

A novel quinone-based polymer electrode for high performance lithium-ion batteries

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ABSTRACT Designing of high electrochemical performance organic electrode materials has attracted tremendous attention. Recent investigations revealed that quinone-based polymers along with the stable thioether bonds could achieve a high specific capacity and a good cycling stability simultaneously. In this study, we synthesized a novel ladder-structured polymer poly(2,3-dithiino-1,4-benzoquinone) (PDB) through a simple two-step polymerization. The electrochemical performance indicated that PDB could achieve a high reversible specific capacity of 681 mAh g⁻¹ with 98.4% capacity retention after 100 cycles. A good rate performance was also achieved with a fast recovery of the capacity after testing at different current densities. Ultra-long cycling performance of PDB was also investigated. The promising results of PDB provided us more confidence to continue searching for high performance polymers through the modification of organic structures.

Keywords lithium battery, electrode, polymer, carbonyl, thioether

The invention of lithium-ion battery (LIB) has brought huge convenience in our daily life. Owing to LIB's light weight, high specific capacity and long cycling stability, successful investigations have been devoted to the applications for portable devices and electric vehicles [1,2]. However, due to the large-scale industrial production of the transition metal-based electrode materials, more and more toxic and non-renewable chemical wastes have been created [3]. Recently, new strategies including the designing of binder-free and composite electrode materials have been proposed [4–6]. Moreover, to search for potential greener electrode materials, organic compounds have attracted a lot of attention [1,7–9]. Although many small molecules have been synthesized and investigated as the electrode materials for LIBs, the reported electrochemical performances in terms of both specific capacity and cycling stability were still far away from the practical applications due to the serious dissolution issue [10–12]. Therefore, it is urgent to design novel organic compounds that can overcome the

dissolution issue without sacrificing the electrochemical performance.

In the past two decades, several strategies have been comprehensively proposed and evaluated. For example, one of the earliest attempts was through the synthesis of lithium salts [8,9,13–15], which delivered relatively better cycling stability and specific capacity compared with the previously reported small molecules. It was reported that Li₂C₈H₄O₄ (Li terephthalate) could accept two lithium ions to give an initial reversible capacity of 300 mAh g⁻¹ at 1 C [9]. In addition, all-organic LIBs fabricated by the tetralithium salt of 2,3,5,6-tetrahydroxy-1,4-benzoquinone (Li₄C₆O₆, THQ) and the tetralithium salt of 2,5-dihydroxyterephthalic acid (Li₄C₈H₂O₆, Li₄DHTPA) were evaluated respectively [8,14]. The cells were able to provide reversible capacities of 120 and 200 mAh g⁻¹ after 50 cycles and 20 cycles, separately at low current densities. Although these organic salts displayed better electrochemical performances as compared with the old-designed organic molecules, the cycling ability of them was still not stable and the specific capacities were still low as compared with the inorganic electrode materials. From the perspective of molecular design, another strategy is to increase the molecular weight of organic compounds by polymerization [16]. Especially, these polymers with large conjugated structures are not easily dissolved into the electrolytes. Nevertheless, increasing the molecular weight through polymerization could only somewhat resolve the dissolution issue. More importantly, the specific capacity of the larger structures will decrease accordingly.

Hence, in order to achieve a compromising result between the cycling stability and the specific capacity, our strategy is to develop quinone-based rigid backbone polymers with the chemically stable thianthrene structures. Recently, polymers containing redox-active carbonyl groups (C=O) have been thoroughly investigated [12,17–27]. Especially, quinones are regarded as the most promising types

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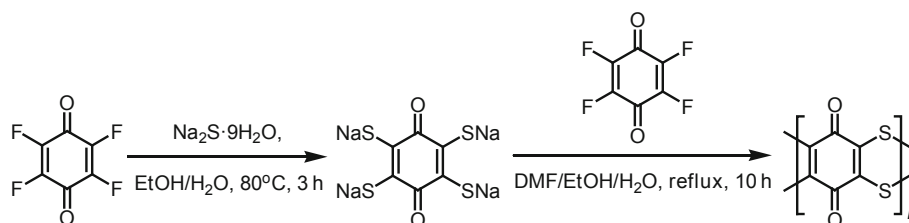
of organic electrode materials [12,18,20,21,23,24]. The redox mechanism of the electrochemically reactive carbonyl groups is well explained by the enolation process between the lithium ions and the carbonyl groups. Further investigations found that each C_6 ring can reversibly accept six lithium ions to form a Li_6/C_6 complex [17,28]. The results were supported by both the experimental and calculation studies. It was found that polymers with the thioether bonds (C–S–C), which do not undergo bond cleavage during the redox reactions, could behave more stable as compared with those with disulfide bonds [23]. Additionally, the thioether bond could provide fast electron transfer caused by the π -electron delocalization between the lone pair of sulfur and the quinonyl rings [26]. A sulfide polymer was synthesized based on 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [26]. Apart from the carbonyl bonds that provided the reactive centers for the redox reactions, the thioether bonds was found to greatly enhance the conductivity of the electrode and thus led to a high stability of the electrode. More recently, polyanthraquinone (PAQ) and lithium salt of poly(2,5-dihydroxy-*p*-benzoquinonyl sulfide) (Li_2 PDHBQS) were also discovered to have the ability to deliver excellent cycling stability after ultra-long charge-discharge cycles [18,20]. The extraordinary electrochemical results of these polymers indicated that quinone-based polymers with the thioether bond could effectively improve the redox reactivity as well as prevent the

unwanted dissolution of the organic compounds.

Combining the merits of quinone-based polymers, herein, we report a novel ladder-structured polymer poly(2,3-dithiino-1,4-benzoquinone) (PDB), which showed excellent electrochemical performance in terms of specific capacity (initial reversible capacity, 1050 mAh g^{-1}), cycling stability (100 cycles at 0.1 A g^{-1} and 1000 cycles at 2 A g^{-1}) and rate capability (0.1 to 4.2 A g^{-1}). The polymer sample was synthesized through a simple two-step polymerization between 2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione and $Na_2S \cdot 9H_2O$ at 80°C (Scheme 1).

Field-emission scanning electron microscopy (FESEM) was performed on JEOL/JSM-6340F at 5 kV to characterize the morphology of PDB. Fig. 1 shows that the diameters of the polymer particles are in the range of 500 nm to $1 \mu\text{m}$. Compared with those bigger-sized polymers, the micro-sized PDB with larger surface areas would be able to promote an enhanced connection between the polymer particles and the carbon nanotubes (CNTs), and hence results in an improved conductivity of the electrode material.

The chemical structure of the as-prepared sample was characterized by Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 2a, the strong absorption band near 1630 cm^{-1} corresponds to the stretching vibration of the carbonyl group (C=O) [23]. The peaks at 1423, 1382, 1176 and 1089 cm^{-1} can be assigned to the carbon sulfur bond (C–S) [12,23,26,29,30], indicating the successful for-



Scheme 1 The synthesis route of PDB.

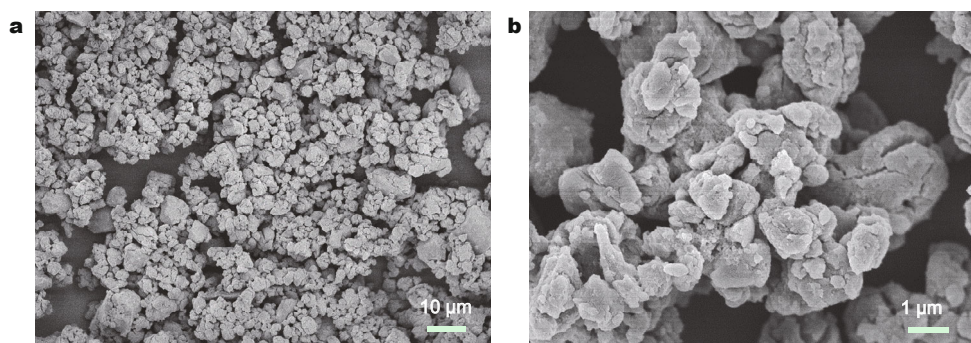


Figure 1 FESEM images of PDB micro-particles: (a) low-resolution image, (b) high-resolution image.

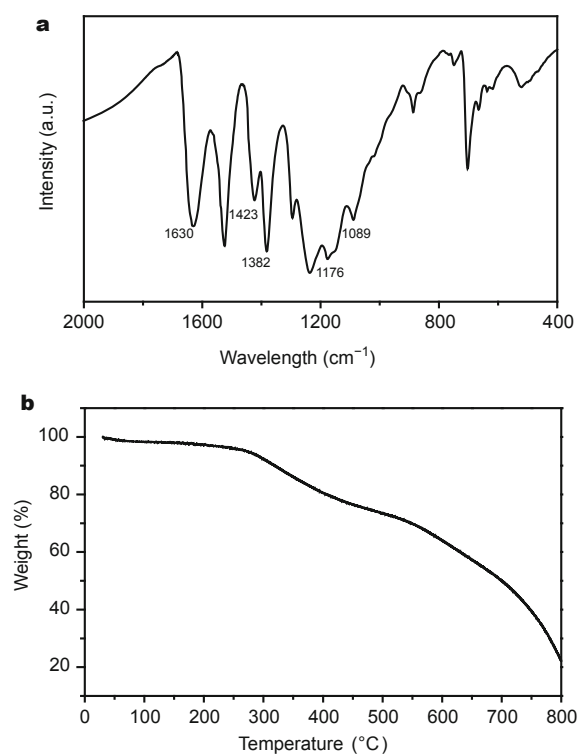


Figure 2 (a) FTIR spectra of PDB and (b) TGA curve of PDB in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$.

mation of the thioether bond (C–S–C) during the polymerization process. To further evaluate the thermal property of PDB, Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere between room temperature and 800°C . As shown in Fig. 2b, the decomposition of PDB starts at approximately 300°C , followed by another weight loss at around 500°C . This two-step weight loss could be due to the incomplete polymerization of the polymer sample. Therefore, the molecules with relatively smaller molecular weight decompose faster than the completely polymerized molecules. Nevertheless, the onset decomposition temperature of 300°C , which is consistent with majority of the polymers, still suggests a good thermal stability of PDB.

In order to evaluate the electrochemical performances of the PDB electrode, the active material (80 wt.%) was mixed with 10 wt.% CNTs and 10 wt.% polyvinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) solvent. Various measurements were carried out, including cyclic voltammetry (CV), galvanostatic charge-discharge profiles, rate performance and long-term cycling. Fig. 3a shows the CV curves of the initial three cycles between 3.0 and 0.0 V at a scanning rate of 0.2 mV s^{-1} . Obviously, there are some differences between the first cycle and the following cycles, especially during the lithiation process.

For the first cathodic scan, the large broad peak below 1.04 V is associated with the lithiation process occurred on the carbons of the C_6 rings along with the formation of a solid electrolyte interphase (SEI) film [17,28]. On the reverse anodic scan, a corresponding peak near 1.05 V is attributed to the delithiation process [17]. For the second and the third scans, the peak in the range of 2.25–2.5 V during the anodic scan is associated with the enolation process, which can be attributed to the reoxidation of the lithium enolate to form the carbonyl group [23,26]. It can be observed that, the CV curves of the 2nd and 3rd cycles almost overlapped, indicating the good stability of PDB during the electrochemical process.

The galvanostatic charge-discharge process was performed between the potential of 0.01 and 3.0 V at a current density of 100 mAh g^{-1} . The charge-discharge profiles of the 1st, 2nd, 3rd, 10th and 100th cycles are displayed in Fig. 3b. It can be observed that PDB delivered an initial discharge capacity of 1614 mAh g^{-1} and a high reversible capacity of 1050 mAh g^{-1} in the subsequent charge process, corresponding to a Coulombic efficiency of 65.1%. The loss of 564 mAh g^{-1} is attributed to the irreversible capacities from the formation of the SEI film, which can also be detected from the CV curves. It is widely known that the formation of the SEI film is a very common phenomenon for the anode materials during the initial discharge process [31,32]. Even though, the initial reversible capacity is much better than most of the thioether or thianthrene bond-containing compounds [20,33–36], indicating a superiority of PDB over them. Additionally, the potential plateaus observed in the charge-discharge profiles show good consistent with the redox peaks in the CV curves.

As shown in Fig. 3c, the rate capability of the sample was further examined at different current densities including 0.1, 0.2, 0.5, 1.0 and 4.2 A g^{-1} . Each current density corresponds to five cycles of charge and discharge processes. The results indicate that PDB could deliver reversible capacities of 887, 692, 500, 357 and 107 mAh g^{-1} , respectively, at different current densities mentioned above. It is worthy to note that, a high reversible capacity of 748 mAh g^{-1} could still be achieved when the current density returned back to 0.1 A g^{-1} . This reversible capacity of 748 mAh g^{-1} was quite consistent with the reversible capacity of 793 mAh g^{-1} at the same cycle during the charge and discharge process at 100 mA g^{-1} , indicating a good repeatability and an excellent structure stability of the PDB electrode material.

To investigate the cycling stability of PDB, specific capacity vs. cycle number was plotted as shown in Fig. 3d. It can be seen that, even after 100 cycles, PDB could still display a high specific capacity of 681 mAh g^{-1} , retaining

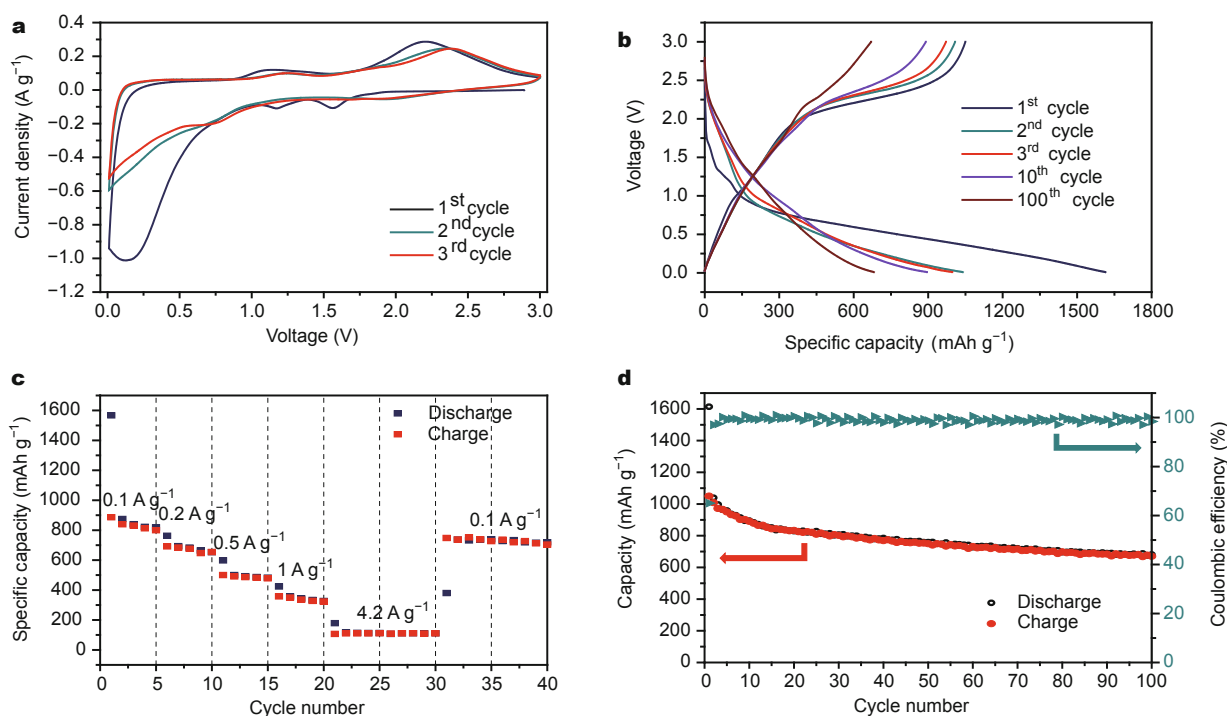


Figure 3 (a) CV curves of PDB at a scan rate of 0.2 mV s^{-1} . (b) Galvanostatic charge-discharge profiles of PDB at a current density of 100 mA g^{-1} . (c) Rate performance of PDB at different current densities. (d) Cycling performance and Coulombic efficiency of PDB at a current density of 100 mA g^{-1} .

71% of its specific capacity as compared with its 5th cycle. This good specific capacity is among the best performances of pure organic electrode materials that have been reported so far. Moreover, apart from the first cycle, the average Coulombic efficiency of each cycle (the 1st cycle excluded) is as high as 99.1%, further confirming the good stability of PDB. Fig. S1 shows the ultra-long cycling capability of the sample. The reversible specific capacity of PDB was maintained at 161 mAh g^{-1} after 1000 cycles at a high current density of 2 A g^{-1} . Although the result suggests a moderate specific capacity of PDB at high current density, the performance is still better than those of majority of the reported lithium salt anode materials for LIBs [37].

In conclusion, we have developed a novel polymer PDB that can be used as the electrode material for LIBs. For the characterizations of PDB, FTIR result indicates the successful formation of the thioether bond and TGA shows a good thermal stability of PDB at high temperatures. The electrochemical performance reveals that PDB possesses a high initial reversible capacity of 1050 mAh g^{-1} and still maintains a reversible capacity of 681 mAh g^{-1} after 100 cycles. Additionally, the good rate performance and the ultra-long cycling capability suggest the good stability of PDB. Our results show that carbonyl and thioether bonds containing polymers are promising high performance can-

didates as organic electrode materials for LIBs. Utilizing the advantages of carbonyl and thioether bonds, we are continuing searching for potential high performance organic electrodes through designing and modification of organic structures.

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- Author contributions** Xie J wrote the paper. Xie J and Wang Z conceived the experiments. Xie J, Gu P and Zhao Y collected the data and analyzed the results. Xu ZJ provided the glovebox for cell assembling and necessary discussions. Zhang Q supervised the project, conceived the experiments, analyzed the results and wrote the paper. All authors contributed to the general discussion.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Experimental details are available in the online version of the paper.



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基于苯醌结构的新型聚合物电极用于高性能的锂离子电池

谢健, 王子龙, 顾培洋, 赵毅, 徐栳川, 张其春

摘要 近年来, 设计和合成高性能的锂离子电池用有机化合物电极吸引了许多的关注. 很多研究表明基于苯醌和硫醚结构的聚合物可以同时具有高比容量和稳定的循环效率. 本研究用一个简单的聚合方法合成了一个新型的梯形聚合物聚(2,3-二噻烯-1,4-二苯醌) (PDB). 分析发现此聚合物具有 1050 mAh g^{-1} 的初始可逆比容量, 并且在循环一百次之后还保留有 681 mAh g^{-1} 的比容量和98.4%的库伦比效率. 当此聚合物在不同电流下充放电后并且重新设置回小电流时, 其比容量还可以恢复到之前小电流充放电时的性能, 证明了此聚合物有很好的倍率性能. 进一步大电流充放电表明此聚合物可以一直持续1000个循环, 再次说明了此聚合物电极的循环稳定性.