Phenothiazine-based polymer cathode materials with ultrahigh power densities for lithium ion batteries

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Phenothiazine-Based Polymer Cathode Materials with Ultrahigh Power Densities for Lithium Ion Batteries

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Supporting Information

ABSTRACT: Lithium ion batteries (LIBs) currently deliver the highest energy density of any known secondary electrochemical energy storage system. However, new cathode materials, which can deliver both high energy and power densities, are needed to improve LIBs. Herein, we report on the synthesis of a new organic-based redox-active material centered about phenothiazine and phenylenediamine units. Improved Coulombic efficiencies and greater capacity retention during cycling are observed through the copolymerization of a phenothiazine-based monomer that yields cross-linked materials. With this as the positive electrode in Li-coin cells, high specific capacities (150 mAh/g) are delivered at very positive operating voltages (2.8–4.3 V vs Li+/Li), yielding high energy densities. The material has low charge transfer resistance as verified by electrochemical impedance spectroscopy, which contributes in delivering previously unseen power densities in coin cells for organic-based cathodes. Excellent retention of capacity (82%) is observed at ultrastate discharge rates (120 C).

KEYWORDS: lithium ion batteries, organic cathode materials, polymer cathode materials, secondary batteries, phenothiazine

Organic and polymeric materials are excellent candidates for next generation electrode materials in high-power and high-energy density electrochemical energy storage applications, namely, lithium ion batteries (LIBs). Relative to traditional metal oxide cathodes, organic materials are structurally tunable, environmentally benign, and elemental abundant, lending to their continued study as potential cathodes. Polymers centered about conductive, carbonyl-based, nitrooxide radical, and organosulfur functionalities have shown exceptional performance and promise as cathodes in LIBs (see Supporting Information Figure S1). However, designing organic cathodes which exhibit both high power density, characteristic of capacitors, and high energy density, often associated with batteries, remains intrinsically challenging.

In the quest for high energy density organic cathodes, p-type polymers are particularly enticing, owing in part to their high operating voltages. Recently reported phenothiazine-based p-type polymer cathodes exhibit stable cycling and high working voltages. However, low capacities are delivered due to only a single electron being exchanged (via oxidation) per repeat unit. Encouraged by these reports, we sought to design a class of phenothiazine main-chain polymers which would undergo multiple electron oxidations and deliver high capacities (Figure 1). Incorporation of redox functionality directly into the main chain minimizes supporting mass per redox event, affording high theoretical gravimetric capacities. Furthermore, a partially conjugated structure should provide a framework for low resistance toward electronic conduction throughout the cathode. Adhering to these design principles, we present a redox-active phenothiazine centered polymer cathode, which effectively couples high energy density and power density.

Through rational design, we sought to synthesize phenothiazine-based polymer cathodes capable of delivering high power densities at fast charging and discharging rates. We hypothesized that copolymerization of N-methylphenothiazine (1) with electron rich and redox-active aryl diamines would afford polymers with high theoretical capacities and stable charged states by mimicking the stabilized oxidized state of methylene blue. Two aryl amines, N,N,N′,N′-tetramethyl-p-phenylenediamine (2) and N,N,N′,N′-tetramethylenylbenzidine (3), were natural candidates considering their multiple oxidation events to a stabilized quinoidal dication at potentials greater than 3.3 V vs Li+/Li. We further hypothesized that...
copolymerization through the 3 and 7 positions of phenothiazine would facilitate fast charging and discharging rates, since partial conjugation throughout the entire backbone would allow for facile electron transfer to and from the current collector.

Poly(N-methylphenothiazine dimethylphenylenediamine) (PT-DMPD, \( m = 1 \)) and poly(N-methylphenothiazine benzidine) (PT-BZ, \( m = 2 \)) were synthesized from inexpensive starting materials using a Buchwald–Hartwig cross-coupling of 3,7-dibromo-N-methylphenothiazine (1a) with dimethylphenylenediamine (2a) or dimethylbenzidine (3a) (Figure 2a).23,24 The resulting linear polymers were insoluble in their neutral state, and their electrochemical properties were probed using cyclic voltammetry (CV), measured as slurries deposited on a glassy carbon electrode in contact with a solution of LiPF_6 (1 M) in ethylene carbonate/diethyl carbonate (EC/DEC). The neutral and oxidized redox states of PT-DMPD are displayed in Figure 1. The three discrete redox couples of each polymer were observed by CV (Figure 2a), occurring at 3.3, 3.6, and 4.3 V vs Li/Li^+.

These redox couples are among the highest for organic electrodes reported for electrical energy storage applications. Coin cells employing PT-DMPD or PT-BZ as the cathode and Li metal as the anode were assembled to explore the performance of the polymers in devices. Due to the limited stability window of the electrolyte medium (EC/DEC), only the first two redox couples were accessed in coin cell cycling (see Supporting Information for coin cell fabrication). Figure 3a displays the first cycle charge–discharge profiles of PT-DMPD and PT-BZ at 1 C, over the voltage range from 2.8 to 4.3 V. Both exhibit reversible two-stage charge–discharge behavior, which is consistent with the two major redox couples observed in the CV. The discharge capacities of PT-DMPD and PT-BZ were 128 mAh/g and 97 mAh/g, representing 82% and 76% of theoretical capacity, respectively. However, both materials exhibited a relatively low Coulombic efficiency (35% for PT-DMPD and 44% for PT-BZ). The cycling performances of the PT-DMPD and PT-BZ cathode materials are shown in Figure 3b. Both cells were cycled at 25 °C over the same voltage range at 1 C. The discharge capacity of PT-DMPD was 82 mAh/g after 50 cycles (64% retention), while that of PT-BZ was 64 mAh/g after 50 cycles (66% retention). Since the PT-DMPD polymer exhibited higher capacity than PT-BZ polymer, further work focused on the former.

We hypothesized that the low Coulombic efficiency and capacity fade upon cycling were caused by dissolution of the polymer upon oxidation. This dissolution could be observed visually as green dissolved polymer diffused away from the electrode during CV cycling. To address these limitations, a second class of increasingly cross-linked materials was synthesized to generate polymers with decreased solubility in the electrolyte medium (Figure 4a). This class of cross-linked cathode materials is referenced according to the mol percentage of cross-linker relative to 1a. The first charge–discharge cycles of PT-DMPD, PT-DMPD (5% cross-linked, 5% CL), PT-DMPD (10% CL), and PT-DMPD (33% CL) at 5 C are shown in Figure 4b. Increased discharge capacities trended with an increase in mol percentage of cross-linker, with PT-DMPD (10% CL) exhibiting the highest discharge capacity of 150 mAh/g (97% of the theoretical value of PT-DMPD).
addition, a decrease in charging capacity led to significant improvements in Coulombic efficiency with increasing copolymerization of cross-linker. It is likely that the decrease in charging capacity results from either a suppression of polymer degradation or a decrease in small, soluble oligomers, which can act as electron shuttles between electrodes during charging.\textsuperscript{26–28} The Coulombic efficiency at 5 C increases from 49\% to 82\% between linear (no cross-linker) and 33\% cross-linked polymer. By limiting dissolution through cross-linking, both the capacity and Coulombic efficiency were dramatically improved.

The cycling performance of PT-DMPD, PT-DMPD (5\% CL), PT-DMPD (10\% CL), and PT-DMPD (33\% CL) materials was investigated between 2.8 and 4.3 V at 5 C, as shown in Figure 4c. Increasing the mol percentage of cross-linker resulted in materials exhibiting better cycling performance when compared to that of linear PT-DMPD. As the mol percentage of cross-linker increased from 0\% to 5\% to 10\% to 33\%, the capacity retention after 50 cycles increased from 65\% to 73\% to 74\% to 82\%, respectively. These results suggest that dissolution of the polymer from the cathode was largely mitigated in the cross-linked materials.

For use in high power applications, the proposed materials must be able to deliver high discharge capacities at fast discharge rates. To better understand the relationship between mol \% cross-linker and the materials capacity retention at increasing discharge rates, the rate capabilities of PT-DMPD (10\% CL) and PT-DMPD (33\% CL), the two materials displaying the highest discharge capacities, were investigated.
between 2.8 and 4.3 V. Figure 5 compares the discharge capacities of these materials charged at 1 C and discharged at C-rates of 1, 5, 10, 20, 40, 60, and 120 C. Significantly, excellent capacity retention (82%) was observed in PT-DMPD (10% CL) between even the most extreme discharging rates, 1 to 120 C. While similar capacities are observed at the lower rates for both materials, an apparent decrease in capacity is evident in PT-DMPD (33% CL) at higher discharge rates. We attribute this to a decrease in the rate of counterion transport through the more densely cross-linked material. Notably, the PT-DMPD (10% CL) material retained a very high discharge capacity of 122 mAh/g at the ultrahigh C-rate of 120 C.29

Encouraged by the fast discharge rates exhibited by these materials, electrochemical impedance spectroscopy (EIS) was used to measure the charge transfer resistance of PT-DMPD (10% CL) in a coin cell to explore the origin of the ultrahigh rate behavior.30−32 In impedance measurements, a high frequency semicircle is attributed to the double layer and the kinetics of the active material (Figure 6). In addition, the low frequency behavior is attributed to transport effects. The high frequency semicircle was fit to a simplified Randles model, and the charge transfer resistances obtained are given as an inset.

As expected, the charge transfer resistance was a function of the oxidation state of the polymer. The charge transfer resistances near the redox couple around 3.6 V are much lower than the charge transfer resistances near 4.1 and 3.1 V. Overall, the charge transfer resistance was between 80 and 230 Ω. When compared to literature reports, these values are similar to or lower than comparable systems, reflecting fast charge transfer kinetics.37,9,30−33 This facile kinetic behavior allows the battery to operate at high C-rates without excessive overpotentials. The low overpotentials, in turn, are one of the reasons for the high rate cycling capability without significant loss of capacity. The low charge transfer resistance of this material is exemplified by retention of capacity and stable cycling in coin cells with 75% active material loading (Figure S4).

In conclusion, we have designed, synthesized, and tested a class of high energy phenothiazine-derived redox-active polymers that deliver high capacities at ultrafast discharge rates and high operating voltages in lithium ion batteries. The initial capacity fade, due to electrode dissolution, was largely mitigated through the implementation of cross-linked materials, which led to dramatically improved cycling performance, discharge capacity, and Coulombic efficiency without compromising the material’s rate capability. PT-DMPD (10% CL) retained 82% capacity at an unparalleled 120 C rate. These results validate our design principles and are highly instructive for future discoveries of organic electrodes with competitive energy densities and superior power densities for electrical energy storage applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00778.

General experimental considerations, experimental procedures, coin cell construction, electrochemical measurement procedures, and additional supporting data (PDF)

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Notes

The authors declare no competing financial interest.

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(25) We hypothesize the two small redox couples at 3.6 and 4.0 V vs Li/Li’ correspond to redox active end groups of the polymers.


(29) By comparison, the reported materials retain 82% of initial capacity (150 mAh/g) at 120 C, whereas the phenothiazine-based material reported in 20 retains 52% of initial capacity (79 mAh/g) at 100 C.


