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

Chang Su\textsuperscript{a,b}, Xiaogang Zhu\textsuperscript{a}, Lihuang Xu\textsuperscript{b,*}, Ningning Zhou\textsuperscript{b}, Huihui He\textsuperscript{a}, Cheng Zhang\textsuperscript{a,*}

\textsuperscript{a} State Key Laboratory Breeding Base for Green Chemistry Synthesis Technology, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Chaowang Road 18\textsuperscript{b}, Hangzhou 310014, PR China

\textsuperscript{b} College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang 110042, PR China

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In this work, the triphenylamine derivatives with the different electron donating/with-drawing groups, such as 4-[(diphenylamino)benzonitrile (TPA-CN), 4-methyltriphenylamine (TPA-CH\textsubscript{3}) and 4-methoxytriphenylamine (TPA-OCH\textsubscript{3}) 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 electrochemical effect groups affected obviously the redox potential of polytriphenylamine, in which the electron with-drawing group improved the potential plateau 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 plateau 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 LiCoO\textsubscript{2}, LiMnO\textsubscript{4} and LiFePO\textsubscript{4}, 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 (PTPA)n 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 main 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 x 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, organicics prefer to be applied as the cathode rather than anode, since their redox potentials are usually between 2.0 and 4.0 V vs. Li+/Li. Usually, p-type organicics possess a higher redox potential than n-type organicics. For instance, nitroxy radical (2,2,6,6-tetramethylpiperidinoxy-4-yl) and conducting polymer polyaniline always show a similar average charge/discharge potential of about 3.5 V, while organosulfide and n-type conjugated carbonyl compounds including quinones and dihydrides show redox potentials below 3.0 V. Beside the functional group or moieties, the adjacent electron with-drawing 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-(diphenylaminobenzonitrile (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-fluorobenzonitrile (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 C20H16N2: 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-ButOK (1.5 g) were dissolved in 40 mL of xylene. Then, 0.1 M Pt[t-Bu]2 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 C28H78N2: 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 (dd, 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 C29H78NO: 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 molar 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 re-precipitated 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 preformed on a Q5000IR (Ra, 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 CT2001A in the voltage range of 2.5–4.2 V vs. Li/Li\textsuperscript{+}, using a constant current density at room temperature. The
cyclic voltammograms (CV) tests were performed with CHI 660E electrochemical working station in 0.1 M LiClO4/CH3CN versus Ag/AgCl at a scan rate of 10 mV s⁻¹. Electrochemical Impedance Spectroscopy (EIS) experiments were carried out using the assembled CR2032-type coin cell at a charge stage with the target active material as the cathode material, in which the electrolyte in the coin cell was composed of 1 M LiPF6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC = 1:1, v/v). And the measurements were performed with CHI 660E electrochemical working station over the frequency ranges from 0.1 Hz to 1 MHz, with the applied amplitude of 5 mV.

3. Results and discussion

3.1. Material characterization

Fig. 1 showed the FTIR spectra of the as-prepared PTPAn, PTPA-CN, PTPA-CH₃ and PTPA-OCH₃. As shown in Fig. 1, the main characteristic peaks of triphenylamine moieties can be observed in PTPAn for C=C ring stretching at 1595 cm⁻¹, C—C ring stretching at 1489 cm⁻¹, and C—H bending at 1321 cm⁻¹ and 1177 cm⁻¹. Also, the C—N stretching from tertiary amine and a C—H out-of-plane vibration from 1,4-disubstituted benzene rings are shown clearly.

![Scheme 1. Molecular structure of both polytriphenylamine and its derivatives.](image)

![Fig. 1. FTIR spectra of the as-prepared PTPA-CN, PTPAn, PTPA-CH₃ and PTPA-OCH₃ samples.](image)
at the wavenumbers of 1274 cm⁻¹ and 817 cm⁻¹, respectively. Compared with typical IR spectrum of PTPAn, the main characteristic peaks of triphenylamine moieties are also be presented in all of the other samples. Otherwise, a series of new bands can be obviously found in the spectrum of PTPA-CN, PTPA-CH₃ and PTPA-OCH₃, in which the absorption peak at 2218 cm⁻¹ is related to C=N stretching, the absorption peak at 1387 cm⁻¹ is due to C—H bending of methyl and the absorption peak at 1155 cm⁻¹ can be ascribed to the C—O stretching, respectively. All those indicate that the cyan, methyl and methoxy groups are included in the corresponding polymers and the PTPA-CN, PTPAn, PTPA-CH₃ and PTPA-OCH₃ polymers have been successfully prepared.

UV-vis spectra (normalized absorbance) were further measured in DMF solution to explore on characteristics of PTPAn, PTPA-CN, PTPA-CH₃ and PTPA-OCH₃. As shown in Fig. 2, all of the samples exhibit only one sharp absorption peak, which can be attributed to the π-π' electron transition of triphenylamine units in PTPAn as well its derivatives. For PTPAn, the typical absorption peak for the π-π' electron transition of triphenylamine units present at 356 nm. In contrast, the corresponding absorption peaks for the PTPA-CH₃ and PTPA-OCH₃ are at 355 and 354 nm, respectively, in which the slightly blue-shifts occur compared to PTPAn. This phenomenon can be attributed to the electron-donating effect of both methyl and methoxy groups in PTPA-CH₃ and PTPA-OCH₃, which can increase the electron cloud density of the central N atom, leading to the limited π-π' electron transition ability on triphenylamine units and the blue-shift of UV-vis spectra compared to PTPAn. For PTPA-CN, however, with the electron-withdrawing group (—CN) linked to the triphenylamine units instead of the electron-donating groups (—CH₃ and —OCH₃), an obviously red-shift for the absorption peak of the π-π' electron transition of triphenylamine units can be observed in Fig. 2, which shifts from 356 nm of PTPAn to 361 nm of PTPA-CN. It still can be ascribe to the electronic effects of the —CN group in the PTPA-CN, in which the electron-withdrawing effect together with the extended conjugation of —CN group results in the decrease of the electron cloud density on the 4-(diphenylamino) benzonitrile (TPA-CN) units, leading to the valid π-π' electron transition in PTPA-CN.

The thermal stability of the polymers (PTPAn, PTPA-CN, PTPA-CH₃ and PTPA-OCH₃) was investigated by thermogravimetric analysis (TGA) under the N₂ atmosphere. As can be seen in Fig. 3, all samples show a small weight loss (~3 wt %) below 150 °C, presumably caused by the loss of water and small molecular. For the PTPA-CN, the weight loss between 150 and 480 °C corresponds to the degradation of the oligomer molecular, while the obvious weight loss above 480 °C is attributed mainly to decomposition of the PTPA-CN back-bone. Comparatively, the thermogram of PTPAn shows two main steps of decomposition in the temperature range 200–800 °C, and PTPA-CH₃ shows only one thermogravimetric loss from 260–450 °C, respectively. For PTPA-OCH₃, however, there is not the obvious thermogravimetric loss platform presented, and only a gradually thermal degradation process is observed in all testing. The different thermogravimetric loss is possible due to the different thermal stability of polytriphenylamine derivatives with the various electron groups; furthermore, the different molecular weight as well as the molecular distribution of four polymers is also responsible to the thermal stability characteristics of the polymers.

Fig. 4 showed the SEM images of PTPA-CN, PTPAn, PTPA-CH₃ and PTPA-OCH₃. The PTPA polymer presents a serious aggregation structure with the plane surface (Fig. 4b). The nature of the big triphenylamine units in PTPAn may be responsible for this structural feature. However, under the same experimental conditions, the morphologies of PTPA-CN, PTPA-CH₃ and PTPA-OCH₃ are different from that of PTPAn. For the PTPA-CN, it exhibits the similar morphology to PTPAn, but comprising of the large particles with the diameter of 0.5 μm-2.0 μm; these particles aggregate together to form the densely stacking structure. For PTPA-CH₃ and PTPA-OCH₃, both polymers show a loose particle-like and open morphology with the improved dispersion. The different morphologies can be attributed to the different molecular structures of PTPA-CN, PTPA-CH₃ and PTPA-OCH₃ from PTPAn, in which the produced linear molecular structure of PTPA-CN, PTPA-CH₃ and
PTPA-OCH$_3$ has an obvious effect on the molecular aggregation behavior as well as the resulted morphology of polymers. This open micro-structural feature of the linear PTPAn derivatives will be favor of both the electrolyte diffusion and the lithium ionic migration in polymeric electrode, benefiting to the improvement of the electrochemical properties during the charge/discharge reaction.

3.2. Electrochemical performance

The chemical characteristics for PTPAn, PTPA-CN, PTPA-CH$_3$ and PTPA-OCH$_3$ were also researched and the CV curves (sweeping potentials from 0 to 2.0 V) at a scan rate of 10 mV/s in 0.1 M LiClO$_4$/CH$_3$CN solution were shown in Fig. 5. All samples present only one pair of anodic and cathodic peaks in the CV curve, which corresponds to the redox reaction of triphenylamine unit in the polymers. For PTPAn, one pair of redox peaks presented is located at 0.70 V (reduction) and 1.10 V (oxidation), respectively, with the approximately symmetric peak shape and the approximately 0.40 V of potential separation for both the oxidation and reduction peaks, suggesting the potentially good insertion/extraction reversibility of PTPAn. Comparatively, the CV curves of the PTPA-CN displays one pair of oxidation and reduction peaks appearing at 1.15 and 0.87 V, respectively, which are the obviously

![Fig. 3. TGA thermograms of the PTPA-CN, PTPAn, PTPA-CH$_3$ and PTPA-OCH$_3$ measured from room temperature to 800 °C at a heating rate of 10 °C/min in nitrogen.](image1)

![Fig. 4. SEM images of power samples (a) PTPA-CN, (b) PTPAn, (c) PTPA-CH3 and (d) PTPA-OCH$_3$, respectively.](image2)
higher than that of PTPAn. The improved potential for PTPA-CN can be attributed to the electron with-drawing effect of —CN groups linked to the triphenylamine units, which decreases the electron cloud density in the central nitrogen atom of triphenylamine and makes the gain and loss process of the radical electron in the central nitrogen atom difficult. Also, the redox peaks separation exhibited by the PTPA-CN electrode is about 0.25 V, which is about 0.15 V smaller than that of the PTPAn electrode, suggesting the lower degree of polarization and the potentially better cycle stability for the electronic materials during the charge-discharge reaction process. With the introduction of electron-donating groups (—CH₃ and —OCH₃) into PTPAn, PTPA-CH₃ exhibits one pair of anodic and cathodic peaks at ~0.104 V and ~0.54 V, and for PTPA-OCH₃ presents one pair of anodic and cathodic peaks at ~0.8 V and ~0.65 V, which are lower than that of PTPAn. The opposite shifting for the anodic and cathodic peaks compared to PTPA-CN with the electron with-drawing groups can still be attributed to the electronic effect of the functional groups linked to triphenylamine, in which the electron-donating effects of both —CH₃ and —OCH₃ groups in PTPA-CH₃ and PTPA-OCH₃ are in favor of the enhanced electron cloud density on the central nitrogen atom of the triphenylamine moiety. This will lead to the delocalization energy of the radical electron in the center nitrogen atom decrease and the redox potential decrease, in contrast to PTPAn. These results are in good agreement with the electrochemical cycling performances of the polymer cathodes, as described below.

3.3. Molecular orbitals and energy levels

The molecular orbital of the functional monomers TPA-CN, TPA, TPA-CH₃ and TPA-OCH₃ was further calculated by means of density functional theory (DFT) at the level of B3LYP/6-31G. As can be seen from Fig. 6a, the electron orbital for TPA molecular distribute uniformly in three phenyls of the TPA. However, for the TPA-CN, the electron density distributions are partially spread to cyan group due to its electron-drawing effect. As the electron-donating group (—CH₃ and —OCH₃) are introduced in the TPA, the different changes have happened. Therein, the electron density distribution has no obvious change for the TPA-CH₃ molecular, while for TPA-OCH₃, the electron density distribution even more focuses on the triphenylamine moiety of TPA-OCH₃ with the introduce of —OCH₃, which can be attributed to the stronger electron-donating effect of —OCH₃ than that of —CH₃ group. As a result, the introduction of

Fig. 5. Cyclic voltammograms (CV) of TPTA-CN, TPTA-C,H, and TPTA-OCH₃ in 0.1 M LiClO₄/CH₃CN versus Ag/AgCl at a scan rate of 10 mV/s.
substituent on the triphenylamine will lead to the different electron density distributions in the molecular. Furthermore, the HOMO energy levels of the prepared polymers were also be calculated base on the formula \( \text{HOMO} = -(E_{\text{OX}} + 4.38 \text{ eV}) \), in which the \( E_{\text{OX}} \) refers to the onset oxidation potential of the corresponding polymers, obtained from the CV curves (Fig. 5). It can be found that the onset oxidation potential (\( E_{\text{OX}} \)) for PTPA-based derivatives are 0.95 V for PTPA-CN, 0.78 V for PTPAn, 0.70 V for PTPA-CH\(_3\) and 0.51 V for PTPA-OCH\(_3\), respectively. And the calculated HOMO energy levels were \(-5.33 \) eV for PTPA-CN, \(-5.16 \) eV for PTPAn, \(-5.08 \) eV for PTPA-CH\(_3\) and \(-4.89 \) eV for PTPA-OCH\(_3\), respectively (as shown in Table 1 and Fig. 6b). The results indicate that the introduction of the electron-with-drawing substituent on the triphenylamine reduce the highest occupied molecular orbital (HOMO) energy level of the polymer. Conversely, the electron-donating groups make it increase. From above results, it can be observed that there is certain relationship between the HOMO energy levels of the PTPAn derivatives and the its oxidation peak in the CV curve as well as the voltage plateaus as described below. It is expected that the gain/loss process of the electron from the HOMO energy levels of the molecular is in some degree related to the oxidation/reduction process occurred in the CV and the charge/discharge testing, and the introduction of the with-drawing groups (\(-\text{CN}\)) makes the loss process of the radical electron of the central nitrogen atom in the HOMO energy levels more difficult than that of the donating groups.

### Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( E_{\text{OX}} ) (V)</th>
<th>HOMO (eV) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPA-CN</td>
<td>0.95</td>
<td>-5.33</td>
</tr>
<tr>
<td>PTPAn</td>
<td>0.78</td>
<td>-5.16</td>
</tr>
<tr>
<td>PTPA-CH(_3)</td>
<td>0.70</td>
<td>-5.08</td>
</tr>
<tr>
<td>PTPA-OCH(_3)</td>
<td>0.51</td>
<td>-4.89</td>
</tr>
</tbody>
</table>

* \( \text{HOMO} = -(E_{\text{OX}} + 4.38 \text{ eV}) \).

### 3.4. Charge-discharge performance

The charge-discharge behaviors of the as-prepared polymers as the cathode of lithium ion batteries have been systematically investigated by simulated lithium ion half-cell method. The initial charge-discharge profiles of the polymers at 20 mA/g between 2.5 and 4.2 V are shown in Fig. 7(a). As can be seen, the initial discharge capacity of the PTPAn is \( \sim 105.3 \) mA h/g with a discharge potential plateaus at 4.0–3.5 V, which is in accord with the reported results [22]. Comparatively, the PTPA-CN shows an initial discharge capacity of \( \sim 88.3 \) mA h/g at initial cycle, which is less than that of PTPAn due to its small theory capacity. Furthermore, it can be noticed that PTPA-CN presents a more flat discharge potential curve with the potential platform with at 4.0–3.8 V which is obviously higher than that of PTPAn. The outstanding improved potential characteristics can be attributed to the introduction of \(-\text{CN}\) as the electron with-drawing group, which affects the molecular energy level and leads to the change of the redox potential for the PTPA-CN. With the introduction of electron-donating groups, the initial capacities for PTPA-CH\(_3\) and PTPA-OCH\(_3\) decrease to 62.9 and 29.2 mA h/g, respectively. The obviously decreased capacity can be partly attributed to the decreased theory capacity of the PTPA-CH\(_3\) and PTPA-OCH\(_3\), and more importantly, is possible due to their dissolubility in the electrolyte which decreases the real availability of the electro-active polymers. Meanwhile, it can be observed that the discharge potential plateaus of PTPA-CH\(_3\) becomes obviously lower than that of PTPAn, and specially for PTPA-OCH\(_3\), its discharge potential plateau decreases to \( \sim 3.2 \) V with no obvious potential plateau. The potential changes of PTPAn derivatives with the different electronic effect groups are in accord with the results of the cycling voltammetry as mentioned above. The electrochemical mechanism during the charge/discharge process can be described just like that of PTPAn [21], in which the electro-oxidation/reduction process for PTPAn-based derivatives can be regarded as a reversible gain/loss of the electron in the central N atom of the triphenylamine moieties and the corresponding electrochemical...
p-doping/dedoping process which companies with the insertion/de-insertion of both \( \text{Li}^+ \) and \( \text{PF}_6^- \).

The cycling stability of the prepared electroactive polymers (PTPA-N, PTPA-CN, PTPA-CH\_3 and PTPA-OCH\_3) as the cathode was also measured at 20 mA/g between 2.5 and 4.2 V, and the results were shown in Fig. 7(b) and 7(c). As described in the picture, the PTPA-N electrode exhibits an unstable cycling performance with a fluctuant capacity during the cycling process, and after 50 cycles the specific capacity change from the initial 105.3 mA h/g to 100.4 mA h/g, with about 4.7% loss of capacity. For PTPA-CN, the electrode shows the similar cycling performance, with the specific capacity decrease from the initial 96.4 mA h/g to 85.4 mA h/g with about 11.4% loss of capacity. The unstable and fluctuant cycling performance indicates the serious aggregated morphologies of PTPA-CN and PTPA-N, which may possibly cause by the volume change of the polymers during the doping/dedoping process, leading to the degradation of capacity and the unstable cycling performances. Comparatively, both PTPA-CH\_3 and PTPA-OCH\_3 electrodes show a comparatively stable cycling performance, with the less capacity decline during the cycling process. The stable cycling performances can be attributed to the open and dispersing morphology architecture of the PTPA-CH\_3 and PTPA-OCH\_3, which suffers from less morphology destroy by the insert and de-insert process of ions (\( \text{Li}^+ \) and \( \text{PF}_6^- \)) during charge/discharge process.

Also, it can be found in Fig. 7(c) that, even after 50 th cycles, four electrodes still keep almost the similar curve characteristics, implying that the composite electrodes have a lower polarization during the charge-discharge cycling process.

The rate cycling performances of PTPA-N, PTPA-CN, PTPA-CH\_3 and PTPA-OCH\_3 electrodes were also examined at different current rates of 50, 100, 300 and 500 mA/g, respectively. As can be seen, all polymers exhibit the similar discharge rate characteristics, namely, the discharge capacities of the polymer cathode decrease with enhancing the current rate, which can be attributed to the serious polarization of the electrodes with increasing the current density. Compared with PTPA-N, the PTPA-CN displays an slightly improved rate capability with an enhanced current rate from 50 to 500 mA/g, as shown in Fig. 7(d), and the specific capacities change form 71.9, 66.6, 58.3, 56.1 mA h/g of PTPA-N to 74.6, 70.7, 60.5, 57.6 mA h/g of PTPA-CN, with a 10 times increase in the current from 50 to 500 mA/g. In addition, the polymer presents a quickly recovered ability of capacity with the current rate going back to 50 mA/g from 500 mA/g. The possible reasons for the improved high rate capability of PTPA-CN can be partly ascribed to the novel molecular structure, in which introduction of the —CN groups on the PTPA makes the molecular structure of polymer from the bulk structure of PTPA to linear structure of PTPA-CN. The formed linear molecular structure will benefit to the ions transportation in...
the composite cathode, leading to the improved rate performance. Furthermore, the improved morphology of PTPA-CN compared to PTPAn will in favor of the insertion-extraction of ions (Li⁺ and PF₆⁻) in the electrode during the charge-discharge process, which is also responsible for the improved rate capability. For the PTPA-CH₃ and PTPA-OCH₃, both reveal a lower rate capability than that of PTPAn, in which the specific capacities for PTPA-CH₃ and PTPA-OCH₃ are 30.0, 29.3, 27.0, 26.2 mA h/g and 17.7, 14.5, 10.2, 7.9 mA h/g respectively, with a 10 times increase in the current from 50 to 500 mA/g, and such low specific capacities at the different rate is mainly due to the low initial capacities for both PTPAn-based polymers.

Fig. 8 further showed electrochemical impedance spectra of pristine PTPA-CN, PTPAn, PTPA-CH₃ and PTPA-OCH₃, respectively. The impedance spectra can be explained on the basis of an equivalent circuit with electrolyte resistance (Rₑ), charge transfer resistance (Rₓ), double layer capacitance and passivation film capacitance (CPE) and Warburg Impedance (Zw). In these impedance plots, the initial intercept of the spectrum at the Zₑ axis in high frequency corresponds to the resistance of the electrolyte (Rₑ). The semicircle at low frequency represents the charge-transfer reaction resistance (Rₓ), while the straight line at low frequencies indicates the Warburg impedance (Zw), which displays the diffusion-controlled process. As can be seen in Fig. 8, the Rₑ is almost same for all cells with different cathode material, indicating that no significant change in ionic conductivity of the electrolyte or mobility of ions with the different cathode-based cell during the cycling process. However, Rₓ varied with different cathode: 167 Ω for the PTPA-CN electrode, 244 Ω for PTPAn electrode, 513 Ω for PTPA-CH₃ electrode and 856 Ω for PTPA-OCH₃ electrode, indicating the charge-transfer reaction resistances for the PTPA-CN cathode are less than that of the PTPAn in the simulated cell, which is further explained why does the PTPA-CN cathode exhibits the improved rate performance.

4. Conclusions

A series of triphenylamine derivatives with different electronic effect groups (—CN), —CH₃ and —OCH₃ have been designed and synthesized successfully, and the corresponding polymers were then prepared by the chemical oxidation polymerization. The electrochemical properties of the polymers as the cathode material were further tested by lithium ion half-cell method. The results showed that the incorporating electronic effect substituent at para-position of triphenylamine obviously affected the spectra characteristics, the electrochemical properties and the molecular energy levels. What’s more, the introduction of the electron-drawing group into PTPA had significantly enhanced the potential plateaus of the organic cathode from 3.6 V of PTPAn to 3.8 V of PTPA-CN and improved the acceptable cell rate performance, all of which would pave a valuable way for the design of high potential organic cathode. In general, above works will provide the valuable references to the molecular design and the cell performance research of the advanced organic cathode materials.

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