

Properties of poly (4-nitro)triphenylamine-thiophene Composite based Cathode Material for Rechargeable Lithium-ion Battery

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A triphenylamine-based conjugated polymer (PTPA-NO₂)-PTH poly[4-(nitro)triphenylamine-thiophene] with multiple active polymerization sites has been prepared as the cathode material. First, the crystal phase structure, surface morphology and element states were characterized by XRD, SEM and XPS in turn, the dispersed porous arthiicstructure supply a rich electrochemical interface and ion channels to improve its electrode reactivity. By calculating the energy level of HOMO and LUMO orbitals, we find that the conductivity and conjugation ability are enhanced. Then the electrochemical charge and discharge performance, CV and EIS of the battery were also tested, because of the nitro electron-absorbing functional unit are introduced in the triphenylamine skeleton, the copolymer perform a reversible specific capacity of 772.4 mAh/g with two significant charge-discharge voltage platforms under different reaction mechanisms after 500 cycling, even when the current density is 1600mA/g, this composite material still maintain a high capacity of 550mAh/g with the efficiency $\geq 99\%$.

Keywords: triphenylamine-based conjugated polymer; nitro; electrochemical; lithium-ion battery

1. INTRODUCTION

Electroactive conductive polymers are a class of macromolecules [1, 2] with high conductivity and practicable fast chemical kinetics properties that can store and transfer electrical energy efficiently. Over the past few years, various conducting polymers, such as polyaniline (PAn) [3, 4], polythiophene (PTh) [5, 6] and their derivatives, have been investigated as cathode active materials for lithium ion batteries or supercapacitors [7, 8] because of its excellent cycling stability and stable voltage platform.

Polytriphenylamine (PTPAn) is a kind of conjugated and mixed valence polymer with super-fast electron transfer rate constant and excellent hole transport ability [9-12]. As a typical p-dopable radical polymer, it can realize the reversible free radical redox reaction in the charging and discharging process

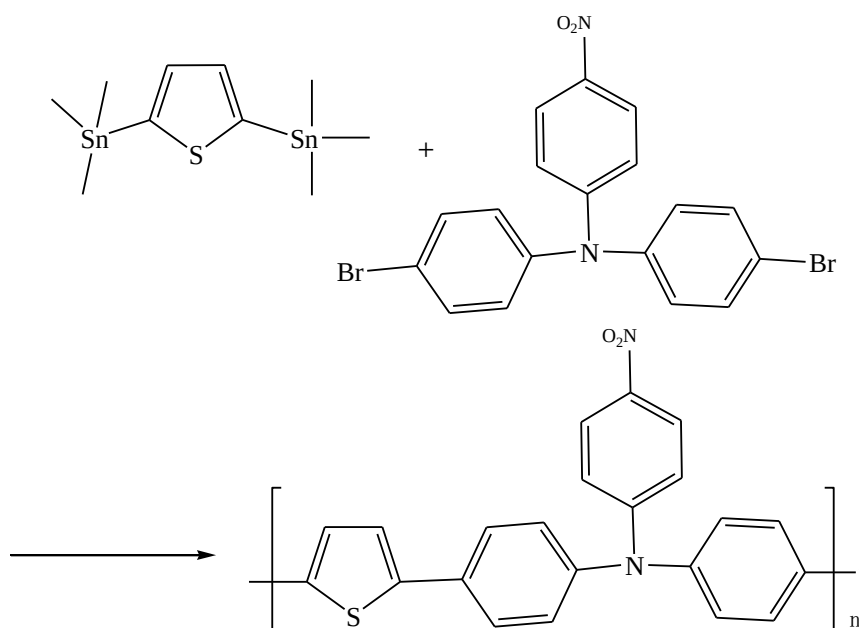
of organic rechargeable batteries [10], exhibiting the well-defined high voltage plateau of 3.6V [9] and long-term cycling performances. But it also confront with the problems of low actual capacity (about 109 mAh/g) that still need to be improved, this is mainly due to the dense aggregation in the electrode which prevents the contact between active sites and the electrolyte, leading to the low utilization of active matter and slow diffusion of lithium ions.

In order to enhance the energy density of the battery, we can introduce some functional neighboring groups into the PTPA system to make a novel structure, such as the electron with-drawing groups (Cl, F, CN and NO₂) [13-15], which can increase the numbers of redox center per repeating unit, and also raise the redox potential can be forecasted by theoretical chemical calculations [16, 17]. In addition, in the search for n-type organic polymer materials, we focus on the polythiophenes and try to design a simple organic synthesis route by coupling with p-type polytriphenylamine (PTPAn) derivative, to construct a new type of composite conductive polymer cathode material.

In this paper, a high capacity cathode material (PTPA-NO₂)-PTH for lithium secondary batteries is reported, and discuss the possible mechanism between its molecular structure and electrochemical performances, as well as the details of charge-discharge process. It is of great significance to probe the effect of molecular structure on the redox potentials and the change of micro-morphology on their charge storage state. These work provide valuable references for obtaining advanced polymer cathode materials.

2. EXPERIMENTAL

2.1 Synthesis of (PTPA-NO₂)-PTH



Scheme 1. Synthesis route of (PTPA-NO₂)-PTH

In this paper, a new triphenylamine-based derivative polymer containing the thiophene was

synthesized.

First, we weighed 300mg of nitrodibromotribenzidine(molecular weight is 448.11), then we weighed 274.4mg of the thiophenediacetol, and 50mg of dichlorotriphenyl phosphorus-based Palladium as Catalyst, carbon powder 900mg. All these were reacted for 48 hours in 60 mg toluene under the argon atmosphere. Finally, we used n-hexane, methanol, acetone, and dichloromethane for the extraction process 3 days successively. Powder material was obtained as an electrode material.

2.2 Material characterizations

The crystal phase of the synthetic sample was collected by x-ray diffraction (XRD) on a X'Pert PRO diffractometer (PANalytical B.V, Holland) with Cu Ka radiation ($\lambda = 0.1541 \text{ \AA}$) at 40 kV and 20 mA operating conditions, the scanning range was $5 \sim 80^\circ$ at a step length of 0.0167° . The surface morphology were observed by Scanning electron microscopy of JSM6380LV (Japanese electronics) under 30 kV voltage and vacuum gold plating. XPS analysis of the polymer film sprayed on the ITO substrate was performed on an Escalab 250 (Thermo Scientific, USA) x-ray photoelectron spectrometer.

2.3 Electrode cell assembly

The copolymer powder, acetylene black and PVDF were mixed at the mass ratio of 70:20:10 with N-methylpyrrolidone as solvent, they were stirred down to well-distributed, and the slurry were manually coated on the clean copper foil with a spatula to form a 0.1 mm thick membrane. The copper foil was then dried at 60°C for 24 hours in a vacuum oven and cut into 12mm diameter electrode plate by microtome. By weighing the content of per unit area is about $0.33\text{mg}/\text{cm}^2$.

The CR2032-type button cells were assembled in the high-purity Ar gas glove box (water and oxygen are below 0.1ppm) with lithium tablet as the anode, the electrode prepared above serve as the cathode and separated by a micro-porous polypropylene (PP, Celgard 2400) film, 1M LiPF_6 in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) purchased from Merck as the electrolyte.

2.4 Electrochemical measurements

Leave the assembled battery for 12 hours, charge and discharge tests were measured at a constant current on LAND CT2001A battery test system (Wuhan, China) controlled by programmable computer, and circulated 500 times in two voltage ranges of $0.05 \sim 2.5 \text{ V}$ and $0.05 \sim 4.0 \text{ V}$ (vs Li/Li^+).

The cyclic voltammetry were conducted at the CHI600D electrochemical station (Chenhua, Shanghai), the cathode was used as the working electrode, the lithium metal plate was used as the auxiliary electrode and the reference electrode, the scanning rates were 10 mV/s and 50 mV/s , the voltage range was $0 \sim 4.0 \text{ V}$. The AC impedance of the battery before and after 500 cycles of charge-discharge tests were carried out on Gamry electrochemical station (Reference3000, America), the frequency range was $0.01 \text{ Hz} \sim 0.1 \text{ MHz}$ and the amplitude of the alternating signal was 3 mV .

3. RESULTS AND DISCUSSION

3.1. XRD analyses

The structure of the polymer is determined by XRD for the first time, the result is showed in Figure 1. We can see that two wide and dispersed diffraction peaks appear at $2\theta=25^\circ$ and 42.5° respectively, indicating that the synthesized polymer is reflected mainly in the amorphous state, in which the $2\theta=25.1^\circ$ peak is due to the periodic vertical scattering of the polyphenylamine chain [18]. In addition, due to the large benzene group in this macromolecule chain, the torsion angle of the polythiophene segment is reduced, the local regularity is high, and the crystallization degree is higher, there is a strong diffraction peak in $2\theta=20^\circ$.

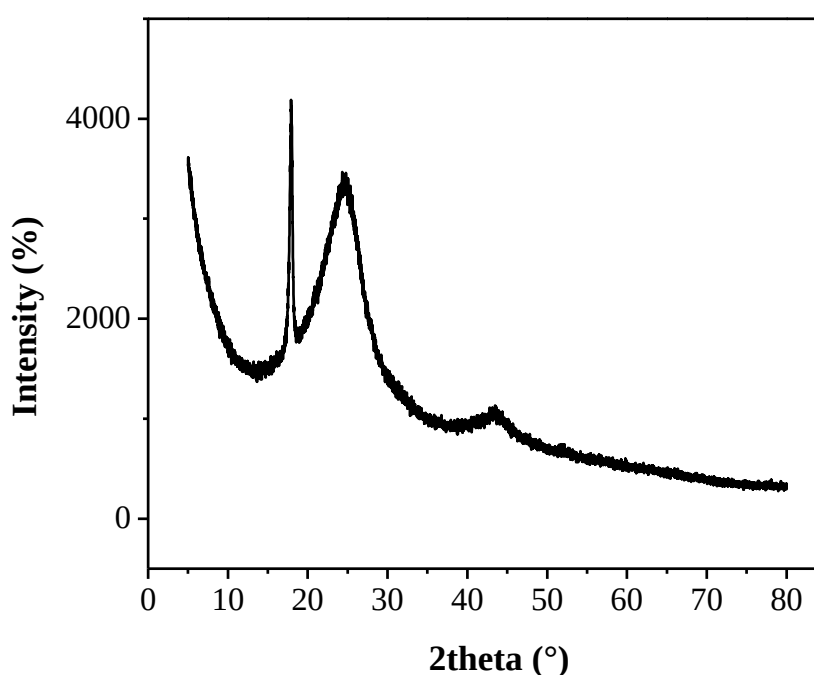


Figure 1. XRD spectra of the copolymer

3.2. SEM measurement

Fig. 2 show the scanning electron microscope (SEM) images of the cathode before and after 500 charge-discharge cycles, and they were magnified 5k and 50k times, respectively. Before discharge, the particle size distribution of the composite material is uniform, this derivative exhibit a dense granule and open morphology, the microstructure is beneficial to the diffusion of electrolyte and the migration of lithium ions. After 500 cycles, the surface appearance of the electrode has hardly changed and the whole reaction frame is intact, there is only a slight aggregation which may be caused by large triphenylamine molecular structure, including big sizes of 0.2 μm -0.5 μm and it still smaller than some polymer that have been reported [19]. As can be see, the electrode has a honeycomb arthicstructure and a large number of interconnected holes, in favor of the cathode material to participate in the charge and discharge course effectively and improve its electrochemical properties as macromolecular storage batteries.

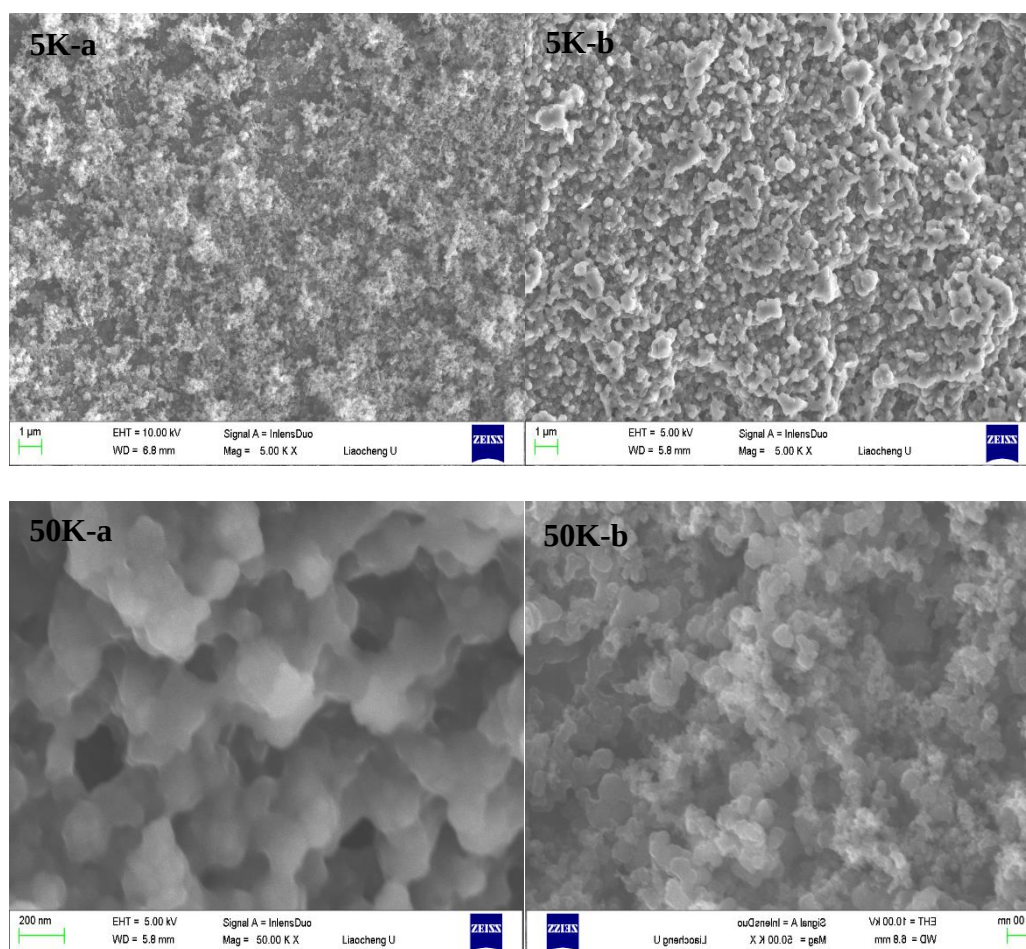
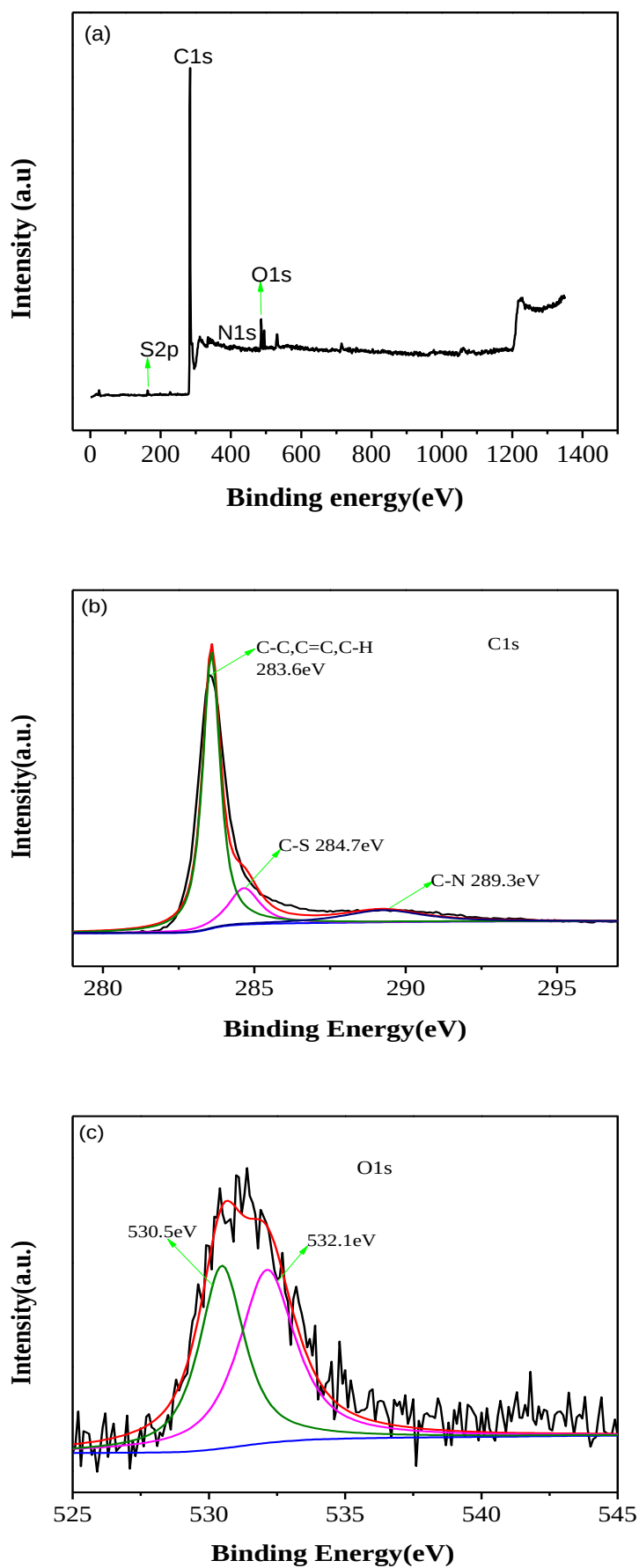


Figure 2. SEM pictures of the cathode sheets (a) before cycle (5k, 50k), (b) after 500 cycles (5k, 50k)

3.3. XPS investigation results

X-ray photoelectron spectroscopy is used to identify the surface distribution of element types, chemical valence states and relative strength contrast of the synthetic copolymer. Fig. 3(a) confirm that there are four characteristic elements of C, N, O, S existing in the sample material. In figure 3(b), the high-resolution C1s spectra are fitted into three peaks, the peak at 283.6 eV prove the existence of sp^3 and sp^2 hybridized carbon atoms, which come from carbon-carbon single bond, carbon-carbon double bond and carbon-hydrogen bond of the benzene ring and the thiophene ring; the signal at 284.7 eV correspond to C-S bond and the signal at 289.3 eV correspond to C-N bond [20]. The O1s spectrum are fitted into two peaks: containing lattice at 530.5 eV and absorbed oxygen at 532.1 eV, as showed in Fig. 3(c), they are ascribed to the existence of O-N-O. Fig. 3(d) show the high resolution S2p spectrum is divided into two parts by fitting the peak at 163 eV ($S2p_{3/2}$) and the peak at 164.2 eV ($S2p_{1/2}$) [21].



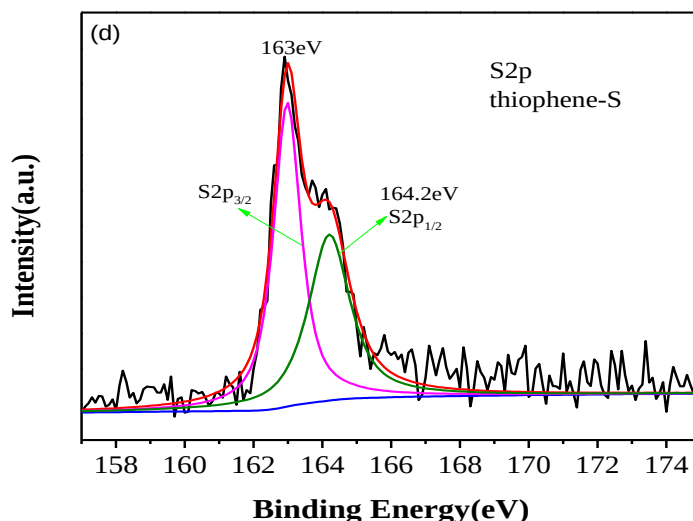


Figure 3. Full XPS spectrum of the composite (a), high-resolution signals for C1s (b), O1s (c) and S2p (d)

3.4. Molecular orbitals and energy levels

The orbitals of the constituent monomers were simulated using the Density functional theory method in Gaussian quantum chemistry computing software, as shown in Fig. 4. HOMO have the properties of electron donor and LUMO has electron affinity and electron acceptor properties, both of which play an important role in chemical reactions. We can see from table. 1, the energy levels of different monomer polymers were also acquired. From the electron clouds distribution of thiophene, it can be seen that the LUMO orbit is distributed according to the S-type, besides, the LUMO energy of the thiophene is -6.49 eV, is the smallest of the three monomers, which proves that it can be used as a cathode material. According to the reported literature [22], the electron orbitals in triphenylamine (TPA) are distributed evenly, however, for the TPA-NO₂, due to the electron attraction function of the nitro, most of the electron cloud on triphenylamine are extended to the nitro group, compared with PTPA-CN (-5.33 eV), it has a stronger electric absorption effect, its HOMO energy level is calculated to be lower, at -5.68 eV. From the LUMO orbital in the third row, there are almost no electrons in the thiophene ring after the combination, and it is presumed that the nitro group and the linked triphenylamine should be the main reactive center. By subtraction, we find that the band gap (energy level difference between the valence band and the conduction band) of the newly synthesized copolymer is the smallest of 3.03 eV, which make clear the conductivity of the conjugate system is enhanced, the oxidation-reduction activities of n-type doped thiophene and p-type substituted triphenylamine are both strengthened.

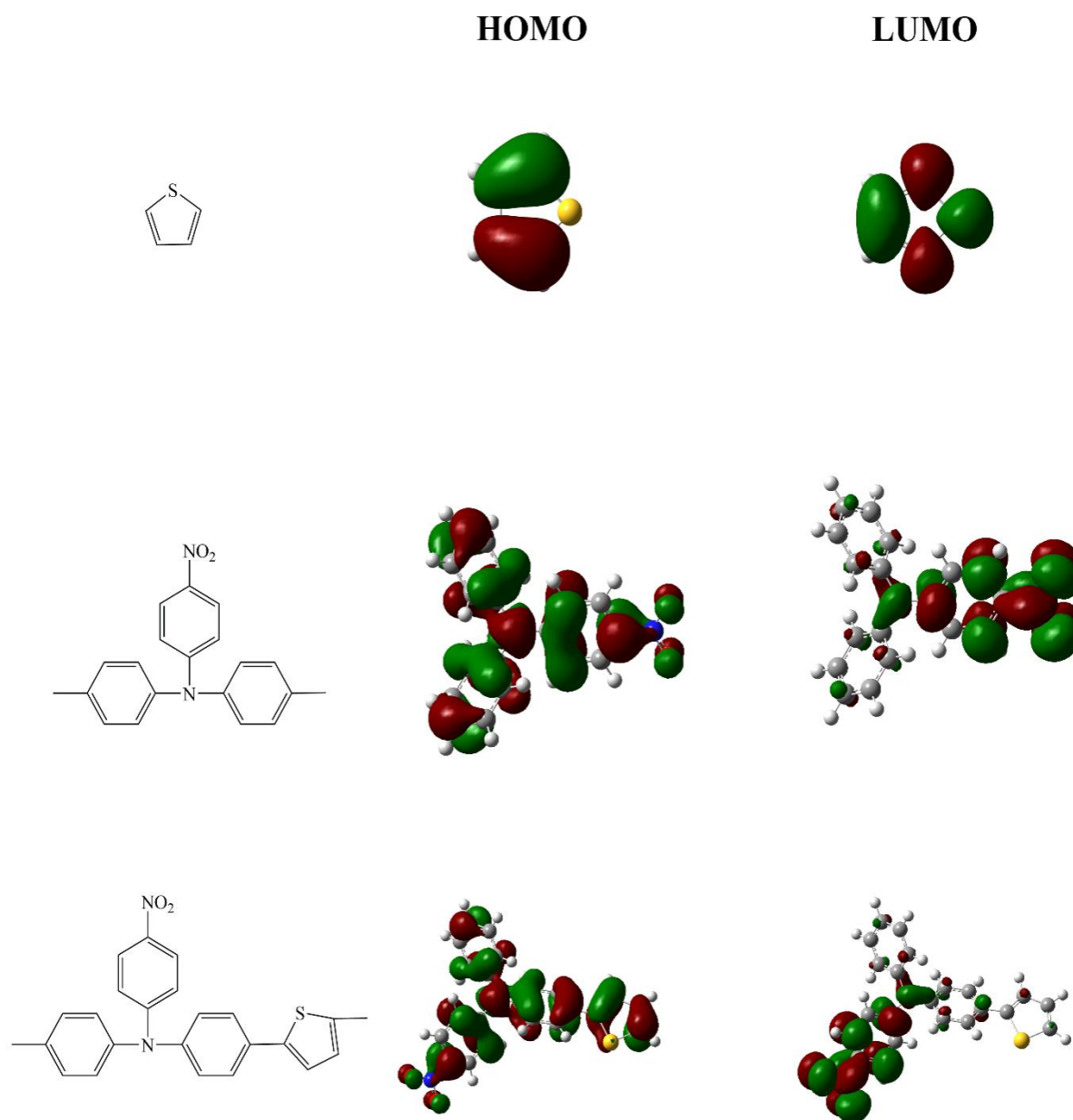


Figure 4. Molecular orbitals (HOMO and LOMO) of the functional monomers

Table 1. HOMO and LUMO energy levels of three polymers

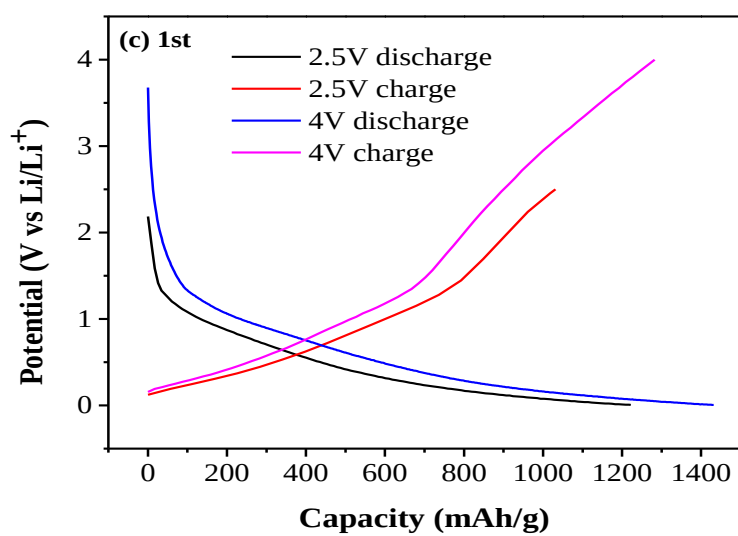
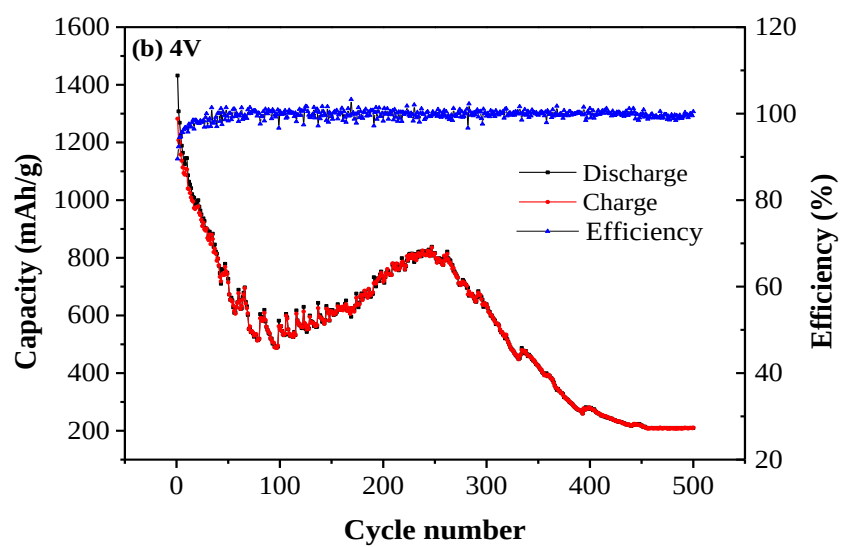
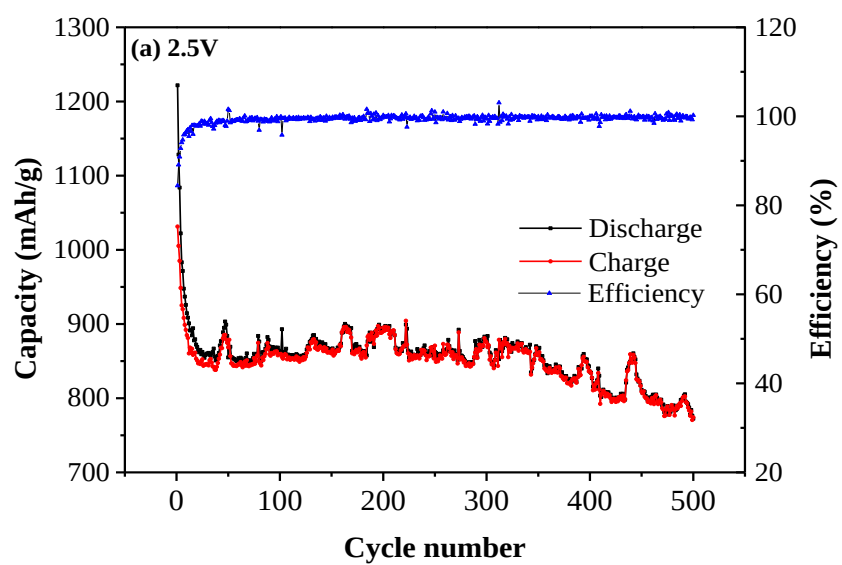
Monomer	HOMO (eV)	LUMO (eV)	Forbidden Band (eV)
PTPA-NO ₂	-2.46	-5.68	3.22
PTH	-0.41	-6.49	6.08
(PTPA-NO ₂)-PTH	-2.51	-5.54	3.03

3.5. Electrochemical performances

The charge and discharge behaviors of this polymer as the cathode material have been studied systematically. As described in picture 5(a), when charged to 2.5 V at the current of 200 mA/g, the (PTPA-NO₂)-PTH display an primary discharge capacity of 1221.8 mAh/g, after 50 cycles the specific capacity decline to 854.9 mAh/g, with a loss of about 2% per cycle, during the following cycles, it exhibit a comparatively stable cyclic performance, and then the capacity decline slowly, after 500th cycle, the capacity is stabilized at 772.4 mAh/g, charge-discharge efficiency is more than 99%. In the back-and-forth of doping and de-doping, changes in the electrode volume may cause the fluctuation and resulting in reduced capacity. Nevertheless, in general, the excellent cyclic characteristic can be attributed to open and dispersed multi-void morphology as seen in the previous SEM images, obviously, it can provide a rich electrochemical interface and ions channels. Meanwhile, p-conjugated conducting skeleton of the polymer is helpful to enhance the rate of electron transfer.

Relatively, as described in picture 5(b), when charged to 4 V, in the first 100 cycles, it also show a downward trend, compared to the discharge specific capacity of 2.5 V (864 mAh/g), which is smaller, it is 551 mAh/g. And yet, from 100 to 250 cycles, the capacity of 2.5 V has stabilized, but when charged to 4 V, it rise from 551 mAh/g to 816 mAh/g, which is a unique phenomenon compared with the previous cathode materials, this increase indicate that the electroactive conductive copolymer has been fully used in the process of charging and discharging. After 250 cycles, the specific capacity begin to drop again, until by the time the loop is 500 times, the specific capacity drops to 210 mAh/g, as a whole, during the cycles of high oxidation potential, the damage of electrode material structure and the dissolution in the electrolyte are the main reasons for the subsequent capacity degradation. We can explore a number of measures to make the battery received over-charging protection, to prevent further oxidation of cathode materials and electrolytes [23]. It's like being charged to 2.5 volts, the coulomb efficiency is also very high and staying close to 98%.

The initial charge and discharge curves of the battery when be charged at 2.5 V and 4 V are showed in figure 5(c). Both of the discharge profiles have two slanting discharge platforms at 1.4 V- 2.4 V and 0.5 V-1.0 V, based on the estimates ahead [24, 25], the results corresponding to the doping/de-doping of PF₆⁻ ions on nitrogen radical in the main chain of triphenylamine at high potential (in Scheme 2) and the insertion and de-insertion of lithium ions on the nitro part at low potential (in Scheme 3) separately, these are consistent with the redox peak voltages of the CV curve that will follow, it is evident that the bulk capacity to be concentrated in the nitro group.



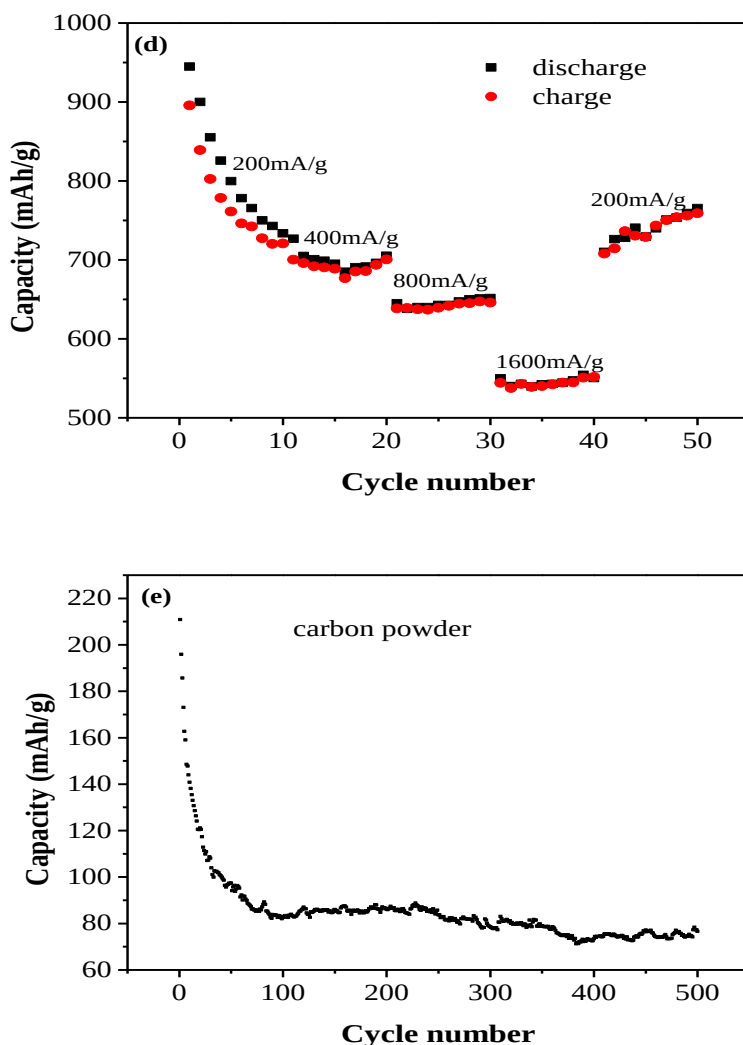
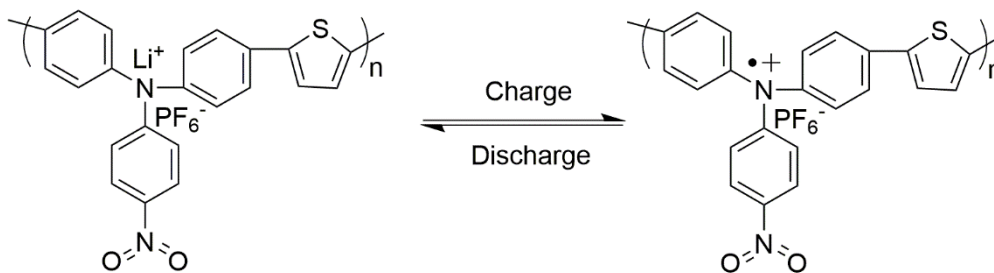
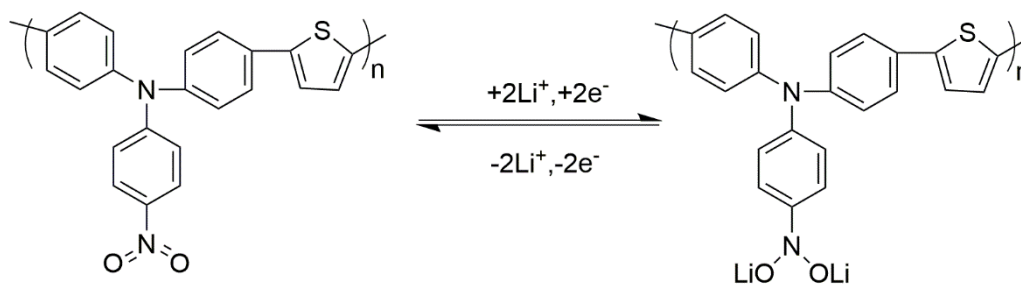


Figure 5. (a) The charge-discharge cycling performance and efficiency when be charged to 2.5 V within 500 cycles; (b) The charge-discharge cycling performance and efficiency when be charged to 4 V within 500 cycles; (c) Initial charge/discharge profiles of two charged voltage 2.5 V and 4 V at the current of 200 mA/g (vs Li/Li⁺); (d) The cycling capacities of the battery at different charge and discharge currents as shown above in the voltage from 0.05~2.5 V; (e) The discharge cycling performance of pure carbon powder (the mass ratio with acetylene black and PVDF is also 70:20:10, at the same current and charged voltage of 200 mA/g, 2.5 V).



Scheme 2. The charge-discharge mechanism of (PTPA-NO₂)-PTH at high potential



Scheme 3. The charge-discharge mechanism of (PTPA-NO₂)-PTH at low potential

By the way, rate performance is another important index to judge the battery, which reflects the capacity retention and resilience percentage of an electrode active matter at high current. The cell is studied each 10 cycles at different current densities of 200 mA/g, 400 mA/g, 800 mA/g, 1600 mA/g respectively, and finally go back to 200 mA/g, the changes in charge-discharge capacity are showed in Fig. 5(d). From 200 mA/g to 1600 mA/g, the capacity decreases with the increase of current density, which descend from 900 mAh/g to 550 mAh/g, these may be caused by the polarization signs, but this composite material still maintain a high capacity, and when the current return to 200 mA/g, the capacity restore to 766 mAh/g. The good hole transport ability of the triphenylamine unit and the stable free radical center embedded in the polymer skeleton [26] is a key factor in its good rate performance.

In order to enhance the electrochemical reactivity of the copolymer, a number of carbon powder was put in the polymerization system to form a conductive network around it. Therefore, we should remove the contribution to the reversible capacity, so under the same test conditions repeating 500 times, the cycling property was reappeared. As you can see from the diagram 5(e), the toner offer a lithium ion intercalation/exit capacity up to 210 mAh/g and remains stable over a long period of time, taking the intermediate value at the active substance weight ratio of 7:3 ($7/3 \times 140 = 233$ mAh/g), the residual specific capacity is about 445 mAh/g. To sum up, due to the n-type doping potential of thiophene rings is low [24], the new composite conductive cathode material has a relatively low redox potential compared to the same class of polytriphenylamine derivatives, but it shows superior reversible circulation capacity, which is higher about 4-5 times [19, 22, 25, 27-28].

The completed papers have shown that there is one electron [9] involved in the electrode reaction at a time, in addition, each nitro group has two electrochemical active centers (in Scheme 3), even if every thiophene unit [29] can undergo one electron redox reaction, according to the formula for calculating the theoretical specific capacity: $C_m \text{ (mAh/g)} = 1000nF/3600M$ [27], the theoretical value of the copolymer is to be 287.28 mAh/g. As far as we know, it's high among similar conjugated polymers we've seen, but it is below the reversible capacity after cycling, we speculate that there may be two reasons for this results. First, the polythiophene substituted by nitro-triphenylamine has a long twisted [30] conjugated chain structure, which resulting in the expansion of the electron transfer band that allow each repeating unit to actually have more than four electrons involved in the electrode charge-discharge reactions. Second, the wrapped composition of carbon powder play as the gargantuan conductive environment, which facilitates the fast electron/ion migrate in contact between active substances, and also can adsorb soluble electrolytes in the polymer layers.

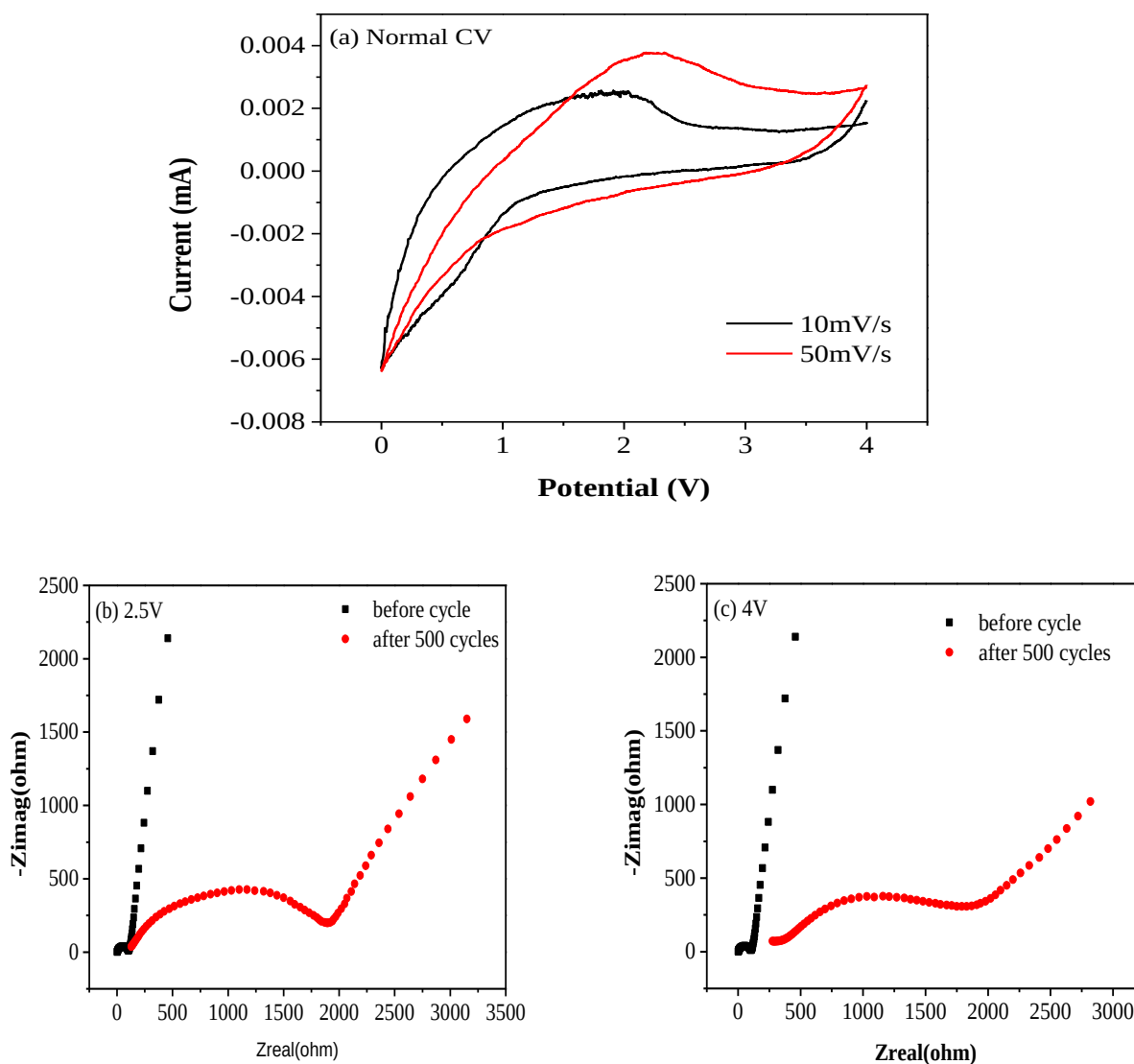


Figure 6. (a) The CV curves of the polymer at the rates of 10 mV/s and 50 mV/s from 4 V to 0 V; (b) EIS of the copolymer electrode before and after 500 cycles when be charged to 2.5 V; (c) EIS of the copolymer electrode before and after 500 cycles when be charged to 4 V.

Figure 6(a) show the cyclic voltammetric characteristic rule of (PTPA-NO₂)-PTH positive at scan rates of 10 mV/s and 50 mV/s (scan voltages range from 0 to 4 V). Two pairs of anode and cathode peaks appear on the CV curves, which match with two charge and discharge platforms of the battery. The oxidation peaks of this polymer locate at 0.80 V and 2.0 V (10 mV/s), 2.5 V (50 mV/s), the oxidation peak area is larger than the reduction peak area, which indicates that the material has high oxidation electrode activity, and the oxidation rate of the PF₆⁻ anions in the electrolyte moving towards the conductive copolymer is very fast.

The impedance diagrams are continue to be studied before and after 500 cycles and fitting curves are showed in Fig. 6b (2.5 V) and 6c (4 V), where initial acquisition of frequency spectrum on high frequency represents the electrolyte resistance (R_e), a semicircle at low impedance frequency represents the charge transfer reaction resistance (R_{ct}) and the low frequency line represents the diffusion

impedance (Z_w) of the ions. As can be seen, R_e increase slightly after 500 cycles, especially for batteries when be charged to 4 V, indicating that some electrode materials are flow into the electrolyte during cycling process. In addition, both the R_{ct} and the Z_w are higher than those before the cycle, for example, R_{ct} varies 50 Ω , 1000 Ω for charging state of 2.5 V, 50 Ω , 750 Ω for charging state of 4 V, the results indicate that the cathode has good conductivity before cycling, 50 Ω for the (PTPA- NO_2)-PTH electrode is almost the smallest compared to 244 Ω for PTPAn, 167 Ω of electron-withdrawing substituent PTPA-CN and 513 Ω of electron-donating substituent PTPA- CH_3 [22], and it also provide further evidence of the capacity decay during the charge-discharge cycles.

4. CONCLUSION

A new type conductive copolymer of nitro-substituted triphenylamine with thiophene was synthesized through a simple organic synthesis route, XRD and XPS confirm the polymer has been prepared successfully. CR2032-type button cells were assembled with lithium tablet as the anode, (PTPA- NO_2)-PTH serve as the cathode, the surface appearance of the cathode has hardly changed after 500 cycles as seen in the SEM images, and forbidden band between HOMO and LUMO energy level is the smallest of 3.03eV among three constituent monomer polymers, demonstrate that the oxidation-reduction activities of n-type doped thiophene and p-type substituted triphenylamine are both strengthened. The battery display an primary discharge capacity of 1221.8 mAh/g when be charged to 2.5 V, the discharge profiles show that the bulk capacity is concentrated in the nitro group, after 500th cycles, the capacity is stabilized at 772.4 mAh/g, with a high current efficiency of $\geq 99\%$, deducting the contribution of carbon powder to the reversible capacity, there is still about 445 mAh/g, which is higher than that of be charged to 4 V. The good hole transport ability of the triphenylamine structural unit is a key factor in its good rate performance, even at a current of 1600 mA/g, it still have a high capacity retention of 550 mAh/g. In conclusion, although the new cathode material has a relatively low redox potential, but it shows superior reversible circulation capacity, which is about 4-5 times higher than the same class of polytriphenylamine derivatives.

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