

Short communication

Polytriphenylamine: A high power and high capacity cathode material for rechargeable lithium batteries

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Abstract

Polytriphenylamine (PTPAn) was chemically synthesized and tested as a cathode material for high-rate storage and delivery of electrochemical energy. It is found that the polymer has not only superior high power capability but also high energy density at prolonged cycling. At a moderate rate of 0.5C, PTPAn gives a high average discharge voltage of 3.8 V and quite a high capacity of 103 mAh g⁻¹, which is very close to the theoretical capacity (109 mAh g⁻¹) as expected from one electron transfer per triphenylamine monomer. Even cycled at a very high rate of 20C, the polymer can still deliver a capacity of 90 mAh g⁻¹ at 1000th cycle with a nearly 100% coulombic efficiency. The excellent electrochemical performances of PTPAn are explained from the structural specificity of the polymer where the radical redox centers are stabilized and protected by conductive polymeric backbone, making the radical redox and charge-transporting processes kinetically facile for high-rate charge and discharge. © 2007 Elsevier B.V. All rights reserved.

Keywords: Polytriphenylamine; Radical redox polymer; Cathode material; Lithium batteries; High-rate capability

1. Introduction

Rechargeable batteries are required to have not only a high energy density but also a high power capability in many new applications such as hybrid electric vehicles, portable electric tools and power backup [1,2]. During past years, Li-ion batteries have gained remarkable progress in energy density; however, their power densities are still insufficient for many high-rate applications due partly to the slow kinetics of lithium intercalation chemistry of the battery systems [3–5]. For currently commercial rechargeable Li batteries, the cathode materials are mostly crystalline transition-metal oxides, which are intrinsically poor conductor both for electrons and inserting Li⁺ ions and are therefore restricted to charge and discharge at moderate rate.

Electroactive conducting polymers are a large family of the molecules capable of high-rate storage and delivery of power because of their high electronic conductivity and feasible rapid electrochemical kinetics. In past years, various conducting polymers, such as polyaniline (PAn) [6,7], poly(*p*-phenylene) (PPP)

[8,9], polythiophene (PTh) [10,11] and their derivatives, have been investigated as positive electrode materials for electrochemical batteries or supercapacitors. However, most of the conducting polymers reported so far can only have either high discharge capacity or high-rate capability. For example, PPP and PTh can be charge and discharged at high rate of $\geq 10C$, but their capacity output is very low only about 50 mAh g⁻¹ [9–11] due to their low doping depth. Although PAn and polysulfides can have a quite high specific capacity ≥ 140 mAh g⁻¹, the power density of these materials is quite poor [6]. If a conducting polymer is integrated of redox moieties compactly in a fast charge-transporting backbone, the polymer may have not only high energy density but also high power capability.

Polytriphenylamine (PTPAn) seems to be the polymer molecule as required to have a highly conductive PPP backbone combined with high energy density of electroactive PAn unit. In the studies of organic optoelectronic materials, it has been revealed that PTPAn is a polymeric mixed valence compound with ultrafast electron-transfer rate constant and good hole-transporting ability [12,13]. Also, previous electrochemical evidences demonstrated the reversible redox behaviors of PTPAn and its derivatives [14]. Unfortunately, there have been no further studies reported for the electrochemical properties of PTPAn as an electroactive material in energy storage devices.

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Recently, we studied the reversible change in the electronic conductivity of PTPAn with applied potential and found possible use of this material as a potential-switchable separator [15]. In this paper, we report high-rate charge–discharge properties of PTPAn as a high capacity cathode material for rechargeable lithium batteries and discuss the possible mechanisms responsible for superior high power and high energy density capability of the conducting polymer.

2. Experimentals

2.1. Material synthesis and characterizations

PTPAn was prepared by chemical oxidative method similarly as reported in literature [16]. A typical experimental procedure is to add 100 ml of a mixed solution of 0.25 mol l^{-1} triphenylamine (TPA) and CHCl_3 into a three-necked 250 ml flask under magnetic stirring, and then add 0.025 mol FeCl_3 oxidant into the reaction solution at the interval of 1 h. The total amount of FeCl_3 used was four times of TPA. The oxidative polymerization of TPA usually takes 2 h in the solution at aerating of nitrogen. After completion of the solution polymerization reaction, the reaction mixture was poured into methanol to deposit the polymer product, which was then filtered and washed with methanol several times. For purifying the synthetic PTPAn, the collected polymer powders were dissolved again in CHCl_3 solvent to remove the insoluble residues by filtration. The filtrate was concentrated and then re-precipitated with acetone solution containing 5% of aqueous ammonia. Finally, the polymer product was filtered and dried in vacuum at 50°C for 12 h.

All the chemicals were obtained commercially and used without further purification except otherwise noted. Chloroform was distilled over CaH_2 before use.

The FT-IR spectra of PTPAn were recorded on a NICOLET AVATAR360 FT-IR spectrometer with KBr pellets. Elemental analysis was performed on VarioEL III instrument. The particle morphology of PTPAn powder was examined by scanning electron microscopy (SEM) on a Sirion2000 machine (Holland). ^1H NMR spectra of PTPAn were recorded on a Mercury VX-300 (300 MHz) spectrometer with tetramethylsilane (TMS) as internal standard and CDCl_3 as solvent. Average molecular weight ($M_{n,\text{GPC}}$) of PTPAn was measured by gel permeation chromatography and determined by the universal calibration method using a viscosity detector. UV–vis spectra of PTPAn were measured using a Shimadzu 160A spectrometer.

2.2. Electrochemical measurements

The cyclic voltammograms (CV) of the PTPAn powder were recorded by powder microelectrode using a two-electrode cell with a larger lithium sheet served as both counter electrode and reference electrode. The preparation method for powder microelectrode has been described in detail in Ref. [17].

The AC impedance and charge–discharge measurements were carried out using conventional three-electrode cells. The test cells were composed of a PTPAn film electrode (1.5 cm^2 , 0.1 mm thick) and a lithium sheet separated with a porous

polypropylene separator (Cellgard 2400). The PTPAn electrode film was consisted of 70% PTPAn powder, 20% acetylene black and 10% PTFE (wt.%) and prepared by roll-pressing the mixture into an 0.1 mm thick film and then pressing the electrode film onto an aluminum net. The electrolyte was 1 M LiPF_6 in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v, Merck). The AC impedance spectra were recorded using a CHI 660A electrochemical workstation (Shanghai, China) within a frequency sweep range of 10,000 kHz–1 Hz and the charge–discharge experiments were carried out using a programmable computer-controlled battery charger (BTS-0518001 type, Shenzhen, China).

The electronic conductivity of the doped PTPAn was estimated by direct measurements of electronic resistance of the charged PTPAn film. The samples for ohmic measurements were taken out from fully charged test cells, washed with acetone and then dried in vacuum oven.

3. Results and discussion

3.1. Material characterizations

PTPAn can be synthesized by chemical or electrochemical oxidation of TPA [16]. In comparison, PTPAn produced from chemical oxidation polymerization has a higher degree of polymerization and structural homogeneity. Therefore, we used the oxidative polymerization for preparation of PTPAn using excessive oxidant. Fig. 1 shows the FT-IR spectrum of the as-prepared PTPAn sample. Compared with typical IR spectrum of TPA molecule, the main vibration bands characteristic of TPA moieties can be found in Fig. 1 for C–C ring stretching at 1550 cm^{-1} , C–C stretching at 1491 cm^{-1} and C–H bending at 1321 cm^{-1} and at 1154 cm^{-1} . The C–N stretching from tertiary amine and a C–H out-of-plane vibration from 1,4-disubstituted benzene rings are shown clearly at the right wavenumbers of 1274 cm^{-1} and 818.6 cm^{-1} , respectively. Appearance of a number of new bands at 1274 and 819 cm^{-1} indicates the C–C bonding between the benzene rings of TPA and the bands at 1596 and at 1109 cm^{-1} represent the vibrations from C=C stretching and from C–H bending due to the quinoid structures formed

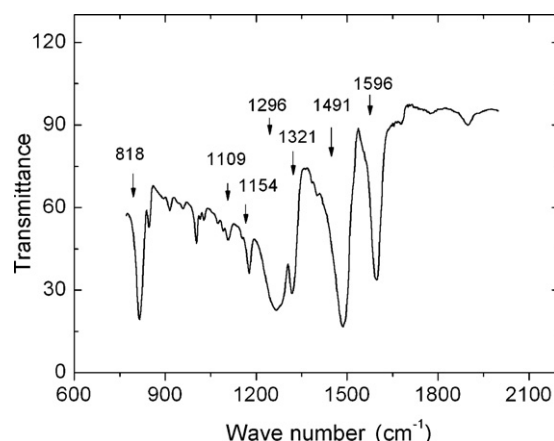


Fig. 1. FT-IR spectrum of the as-prepared PTPAn sample.

after polymerization of TPA. All the IR features in Fig. 1 suggests a highly crosslinked structure of the PTPAn polymer and agrees very well with the well-documented data for chemically synthesized PTPAn compounds [18].

Elemental analysis also supports the homogeneity of the as-prepared PTPAn polymer. Compared with the theoretical H-contents of TPA (6.12%) and PTPAn (4.89%), the experimental H-contents measured from TPA and PTPAn are 6.02% and 4.97% respectively, which are very well agreed with the theoretical values, indicating that a complete polymerization of PTPAn takes place by oxidative dehydrogenation polymerization of TPA. Also, the ^1H NMR data (6.8–7.5 ppm, 12.2H) of the as-prepared PTPAn showed a decreased content of H atoms as compared with the ^1H NMR data (6.9–7.4 ppm, 15H) of TPA, further confirming the PTPAn produced from the dehydrogenation polymerization of TPA. The average molecular weight (M_n) of the as-prepared PTPAn is about $16\text{--}17 \times 10^3$, suggesting that each PTPAn molecule contains 64–72 TPA units. The UV absorption maximum of PTPAn was dramatically red-shifted from 291 to 372 nm in comparison with TPA monomer. This red-shift can be attributed to the extended conjugation by polymerization of TPA monomers, which lowers the ionization potentials of the polymer.

The morphology of the as-prepared PTPAn polymer is shown in Fig. 2. The polymer showed a porous structure with particle size of a few micrometers and each particle has a coralloid surface with abundant holes mutually connected. This structural feature is possibly due to the twisting and folding of the polymer chains themselves and may provide sufficient surface area and ionic channels for polymeric electrode reactions.

The electronic conductivity is an important factor to determine the power capability of an active electrode material, particularly at high-rate charge and discharge. To estimate the electronic conductivity of the PTPAn material, we used the pure PTPAn film fully charged to 3.8 V as doped PTPAn samples for ohmic measurements and found that the conductivity of the powdered polymeric PTPAn film is $\sim 1.0 \text{ S cm}^{-1}$, about 1×10^6 times higher than the undoped samples. This value of conductivity is in a close agreement with that reported previously for

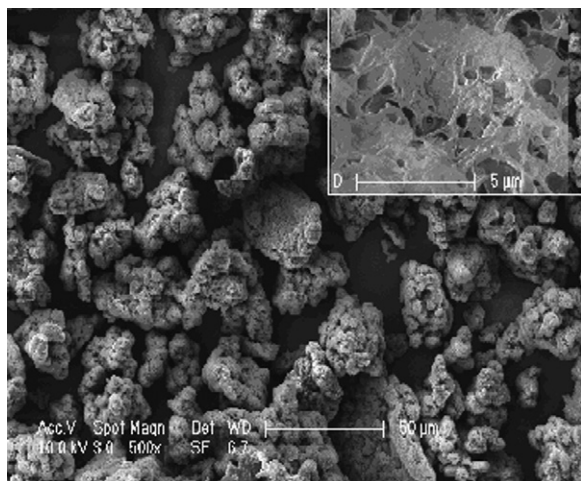


Fig. 2. SEM image of the as-prepared PTPAn sample.

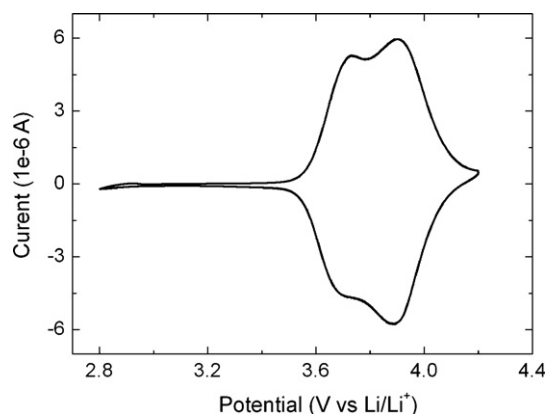


Fig. 3. The CVs of PTPAn in 1 M LiPF_6 EC/DMC (v/v 1:1) measured at a scan rate 1 mV s^{-1} .

iodine-doped PTPAn (ca. 1 S cm^{-1}), indicative of the hole conducting nature of this polymer material [19–21].

3.2. Electrochemical behaviors

Fig. 3 shows a typical CV curve of PTPAn measured in 1 M $\text{LiPF}_6 + \text{EC/DMC}$ (v/v 1:1) solution. The main CV feature of the PTPAn is two pairs of reversible redox peaks at 3.7 and 3.9 V, which displayed almost the same peak positions and peak areas for the cathodic and the anodic branches of the redox bands, suggesting that the electrochemical redox reactions of this polymer electrode were highly reversible and kinetically very fast. In previous studies of electrochemical polymerization of TPA [22] and their derivatives [19–21], very similar features of these two redox bands were also observed in different electrolytes and experimental conditions, however, the origin of these two bands remains unrevealed. If a TPA unit produced a hole or a TPA^+ cation during electrooxidation of PTPAn as convinced by spectral evidences [19–22], there should be only one pair of redox peaks observed in the CV curve and thus the appearance of two pairs of redox bands in the CV curve of PTPAn is really difficult to explain. Taking into account that the *para*- and *meta*-positions of each phenyl ring in TPA are possible positions for polymerizing to produce two types of structurally and energetically similar conformational isomers of PTPAn, we attributed the two pairs of closely overlapped CV peaks to be brought about by the two types of isomers of PTPAn (Fig. 4), which may be formed simultaneously as fragments in the polymer chains, or as independent parts in the polymeric material. Molecular orbital study of methyl substituted TPA supports this suggestion. It is revealed that *para*- and *meta*-substituted TPAs showed a slightly affected electronic structure and their HOMO energies change only 0.1–0.2 eV [23]. Because the two CV peaks of the *p*- and *m*-PTPAn have similar areas, we can think of the ratio *p*-PTPAn and *m*-PTPAn to be close to 1:1.

It can also be seen from Fig. 3 that the redox potentials of PTPAn were considerably higher than those observed for PAN and its derivatives [6,7], and the maximum redox currents appeared at 3.9 V, which is indicative of the high operating voltage of this material when used for energy storage and delivery. Probably, the high redox voltage of PTPAn is resulted from a

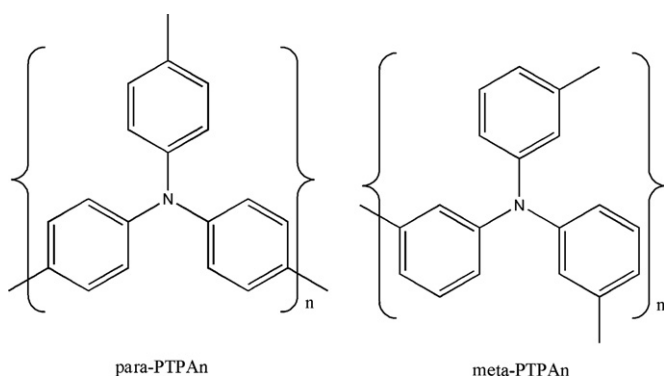
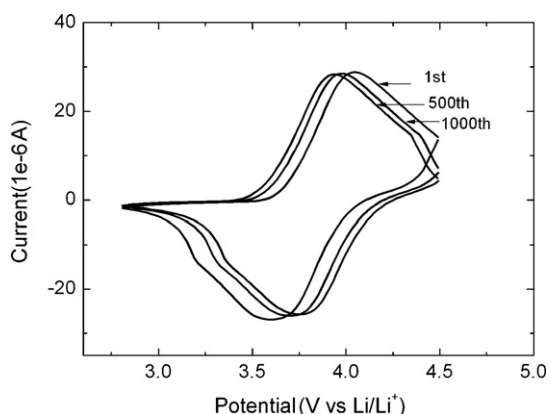
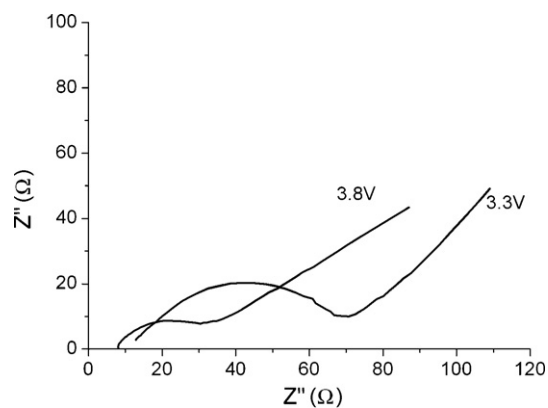


Fig. 4. Two possible isomers of PTPAn.

strong electron-withdrawing ability of three phenyl groups in a TPA unit.

When the scan rate was increased to 10 mV s^{-1} , the two pairs of redox peaks of PTPAn were overlapped to one pair of redox peaks, as shown in Fig. 5. After successive scans of 1000 cycles, the CV curves changed very slightly and remained almost the same areas of anodic and cathodic bands, showing excellent electrochemical reversibility and cycling stability. In general, the capacity decay is a problem for electroactive polymers due to breakdown of the polymeric structures, occurring particularly during cycling at high oxidation potentials. As discussed in optoelectronic applications of PTPAn materials, it has been revealed that because the amine redox centers in PTPAn were located in the center of the polymer backbone and bridged alternately by triphenyl units, thus, the nitrogen centers can undergo reversible oxidations while its radical cations were sufficiently stabilized and no further chemical reaction took place [24].

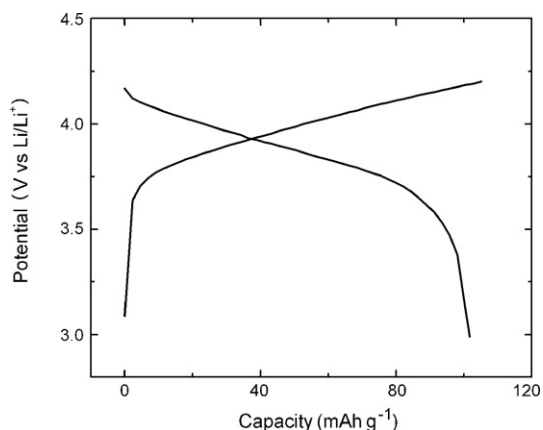
Fig. 6 gives the electrochemical impedance spectra of the PTPAn film electrode measured at $+4.0 \text{ V}$ and $+3.5 \text{ V}$, corresponding to a fully charged (doped) state and a discharged (de-doped) state, respectively. In these impedance plots, the semicircles at higher frequencies represent the charge-transfer reaction, while the straight lines at low frequencies display the diffusion-controlled process. For the discharged PTPAn electrode, both the semicircular part and the linear part of the impedance are well defined; suggesting that the charge trans-

Fig. 5. Successive cyclic voltammograms of a PTPAn microelectrode at 10 mV s^{-1} .Fig. 6. Impedance plots of the PTPAn film electrode: (a) charged to 4.2 V and (b) discharged to 3.5 V .

fer and the mass transfer reactions were combined to determine the kinetic behaviors of the polymer electrode. However, when the PTPAn electrode was charged to 4.2 V , the impedance plot appeared mainly as a Warburg impedance and the semicircular part became small and not well defined, implying that the electrode system was kinetically very facile and the mass transfer was a rate-determining process. By comparison of the two spectra in Fig. 6, it can be concluded that once doped the PTPAn material becomes highly conductive and kinetically facile for charge transfer and transport.

3.3. Charge–discharge performances

Typical charge and discharge curves of the PTPAn electrode are shown in Fig. 7. As it can be seen, both the charging and discharging curves show an approximately linear relationship between voltage and capacity at $4.2\text{--}3.6 \text{ V}$, seemingly behaving like an electrochemical capacitor. The charge and discharge voltages are also symmetric in accord with the oxidation and reduction potentials of PTPAn in the CV curves as shown in Fig. 3. At a moderate discharge rate of $0.5C$, the discharge capacity attained to 103 mAh g^{-1} , $\sim 94\%$ of the theoretical capacity (109 mAh g^{-1}) as expected from one electron transfer per TPA unit. This means that PTPAn can be almost 100% doped and

Fig. 7. The Charge–discharge curves of Li–PTPAn test cells at a constant current of 50 mA g^{-1} .

de-doped, which is considerably higher than the doping levels of most conducting polymers reported so far.

In general, polymeric cathode materials have a common problem of structural degradation when cycled at high oxidation potentials. For example, the structure of PAN and PPy would be destroyed when charged to higher potential than 4.0 V [7,25]. However, the PTPAn electrode exhibited an excellent structural stability even charged to a high potential of 4.4 V and remained its initial capacity after hundreds of charge–discharge cycles. As discussed above, the electrochemical stability of PTPAn may be due to its structural specificity that the radical cations were embedded in and stabilized sufficiently by the PPP-like polymeric backbone.

A superior electrochemical performance of the PTPAn material is its high-rate charge and discharge capability. Fig. 8 compares the discharge curves of the PTPAn cathode at different charge rates. It is shown that even though the charging rate was 100 times increased from 0.3C to 20C, the PTPAn electrode showed a slightly decreased discharge capacity and still remained 90% of its capacity obtainable at low rate charge of 0.5C. Also, the PTPAn electrode exhibited a strong dischargeability at very high rate. At a very high rate of 20C (2000 mA g⁻¹), the PTPAn electrode can deliver a discharge capacity of 91 mAh g⁻¹, about 90% of its discharge capacity at 0.5C.

Fig. 9 shows the cycling properties of the PTPAn electrode at fast charge and discharge. After 1000 cycles at a rate of 20C, the discharge capacity dropped very slightly from its initial 91 mAh g⁻¹ to 84 mAh g⁻¹, with only about 5% loss of its capacity. At the same time, the coulombic efficiency for the charge–discharge of this electrode rapidly rose up from 92% at first cycle to nearly 100% at third cycle and then kept stable at prolonged cycles. These data demonstrated excellent cycleability and cycling stability of the PTPAn material at high-rate applications.

Usually, polymer electrodes have much higher self-discharge rates than conventional oxide electrodes, which has been a problem of concern for practical applications of electrochemical energy storage. However, it is found in our experiments that the Li–PTPAn test cells have shown quite good capacity retention, about 90% of its initial capacity when stored at room tempera-

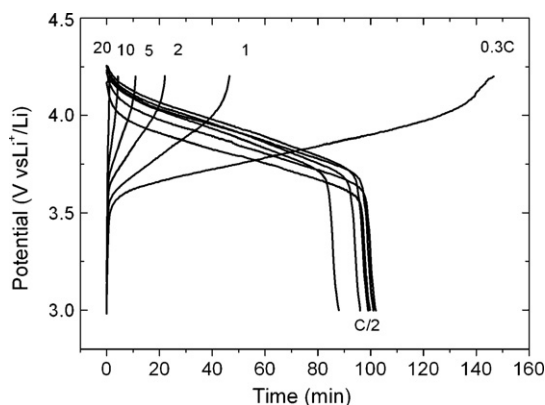


Fig. 8. The C/2 discharge curves of PTPAn electrode at various charging rates as labeled each charging curves.

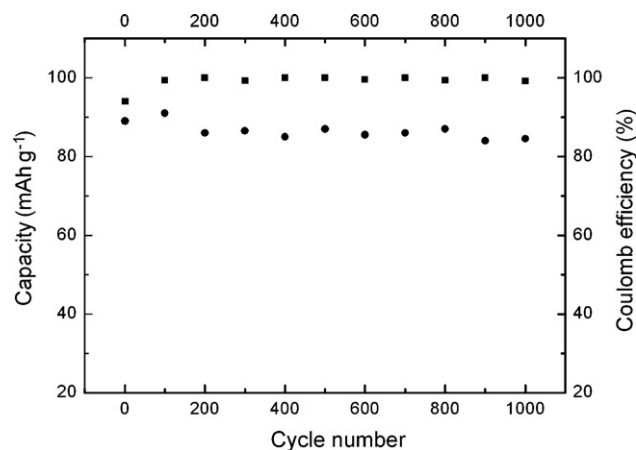


Fig. 9. The cycling performance of PTPAn at charging and discharging rate of 20C.

ture for 2 weeks, which is comparable to most of commercial rechargeable batteries. Although we cannot give a definitive interpretation of this low self-discharge at present understanding, it is reasonable to attribute the very stable oxidative state of this polymer to its largely conjugated structure in which the charge on each redox center is delocalized and protected by surrounding three phenyl-rings from chemical attack.

3.4. Possible operating mechanisms of the PTPAn electrode

The experimental results given above clearly demonstrated the superior high-rate capability of the PTPAn material coupled with quite a high energy density capability. However, the question arises why PTPAn can show such a high power capability but not most of other electroactive polymers. Although it is difficult to answer this question for lack of detailed understanding of the electrochemical kinetics of the PTPAn material, we can still find out the possible mechanisms responsible for the excellent charge and discharge behaviors of the polymeric PTPAn electrode.

First, PTPAn is considered as a radical polymer with the inter-valence charge-transfer similar to those in monomeric radical compounds, i.e. the charge-transfer processes taking place from triarylamine radical cation centers to neutral triarylamine moieties [21]. Also, it is reported that electron transfer processes can be extremely fast in triarylamine redox centers, which is a consequence of the strong electronic coupling compared to its small reorganization energy, because the charge is partly delocalized in the triarylamine moieties [20]. Thus, we can ascribe the charge–discharge mechanism of PTPAn to be a radical redox reaction. Since the radical redox process does not involve bond cleavage and structural rearrangements, it is therefore expected that the charge transfer process of the PTPAn electrode is sufficiently fast for high-rate storage and delivery of electrochemical energy.

Secondly, TPAs are well known to be a hole-transporting material and currently used in organic optoelectronic devices [20,21]. Composed of π -conjugated TPA substructure, PTPAn should have a similar conductivity of long-range electron or hole transfer as TPA materials. Due to the electronic wiring

of each redox centers of TPA by conductive polymeric chains, the current collecting and conduction are no longer a serious problem of much concern for high-rate charge and discharge.

Furthermore, PTPAn is theoretically a planar macromolecule. Although PTPAn may not appear as a complete plane, it must be composed of large amount of planar oligomers of TPA structure. We can conceive of the as-prepared PTPAn as a macroscopically porous material consisted of planar oligo-triphenylamine fragments. In such a polymeric structure, the electrolyte salt can approach to the electroactive surfaces very easily without much steric hindrance and therefore the radical cations produced during charge process could be very quickly electrostatically balanced by neighboring phosphorus hexafluoride anions in the electrolyte with no need for the anions undergoing long-distance diffusion in the solid polymer phase.

4. Conclusions

In summary, we have shown above that PTPAn can be simply synthesized and utilized as a high capacity cathode material for high-rate storage and delivery of electrochemical energy. It is found in this work that the polymer can be p-doped to a degree of ca. 95% per triarylamine unit at a moderate rate of 0.5C, giving a discharge voltage of 3.8 V and quite a high capacity of 103 mAh g⁻¹. Of particular interest is the superior high-rate capability and cycling stability of the PTPAn material. Even cycled at a very high rate of 20C, the polymer can still deliver a capacity of 90 mAh g⁻¹ at 1000th cycle with a nearly 100% coulombic efficiency.

The excellent electrochemical performances of PTPAn are suggested to arise from the structural specificity of the polymer where the radical redox centers are embedded in and stabilized by conductive polymeric backbone, which makes the radical redox and charge-transporting processes kinetically facile for high-rate charge and discharge.

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