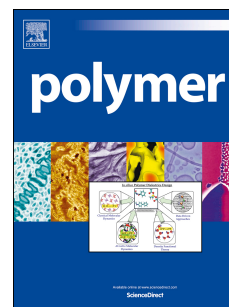


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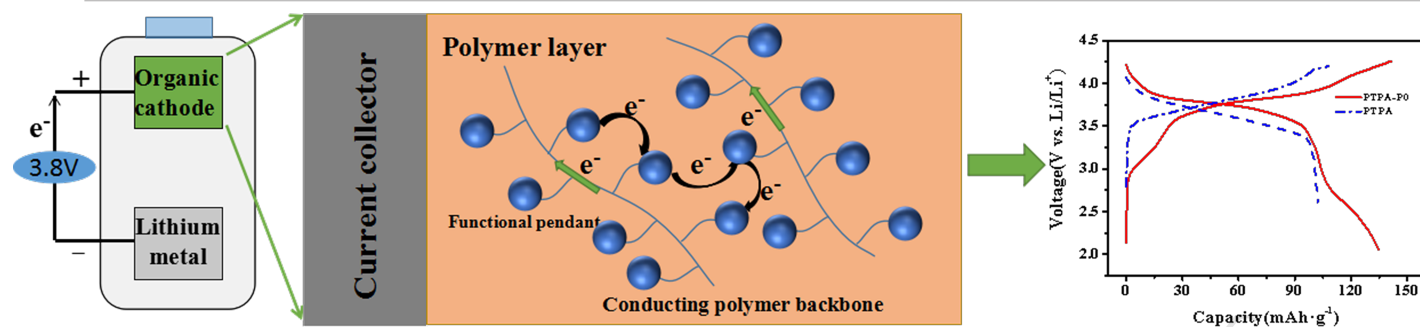
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Polytriphenylamine derivative with enhanced electrochemical performance as the organic cathode material for rechargeable batteries

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HIGHLIGHTS

A novel and linear polymer is synthesized and investigated as the organic cathode material of rechargeable batteries for the first time.

Connection between the molecular structure and electrochemical performance is explored using electrochemical techniques.

The initial specific discharge capacity of the battery is 134.5 mAh·g⁻¹.

Capacity retention greater than 90% for 100 cycles at 25 °C.

ABSTRACT

A novel polytriphenylamine derivative, poly(4-carbamoyl-N,N-diphenylaniline-2,2,5,5-tetramethyl-pyrrolin-1-oxyl) (PTPA-PO) has been synthesized and utilized for the fabrication of the cathode material for organic rechargeable batteries for the first time. The molecular structure, morphology, and electrochemical performance of the obtained polymers were characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis), scanning electron microscopy (SEM), cyclic voltammetry (CV), respectively. Additionally, the charge-discharge performance of the obtained polymers as cathode material were explored by galvanostatic charge-discharge tests. As a result, compared with PTPA, the as-prepared polymer presented an enhanced discharge capacity of $134.5 \text{ mAh}\cdot\text{g}^{-1}$ with two well-defined plateaus. Besides, the PTPA-PO, as the cathode material, exhibited an improved rate performance and remained above 90% of the initial capacity over 100 cycles. These outstanding electrochemical performances were attributed to the combination of the conducting polymer PTPA and the radical pendant PO together with the novel linear molecular structure, which not only provided a two-electron redox process, but also enhanced the charge carrier transportation along the polymer chain.

Keywords: Polytriphenylamine derivative, Novel linear molecular structure, Two-electron redox characteristics, Rechargeable batteries, Electrochemical properties

1. Introduction

Nowadays, batteries are being developed to power diverse electronic devices such as laptop computers, cell phones, and electric vehicles. [1-3] Hence, it is necessary for researchers to pursue new rechargeable batteries with distinguished properties such as sustainability, smaller size, light weight, safety, and environmental compatibility as well as high power and energy density. Currently, the lithium rechargeable battery has played a significant role in the area of energy conversion and storage owing to its remarkable energy density and cyclability. [4,5] Whereas, with the concept of eco-friendly organic rechargeable batteries appearing in public sight, the development of traditional lithium batteries, the majority of cathode materials used in which are inorganic tradition charge storage materials, such as LiCoO_2 or LiMn_2O_4 , has met some drawbacks. These drawbacks, involving the limited mineral resources (Co) and the high energy consumption together with the large CO_2 emission during the producing process, hamper the large scale applications of these traditional inorganic electrode-based lithium batteries. [6-8] Consequently, to keep pace with the increasing demands for sustainable and high-performance batteries, more and more attention has been paid on organic compounds as potentially novel electrode materials for rechargeable batteries, most of which can be derived from natural product and biomass. [9-11] Additionally, diverse properties of organic electrodes can be obtained by designing their structures together with the introduction of functional groups, which may offer better electrochemical properties than those inorganic electrodes. In the future, the polymers with outstanding electrochemical properties as the cathode materials are promising to be substitutes for LiCoO_2 , [12-14] although they also have a few well-known drawbacks, such as lack of cycling stability and relatively poor capacity. In recent years, several significant organic compounds have been proposed and used as electronic materials for rechargeable batteries,

including organic carbonyl compounds, [15-17] organosulfur compounds, [18,19] and conducting polymers, [20,21] as well as organic radical polymers, [22,23] etc.

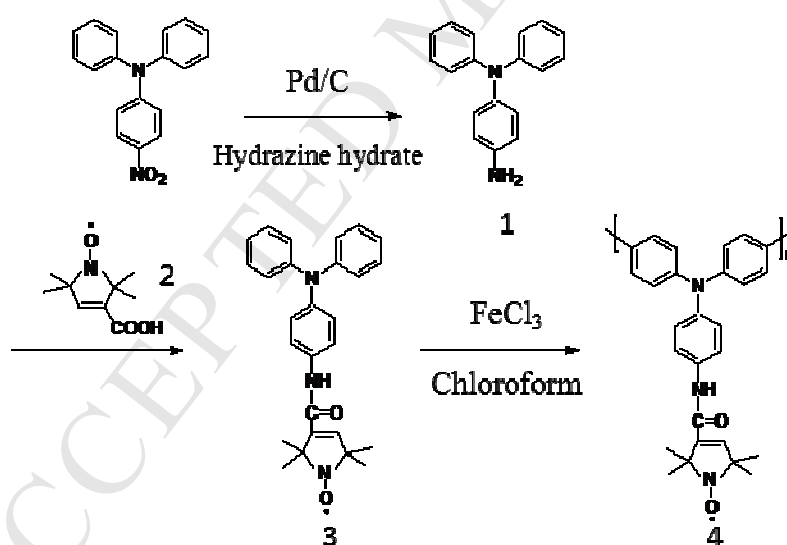
Recently, conducting polymers have been probed by researchers intensively as electrode materials for novel rechargeable batteries. Particularly, polytriphenylamines (PTPA), as a decent type of the electronic conductive polymers, has been widely employed as pseudo-capacitors materials, photo-conduction materials, and organic rechargeable batteries owing to its intrinsic structure that possesses a polyphenylene as conducting backbone together with an electroactive polyaniline unit, which has high energy density. As reported, the polytriphenylamine (PTPA) exhibited high power capacity and excellent charge transport together with a well-defined high voltage plateau of 3.8 V as the cathode materials for organic rechargeable batteries. [24] However, its further application as cathode materials for organic rechargeable batteries has met a bottleneck, because the practical capacity of polytriphenylamines (PTPA) is approximately 109 mAh·g⁻¹, which is lower than the practical specific capacity of the currently used LiCoO₂. Consequently, some progress has been made by tuning of the polymer structure to enhance the cell performances of PTPA-based electrode active material. For example, poly(1-N,1-N,4-N-triphenyl-4-N-[4-(N-[4-(N-phenylanilino)phenyl]anilino)phenyl]-benzene-1,4-diamine) (PFTP) [25] and poly[N,N,N,N-tetraphenylphenylenediamine] (PDDP) [26] have been studied and explored as potential electrode materials. [27,28] In order to increase the energy density for better battery, the above polytriphenylamine derivatives always increase number of redox centers per repeating unit by introducing the similar triphenylamine radical units into the PTPA system. However, these polymers still have some problems, such as expensive catalyst demand during the synthesis, relatively poor rate capability, and long-term cyclability, owing to their design of synthesis route and intrinsic cross-linked structure. Therefore, we can make an attempt to design

a novel synthesis route to improve the cell performance of the PTPA-based cathode material by introducing some functional pendant groups into the PTPA system, such as nitroxide radical. Meanwhile, it is necessary for us to make the further exploration of the connection between the molecular structure of the target polymer and its electrochemical performances or of the details of the charge-discharge process.

2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (PO), an oxygen-centered nitroxide radical, containing a stable structure and undergoing both the p-type and the n-type doping, respectively, may be employed as the pendant group bound to the target polymer for better electronic properties. Meanwhile, as nitroxide radical pendant group, PO not only can undergo a one-electron redox reaction, but also has smaller molecular weight compared to the reported radical pendant 2,2,6,6-tetramethylpiperidiny1-N-oxyl (TEMPO) [29] and possesses these outstanding features [30], such as excellent reversible electrochemical performance and fast electron-transfer, which all contribute to increase the energy density for better battery. As reported, [31] Kenichi Oyaizu and his group designed a novel polymer constructed with poly(ethylene oxide) (PEO) as polymer backbone and PO as radical pendant groups. The cell performance of the novel polymer with PO radical as the pendant group has been studied by a simulated three-electrode method. These results exhibited its remarkable cathode performance, such as high capacity and excellent charge hopping process, etc. As a solution, we intend to design a simple organic synthesis route to produce a novel polymer with the linear molecular structure, which is composed of the polytriphenylamines (PTPA) as conducting main chain and PO as the radical pendant groups.

In this paper, we designed and prepared a novel linear polymer poly(4-carbamoyl-N,N-diphenylaniline-2,2,5,5-tetramethyl-pyrrolin-1-oxyl) (PTPA-PO), in which PTPA was the main chain bearing the PO as functional radical pendant. The chemical structure and cell performances

of the obtained radical polymer as the cathode active material for rechargeable batteries were investigated systematically. Moreover, the possible connection between the introduction of the radical pendant (PO) and the improved electrochemical properties was discussed in detail. Thanks to the introduction of a low molar mass PO functional pendant group into the PTPA system, the obtained polymer PTPA-PO as the cathode material exhibited enhanced electrochemical properties compared to the prepared PTPA-based electrode. Hence, the novel linear polymer would be employed as an organic cathode material with great promise for rechargeable batteries.



Scheme 1. The synthesis route of PTPA-PO.

2. Experimental

2.1. Materials preparation

N-(4-nitrophenyl)-N-phenylbenzenamine, Palladium 5% on Carbon (Pd/C, 5%), N-methyl-2-pyrrolidone (NMP, AR), N,N'-dicyclohexylcarbodiimide (DCC, 99%), Ferric-chloride anhydrous (FeCl_3 , AR), and 4-dimethylaminopyridine (DMAP, 99%) were purchased from Aladdin. 3-Carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (nitroxide radical, 99%) was purchased from Sigma-Aldrich., Hydrazine hydrate (85%), Trichloromethane, Acetone, methanol, Ether, dichloromethane, and ethyl alcohol absolute were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of PTPA-PO.

As shown in Scheme 1, the synthesis of PTPA-PO was conducted with four steps.

2.2.1 Synthesis of N',N'-diphenylbenzene-1,4-diamine (1)

The N',N'-diphenylbenzene-1,4-diamine was prepared by reduction reaction using Pd/C and Hydrazine hydrate as the catalyst and the reducing agent, respectively. [32] ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.15-7.23 (t, 4H), 7-7.04 (t, 4H), 6.93-6.95 (d, 2H), 6.89-6.91 (d, 2H), 6.74-6.76 (d, 2H), 3.89 (s, 2H, broad, NH_2). MS (EI): calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2$ m/z: 260, found m/z: 260.00. IR (KBr, cm^{-1}): ν 3431 ($-\text{NH}_2$), 3352 ($-\text{NH}_2$), 1588, 1490, 1328, 1275, 1162, 1074, 1021, 824. (Figure S1)

2.2.2 Synthesis of 3-Carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (2)

The 3-carboxyl-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl was prepared by hydrolysis reaction in 10 wt % aqueous NaOH solution. [31] FAB-MS (m/z): calculated for M^+ 184.21; found 184.01. IR (KBr, cm^{-1}): 1720 ($\nu_{\text{C=O}}$). (Figure S2)

2.2.3 Synthesis of 4-carbamoyl-*N,N*-diphenylaniline-2,2,5,5-tetramethyl-pyrrolin-1-oxyl (3)

3-Carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (0.736 g, 4 mmol) and *N,N'*-diphenylbenzene-1,4-diamine (1.04 g, 4 mmol) together with dichloromethane (30 mL) as a solvent were added and sealed in a three-necked flask with nitrogen charged. Then 4-dimethylaminopyridine (0.048 g, 0.39 mmol) as acylating catalyst and dicyclohexylcarbodiimide (0.824 g, 4 mmol) as dehydrating agent were put in, which was stirred overnight at room temperature. The residue was filtered with ethyl acetate to remove the unconverted reactants. After washing with dilute hydrochloric acid, sodium bicarbonate and distilled water, respectively, the crude product was purified by column chromatography to produce a claret-red solid (39%). MS (EI): calculated for $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}_2$ m/z : 426, found m/z : 426.06. (Figure S3) Anal. Calcd.(%) for $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}_2$: C: 76.06; H, 6.57; N:9.86. Found:C: 76.04; H, 6.61; N:9.84. The nitroxide radicals of the monomer was characterized by the g -value (2.1024) of the ESR signal, which was close to that of PO at 2.1018. (Figure S4)

2.2.4 Polymerization of PTPA-PO (4)

The monomer TPA-PO (0.6 g, 1.408 mmol) and ferric chloride (0.684 g, 4.224 mmol) as oxidant were introduced to a three-necked flask. Dry CHCl_3 (20 mL) was added which was kept stirring for 24 h at room temperature in a nitrogen atmosphere. The final mixture was centrifuged with methanol, and then washed with methanol. Polymerization of PTPA was conducted with

similar procedure. The final polymer products were purified by column chromatography and dried to yield PTPA-PO and PTPA as gray and yellow solid, respectively.

2.3. Electrode cell assembly

The electrodes were prepared in an Ar-filled glove-box using CR2032 casing. [33] The prepared polymers were used as an important component of positive electrode material, which was accomplished by coating a mixture, which contains 50% of obtained polymers and 40% acetylene black as conductive agent together with 10% PVDF binder. The proportion of prepared polymers to conducting agent was confirmed by charge-discharge tests of the PTPA-based electrodes. (Figure S5) The electrode mixture was collected on aluminium current collector foils. The geometric surface area of aluminium current collector foils was 1.54 cm^2 . And the active material loading of the cathode was approximately 0.33 mg/cm^2 . Then the cathode was dried at 50°C for 24 h before further use. Lithium metal foil was used as the counter electrode. The solution of 1 M LiPF_6 dissolved in EC/DEC (ethylene carbonate/dimethyl carbonate, 1/1, v/v) served as the electrolyte. The polypropylene micro-porous film (PP, Celgard 2400) was used as separator and the nickel foam was used as the collector of negative electrode.

2.4. Characterization and electrochemical evaluation

^1H -Nuclear Magnetic Resonance (^1H NMR) measurements were obtained on a Bruker AMX-400 MHz (Bruker, Switzerland). Infrared measurements were conducted with an FTIR spectrometer (Thermo Nicolet Nexus) using KBr pellets. Ultraviolet-visible spectroscopy were recorded on a Varian Cary 100 UV-vis spectrophotometer (Varian, USA). The radical concentrations were obtained through Electron Spin Resonance (ESR). The conventional elemental analysis were performed by a Vario EL cube analyzer (CHNSO). Scanning electron microscopy (SEM)

measurements were observed on a Carl Zeiss AG /Zeiss Ultra Plus scanning electron microscope (Carl Zeiss AG, Germany). Molecular weight data was obtained through gel permeation chromatography (GPC).

The charge-discharge tests were conducted with a LAND CT2001A at a current density of 20 mA g^{-1} . The cyclic voltammograms (CV) experiments were conducted with a SZCL-ZA electrochemical working station at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$. The cycling stability and rate performances were obtained by repeating charging-discharging process at different current densities.

3. Results and Discussion

3.1. Characterization of the obtained polymers

The Fourier transform infrared (FTIR) spectra of the obtained PTPA and PTPA-PO are shown in Figure 1 with absorption peaks marked for comparison. The fundamental vibration bands of the TPA moieties can be all observed in the spectra of PTPA and PTPA-PO, [34] including the vibrations from C=C ring stretching at 1594 cm^{-1} , from C-H bending at 1322 cm^{-1} and from C-C stretching at 1490 cm^{-1} . Besides, the vibrations from C-N stretching at 1274 cm^{-1} and the vibrations from a C-H out-of-plane at 819 cm^{-1} , which can be corresponded to tertiary amine and 1,4-disubstituted benzene rings, respectively, indicate that the chemical polymerization occurs. Additionally, it is worth noting that some new bands and characteristic peaks appear in the spectrum of PTPA-PO, and involves the hydrogen bonded N-H stretching at 3305 cm^{-1} , the C=O stretching vibrations (amide I mode) at 1645 cm^{-1} , the combination of C-N stretching and N-H bending (amide II mode) at 1542 cm^{-1} , the absorption peak from the deformation of the CNH groups (amide III mode) at 1300 cm^{-1} . Above new absorption peaks are the typical amide

absorption peaks, which proves that the organic chemical reaction successfully happens and the covalence bond (NH-C=O) has been contained in the PTPA-PO. [35,36] Additionally, the band at 1365 cm^{-1} corresponds to nitroxide radical pendant (PO) in the obtained PTPA-PO. [37] The new absorption peaks prove that the functional pendant group (PO) has been successfully introduced into polytriphenylamine (PTPA) structural unit by organic synthesis method and has not been destroyed in the chemical oxidation polymerization.

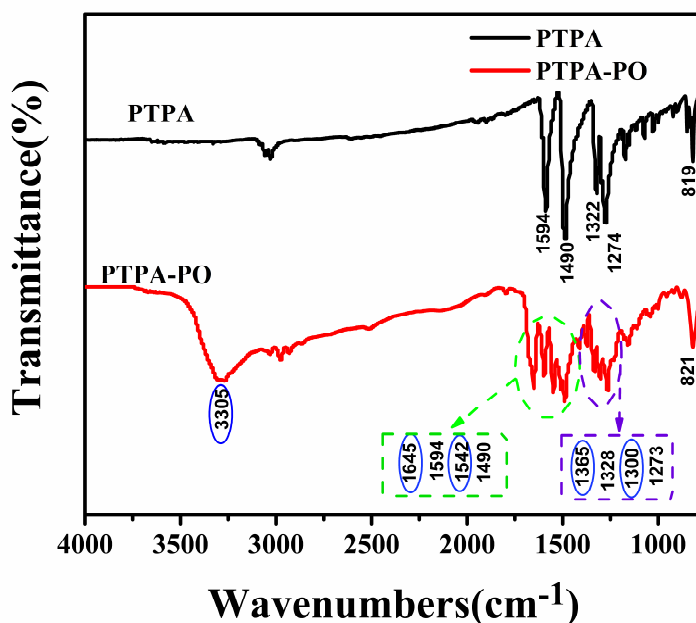


Figure 1. The Fourier transform infrared spectra of the obtained PTPA, and PTPA-PO.

In order to make further exploration of the properties of PTPA and PTPA-PO, the UV/Vis spectroscopy (normalized absorbance) were obtained with DMF (10^{-3} g/L^{-1}) as solvent. As depicted in Figure 2 (a), only one distinct absorption peak at 355 nm is observed in the UV/Vis spectrogram of PTPA, which is ascribed to the π - π^* electron transition from the TPA moieties.

[38] In comparison, the PTPA-PO presents two obvious absorption peaks. We found that one of the absorption peak, corresponding to the π - π^* electron transition from the TPA moieties, red-shifts from the 355 nm of PTPA to 375 nm, indicating that the introduction of PO into PTPA system leads to the extended electron delocalization and enhanced charge carrier transmission in the main chain of the obtained polymer. The explanation of this phenomenon can be that the introduction of the PO pendant groups leads to the molecular structure changing from the previous cross-linked structure of PTPA to a novel linear molecular structure, which reduces the steric torsion between the neighboring TPA units and leads to the enhancement of π conjugation along the main chain of the obtained polymer. As a result, the enhanced π conjugation will be beneficial to the electron transfer along the polymer chain, which is crucial for better organic rechargeable battery. Furthermore, another absorption peak appears at 452 nm, corresponding to the n - π^* transition absorption of the functional pendant (PO) in PTPA-PO. [39] The new absorption peak further proves that the pendant group (PO) has been successfully introduced into the polymeric backbone (PTPA). The molecular weight of PTPA and PTPA-PO was analyzed by gel permeation chromatography using polystyrene and THF as the external standard and the eluent, respectively. The molecular weight of PTPA was $M_n = 117708$ with a dispersity of $M_w/M_n = 1.05$. The molecular weight of PTPA-PO was $M_n = 108273$ with a dispersity of $M_w/M_n = 1.09$, which is similar to that of PTPA. (Figure S6 and Figure S7)

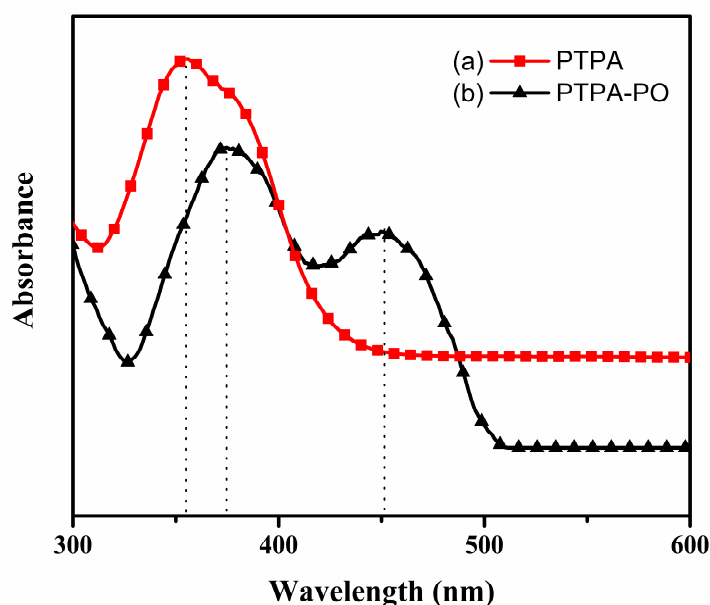


Figure 2. Ultraviolet-visible spectroscopy of samples a) PTPA, b) PTPA-PO

The morphologies of the obtained samples have also been investigated by SEM. Fig.3 (a) and Fig.3 (b) show a low-magnification SEM image of PTPA and PTPA-PO. The samples both have an irregular porous structure with a size of about thirty micrometers. As can be seen in high-magnification SEM image (Fig.3 (c) and Fig.3 (d)), under the same experimental conditions, there are some different places between the morphology of the obtained PTPA-PO and that of PTPA. Although, the shape of PTPA and PTPA-PO particles are both coral-like, and wove into nets. However, compared to PTPA, it can be clearly seen that PTPA-PO exhibits a looser assembled coral-like structure consisting of many small particles with well dispersion which constitute a network. The stable radical group (PO) which is introduced into polytriphenylamine (PTPA) may be responsible for this structural feature. (Figure S8) Comparatively, this structural feature of PTPA-PO may offer larger surface area and more ionic channels, which will be

beneficial for Li-ion migration in the electrode material and full utilization of the produced cathode materials as well the polymeric electrode reactions during the charge-discharge process, accelerating the improvement of the electrochemical performance of the obtained polymer as the cathode material for organic rechargeable battery.

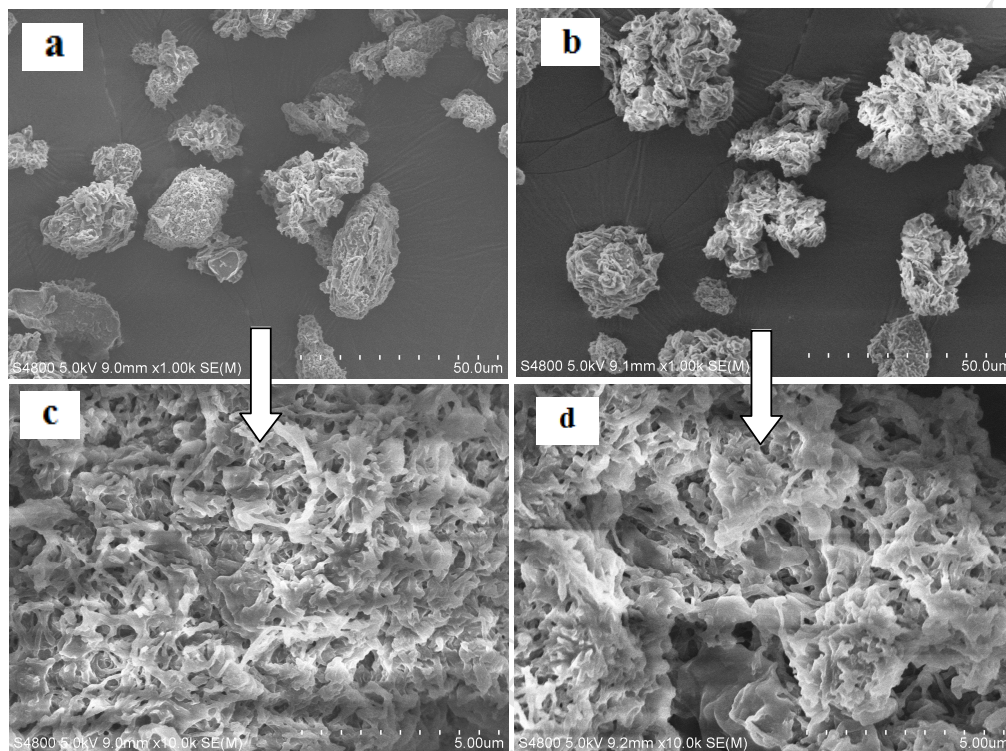


Figure 3. Scanning electron microscopy images of (a) PTPA, (b) PTPA-PO and partially enlarged scanning electron microscopy images in (c), (d)

3.2. Electrochemical properties of the obtained polymers

The cyclic voltammetry (CV) profiles of the obtained polymers were measured in 1 mol / L LiPF_6 EC / DMC (v / v, 1: 1) solution and are shown in Figure 4. As depicted in the Figure 4(a), the PTPA exhibits two couples of distinct redox peaks, in which one pair of oxidation and

reduction peaks appears at 3.75 V and 3.61 V, and another pair of redox peaks appears at 3.59 V and 3.38 V, all corresponding to the redox reactions of TPA moieties during charge-discharge process. The relatively narrow potential separations of the produced PTPA is approximately 0.14 V, implying the good redox reversibility of the obtained polymer as the cathode material. In comparison, under the same experiment condition, PTPA-PO shows some different CV features. As shown in the Figure 4 (b), the PTPA-PO displays four pairs of reversible redox peaks, which are located in 3.89/3.76, 3.68/3.62, 3.23/3.14 V/V and 2.62 V, respectively. Same with the PTPA, the two pairs of oxidation and reduction peaks appearing at 3.89 V/3.76 V and 3.68 V/3.62 V are also corresponded to the electrochemical redox reactions of TPA moieties of PTPA-PO during charge-discharge process. It's worth noting that another couple of weak redox peaks appears at 3.23V/3.14 V, which can be assigned to the p-type doping of radical pendant (PO) (from the nitroxide radicals to the oxoammonium cations), [40] which is introduced into polytriphenylamine (PTPA) structural unit. The corresponding potential separations of the PTPA-PO cathode materials are obviously narrower than that of PTPA electrode, which are 0.13, 0.06 and 0.09 V, respectively, implying the superior oxidation/reduction reversibility of the as-prepared polymer as the cathode material. Additionally, the narrow potential separation of PTPA-PO also implies the good electrochemical kinetics for the electrode applications, which is beneficial to obtain high rate performance during the charge and discharge process of electrode reaction. Furthermore, there is a relatively weak redox peaks appearing near 2.62 V in the cyclic voltammetry (CV) profile of PTPA-PO, which can be assigned to the n-type doping of radical pendant (PO) (from the aminoxy anion to the nitroxyl radicals). However, this phenomenon is not observed in that of PTPA. It indicates that the electrocatalysis function of PTPA as the electroactive main chain of PTPA-PO promotes the redox process between aminoxy anion and

the nitroxyl radicals, resulting in the appearance of the redox peak at 2.62 V. This similar electrocatalysis phenomenon has been presented in previous reports. [41] Meanwhile, the result indicates that the radical pendant PO of PTPA-PO offers another reversible redox process for each and every repeating structure units, which will be beneficial to produce novel organic rechargeable batteries with enhanced cell performance.

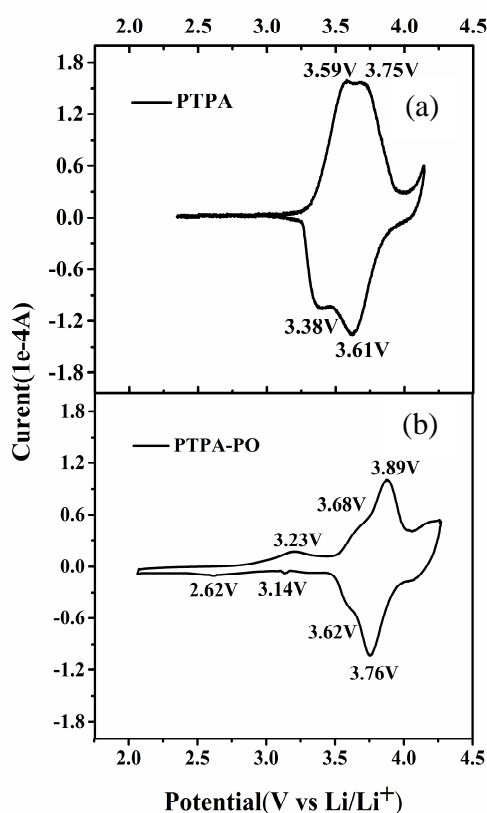


Figure 4. Electrode CV of PTPA and PTPA-PO as the cathode materials in 1.0 M LiPF₆-EC/DMC at a scan rate of 0.1 mV s⁻¹. (a) PTPA; (b) PTPA-PO.

3.3. Charge-discharge behavior of the obtained polymers

In order to further explore the charge-discharge behavior of the obtained polymers as the organic electrode material for rechargeable batteries, the charging and discharging measurements were conducted by galvanostatic method. The charge-discharge capacity of $108.2/102.2 \text{ mAh}\cdot\text{g}^{-1}$ with a clear voltage plateau at 3.5-4.1 V was observed in the charge-discharge curve of PTPA at the initial cycle, as depicted in Fig.5 (a), which is in accord with the reports. [42] However, under the same experiment conditions, an improved initial charge-discharge capacity of $141.6/134.5 \text{ mAh}\cdot\text{g}^{-1}$ with two distinct discharge voltage plateaus can be clearly observed in the charge-discharge profiles of PTPA-PO, which appear at about 3.8 V and 2.7 V, respectively. The higher plateau is attributed to the redox process of TPA moieties of PTPA-PO. The lower discharge voltage platform at 2.7 V is assigned to the n-type doping process of the nitroxide radical (PO). This characteristic is similar to that in previous report. [43] Moreover, as depicted in the CV curves of PTPA-PO, the redox peak of PTPA is obviously stronger than that of PO part. Therefore, the high voltage plateau can be in accord with the stronger redox peak, which can provide the majority of capacity, and the low voltage plateau can be in accord with the relatively weak redox couple, which provide the minority of capacity. As a result of that, the whole voltage plateau can be regarded as 3.8 V, which is beneficial for obtaining better cathode materials with high energy density. Furthermore, compared with PTPA, the discharge capacity of PTPA-PO at initial cycle is increased to $134.5 \text{ mAh}\cdot\text{g}^{-1}$. The improved capacity of PTPA-PO can be due to the introduction of the functional radical pendant groups (PO) to PTPA system, providing another redox process caused by the electrocatalysis function of the conducting backbone (PTPA) to PO. Meanwhile, the conductive polymer (PTPA) as backbone and the design of the linear molecular structure, contributing to the enhancement of π conjugation and the electron transfer along the polymer chain, which will be beneficial to the full utilization of

the increased capacity of the cathode during charge-discharge process, may also be another factor of the improved capacity. The enhanced charge-discharge behavior of the obtained polymers as cathode of rechargeable batteries can satisfy the requirement of the currently used batteries for energy storage system.

To further explore the electrochemical performance of the obtained polymers, the cycling performance was also measured by 100 cycling tests. As shown in Fig.5 (b), the practical capacity of PTPA decreases from $104.1 \text{ mAh}\cdot\text{g}^{-1}$ at first cycle to $88.7 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles, with approximately 14.8% loss of capacity. Comparatively, the practical capacity of PTPA-PO decreases from $134.5 \text{ mAh}\cdot\text{g}^{-1}$ at first cycle to $121.2 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles. We can note that the practical capacity of PTPA-PO over 100 cycles is still superior to the initial capacity of PTPA, indicating that the obtained PTPA-PO as electrode has outstanding cycle-life characteristics. The drop in the specific capacity during extensive cycling process is mainly influenced by some factors, containing the structure changes of the obtained polymer as the cathode materials and the dissolution issues of the polymer. The dissolution test of PTPA and PTPA-PO was conducted, as shown in Fig. S9, the PTPA polymer and PTPA-PO polymer were barely dissolved in the electrolyte, even after two weeks at room temperature. After dissolution for two weeks in the electrolyte solution of $\text{LiPF}_6\text{-EC/DMC}$ at room temperature and following filtration, there was hardly any loss of the obtained polymers, and more than 98 wt% of both PTPA and PTPA-PO remained, respectively. It proved that the obtained polymers had almost no solubility in the electrolyte solution, which could be attributed to the existence of the cross-linked structure of PTPA and the high molecular weight and rigid chain of PTPA-PO, respectively. It is beneficial to the good capacity retention behavior of PTPA and PTPA-PO. Therefore, above results indicate that the structure of PTPA-PO are destroyed less and relatively

stable during the redox reaction, which can be assigned to the novel chemical structure of the obtained polymer and the stability of its micromorphology.

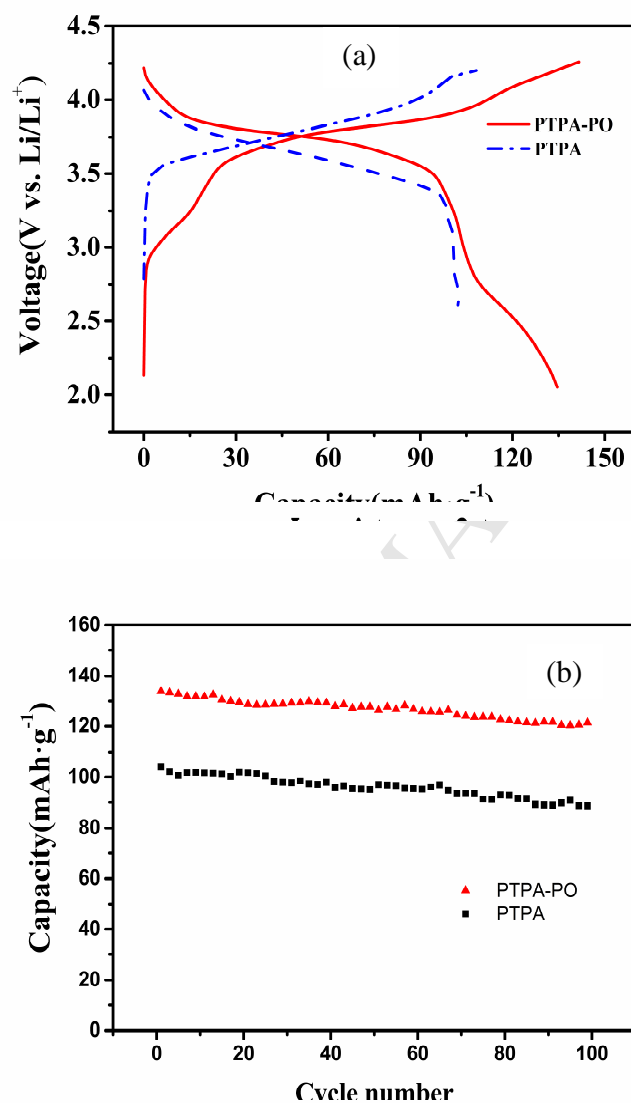


Figure 5.(a) Initial charge-discharge performance and (b) cycle-life performance of the obtained polymers as the cathode materials in 1.0 M LiPF₆-EC/DMC at a current rate of 20 mA·g⁻¹ between 2.0 and 4.2 V

As shown in Figure 6, the rate and cycling behavior of the obtained polymers as the cathode materials for rechargeable batteries were also measured in the voltage range of 2.0-4.2 V with different current densities. The specific capacity for PTPA and PTPA-PO are 101, 99, 95, 86, 76 $\text{mAh}\cdot\text{g}^{-1}$ and 134, 127, 114, 100, 90 $\text{mAh}\cdot\text{g}^{-1}$, respectively, with an enhanced current rate from 20 to 500 $\text{mA}\cdot\text{g}^{-1}$. Compared to PTPA, PTPA-PO exhibits an improved rate capability during the cycling tests, with enhanced specific capacity at high current density. Moreover, the cycle retention rate of the obtained PTPA-PO as electrode is still over 67% with the current increasing from 20 to 500 $\text{mA}\cdot\text{g}^{-1}$. Remarkably, when the current density gets back to 20 $\text{mA}\cdot\text{g}^{-1}$, the specific capacity of PTPA-PO can still recover to 126 $\text{mAh}\cdot\text{g}^{-1}$, and that of PTPA can recover to 95 $\text{mAh}\cdot\text{g}^{-1}$, which both of them exhibit a quickly renewed ability of capacity. The improved capability and cycle stability can be attributed to the novel chemical structure which contains both the conducting polymer backbone and the nitroxide radical pendant (as indicated in the UV/Vis), leading to the improved electron-transportation properties of PTPA-PO, even at high current rate. Particularly, the introduction of PO and the construction of novel linear structure not only reduces the steric torison between triphenylamine units in PTPA, but also enhances the charge carrier transportation along the polymer chain, which is beneficial to the rapid electron migration along the polymer chain of PTPA-PO. Furthermore, the loosely assembled coral-like structure of PTPA-PO provides sufficient ionic channels and reduces the surface hindrance for the conduction of organic electrode material and electrolyte solution, which is another important reason of its high rate capability. Although, compared with PTPA, the rate and cycling behavior of the obtained polymer as novel organic cathode material is enhanced, but it still needs to be improved by further exploration for meeting the requirement of the currently used conventional cathode material of rechargeable batteries.

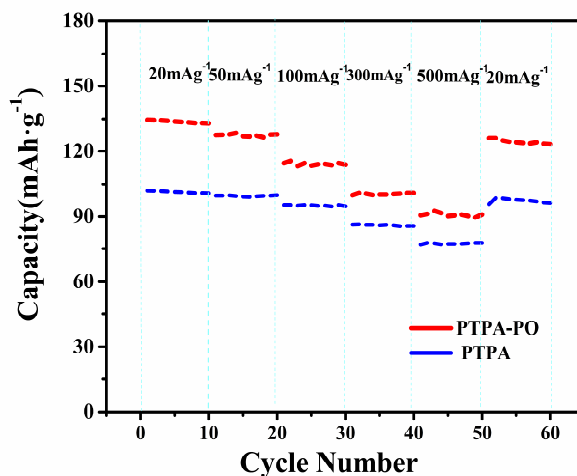


Figure 6. Rate performances for the obtained polymers as the cathode materials at different current rates of 20, 50, 100, 300, and 500 mA·g⁻¹ between 2.0 and 4.2 V

4. Concluding Remarks

A novel linear polymer poly(4-carbamoyl-N,N-diphenylaniline-2,2,5,5-tetramethyl-pyrrolin-1-oxyl) (PTPA-PO), in which PTPA is the main chain bearing the PO as functional radical pendant groups, has been synthesized by organic synthesis method. In order to explore the electrochemical properties of the obtained polymer, PTPA-PO was prepared as the organic cathode material of rechargeable batteries. Compared with PTPA, PTPA-PO presented an enhanced initial discharge capacity of 134.5 mAh·g⁻¹, which was attributed to PTPA as backbone with the excellent electrochemical activity and PO as the pendant groups providing another reversible redox reaction. Besides, the discharge capacity of PTPA-PO retained over 90% of the initial capacity after 100 cycles, which is significant for the use of organic cathode material for rechargeable batteries. What's more, the rate performance of the PTPA-PO as cathode material

was also obviously enhanced, which was attributed to the introduction of the radical pendant PO and the construction of the linear molecular structure, which will enhance the charge carrier transportation along the polymer chain during the charge-discharge process. All above excellent electrochemical performances of PTPA-PO show that the novel linear radical polymer PTPA-PO have great potential for the use of organic cathode material for appropriate battery system.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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