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PAPER

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## Polytriphenylamine derivative with high free radical density as the novel organic cathode for lithium ion batteries

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Polytriphenylamine derivative, poly [N, N, N, N-tetraphenylphenylenediamine] (PDDP) with a high free radical density had been synthesized and studied as a cathode material of organic free radical batteries for the first time. The chemical structure, morphology and electrochemical properties of the prepared polymers were characterized by Raman spectra (RS), electron spin resonance (ESR), ultraviolet visible spectroscopy (UV-vis), scanning electron microscopy (SEM), cyclic voltammograms (CV) and electrochemical impedance spectra (EIS), respectively. Also, the charge-discharge properties of the prepared polymers were studied by galvanostatic charge-discharge testing. Compared to polytriphenylamine (PTPA), the fabricated lithium ion half-cells based on PDDP as the cathode exhibited two well-defined plateaus at two discharge voltages of 3.8 and 3.3 V vs Li/Li<sup>+</sup> and an improved capacity of 129.1 mAh·g<sup>-1</sup> which was very closed to its theoretical capacity (130 mAh·g<sup>-1</sup>). The excellent electrochemical performances of PDDP electrode were due to its stable chemical structure and high free radical density, which makes the PDDP be a promising free radical cathode material for organic lithium secondary battery.

### 1. Introduction

In today's modern society, the growing public demands for the use of electric devices such as electric vehicles (EVs), laptop computers, and cell phones make it necessary for the fabrication of new secondary batteries with improved properties. Compared with the anode materials, it is a challenge to design high capacity, low-cost and environmental benignity cathode materials.<sup>1</sup> For the traditional inorganic transition metal oxide-based cathode materials (e.g., LiCoO<sub>2</sub>), the environmental requirements, toxicity, recycling, limited capacity and disused of battery components are becoming hot issues, which hinder their large scale applications for upcoming portable electronic devices.<sup>2-4</sup> As an alternative, organic compounds have been investigated as novel energy storage materials for the positive-electrode of lithium batteries, which mainly include organic conductive polymers (polyaniline, polythiophene and polyimide),<sup>5, 6</sup> organosulfur compounds,<sup>7</sup> carbonyl-based compounds<sup>8-11</sup> and stable radical polymers<sup>12, 13</sup>, etc.

Recently, stable radical polymer is emerging as one of promising candidates for organic cathode materials. Among them, polytriphenylamine (PTPA) and its derivatives have been studied intensively for their interesting physical properties, including excellent charge transport, electroluminescence, and thermal and morphological stabilities.<sup>14</sup> Moreover, PTPA containing repeat triphenylamine radical units belongs to the family of radical

polymer, in which a reversible radical redox process has been demonstrated to occur during charge and discharge process.<sup>15</sup> It makes the triphenylamine-based polymer materials be explored recently as the electrode material applied in the energy storage field, such as super capacitors and lithium ion battery.<sup>16, 17</sup> As reported,<sup>18</sup> the PTPA electrodes show good electrochemical performances and well-defined voltage plateaus (~3.6 V) as the cathode of lithium ion batteries, which could be contributed to the reversible redox radicals nature of PTPA. However, the theoretical capacity of PTPA is only 109 mAh·g<sup>-1</sup> presently, which is still lower than that of the currently used LiCoO<sub>2</sub> (about 140 mAh·g<sup>-1</sup>), limiting its further research as the desired cathode of high energy batteries with the high energy density. As a solution, it will be an effective strategy to improve either the theoretical capacity (C) or the discharge voltage of PTPA (V) by the molecular structure design strategy for obtaining the high energy density batteries (Energy density= C×V).

Poly [N, N, N, N-tetraphenylphenylenediamine] (PDDP) has a similar triphenylamine structure but the higher free radical density than PTPA due to the increased number of radicals in per repeating unit, which has a 130 mAh·g<sup>-1</sup> of the theoretical specific capacity and can be a potential electrode material with multi-electron reactions, even though this type of polymer has some disadvantages, such as energy/power density, expensive catalyst need for the synthesis, long term cyclability and solubility of organic radical polymers in electrolyte, and so on.

Recent studies have demonstrated that PDDP and its derivatives generally showed excellent charge transport and electroluminescence, which have been widely applied as organic electroluminescence (EL) material, photo-conduction material and organic solar cells material.<sup>19</sup> However, to the best of our knowledge, there have no relative reports for application of PDDP as an electroactive material in lithium ion batteries. Herein, a novel strategy had been first explored to obtain the high performance of triphenylamine free radical-based cathode by using the increased free radical density polymer (PDDP) as the cathode material for higher specific capacity Li-ion battery. Also, the electrochemical properties and the charge/discharge mechanism of the prepared polymer during charge/discharge process were also systematically investigated.

## 2. Experimental

### Material synthesis

**Material** Diphenylamine (98%), 1,4-Dibromobenzene (99%), Triphenylamine (98%), Tri-tert-butylphosphine (PtBu<sub>3</sub>, 1.0 M), Sodium tert-butoxide (NaO<sup>t</sup>Bu, 98%), Palladium acetate (Pd(OAc)<sub>2</sub>, AR) were purchased from Energy Chemical Reagent Co. All other reagents were received as analytical grade and used without further purification.

**Synthesis of DDP monomer** N,N,N,N-tetraphenylphenylenediamine (DDP) was synthesized according to the reference<sup>20</sup>: 0.020 mol Diphenylamine, 0.010 mol 1, 4-Dibromobenzene and 0.020 mol NaO<sup>t</sup>Bu were dissolved in 40 mL toluene, 0.1 g Pd(OAc)<sub>2</sub> and 3 mL PtBu<sub>3</sub> were added. The mixture was stirred in Ar atmosphere at 110 °C for 12 h. The final solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and water. Then CH<sub>2</sub>Cl<sub>2</sub> was removed by rotary evaporation to afford the crude product, which was purified by column chromatography on silica gel with petrol ether as the eluent. The product was obtained as white crystal in an 88.5% yield. MS (EI): calculated for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub> m/z: 412.5, found m/z: 412.5.

**Chemical polymerization of PTPA and PDDP** The polymers of poly(N,N,N,N-tetraphenylphenylenediamine) (PDDP) and poly(triphenylamine) (PTPA) were prepared by chemical oxidative polymerization in chloroform (20 ml) using ferric chloride as oxidant. The solution was stirred over night at room temperature under N<sub>2</sub>. 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. Finally, the polymer product was filtered and dried in vacuum at 60 °C for 12 h. The colours of the PTPA and PDDP were yellow and green, respectively. Pyrolysis-gas chromatography chromatography-mass spectrometry (PTPA): Retention time (31.86 min), Molecular weight (245.10), Pyrolysis-gas chromatography-mass spectrometry (PDDP): Retention time (55.03 min), Molecular weight (412.26).

### Material characterization

Pyrolysis-gas chromatography-mass spectrometry (Py-GC) was carried out on a vertical microfurnace pyrolyzer (PY2020iD, Frontier Lab Ltd, Fukushima, Japan), which was directly attached to a gas chromatograph (CP-3800, Varian, USA) equipped with a flame ionization detector (FID). Raman spectra were recorded on

a Lab RAM HR UV800 (JOBIN YVON, France). UV-vis spectra were recorded on a Varian Cary 100 UV-vis spectrophotometer (Varian, USA). The electron spin resonance (ESR) spectra were recorded on BRUKER A300 spectrometer (Switzerland). Scanning electron microscopy (SEM) measurements were taken using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). The cyclic voltammograms (CV) tests were performed with a CHI 660 C electrochemical working station in 0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN versus Ag/AgCl at a scan rate of 10 mV·s<sup>-1</sup>. Spectroscopy (EIS) experiments were carried out at open circuit voltage (OCV) of frequency ranges from 0.1 Hz-1MHz in CHI 660 C electrochemical working station by the assembled stimulant lithium ion half-cells.

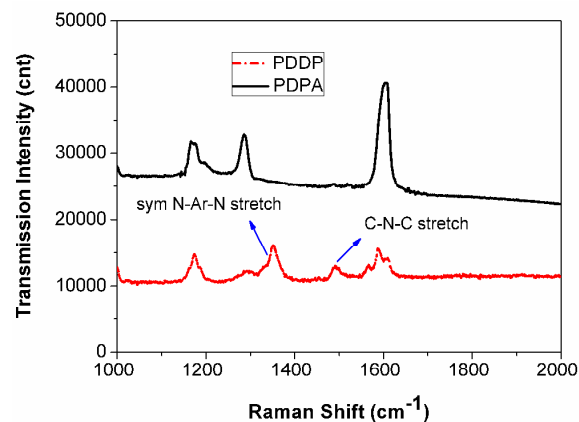
### Electrochemical measurements

For cathode characterization, CR2032 coin-type cell was used, which was assembled in an argon-filled glove box. The cathode electrodes were prepared by coating a mixture containing 50 % the prepared polymers, 40 % acetylene black and 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 LiPF<sub>6</sub> dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC = 1:1 v/v) as the electrolyte. The charge/discharge measurements were carried out on a LAND CT2001 using a constant current density at room temperature.

## 3. Results and discussion

### 3.1 Material characterization

**RS** Fig. 1 showed the Resonance Raman spectra of the as-prepared PTPA and PDDP. The main characteristic peaks of the triphenylamine moieties have been displayed in the two samples which are assign as follows: 1167 cm<sup>-1</sup> (C-H in-plane stretching), 1287 cm<sup>-1</sup> (C-C inter-ring stretching), 1489 cm<sup>-1</sup> (C=N stretching) and 1606 cm<sup>-1</sup> (C-C ring stretching).<sup>21-23</sup> In contrast to PTPA, a new band at 1350 cm<sup>-1</sup> appears in the spectrum of PDDP, which is attributed to the symmetric N-Ar-N stretching. These indicate that p-phenylene moiety have been successfully contained in PDDP polymer, which is absent from PTPA.



**Fig. 1** Resonance Raman spectra of the PTPA and PDDP samples measured at 632.81 nm.

**ESR** Electron spin resonance was employed to further confirm the existence of radical in the products of PTPA and PDDP (Fig.

2). As can be seen, a small and broad peak (g value: 2.00654) is observed in the spectrum of PTPA, corresponding to the existence of free radical in triphenylamine moieties of PTPA. Comparatively, the free radical characteristic peak (g value: 2.00475) for PDDP becomes broad with the obvious enhanced intensity, which can be attributed to the specific molecular structure of PDDP with higher free radical density.<sup>24</sup>

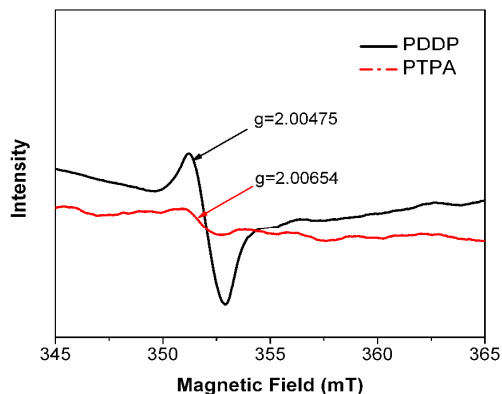


Fig. 2 ESR of PTPA and PDDP measured in the power state

10 **UV-vis.** The UV-vis spectra (normalized absorbance) is very useful tool for the exploring the electro-structure of material and were utilized to explore the characteristics of monomers (TPA and DDP) and the corresponding polymers (PTPA and PDDP). As depicted in Fig. 3, TPA monomer exhibits one pair of absorption peak at 305 nm which is assigned to the  $\pi$ - $\pi^*$  electron transition from the triphenylamine units. Comparatively, the  $\pi$ - $\pi^*$  electron transition of DDP monomer red-shifts to 338 nm due to the extensional  $\pi$ - $\pi^*$  conjugated structure of DDP. After the chemical polymerization, it can be seen that the corresponding absorption peaks of the  $\pi$ - $\pi^*$  electron transition for the obtained PTPA and PDDP become further red-shifting in comparison with that of TPA and DDP monomers, which can be attributed to the expansion of the  $\pi$ -conjugated systems by the produced conjugated polymer system.<sup>25, 26</sup> Still, the absorption peak of PDDP shifts to 390 nm, which is obviously larger than that of PDPA (356 nm). It indicates, due to the higher radical density structure in the repeating unit of PDDP, the charge carrier transportation alone in the polymer main chain of PDDP is even further smoother than that of PDPA.

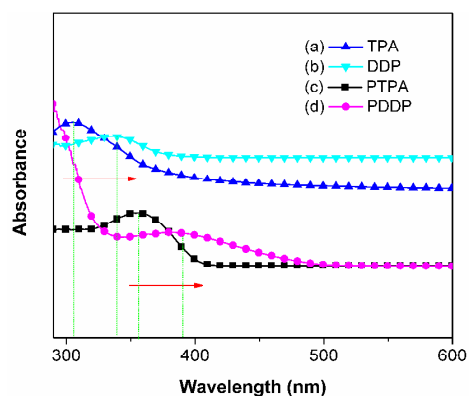


Fig. 3 UV-vis spectra of (a) TPA, (b) DDP, (c) PTPA and (d) PDDP ( $10^{-3}$  g/L) in DMF.

SEM The morphologies of the PTPA and PDDP were also shown in Fig. 4. The PTPA polymer presents a serious aggregation structure with the size of several micrometres (Fig. 4a and 4c). The steric torsion nature of the main chains by the big triphenylamine units may be responsible for this structural feature. However, the morphology of PDDP is different from that of PTPA under the same experimental conditions. As shown in Fig. 4b and 4d, PDDP exhibits regularly spherical structure assembled by many small particles of about 500 nm with well dispersion. The different morphology can be attributed to the different molecular structures of PDDP and PDPA, which has an effect on the molecular aggregation behavior as well the resulted morphology of polymers. This uniform micro-structural feature of PDDP 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.

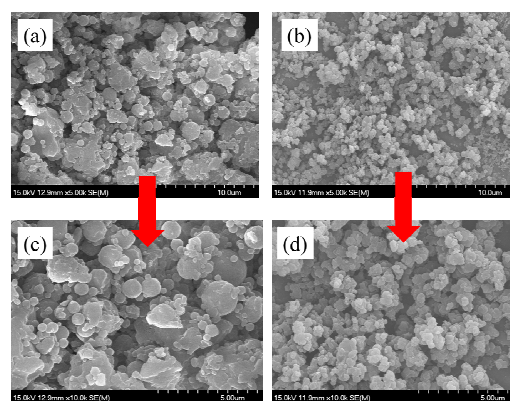


Fig. 4 SEM images of powder samples (a) PTPA, (b) PDDP, (c) and (d) partially enlarged SEM image in (a) and (b), respectively.

### 3.2 Electrochemical performance

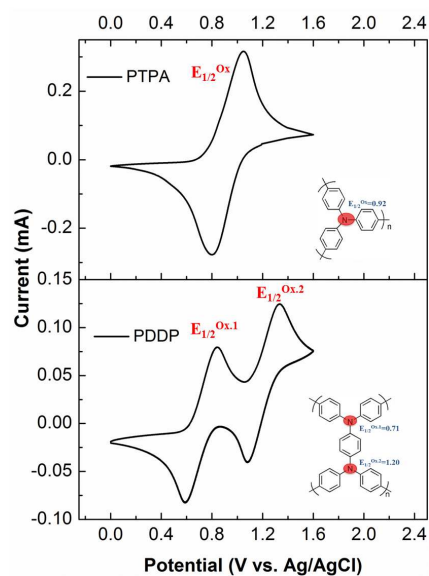
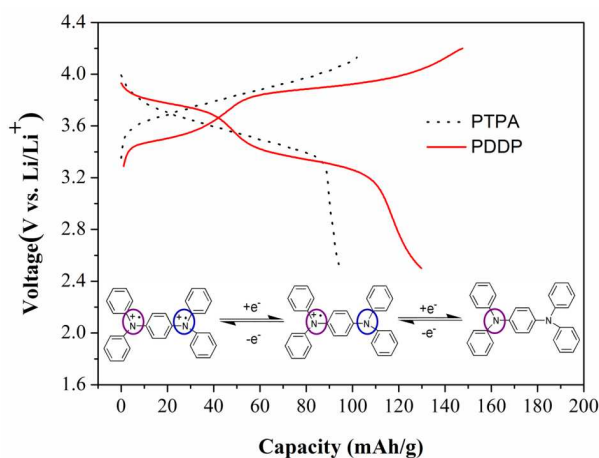


Fig. 5 Cyclic voltammograms (CV) of PTPA and PDDP in 0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN versus Ag/AgCl at a scan rate of 10 mV·s<sup>-1</sup> [Inset: the possible oxidation order of the redox centers of PTPA and PDDP].

Fig. 5 showed the cyclic voltmetry (CV) profile of the PTPA

and PDDP measured in 0.1M lithium perchlorate/acetonitrile solution. The electrode of PTPA exhibits a couple of anodic and cathodic peaks at about 1.05 and 0.8 V, respectively. The potential separation between the oxidation and reduction peaks is about 0.25 V and the approximately symmetrical peaks suggests a good insertion/extraction reversibility of the produced PTPA. Comparably, there are some obvious differences for the CV curves of PDDP, in which it displays two pairs of redox peaks, corresponding to the characteristics of both free radical centers for DDP moieties of PDDP. Therein, one pair of redox peaks located at 0.60 (reduction) and 0.82 V (oxidation) is attributed to the first radical cation reaction during p-type doping process, which is obviously below the redox peaks of PTPA. The other couple of redox peaks at high potential (1.32 and 1.08 V) can be assigned to the formation of the second cation radical. Furthermore, two pairs of anodic and cathodic peaks in PDDP still keep the approximately symmetrical peaks and the almost equal peak areas, suggesting the good insertion/extraction reversibility as the advanced electrode material during the charge/discharge process.

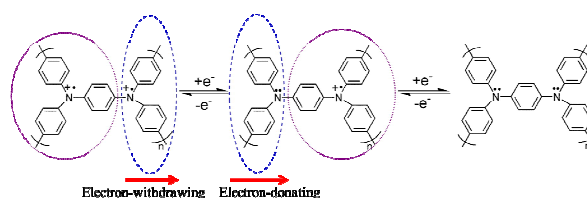
### 3.3 Charge-discharge performance



**Fig. 6** Initial charge/discharge profiles of PTPA and PDDP electrodes material at a constant current of  $20 \text{ mA} \cdot \text{g}^{-1}$  between 2.5 and 4.2 V [Inset: the possible charge/discharge process of PTPA and PDDP].

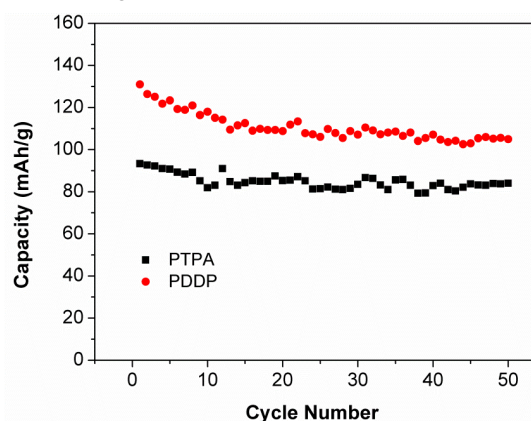
The charge/discharge behaviors of the as-prepared polymers as cathode of lithium batteries had been systematically investigated by simulated lithium ion half-cell method. As exhibited in the Fig. 6, the PTPA shows an initial discharge capacity of  $94.7 \text{ mAh} \cdot \text{g}^{-1}$  with a typical voltage plateau in the voltage range of 3.5–4.1 V at the initial cycle, correspondingly to the report. Comparatively, under the same conditions, the PDDP electrode exhibits an initial discharge capacity of up to  $129.1 \text{ mAh} \cdot \text{g}^{-1}$ , which is higher than that of the measured and reported PTPA, with two obvious voltage platforms at about 3.8 and 3.3 V, respectively, in accord with the redox couples observed in CV analysis (Fig. 5). Therein, the high voltage plateau in the voltage of 3.4–4.2 V is attributed to the higher redox couple, which provides discharge capacity of about  $62.5 \text{ mAh} \cdot \text{g}^{-1}$ , while the other lower plateau in the voltage of 2.5–3.4 V is corresponding to the lower redox couple, which has discharge capacity of about  $67.5 \text{ mAh} \cdot \text{g}^{-1}$ . The almost identical discharge capacity for two stage discharge processes indicates that both free radicals in DDP moieties play the same

action, which is consistent with the symmetrical peak area of two pairs of redox couples (as shown in CV analysis of PDDP). It is reasonable to assume that the redox characteristics of PDDP are exhibited by a one by one two-stage redox reaction. The improved capacity can be attributed to the higher free radical density as well the resulted high theoretical capacities of PDDP. Furthermore, the tiny and uniform particle morphology of PDDP compared to that of PTPA further facilitates the diffusion of the electrolyte solution to the active-polymer center and the improvement of the PDDP performance in some degree (as shown in the Fig. 4 b).



**Fig. 7** Schematic diagram for the possible electron donating/withdrawing effect during two charge/discharge stages

For two symmetrical discharge voltage plateaus displayed by PDDP, the possible reasons can be explained as: during the first stage discharge process, one of the free radical cation centers functions as electron-withdrawing group to another free radical cation center in the same DDP moiety, and this electron-withdrawing effect of the first radical cation tunes the HOMO (highest occupied molecular orbital) energy level of the second radical cation which is closely related to the redox potential. After the first stage of free radical discharge process, one of free radical cation in DDP units accepts one electron to become an electron pair, which further acts as electron donating group to the rest free radical cation. Due to the electron-donating effect of the formed amino-contained group, the SOMO (single occupied molecular orbital) energy level of the last radical cation decreases, leading to the drop of the redox potential during the second stage of free radical discharge. And the related mechanism has been shown in Fig. 7.



**Fig. 8** Cycling stability of the polymer electrodes material at a constant current of  $20 \text{ mA} \cdot \text{g}^{-1}$  between 2.5 and 4.2 V in  $\text{LiPF}_6 \text{ EC/DMC}$  (v/v, 1:1) electrolyte versus  $\text{Li/Li}^+$

The cycling stability of the as-prepared polymers as cathode materials was also examined, as shown in Fig. 8. It is found that both PDDP and PTPA electrodes show a similar cycling

performance, which is decided by nature of organic-based material electrode. Specially, the cycling stability testing of PDDP exhibits a serious capacity degradation in the initial 10 cycles, while the capacity of the following cycles maintains relatively stable. The initial capacity degeneration is possibly caused by the seriously re-aggregation of PDDP during the initial 10 charge-discharge cycles, due to the pristine looser stacking micro-structure of PDDP than that of PTPA. Furthermore, it can be seen that although the discharge capacity of PDDP drops from its initial 129.1 mAh·g<sup>-1</sup> to 110.6 mAh·g<sup>-1</sup> after 50 cycles, it is still higher than the initial capacity of PTPA, demonstrating that PDDP electrode presents an excellent electrochemical stability.

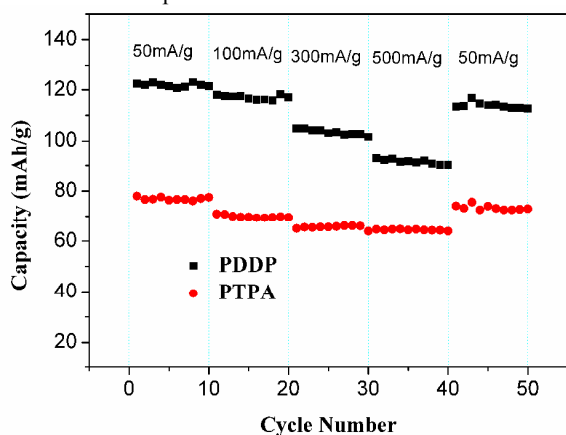


Fig. 9 The rate performances of the polymer electrodes in the voltage from 2.5-4.2 V at various current rates of 50, 100, 300 and 500 mA·g<sup>-1</sup>

The rate performances of the polymer electrodes were further examined at different current rates of 50, 100, 300 and 500 mA·g<sup>-1</sup>, respectively. Compared with parent PTPA, the PDDP electrodes displays an improved rate capability with an enhanced current rate from 50 to 500 mA·g<sup>-1</sup>, as shown in the Fig. 9. The specific capacity for PDDP are 122.4, 118, 104.8 and 92.8 mA·g<sup>-1</sup>, respectively, with a 10 times increase in the current from 50 to 500 mA·g<sup>-1</sup>, which, however, are still higher than that of PTPA at high current rate, although the decay rate of capacity is comparatively high. In addition, PTPA and PDDP presents a quickly recovered ability of capacity, as the current rate further gets back to 50 mA·g<sup>-1</sup>. The possible reasons for the improved high rate capability can be partly ascribed to the higher radical density structure in the repeating unit of PDDP, which leads to that the charge carrier transportation alone in the polymer main chain of PDDP is even further smoother than that of PDDPA. In addition, the uniform micro-structural feature for PDDP will further benefit to the ions (PF<sub>6</sub><sup>-</sup> and Li<sup>+</sup>) insertion-extraction process during the charge-discharge process, which is also responsible for the high rate capability. Thus, PDDP polymer would be a good potential candidate for cathode materials of high-power lithium batteries.

Fig. 10 showed electrochemical impedance spectra of pristine PTPA and PDDP. The impedance spectra can be explained on the basis of an equivalent circuit with electrolyte resistance ( $R_e$ ), charge transfer resistance ( $R_{ct}$ ), double layer capacitance and passivation film capacitance (CPE) and Warburg Impedance ( $Z_w$ ).<sup>29, 30</sup> In these impedance plots, the initial intercept of the spectrum at the  $Z_{re}$  axis in high frequency corresponds to the resistance of the electrolyte ( $R_e$ ). The semicircles at low impedance

frequencies represents the charge-transfer reaction resistance ( $R_{ct}$ ), while the straight lines at low frequencies indicates the Warburg impedance ( $Z_w$ ), which displays the diffusion-controlled process. As can be seen in the Figure, the  $R_e$  is almost same for the 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. For the charge transfer resistance ( $R_{ct}$ ), it varies with different cathodes: 600 Ω for PTPA electrode and only 160 Ω for PDDP. And the reduced charge transfer resistance of PDDP may be ascribed to the delicate molecular structures and high free radical density, which led to the charge migration smoothly along polymer chain. The smooth charge migration for PDDP as compared to PTPA had also been proved by the UV-vis spectra (as displayed in the Fig. 3). In addition, the smaller particles and the loose structure of the PDDP will provide a higher specific surface area, making the electrolyte penetration easily during the redox reaction, which do also facilitate to the decrease of the charge-transfer reaction resistance.

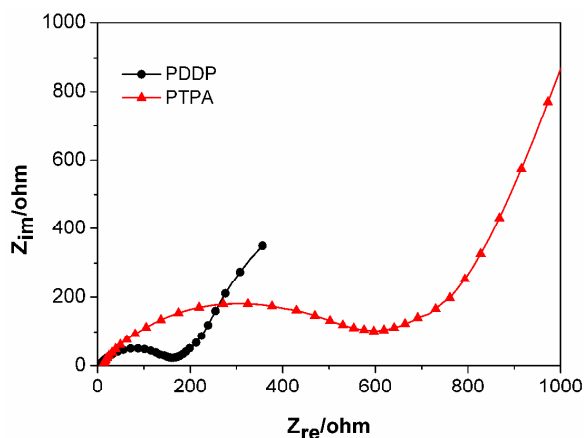


Fig. 10 EIS of PTPA and PDDP sample in Li/Electrolyte/Sample configuration

#### 4. Conclusions

PDDP with high free radical density structure had been firstly applied as cathode material, which presented two well-defined plateaus with quite a high capacity of 129.1 mAh·g<sup>-1</sup>. Moreover, the discharge capacity of PDDP retained over 110.6 mAh·g<sup>-1</sup> after 50 cycles which was still higher than the initial capacity of PTPA. UV-vis spectra and EIS test had illustrated the smoother charge migration in the PDDP polymer bulk than in that of PTPA, which was attributed to the intensive free radical density structure and the improved morphology of PDDP. The excellent electrochemical performances of PDDP indicated that it was a promising strategy to design and prepare the high capacity cathode with the high free radical density structure by increasing the number of radicals in the repeating unit, although.

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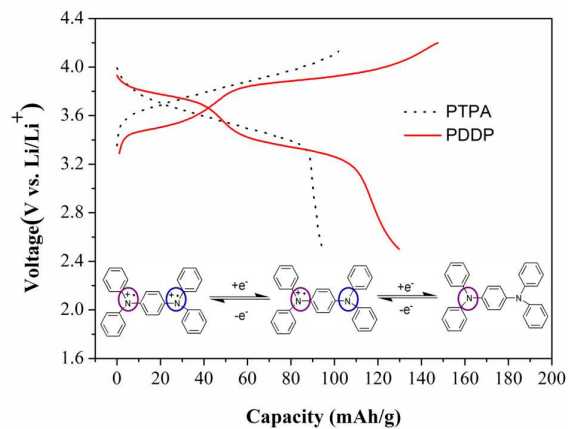
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Graphical abstract:



Initial charge/discharge profiles of PTPA and PDDP with two obvious voltage platforms and the possible electron donating/accepting process during two charge/discharge stages