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Short Communication

p-Dopable Poly(4-nitro)triphenylamine as Cathode Material with High Discharge Voltage for Lithium Ion Batteries

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p-Dopable poly(4-nitro)triphenylamine was prepared by a chemical oxidative polymerization and grafted an electron-withdrawing nitro group onto triphenylamine chains to enhance the redox potential. The electrochemical tests revealed that the polymer exhibits a high potential capability of 3.95 V (*vs.* Li^+/Li) with a reversible capacity of 72 mAh g^{-1} at the current density of 40 mA g^{-1} and remains 63 mAh g^{-1} at a high current density of 320 mA g^{-1}. In addition, the polymer was low cost and easily made, possibly serving as a high-rate charge/discharge and high potential polymer cathode for lithium ion batteries.

Keywords: Poly(4-nitro)triphenylamine; Cathode material; Lithium ion batteries; High voltage; Electrochemical performances

1. INTRODUCTION

Lithium ion batteries with high energy density and excellent cycle life are in growing demand for future large-scale electric storage applications, such as electric vehicles and renewable power stations [1-5]. Compared with the anode materials, it is more challenging to design cathode materials [6]. However, the present commercialized Li-ion batteries use scarce transition metal oxide cathodes [7-10], such as cobalt, manganese and nickel compounds, which are difficult to meet the requirements of large-scale electric storage applications due to their limited theoretical capacities, the unrenewable mineral resources and relatively high cost. Hence, many efforts have been devoted to searching for inexpensive, environmentally-benign and sustainable cathode materials in recent years. To this end, researchers have investigated a vast variety of redox-active organic materials as electro-active cathode, such as polyaniline, polythiophene, polyimide [11, 12], organosulfur compounds [13] and stable radical polymers [14, 15]. Among the redox-active polymer, polytriphenylamine (PTPAn) exhibits high specific capacity, superior rate capability and long cycle life. However, the average discharge voltage of PTPAn is 3.8 V, which is not high enough. We try to substitute electron - drawing groups on the 4 positions of the triphenylamine so as to adjust the electronic properties of the PTPAn and increase the discharge voltage of the polymer. We found by using poly(4-nitro)triphenylamine as cathode materials, the polymer was capable of being reversibly p-doped and dedoped to release high electric capacity at quite positive potential. Base on this result, we herein report the high-rate charge/discharge properties of poly(4-nitro)triphenylamine as cathode material for rechargeable lithium ion batteries and discuss the possible mechanisms of the polymer.

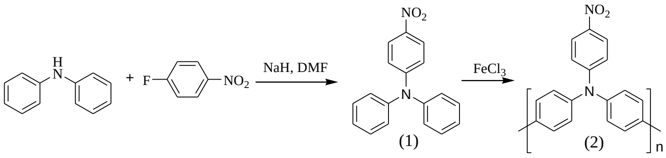
2. EXPERIMENTAL

2.1 Material synthesis of 4-nitrotriphenylamine and poly(4-nitro)triphenylamine

The poly(4-nitro)triphenylamine powder was prepared according to previous reported literature [16, 17]. The synthetic route is shown in Scheme 1. 0.27 g (11.25 mmol) of sodium hydride and 25 mL of Dimethylformamide (DMF) were mixed and stirred at room temperature for 15 min. Then, 1.7 g (10 mmol) diphenylamine and 1.24 g (10.25 mmol) of 4-fluoronitrobenzene were added into the mixture in sequence. The mixture was heated with stirring at 140 ^{o}C for 15 h under nitrogen and then precipitated into 150 mL of ice water. The products were filtered and recrystallized in methanol dried in vacuum at 60 ^{o}C for 12 h to give 1.5 g (56% in yield) of orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.948-7.979 (d, 2 H), 7.271-7.322 (t, 4 H), 7.122-7.187 (m, 6 H), 6.835-7.097 (d, 2 H). (See ESI, Figure S1)

The as-prepared 4-nitrotriphenylamine (0.54 g, 2.0 mmol), $FeCl_3$ (0.81 g, 5.0 mmol), and nitrobenzene (4 mL) were placed in a flask under nitrogen. The solution was stirred at room temperature for 18 h and poured into a mixture of methanol containing 10% hydrochloric acid. The precipitate was collected and washed thoroughly with ammonium hydroxide aqueous solution. Precipitations from chloroform into methanol were carried out twice for further purification to afford the polymer 502 mg (93% in yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08-8.13 (d, 4 H), 7.58-7.64 (d, 2 H), 7.18-7.54 (d, 4 H), 7.087-7.165 (d, 2 H). (See ESI, Figure S2)

All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Solvents were dried and distilled according to standard procedures.



Scheme 1. Synthetic route of poly(4- nitro)triphenylamine.

2.2 Structural characterizations

The FT-IR spectra of poly(4-nitro)triphenylamine were recorded on a NICOLET AVATAR360 FT-IR spectrometer with KBr pellets. The morphology of poly(4-nitro)triphenylamine powder was examined by scanning electron microscopy (SEM) on a Sirion2000 machine (Holland). ^{1}H NMR spectra of poly(4-nitro) triphenylamine were recorded on a Mercury VX-300 (300 MHz) spectrometer with tetramethylsilane (TMS) as internal standard and $CDCl_3$ as solvent.

2.3 Electrochemical measurements

Cyclic voltammetry (CV) was performed with a powder microelectrode using a two-electrode cell, a larger lithium sheet served as both counter electrode and reference electrode. The CVs were recorded using a CHI 660A electrochemical workstation (Shanghai, China). The poly(4-nitro) triphenylamine electrode film consisted of 70% poly(4-nitro)triphenylamine powder, 20% acetylene black, 10% PTFE (wt.%) and prepared by roll-pressing method. The mixture was pressed into a thick film and then pressed the film on aluminum net. The charge-discharge measurements were carried out using 2016 type coin cells. The cells were assembled in an argon-filled glove box, using a Li metal disc as the negative electrode, separated by a Whatman GF/D borosilicate glass fiber sheet saturated with 1M $LiPF_6$ in Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Ethyl Methyl Carbonate (EMC) (1:1:1 v/v/v, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd., China) as the electrolyte. The charge-discharge experiments were executed using a programmable computer-controlled battery charger (LAND CT2001A, Wuhan, China).

3. RESULTS AND DISCUSSION

As displayed in Fig. 1a, the poly(4-nitro)triphenylamine polymer appeared as particle with a coralloid surface. That is possibly ascribed to the twisting and folding of the polymer chains themselves, which may provide sufficient surface area and ionic channels for polymeric electrode reactions. Fig. 1b shown the FT-IR spectrum of the poly(4-nitro)triphenylamine samples. Compared with typical IR spectrum of 4-nitrotriphenylamine monomer, the main vibration bands characteristic of the polymer are attributed to the $–NO_2$ stretching at 1315 cm^{-1}, C–C ring stretching at 1585 cm^{-1}, C–C stretching at 1490 cm^{-1} and C–H bending at 1177cm^{-1}. The C–N stretching from tertiaryamine and a C–H out-of-plane vibration from 1, 4-disubstituted benzene rings are shown clearly at the right wave numbers of 1267 cm^{-1} and 815 cm^{-1}, respectively. A new band appeared at 1109 cm^{-1} is corresponding to quinoid structures formed after polymerization of 4-nitrotriphenylamine. All the IR features in Fig. 1b suggested a highly cross-linked structure of the poly (4-nitro)triphenylamine polymer.

Fig. 2 shown the cyclic voltammograms of the poly(4-nitro)triphenylamine electrode in 1 mol dm^{-3} LiPF$_6$+ EC/DMC/EMC (v/v/v 1:1:1) electrolyte, measured at a scan rate 10 mV s^{-1}. It exhibits a pair of reproducible anodic and cathodic peaks at 3.93 V and 3.85 V (*vs*. Li$^+$/Li), respectively, and the CV curves display almost the same peak areas, indicating that the electrochemical redox reactions of this polymer electrode were highly reversible and kinetically very fast. After successive scans of 50 cycles, the CV curves only slightly changed, showing excellent electrochemical reversibility and cycling stability.

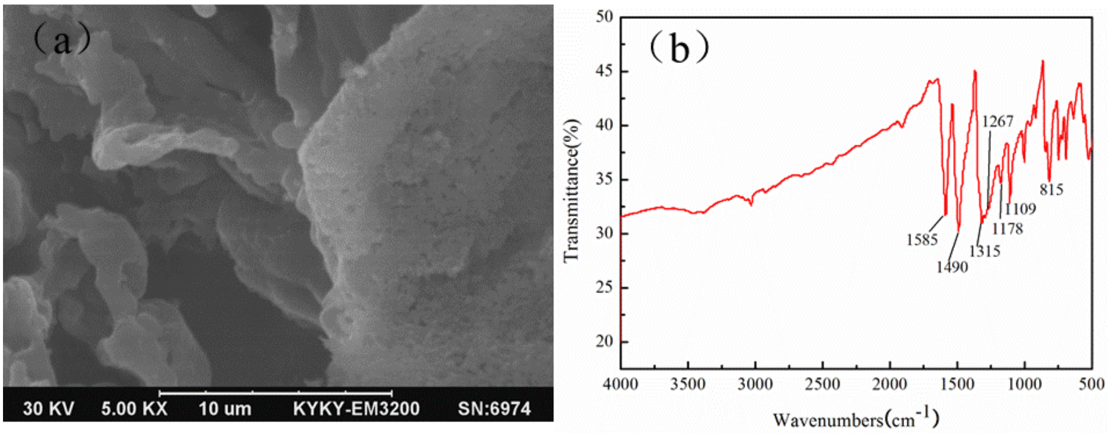


Figure 1. The SEM images of the poly(4-nitro)triphenylamine (a), and the FT-IR spectrum of the poly(4-nitro)triphenylamine (b).

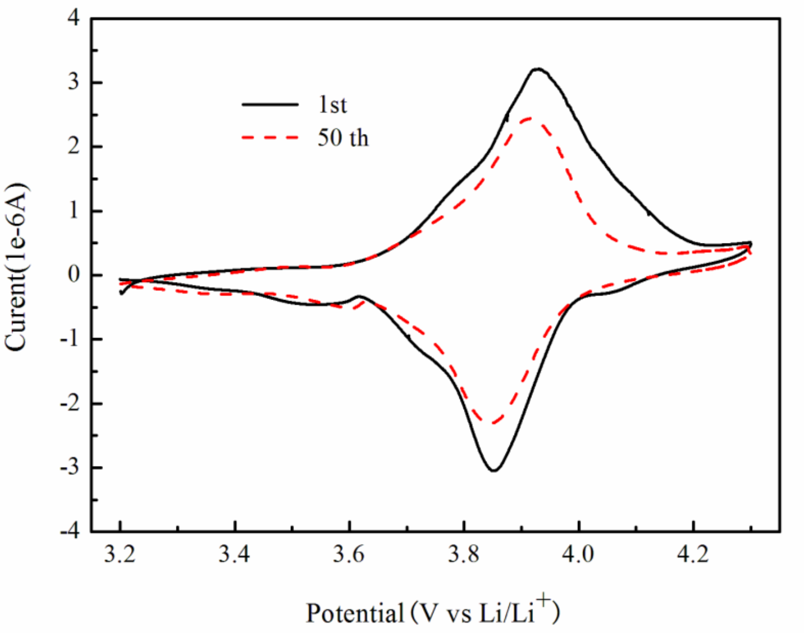


Figure 2. The CV curves of the poly(4-nitro)triphenylamine electrode.

Charge and discharge curves of the poly(4-nitro)triphenylamine electrode in the potential range of 3.0 and 4.2 V at the current density of 40 mA g^{-1} are shown in Fig. 3a. It can be seen that the polymer electrode could deliver a reversible capacity of ~72 mAh g^{-1} with a high Coulombic efficiency except the first cycle. The typical charge-discharge voltage plateaus emerged at 3.95 V, which are also in accord with the oxidation and reduction potentials of the polymer in the CV curves. Even after 90 cycles, the polymer electrode can still keep its capacity steadily without much degradation, demonstrating an excellent cycling stability. Furthermore, in comparison with the PTPAn, the poly(4-nitro)triphenylamine exhibits a ~150 mV higher potential, demonstrating an effective electrochemical activation of the polymer by introducing the electron-withdrawing nitro-groups on the TPA chains. The electrochemical activation of the polymer electrodes can also be visualized from the rate capability as illustrated in Fig. 3b. As seen, the polymer electrode showed a strong rate capability with its reversible capacity from 73 mAh g^{-1} at 40 mA g^{-1} slightly decreased to 63 mAh g^{-1} at 320 mA g^{-1}. More importantly, the polymer showed relatively stable cycling performance and high capacity at step-wise current rates.

Based on the aforementioned results, we can infer the working mechanism occurring on the poly(4-nitro)triphenylamine. In this high potential range, the redox reaction of the polymer must proceed through a p-doping/dedoping mechanism, in which the oxidation and reduction of the polymer occur with insertion and deinsertion of the electrolyte anions (PF_6^-) into/from the polymer chains.

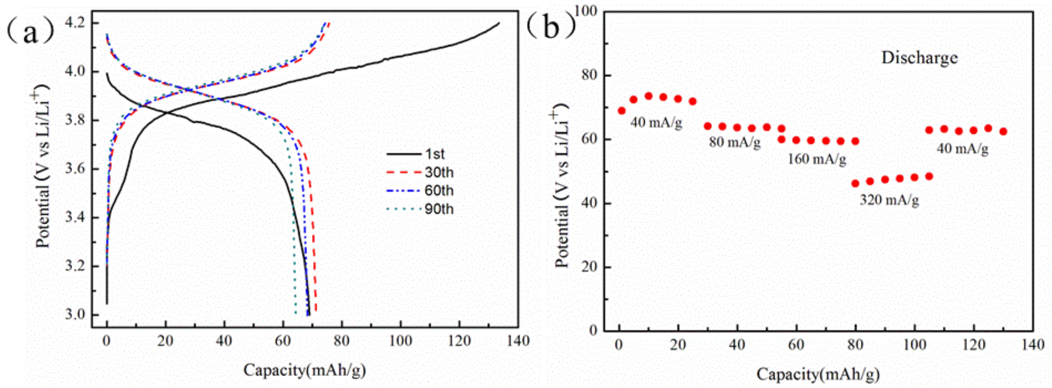


Figure 3. The charge/discharge profiles of the poly(4-nitro)triphenylamine electrode (a) and the evolution of discharge capacity at different current rates as labeled (b).

4. CONCLUSIONS

In summary, the p-dopable poly(4-nitro)triphenylamine was prepared by a simple chemical oxidative route and investigated as a polymeric cathode material for Li-ion batteries. By introducing the electron-withdrawing -nitro groups onto the triphenylamine chains, the polymer demonstrates a high redox potential with the capacity of ~72 mAh g^{-1} at the current density of 40 mA g^{-1} and remains 63 mAh g^{-1} at a high current density of 320 mA g^{-1}, which can possibly serve as a high-redox potential and high-rate cathode materials for Li-ion batteries.

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

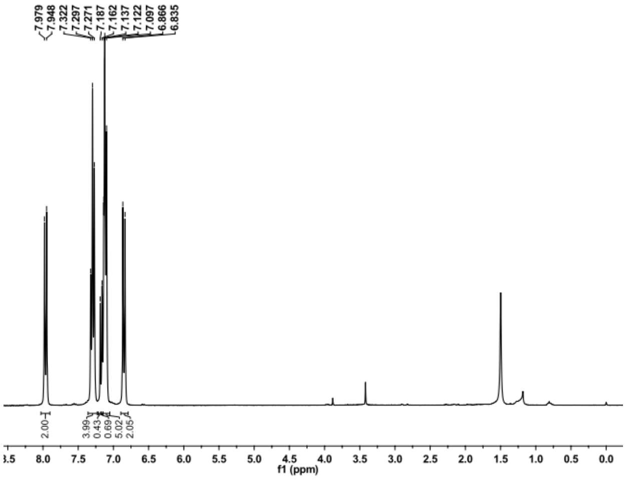

Figure S1. The NMR spectra of the 4-nitrotriphenylamine samples.

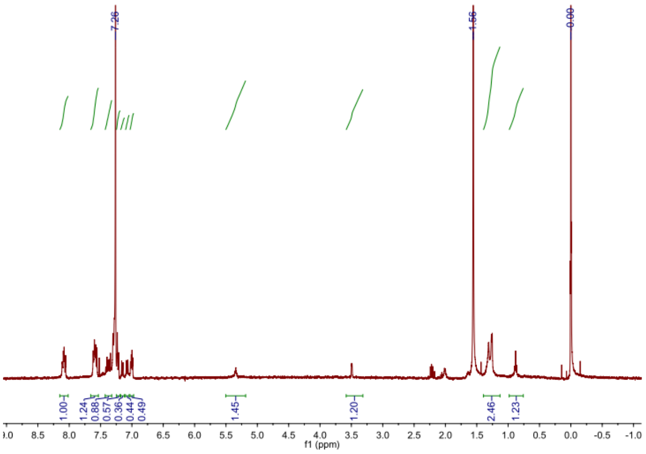

Figure S2. The NMR spectra of the poly(4- nitro)triphenylamine samples.

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