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Poly(diphenanthrenequinone-substituted norbornene) for Long Life and Efficient Lithium Battery Cathode

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Abstract

Redox-active polymers with large charge-storage density are candidates for electrode-active materials in next-generation energy storage devices, due to their swift charge-discharge capabilities and their inherent characteristics of redox reactions that undergo without significant structural changes, leading to their highly energy-efficient and durable performances. Here we report that poly(di-phenanthrenequinone-substituted norbornene) (PQN) as a novel class of the organic electrode-active material. The Li coin cell composed of the PQN/carbon composite electrode as the cathode exhibited 2.8 V (V vs. Li/Li⁺) and great cycle performance maintaining a capacity higher than 100 mAh/g for more than 100 cycles at 60 C (i.e. in 1 min charging and discharging). Among many types of o-quinone-containing polymers for Li-ion batteries reported so far, the present research provides the first example of introducing phenanthrenequinone as the pendant group per repeating unit of polymers, which proved to be especially advantageous in terms of robustness and cyclability by virtue of the fused-ring structure to protect the reactive positions of the o-benzoquinone. We also report that the functional group tolerance against many types of redox-active groups, which we have established for the initiator and the propagating end of norbornene derivatives, apply for the phenanthrenequinone-substituted monomer, giving rise to a reversible redox activity.

1. Introduction

The improvement of technology has always influenced and been influenced by the development of energy storage devices, which started with the non-rechargeable lead-acid battery1-2 and has now changed its form into various kind of primary and secondary batteries.³ Recent progress in the chemistry of reversible charge storage have spawned a variety of organic electrode-active materials.⁴⁻⁸ To enhance the energy density of batteries, the charge-storage capacity of the electrode material is very important.9 For anodes, lithium metal has the highest theoretical capacity (~3600 mAh/g), but has difficulties in the matter of cycle life and safety.¹⁰⁻¹¹ Li-ion batteries (LIBs) have been deeply focused for its excellent power efficiency,12 which utilize lithium metal oxides as the cathode and graphite or carbon electrodes as the anode. LIBs are used from handheld devices to EVs and large energy storage systems, but the rare metals that are used in the cathode has always been a concern in the matter of sustainability.¹³ Compared to the conventional cathodes, organic electrode materials are a choice of replacement since the redox reaction does not relate to almost any morphological changes making the material more stable and energy efficient.¹⁴⁻¹⁵ High-density redox polymers, especially those substituted with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as the redox-active pendant group per repeating unit are one of the promising candidates for its fast charge-discharge, very small chance of side reactions, light weight, and mechanically flexible properties characteristic to organic materials.^{12-13,16-17} We have already reported a highly flexible rechargeable organic battery with an excellent power density and cycle performance in which these properties are derived from the completely reversible and swift redox reaction of the TEMPO^{0/+} couple.^{12-13, 16-21} Not only for the cathode materials, but many types of redox polymers can also be used as the anode material such as organic-air secondary batteries.²²⁻²³ Quinones or carbonyl compounds are often selected for anode materials for their negative potentials and structural robustness.²⁴⁻²⁹ Quinones are focused for its wide availability and high charge capacity for its two-electron reaction at the two carbonyl oxygen atoms.³⁰ Among them, the redox couple of anthraquinone (AQ^{2-/0}) was found to be particularly useful as the electrode reaction in organic anodes²²⁻²³ for its exceptionally stable redox performance and chemically robust structure,³¹ but as a cathode material against Li^{0/+}, AQ only exhibits ~2.4 V (vs. Li/Li⁺) due to its negative potential.³²⁻³³

Recently, Shimizu and Yoshida et al. reported that the redox cyclability in Li-ion battery electrolytes greatly enhanced by replacing p-quinones with o-quinones, which was ascribed to the attenuated RO--Li⁺ interaction as a result of the bidentate coordination of two adjacent carbonyl (or phenolate) oxygen atoms to the Li⁺ ion.^{34,35} This result inspired a variety of relevant research employing o-benzoquinones bound to many types of polymer backbones.³⁶⁻³⁸ Typically, Patil et al recently reported polymers bearing o-benzoquinone with excellent cycle performance of 98% capacity retention after 3400 cycles.³⁶ In search of organic redox couples with high reversibility, robustness and positive potentials suitable for organic cathode in Li-ion batteries, we have focused on phenanthrenequinone (PQ) which shows a moderately positive potential (~0.4 V more positive than AQ) and desired chemical inertness due to the fused aromatic ring structure with the o-quinone or 1,2-diketone framework. PQ showed a better stability than AQ at the reduced state due to the formation of the chelate Li⁺ complex similar to that of the o-benzoquinone oxygen atoms.^{34-35, 39-41} Here we report the first successful attempt to incorporate PQ in an ultimate density per repeating unit of an aliphatic polymer chain.

Poly(diphenanthrenequinone-substituted norbornene) (PON) was synthesized in a sufficiently high molecular weight for electrode fabrication, by monomer synthesis of simple reactions starting from 3-acetylphenanthrene followed by ROMP with the Grubbs 2nd generation catalyst.⁴²⁻⁴⁵ Norbornene was chosen as the main chain for its high polymerization rate, film formability, redox inactivity, and the functional group tolerance against the quinoid group during ROMP.23 Indeed, polymers obtained from monomers with the redox-active pendants have inherent advantages, in terms of charge-storage capacity, over those having the redox-active groups incorporated by polymer-analogous reactions that frequently suffer from the limited degree of incorporation.^{34,48} Interestingly, almost all of the PQ pendant in the polymer maintained its redox capability, characterized by the efficient coupling with the Li⁺ ions.^{40-41,46-47,49} These properties were found to be important for fabricating energy-efficient organic electrodes and directly effected the battery performance, such as voltage, capacity, and cyclability. The Li coin cell composed of PQN as the cathode and Li metal as the anode gave a stable working voltage of 3 V and maintained over 100 mAh/g of capacity for more than 100 cycles without capacity decay.49 This work is sure to give a strong positive possibility to the organic electrode area and should become an influence for futuristic energy storage systems.

2. Experimental

Characterization of prepared materials can be found in the see Supporting Information.

Electrode Fabrication

In a mortar, 2 mg of PQN (PQN1, PQN2, and PQN3), 2 mg of PVdF, 16 mg of VGCF-H, and few drops of NMP were added and mixed. The mixture was coated on a glassy carbon electrode and vacuum dried at 80 °C for 8 h to yield the PQN/carbon composite electrode and these electrodes were used for half-cell experiments (Figure 3-7). For coin cell experiments (Figure 8-10), the substrate was replaced with Al foil.

Electrochemical Measurements.

Electrochemical measurements were carried out using the ALS electrochemical analyzer Model 660C, 660D, and 760EW. All half-cell measurements were performed using a sealed cell under an atmosphere of dry nitrogen. The three-electrode cell was composed by a glassy carbon plate working electrode, a platinum wire counter electrode, and an Ag/AgCl reference Electrolytes prepared electrode. using were gamma-butyrolactone (GBL) and LiClO4 as purchased inside a glove box. The electrolytes were primary degassed by argon before use. 2032 type coin cell batteries were fabricated by polymer/carbon composite as the cathode, Celgard #3501 as the separator, Li metal as the anode, and 1 M LiClO4/GBL as the electrolyte.

Synthesis

Phenathrenequinone substituted polymers were synthesized by the following procedures. A total of three polymers with direct linkage, ester linkage, and di-ester linkage of PQ was synthesized.



Scheme 1. Synthesis of IPQ and PQN1.

(IPQ). Synthesis 2-Iodophenanthrenequinone of 9,10-Phenanthrenequinone (2.08)10 mmol). g, N-iodosuccinimide (3.38 g, 15 mmol), and trifluoroacetic acid (7.4 mL, 100 mmol) were added together and stirred for 15 h at r.t. under N2 or Ar gas atmosphere. The mixture was washed with CHCl₃/sodium thiosulfate aq. to remove excess and unreacted acid and iodides. After purification by silica gel column chromatography using CHCl₃ as eluent, IPQ was obtained as a red solid. Yield: 60%. FAB-MS (m/z): M⁺ 334.1. Found 334.8. ¹H NMR (CDCl₃, 500 MHz, ppm, TMS): δ 8.49 (d, 1H, Ph), 8.19 (dd, 1H, Ph), 8.03 (dd, 1H, Ph), 7.98 (d, 1H, Ph), 7.73 (m, 2H, Ph), 7.50 (t, 1H, Ph).

of 5-Norbornene-2-phenenthrenequinone. Synthesis 2-Iodophenanthrenequinone (1g, 3 mmol) and PdCl₂(PPh₃)₂ (138 mg, 0.12 mmol) was purged by N2 gas and dissolved in 30 mL of toluene. 2,5-Norbornadiene (0.9 mL, 9 mmol) and triethylamine (1.38 mL, 9 mmol) were added to the solution under N₂ gas, and the mixture was heated to 80 °C. Formic acid (0.21 mL, 6 mmol) was added to the mixture and was stirred for 15 h at 80 °C. The mixture was washed with CHCl₃/brine and purified by silica gel column chromatography using CHCl3 as eluent to obtain 5-norbornene-2-phenenthrenequinone as a red solid. Yield: 65%. FAB-MS (m/z): M⁺ 300.4. Found 301.1. ¹H NMR (CDCl₃, 500 MHz, ppm, TMS): δ 8.15 (d, 1H, Ph), 8.08 (d, 1H, Ph), 7.96 (d, 1H, Ph), 7.91 (d, 1H, Ph), 7.68 (t, 1H, Ph), 7.61 (m, 1H, Ph), 7.43 (t, 1H, Ph), 6.27 (dd, 1H, -HC=), 6.19 (dd, 1H, -HC=), 3.02 (s, 1H, -CH-), 2.95 (s, 1H, -CH-), 2.75 (m, 1H, -CH-), 1.73 (m, 2H, -CH2-), 1.51 (m, 2H, -CH2-). Polymerization of 5-Norbornene-2-phenenthrenequinone. The monomer 5-norbornene-2-phenenthrenequinone (100 mg, 0.33 mmol) and the Grubbs 2nd generation catalyst (2.83 mg, 0.01 eq, 0.0033 umol) was added to a round bottom flask and was charged with nitrogen. Dry CHCl₃ (0.5 mL) was added by syringe and was stirred for 20 h at 60 °C. After removing the solvent by evaporation, the polymer solution was centrifuged with methanol, washed with methanol using soxhlet extraction,



and dried to yield PQN1 as a green solid. The polymer was

insoluble in conventional organic solvents after drying.

Scheme 2. Synthesis of PCA and PQN2.

Synthesis of Phenanthrene-3-carboxylic acid. 3-Acetylphenanthrene (1 g, 4.54 mmol) was dissolved in 20 mL of 1,4-dioxane. NaClO solution (64 mL, available chlorine 5 %) and 1 M NaOH aq. (90 mL) was added to the solution and stirred for 6 h at 65 °C. After cooling down to r.t., sodium thiosulfate (26 g, 0.16 mmol) was added and stirred for neutralization. The solution was washed with water and diethyl ether, followed by vacuum drying to yield phenanthrenequinone-3-carboxylic acid as a white solid. Yield: 97%. FAB-MS (m/z): M⁺ 222.1. Found 222.9. ¹H NMR (DMSO-d₆, 500 MHz, ppm, TMS): *δ* 13.1 (s, 1H, -OH), 9.33 (s, 1H, Ph), 8.82 (d, 1H, Ph), 8.12 (d, 1H, Ph), 8.07 (d, 1H Ph), 8.02 (d, 1H, Ph), 7.97 (d, 1H, Ph), 7.90 (d, 1H, Ph), 7.74 (t, 1H, Ph), 7.68 (t, 1H, Ph). ¹³C NMR (DMSO-d₆, 500 MHz, ppm, TMS): δ 168.1, 134.8, 132.3, 130.3, 129.8, 129.6, 129.4, 129.3, 129.2, 128.1, 127.9, 127.1, 126.3, 125.0, 123.3.

Synthesis of Phenanthrenequinone-3-carboxylic acid (PCA). Phenanthrene-3-carboxylic acid (489 mg, 2.20 mmol) was dissolved in 20 mL of acetic acid. In a separate flask, chromium(VI) oxide (808 mg, 8.80 mmol) and 18-crown-6 (6.90 mg, 0.367 mmol) was dissolved in 11 mL of acetic acid/water (v/v = 10/1). After complete dissolution, the latter solution was added to the first solution and was stirred for 16 h at 60 °C. Water was added to the reaction mixture for precipitation and the precipitate was purified by washing with acetic acid/water (v/v = 1/1) and diethyl ether to obtain phenanthrenequinone-3-carboxylic acid as a yellow solid. Yield: 79%. FAB-MS (m/z): M⁺ 252.0. Found 253.4. ¹H NMR (DMSO-d₆, 500 MHz, ppm, TMS): δ 13.5 (s, 1H, -OH), 8.66 (s, 1H, Ph), 8.30 (d, 1H, Ph), 8.09 (d, 1H, Ph), 8.03 (d, 1H, Ph), 7.99 (d, 1H, Ph), 7.76 (t, 1H, Ph), 7.54 (t, 1H, Ph). ¹³C NMR (DMSO-d₆, 500 MHz, ppm, TMS): δ 179.0, 178.9, 167.1, 136.8, 136.0, 135.9, 135.0, 134.6, 132.0, 130.2, 130.0, 129.9, 129.7, 125.3, 125.0.

Synthesisof5-Norbornen-2-ylmethyl9,10-phenanthrenequinone-3-carboxylate.

Phenanthrenequinone-3-carboxylic acid (504 mg, 2 mmol), 5-norbornene-2-methanol (300 2.4 mmol). mg, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium (DMT-MM) (1.1)4 mmol), chloride g, and 4-dimethylaminopyridine (DMAP) (200 mg, 1.6 mmol) were dissolved in 20 mL of DMF and were stirred for 14 h at r.t. Water was added to the reaction mixture for precipitation and the precipitate was washed by CHCl3/brine followed by column chromatography with CHCl3/ethyl acetate to obtain 5-norbornen-2-ylmethyl 9,10-phenanthrene-3-carboxylate as a yellow solid. Yield: 40%. FAB-MS (m/z): M⁺ 358.1. Found 359.3. ¹H NMR (CDCl₃, 500 MHz, ppm, TMS): δ 8.69 (d, 1H, Ph), 8.23 (m, 2H, Ph), 8.10 (m, 2H, Ph), 7.77 (m, 1H, Ph), 7.51 (m, 1H, Ph), 6.25-6.00 (br, 2H, -HC=), 4.51-3.97 (br, 2H, -CH2-), 3.03-2.55 (br, 2H, -CH2-), 1.94 (m, 1H, -CH-), 1.55-0.65 (br, 4H, -CH2-).

Polymerization of 5-Norbornen-2-ylmethyl 9,10-phenanthrenequinone-3-carboxylate. The monomer 5-norbornen-2-ylmethyl-9,10-phenanthrene-3-carboxylate (179 mg, 0.5 mmol) and the Grubbs 2^{nd} generation catalyst (4.2 mg, 0. 01 eq, 5 umol) was added to a round bottom flask and was charged with nitrogen. Dry CHCl₃ (0.5 mL) was added by syringe and was stirred for 12 h at 40 °C. After removing the solvent by evaporation, the polymer solution was centrifuged with methanol, washed with methanol using soxhlet extraction, and dried to yield **PQN2** as a yellow-green solid. GPC (CHCl₃, 40 °C, RID): $M_w = 1.1 \times 10^4$, $M_w/M_n = 1.8$.



Scheme 3. Synthesis of PQN3.

Synthesisof5-Norbornen-2,3-diylmethylbis(9,10-phenanthrenequinone-3-carboxylate).

Phenanthrenequinone-3-carboxylic acid (504 mg, 2 mmol), 5-norbornene-2,3-dimethanol (154 mg, 1 mmol), DMT-MM (1.33 g, 4.8 mmol), and DMAP (200 mg, 1.6 mmol) were dissolved in 10 mL of DMF and was stirred for 15 h at r.t. Water was added to the reaction mixture for precipitation of the product, and the precipitate was washed by CHCl3/brine followed by column chromatography with CHCl3/ethyl acetate obtain 5-norbornen-2,3-diylmethyl to bis(9,10-phenanthrenequinone-3-carboxylate) as a yellow solid. Yield: 45%. FAB-MS (*m*/*z*): M⁺ 622.2. Found 623.4. ¹H NMR (CDCl₃, 500 MHz, ppm, TMS): *S* 8.64 (s, 2H, Ph), 8.20 (m, 4H, Ph), 8.08 (m, 4H, Ph), 7.74 (t, 2H, Ph), 7.51 (t, 2H, Ph), 6.30 (m, 2H, -HC=), 4.73 (m, 2H, -CH2-), 4.46 (m, 2H, -CH2-), 2.92 (m, 2H, -CH-), 2.20 (m, 2H, -CH-), 1.70 (d, 1H, -CH2-). ¹³C NMR (CDCl₃, 500 MHz, ppm, TMS): δ 179.9, 179.4, 165.1, 137.5, 136.3, 136.0, 134.9, 133.5, 131.1, 130.6, 130.3, 129.9, 125.5, 124.4, 67.0, 45.3, 43.1, 40.1.

Polymerization of 5-Norbornen-2,3-diylmethyl bis(9,10-phenanthrenequinone-3-carboxylate). The monomer

5-norbornen-2,3-diylmethyl-bis(9,10-phenanthrenequinone-3-c arboxylate) (124 mg, 0.2 mmol) and the Grubbs 2^{nd} generation catalyst (1.72 mg, 0. 01 eq, 2 µmol) were added to a round bottom flask and were charged with nitrogen. Dry CHCl₃ (2 mL) was added by syringe and was stirred for 16 h at 40 °C. After removing the solvent by evaporation, the polymer solution was centrifuged with methanol, washed with methanol using soxhlet extraction, and dried to yield **PQN3** as a green solid. The polymer was insoluble in conventional organic solvents after drying.

3. Results and Discussion

Quinones are one of the representative organic redox active units for their 2e- reaction giving higher charge-storage density compared to 1e⁻ materials.²⁴⁻³¹ Benzoquinone is the most ideal structure which gives a theoretical capacity of 460 mAh/g, but due to the inherent reactivity of the reduced dianion state and the concurrent formation of quinhydrones, it is usually difficult to accomplish the reversible 2e- reaction without the undesired side-reactions that lead to capacity decay.⁵⁰ In comparison, the rings of anthraquinone (AQ) fused aromatic and phenanthrenequinone (PQ) give durability or robustness that is critical for long cyclability. Also, since the cation involved in the redox reaction of quinones in the battery electrolytes will be only Li⁺, the battery reaction becomes the rocking-chair type.51-53

Our concept is to produce a cathode material to be coupled with the lithium metal anode in the battery, focusing on PQ as the redox active unit. First, we investigated the redox potential of PQ and AQ in lithium-based electrolyte to observe the effect of the *o*-quinone structure on the half-wave potential ($E_{1/2}$) (Figure 1). When compared to AQ ($E_{1/2} = 2.47$, 2.16 V vs. Li/Li⁺), a positive shift of ~0.3 V was observed for PQ ($E_{1/2} =$ 2.75, 2.48 V). This shift has been ascribed to presence of two adjacent carbonyl groups^{34-35,40-41} in the *o*-quinone structure in which the two oxygen atoms serve as the bidentate ligand to coordinate to Li⁺ (Figure 2), resulting in a higher potential compared to AQ.³⁴ Also, according to Yoshida *et al.*,³⁴ a six-membered ring 1,2-diketone group serves as the best candidate for the cathode materials due to the significant stabilization of the reduced state by the increase in aromaticity.³⁴ The positive $E_{1/2}$ for PQ suggested that it should act as a cathode working at 3 V.



Figure 1. Redox reaction of PQ with chelate complex formation with Li ions.³⁴



Figure 2. Cyclic voltammogram of 1mM PQ in 0.1 M LiClO₄ GBL electrolyte at a scan rate of 50 mV/s. The potential was recorded with an Ag/AgCl reference electrode and was converted to that against Li/Li⁺ using E (V vs Li/Li⁺) = E (V vs. Ag/AgCl) + 3.02 V.

Polymer concentration of the electrode was kept low at 10 wt% and the conductive carbon additive, VGCF-H, was set to be 80 wt% to offer sufficient electrical conductivity to the electrode while maintaining the electroactivity of the polymer. This composition does not effect the total capacity of the electrode due to the low capacitance of VGCF-H (lower than 2 $F/g)^{54}$ so that the capacity obtained is derived only from the redox-active polymer. The half-cell performance of the PQN/carbon composite electrode was investigated as follows.

types Three of poly(phenathrenequinone-substituted norbornene) (PQN) were synthesized without unfavorable side-reactions. PQN substituted with direct linkage to norbornene (PQN1) and that substituted via methylester linkage (PQN2) was initially prepared to compare the effect of the electron-withdrawing methyl ester linkage against the redox potential and the charge capacity. Huang et al. has reported the positive potential shift by introduction of ester groups to fluorene-based polymers.⁵⁵ Figure 3 demonstrated that PQN2 exhibited a potential shift slightly to the positive side and from Figure 4, the charge capacity became almost twice of PQN1. These results clarified the effect of the methyl ester linkage between norbornene and PQ to improve the electron withdrawing property and electrolyte affinity for positive potential and larger capacity.



Figure 3. Cyclic voltammograms of PQN1 (dashed line) and PQN2 (solid line)/carbon composite electrode in 1 M LiClO₄ GBL electrolyte at a scan rate of 10 mV/s. The electrode potential was recorded as in Figure 2.



Figure 4. Charge-discharge curves of PQN1 (dashed line) and PQN2 (solid line)/carbon composite electrode in 1 M LiClO4 GBL electrolyte at 10 C. (i) demonstrates the reduction of the polymer (i.e. negative charge being stored at the carbonyl of phenanthrenequinone units), which corresponds to the discharging of the polymer in Li batteries, and (ii) the oxidation. The electrode potential was recorded as in Figure 2.



Figure 5. Cyclic voltammogram of PQN3/carbon composite electrode in 1 M LiClO₄ GBL solution at a scan rate of 10 mV/s. The electrode potential was recorded as in Figure 2.

From cyclic voltammetry, we observed two reversible redox potentials at 3.02 V and 2.60 V (vs. Li/Li⁺) (Figure 5). The galvanostatic charge-discharge curves showed a capacity of 124 mAh/g at 10 C and the capacity was maintained after long time cycling (Figure 6). PQN3 exhibited the best properties of all three PQN polymers and this was accomplished by the two PQ units per repeating unit for high capacity and by the methyl ester linkage introduced to increase the stability of reduced state along with positive shift of the potential. Note that the term 1 C rate is defined as the current density for the material to undergo charging or discharging in 1 h. We investigated the rate performance of the electrode by discharging at various rates after charging the electrode at 10 C. The polymer electrode showed a slight capacity decay but maintained 70 % of the capacity even at 50 C compared to 10 C (Figure 7). As reported previously,³²⁻³³ at high rates of over 10 C, it was difficult to maintain the charge-storage capacity for pendant-type quinone polymers without addition of ionic side-chains for charge compensation. It may be stated that this improved rate performance was accomplished by the enhanced Li⁺ diffusivity derived from the *o*-quinone structure and electron-withdrawing property and electrolyte affinity derived from the ester linkage. Further improvements by optimizing electrode fabrication process and materials are our future topics.



Figure 6. Charge-discharge curves of PQN3/carbon composite electrode in 1 M LiClO₄ GBL solution at 10 C. (i) demonstrates the reduction of the polymer (i.e. negative charge being stored at the carbonyl of phenanthrenequinone units), which corresponds to the discharging of the polymer in Li batteries, and (ii) the oxidation. The electrode potential was recorded as in Figure 2.



Figure 7. Discharging performance of PQN3/carbon composite at various discharging rates of 10-50 C in 1 M LiClO₄ GBL solution. The electrode potential was recorded as in Figure 2.

The polymer electrode was employed as the cathode of a coin cell with lithium metal as the anode. For the coin cells, the PQN/carbon composite electrode was fabricated in the same way as the above process, except that the substrate (i.e. current collector) was an Al foil instead of the glassy carbon electrode. From cyclic voltammetry, we observed two reversible redox peaks and the overall cell voltage was 2.81 V (vs. Li/Li⁺) (Figure 8). These peaks were consistent with the two redox peaks observed for the half-cell. With the AQ polymers, the voltage ends up around 2.4 V (vs. Li/Li⁺) making the

electromotive force of PQ/Li batteries 17% higher than the AQ/Li batteries. The charge/discharge curve of the 3^{rd} cycle cell exhibited a high capacity of >100 mAh/g at both charge and discharge (Figure 9), and maintained >90% of its capacity for over 100 cycles (Figure 10). Not only the voltage but also with the capacity, AQ polymers usually end up losing 60% of its initial capacity at around 50 cycles due to the irreversibility of the quinone-Li interaction (vide supra). These prospects demosntrated that PQN and future PQ electrode materials are true candidates in the field of organic electrode for Li secondary batteries.



Figure 8. Cyclic voltammogram of the Li coin cell battery with PQN3/carbon composite electrode as cathode at a scan rate of 1 mV/s.



Figure 9. Charge-discharge curves of the 3^{rd} cycle of Li coin cell battery with PQN3/carbon composite electrode as cathode at 1 C.



Figure 10. Cycle performance of the Li coin cell battery with PQN3/carbon composite electrode as cathode at 60 C. Inset: Charge/discharge diagram of PQ.

4. Conclusion

To invent a powerful and energy efficient electrode material, specific structural design for high potential and capacity is important. The o-quinone structure (PO) was chosen for its suitability in term of coordination to Li⁺ upon reduction which led to a positive redox potential shift compared to p-quinones (e.g. AQ) by 0.3 V. Norbornene was chosen for the polymer backbone for its high rate of polymerization, linearity of the chain, and the functional group tolerance of the propagating end against the quinoid unit. An ester linkage between norbornene and PQ was introduced for improved stability and capacity which were accomplished by the electron-withdrawing property and electrolyte affinity. PNQ was synthesized by few steps of monomer synthesis and ROMP. The earned polymer was insoluble in conventional organic solvents suggesting a high robustness for long cyclability without exfoliation from the current collector. A coin cell composed of PNQ as the cathode and lithium metal as the anode exhibited an operating voltage of 2.81 V and a capacity of 110 mAh/g. The battery was fully discharged in ~ 1 min and maintained its initial capacity for over 100 cycles at the fast C rate of 60 C. These characteristics were accomplished thanks to the efficient and swift Li⁺ diffusion in the polymer layer during the redox reaction. Further work on electrode fabrication is in progress to enhance the performance of the polymer.

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Supporting Information

Device and material used for electrochemical measurements, equation for formula weight-based theoretical redox capacity, ¹H and ¹³C NMR spectra of the reported molecules are listed in the supporting information.

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