



Organic polytriphenylamine derivative-based cathode with tailored potential and its electrochemical performances



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ABSTRACT

In this work, the triphenylamine derivatives with the different electron donating/with-drawing groups, such as 4-(diphenylamino)benzotrile (TPA-CN), 4-methyltriphenylamine (TPA-CH₃) and 4-methoxytriphenylamine (TPA-OCH₃) were successfully synthesized, and the corresponding polymers were then prepared by chemical oxidative polymerization. The chemical structure, morphology and charge-discharge performance of the prepared polymers as the cathodes were characterized by fourier transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (UV-vis), scanning electron microscopy (SEM), cycling voltammograms (CV) and galvanostatic charge-discharge testing, respectively. The results showed that the different electronic effect groups affected obviously the redox potential of polytriphenylamine, in which the electron with-drawing group improved the potential plateaus of the polytriphenylamine, while the electron donating groups generally led to the opposite results. And specially, the introduction of —CN group as the electron with-drawing group into polytriphenylamine obviously improved the potential plateaus of the lithium ion battery from 3.6 V of PTPAn to 3.8 V of PTPA-CN. The explored work would provide a valuable reference for preparing the organic cathode materials with the high redox potential by the molecular design method.

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1. Introduction

With the development of the society, the growing demands for electronic products such as electric vehicles (EVs), laptop computers, and mobile phones have made it essential for the fabrication of the new rechargeable batteries with excellent properties. Among various types of rechargeable batteries, lithium-ion batteries are the most popular and powerful rechargeable batteries, owing to their convenient and good charge-discharge capacity. However, the currently available lithium battery technologies cannot satisfy the increasing demands for high energy density. At present, the lithium ion battery cathode materials are mostly transition-metal materials (such as LiCoO₂, LiMnO₄ and LiFePO₄, etc), which, however, have a series of defects involving the limited theoretical capacities, the limited mineral resources and the seriously environmental pollution. As an alternative, organic materials for lithium ion batteries have captured worldwide attention due to their high capacities,

designing molecular structure, structural diversity, and resource renewability [1–3]. For many years of exploration, the exciting progress has been made to apply various organic materials as the electrode of lithium ion batteries, which include organic free radical compounds [4–6], organosulfur compounds [7,8], and organic carbonyl compounds [9–16], et al.

Among them, stable radical polymers and their derivatives have been explored as the cathode-active charge-storage materials for lithium-ion batteries due to their good cycling stability and a stable voltage platform. Polytriphenylamine (PTPAn) as well its derivatives is a kind of radical polymer, which possesses ultrafast electron-transfer rate constant and good hole-transporting ability, having been widely applied as organic electroluminescence (EL) material, photo-conduction material and organic solar cells material [17]. Moreover, the triphenylamine-contained radical unit in PTPAn and its derivatives can carried out the reversible radical redox reaction during charge and discharge process [18], resulting in the triphenylamine-based polymers have been explored recently as the electrode material applied in the energy storage field, such as super capacitors and lithium ion battery [19,20]. As reported [21], PTPAn presented not only superior high power capability, but also high energy density as well as prolonged

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cycling performances when used as the cathode of lithium ion batteries. During the charge/discharge process, it gives an average discharge potential of 3.6 V and a high capacity of 103 mA h/g. And the advanced cell performances of the PTPAn can be contributed to the π -conjugated triphenylamine substructure and reversible redox radical nature of PTPAn. As the mainly characteristic of the cell performances, the redox potential (V) of the cathode is a key aspect, which together with the theoretical capacity (C) decides the energy density of the batteries (Energy density = C \times V). Due to the designable molecular structure of the organic material, it is significant to explore about the effects of the molecular structure of the organic electrode materials on the redox potential of the electrode.

Redox potential of the organic cathode is mainly determined by the electroactive organic group or moieties. Different structures usually show huge difference in charge/discharge plateau or average charge/discharge potential. Usually, organics prefer to be applied as the cathode rather than the anode, since their redox potentials are usually between 2.0 and 4.0 V vs. Li⁺/Li. Usually, p-type organics possess a higher redox potential than n-type organics. For instance, nitroxyl radical (2,2,6,6-tetramethylpiperidinyloxy-4-yl) and conducting polymer polyaniline always show a similar average charge/discharge potential of about 3.5 V, while organosulfide and most conjugated carbonyl compounds including quinones and dianhydrides show redox potentials below 3.0 V. Beside the functional group or moieties, the adjacent electron withdrawing groups (e.g., —Cl, —F, —CN and —NO₂) or electron donating groups (e.g., —OH, —NH₂ and —OCH₃) can also affect the redox potential, respectively, which can be forecast by theoretical chemical calculation [22,23].

In this paper, a series of triphenylamine derivative polymers with the different electronic effect (the electron-withdrawing/-donating) groups had been molecular-designed and synthesized by the chemical oxidation polymerization, and the obtained polymer's molecular structure and redox potential of the cathode as well as the electrochemical characteristics were also explored in detail. All the works will provide the valuable references for obtaining the advanced organic cathode materials by the way of the molecular structure-designed strategies.

2. Experimental

2.1. Material preparation

2.1.1. Synthesis of 4-(diphenylamino)benzotrile (TPA-CN)

The monomer of PTPA-CN was synthesized as following: Diphenylamine (5.1 g) and sodium hydride (1.5 g) were firstly dissolved in 50 mL of N,N-dimethylformamide (DMF). Then, 4-fluorobenzotrile (4.5 g) was added into the above solution. The reaction was carried out at 110 °C for 12 h under a nitrogen atmosphere. The resulting solution was then cooled and extracted with chloroform, and the organic fraction was washed with water for several times and dried by anhydrous MgSO₄. Finally, the obtained 4-cyanotriphenylamine was isolated by column chromatography with 61.1% yield as a pale yellow residue. MS (EI): calculated for C₁₉H₁₄N₂ m/z: 270.12, found m/z: 269.6. ¹H NMR (500 MHz, CDCl₃) δ 7.46–7.41 (m, 2H), 7.35 (dd, J = 11.1, 4.7 Hz, 4H), 7.17 (dd, J = 13.0, 7.4 Hz, 6H), 7.00–6.94 (m, 2H).

2.1.2. Synthesis of 4-methyltriphenylamine (TPA-CH₃)

The monomer of TPA-CH₃ was synthesized as following: Diphenylamine (2.0 g, 12 mmol), 4-Bromotoluene (1.7 g, 10 mmol), palladium(II) acetate (0.1 g) and t-BuOK (1.5 g) were dissolved in 40 ml of xylene. Then, 0.1 M P(t-Bu)₃ xylene solution (3.0 ml) was added via a syringe and the mixture was further stirred at 120 °C for 12 h under nitrogen atmosphere. The reaction mixture was

cooled down to 80 °C and water was poured into the reaction mixture. The organic layer was washed with water and concentrated by evaporation, followed by purification using column chromatography to remove by-product (s) and unreacted materials. The white solid of TPA-CH₃ was obtained after evaporation of eluent and then dried in vacuo at 50 °C for 12 h. The yield for the objective product was 51.5%. MS (EI): calculated for C₁₉H₁₇N m/z: 259.14, found m/z: 259.3. ¹H NMR (500 MHz, CDCl₃) δ 7.26–7.18 (m, 4H), 7.12–7.04 (m, 6H), 7.00 (ddd, J = 14.7, 5.8, 2.9 Hz, 4H), 2.33 (s, 1H).

2.1.3. Synthesis of 4-methoxytriphenylamine (TPA-OCH₃)

The 4-methoxytriphenylamine (TPA-OCH₃) was prepared using diphenylamine and 4-bromo-4-(methoxy) benzene as the reactive monomers, and the reaction was carried out under the same experimental procedure as that of TPA-CH₃. The obtained yield of TPA-OCH₃ was 64.2%. MS (EI): calculated for C₁₉H₁₇NO m/z: 275.13, found m/z: 275.1. ¹H NMR (500 MHz, CDCl₃) δ 7.26–7.18 (m, 4H), 7.11–7.07 (m, 2H), 7.05 (dd, J = 5.2, 3.5 Hz, 4H), 6.99–6.93 (m, 2H), 6.88–6.83 (m, 2H), 3.82 (s, 3H).

2.1.4. Polymers preparation

All of the PTPA-CN, PTPAn, PTPA-CH₃, PTPA-OCH₃ were prepared by the same polymerization process. For an instance, PTPA-CN was synthesized as following: To a three-necked 50 ml flask equipped with a magnetic stirrer were added TPA-CN dissolved in CHCl₃ under the nitrogen atmosphere. FeCl₃, which was four times mole ratio of TPA-CN, was added to the reaction mixture at the interval of 20 min. After the polymerization, the reaction mixture was poured into methanol. Collected powder was dissolved in CHCl₃, and then the solution was filtrated to remove the insoluble parts. The filtrate was concentrated and then reprecipitated with acetone solution containing 5% of aqueous ammonia. Finally, the product was filtered and dried in vacuo at 60 °C for 24 h. Molecular structure of both polytriphenylamine and its derivatives have been shown in Scheme 1.

2.2. Material characterization

FT-IR spectra were obtained on a Nicolet 6700 spectrometer (Thermo Fisher Nicolet, USA) with KBr pellets. UV–vis spectra were recorded on a Varian Cary 100 UV–vis spectrophotometer (Varian, USA). ¹H NMR spectra of the compounds were recorded on a Bruker AVANCE III 500 MHz spectrometer (Bruker, Switzerland) using CDCl₃. The mass spectrometry (MS) analysis was measured on a GCT premier spectrometer (Waters, USA) using the electron impact (EI⁺) mass spectra technique. Scanning electron microscopy (SEM) measurements were taken using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). Thermogravimetric analyses (TGA) were performed on a Q5000IR (TA, USA) thermogravimetric analyzer running from room temperature to 800 °C at a heating rate of 10 °C/min in nitrogen.

2.3. Electrochemical measurements

For cathode characterization, CR2032-type coin cell was used and assembled in an argon-filled glove box. The cathode were prepared by coating a mixture containing 50% as prepared polymers, 40% acetylene black, 10% PVDF binder on circular Al current collector foils, followed by dried at 60 °C for 24 h. After that, the cells were assembled with lithium foil as the anode, the prepared electrodes as cathode and 1 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC = 1:1, v/v) as the electrolyte. The charge-discharge measurements were carried out on a LAND CT2001 A in the voltage range of 2.5–4.2 V vs. Li/Li⁺, using a constant current density at room temperature. The

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