40^{th} cycle reaches 170 mAh·g⁻¹, which is very close to the theoretical capacity of 185 mAh·g⁻¹ considering the relatively large discharged current, therefore, we can assume that almost all of the PI material are utilized after the initial activation process. Furthermore, improved reaction kinetics is confirmed in the voltage profile shown in Fig. 3(a), where the polarization between the discharge and charge profiles becomes smaller in the activation process and then keeps relatively stable after the 40^{th} cycle. Therefore, the increase of the specific capacity at the activation process could be related to the increase of the direct

contact surface area of the PI polymer to the electrolyte.

EIS spectra was measured and the results corroborated the evolution of the reaction kinetics of the cell. As shown in Fig. 4(d), the Nyquist plots is composed of a semi-circle at high-intermediate frequency and a sloping line at low frequency [28]. The diameter of the semi-circle reflects the resistance for the Li⁺ migration at the PI film and the charge transfer of the redox process at both the cathode and the anode. It is difficult to separate the resistance for the cathode and the anode from Fig. 4(d), but it is clear that the overall resistance for the redox process becomes smaller during activation, gradually decreases from ~ 34 to ~ 20 Ω , and then stabilizes after the 40th cycles. Besides, the overall resistance increases with the cycle matching well with the voltage profile and the morphology evolution of the Li||PI@CNF cell. These results indicate that both the capacity and reaction kinetics experience an activation process at the early state of cycling.

Figure 4(e) shows that the morphology observed at the 100^{th} cycle looks similar to that observed at the 40^{th} cycle, which indicates that the new morphology generated during the activation process is relatively stable. This also explains why the Li||PI@CNF cell has good cyclic stability. However, as shown in Fig. 4(f), the PI material gradually falls off from the CNF upon long-term cycling. Most of the wrinkled PI polymer has disappeared at the end of the 2,500th cycle. Therefore, the loss of the active PI material shall be an important factor contributing to the capacity decay of the Li||PI@CNF cell. EIS results in Fig. S7(b) in the ESM also show that the resistance of the Li||PI@CNF cell becomes larger in long-term cycling probably due to smaller reaction interface when less PI remains active.

Considering the large contact area between the PI material and the electronic/ionic conductor, good rate capability is expected for this PI@CNF electrode. As shown in Fig. 5(a), rate capability up to 100 C of the LilPI@CNF cell is evaluated after the activation process (cycling for 50 cycles at 1 C). The discharge capacity at 0.5, 1, 5, 10, 20, 30, 50, and 100 C are 175, 170, 168, 166, 162, 153, 146, 110, 132, 123 mAh·g⁻¹, respectively, corresponding to a capacity retention of 100%, 98.0%, 96.4%, 95.1%, 93.0%, 87.3%, 83.8%, 80.0%, 75.8% and 70.5% of that at 0.5 C. Importantly, the higher capacity at a lower discharge rate, i.e. 5 C, are recovered after the rate capability measurement. To the best of our knowledge, this rate capability of PI@CNF electrode is ranked among the bests of organic electrodes that have ever been reported (Table S1 in the ESM). Furthermore, a slurry coated PI electrode with the same PI content as that of the PI@CNF electrode showed only 68 mAh g⁻¹ at the initial cycle when discharged at a current density of 175 mA·g⁻¹ between 1.5 and 3.0 V and had a capacity retention of 88.3% after 300 cycles at 1 C (Fig. S6(c) in the ESM). Besides, the rate performance of the PI electrode was also measured and the discharge capacity at 0.5, 1, 5, 10, 20 and 30 C are 82.6, 72.2, 57.3, 46.4, 31.5, 13.7, 9.8, 8.8 mAh·g⁻¹, respectively,



Figure 4 SEM images showing the morphology of the PI@CNF electrodes that are (a) fresh and after (b) 20, (c) 40, (e) 100, and (f) 2,500 cycles between 1.5 and 3.0 V. (d) Nyquist plots for the Li||PI@CNF cell at different cycles under 1 C rate.



Figure 5 (a) Rate performance of the Li||PI@CNF cell measured after activation (50 cycles at 0.5 C). (b) The corresponding voltage profiles of the Li||PI@CNF cell measured at different C-rates.

which is much worse compared to the PI@CNF electrode (Fig. S6(d) in the ESM). These results indicated that the PI utilization is really low and the reaction kinetic of the redox process is also limited, and further verified that the design of core-shell PI@CNF structure is critically important to the utilization and the rate capability of organic materials.

Impressively, as shown in the voltage profiles measured at various current densities (Fig. 5(b)), the polarization of the first redox pair keeps nearly a constant from 0.5 to 100 C, suggesting very fast reaction kinetics for the first electron transfer process. Considering the electrical insulating properties of the PI material, this fast reaction kinetic can be mostly attributed to the structure design of the core shell PI@CNF in the porous electrode.

Figure S8 in the ESM compares the specific discharged capacity and the rate performance of PI@CNF electrodes with different PI contents. At 51 wt.% of PI, the PI@CNF electrode delivers a lower specific capacity of 149 mAh·g⁻¹ at 1 C rate, and the capacity retention is 45.7% at 50 C. At 60 wt.% of PI, the initial specific capacity further declines to 121.0 mAh·g⁻¹ at 1 C and the capacity retention is only 16.9% at 50 C. These results show that the porous structure of the PI@CNF electrode and the high specific contact area between the PI and the electrolyte are important for electrochemical performance. When too much PI material is loaded to the CNF film, the electrode becomes less porous. Consequently, the material utilization and the rate capability become less pronounced.

Last but not least, the PI@CNF electrode reported above can even realize a four-electron transfer process, which was previously considered unrealistic because it was thought to lead to serious structural damage [29]. As shown in Figs. 6(a) and 6(b), when the cut-off discharge voltage is changed to 1 V, the discharge capacity exceeds 300 mAh·g⁻¹ at a current of 175 mA·g⁻¹, corresponding to more than 3 electrons in the redox process. Even though the capacity



Figure 6 The reversible four-electron process realized at 1 V discharge cut-off. (a) cycling performance and (b) evolution of the voltage profile of the Li||PI@CNF cells. ((c), (d)) SEM image of the PI@CNF electrode after 200 cycles between 1 and 3 V.

decay in this case is faster than that cycled between 1.5 and 3.0 V, the result is still important since it is the first example demonstrating the possibility of high specific capacity PI material [12]. In order to make sure that the cycling capacity in 1-3 V is only contributed by the PI polymer instead of the CNFs, a control Li||CNF cell was assembled and discharged/charged at the same condition. As shown in Fig. S9 in the ESM, the initial discharge capacity is 23 and 12 mAh·g⁻¹ as observed at the 10th cycle. So, capacity contribution of the CNFs in this voltage range is negligible. Interestingly, the morphology of the PI polymer layer on the PI@CNF electrode after cycling at 1.0 and 3 V (Figs. 6(c) and 6(d)) is distinctively different from that cycled between 1.5 and 3 V. The different morphology evolution of PI polymer at different discharge depth may arise from different stress and configuration of the polymer chain. Besides, the IR spectra of the fresh PI@CNF electrode and the PI@CNF electrode discharged to 1 V after the activation process were also measured. As shown in Fig. S10 in the ESM, after discharged to 1 V, the characteristic peaks of C=O (1,774 cm⁻¹ for asymmetric stretching, 1,710 cm⁻¹ for symmetric stretching) of the fresh PI sample disappeared; instead peaks corresponding to N-C-O...Li (1,650 cm⁻¹ for asymmetric stretching vibration) showed up [30], suggesting that all the four carbonyl groups in the PI had been enolated when discharged to 1 V.

4 Conclusions

In summary, we demonstrated a binder free self-supporting PI@CNF electrode with a CNF core and PI coating shell. The CNF framework acts as both highly electronic conductive pathway and current collector. The core-shell PI@CNF structure and the porous structure of the electrode ensure that the PI has very large direct contact area with both electronic and ionic conducting pathway, which is especially important to the stability and the rate capability of organic materials. As a result, the PI@CNF electrode exhibits excellent rate capability and superior cycle performance. Furthermore, the reversible four-electron transfer reaction process of the PI polymer is also realized. We believe the PI@CNF electrode is promising for the application of organic electrode material and inspirational for the electrode design of electronically insulating materials.

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Electronic Supplementary Material: Supplementary material (further details of the preparation of dense CNF films and CNT membranes, the formation of PI, the Raman spectra and wettability measurements of the CNT membrane, TG measurement of the PAA powder, SEM images of the PI@CNF electrode with higher PI content, four-electron redox process scheme and theoretical capacity calculation of the PI, voltage profile evolution of the PI@CNF electrodes, capacity measurements of the Li||CNF cell in 1.5–3 V and 1–3 V, EIS results of the PI@CNF electrode after long cycling, rate performance of PI@CNF electrodes with different PI content, rate performance comparison of the PI@CNF electrode with reported results, and Supplemental Video 1) is available in the online version of this article at https://doi.org/10.1007/s12274-019-2306-y.

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