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Improving the cycle-life of naphthoquinone-based active materials by their polymerization for rechargeable organic batteries

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Abstract

To increase the cycle-stability of rechargeable batteries using an organic positive-electrode material, we synthesized a polymer from a 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) skeleton, which potentially undergoes a four-electron transfer redox reaction. The polymeric material (PDHNQ) was synthesized by the condensation reaction between DHNQ and formaldehyde under acidic media conditions. The initial capacity of the electrode using the monomer (DHNQ), 193 mAh/g, quickly decayed to 56 mAh/g after 100 cycles. On the other hand, the electrode incorporating the prepared PDHNQ showed the higher initial discharge capacity of 256 mAh/g and a longer cycle-life, retaining about 133 mAh/g after 100 cycles.

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1. Introduction

The current rechargeable lithium batteries contain a large amount of minor metal-based materials especially in the positive electrode, which would pose a future resource problem. A solution can be to use organic materials as a positive electrode active material instead of the conventionally used rare-metal oxides [1–3]. We have already determined that certain low-molecular-weight quinone derivatives could deliver high discharge capacities due to their multi-electron redox reactions [4–11]. However, their discharge capacities have a tendency to decrease upon cycling resulting from the loss of the active materials from the electrodes by the dissolution of the organic molecules in the electrolyte solutions. Polymerizing the redox active sites is considered to suppress the dissolution of the active materials [1–3,12–19]. We focused our attention on the 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) skeleton (Fig. 1a) as a redox active site, which is known as the mother skeleton of shikonin, a natural purple dye [11,15,20]. This skeleton can be a high capacity active material based on its four-electron transfer redox reaction (Fig. 1b). In this paper, a polymeric compound carrying the DHNQ skeleton was synthesized from the DHNQ monomer and its cycle-life performances were compared to that of the monomer.

2. Experimental

2.1. Materials

All the raw materials used for the polymer synthesis were purchased and used without further purification. An electrolyte solution (ethylene carbonate and diethyl carbonate containing lithium hexafluorophosphate) (1 mol/L $LiPF_6$ in EC/DEC = 1/1 by vol.) was also purchased and used without further purification.

2.2. Synthesis of a DHNQ-based polymer (PDHNQ)

DHNQ (0.23 g, 1.2 mmol) and paraformaldehyde (0.15 g, 4.8 mmol) were dissolved in glacial acetic acid (13 mL). To this solution, a hydrochloric acid aqueous solution (36%, 1 mL) was added, and the mixed solution was heated at 100°C for 16 h using a Teflon vessel autoclave reactor (internal capacity: 28 mL, Φ 30 mm, L 40 mm). After filtration, the obtained precipitate was washed with acetic acid, water, and methanol, then dried under vacuum for 1 h to yield a polymeric material (0.11 g, yield 45%). See §3.2 for the reaction scheme and the characterization of the product polymer.

2.3. Synthesis of the PDHNQ-lithium salt (PDHNQ-Li)

For the polymer characterization as described in §3.2, a lithium salt of PDHNQ was synthesized. An aqueous solution of the mixture of the prepared polymer (PDHNQ) and lithium hydroxide was stirred for 1 h at room temperature. The solvent water was then evaporated and the resulting residue was washed with ethanol to give a bluish solid in quantitative yield. The obtained polymeric material was characterized by gel permeation chromatography (GPC) and ^{1}H-NMR measurement (JEOL, JNM-ECA series, $v(^1H)$=500 MHz).
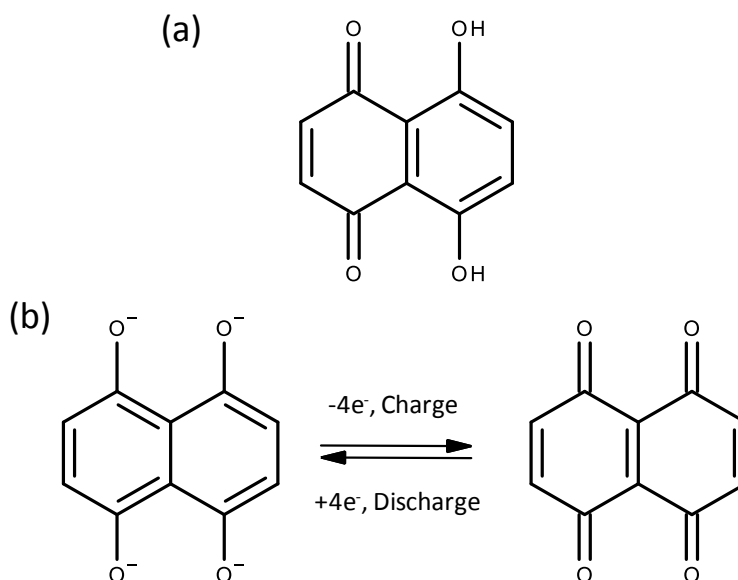
Fig.1. (a) 5,8-Dihydroxy-1,4-naphthoquinone (DHNQ) and (b) conceivable four-electron transfer redox reaction based on the DHNQ skeleton.

2.4. Electrodes preparation and cell assembly

A composite sheet composed of the powders of the active material (DHNQ or PDHNQ), polytetrafluoroethylene as the binder, and acetylene black as the conductive additive in the weight ratio of 4:1:5 was first prepared as a positive-electrode by mixing them. The sheet was then pressed onto a mesh-type current collector and dried. Each electrode contains about 2 mg of active material. A coin-type cell (IEC R2032) was assembled using the prepared positive-electrode sheet, a lithium metal negative-electrode, a glass filter separator, and the electrolyte solution (1 mol/L $LiPF_6$ in EC/DEC = 1/1) under a low dew point (<−70°C) environment.

2.5. Battery testing

The prepared cells were charged and discharged at the current density of 20 mA per gram of the active material with a potential range of 1.8–4.5 V vs. Li^+/Li by a battery evaluation system (BLS series, Keisokuki Center, or ABE system, Electrofield) equipped with a thermostatic chamber at 30°C. As for the first charge process of the electrode incorporating the monomer, DHNQ, the electrode did not reach the stated potential of 4.5 V vs. Li^+/Li; therefore, the process was stopped after a galvanostatic charge for 27 h. The obtained capacities are expressed in terms of per initial mass of the active material contained in the positive electrode in this article.

3. Results

3.1. Battery performance of the monomer

Fig. 2 shows the first discharge curve after the initial charge of the electrode using the DHNQ monomer. The electrode shows a complex discharge curve consisting of many potential steps with the average potential of 2.9 V vs. Li^+/Li. The observed capacity of 193 mAh/g is higher than the practical capacity of the conventional $LiCoO_2$ (*ca.*

140 mAh/g); however, it is less than half the theoretical value of 549 mAh/g based on the assumption of the four-electron transfer redox reaction of the DHNQ moiety shown in Fig.1b.
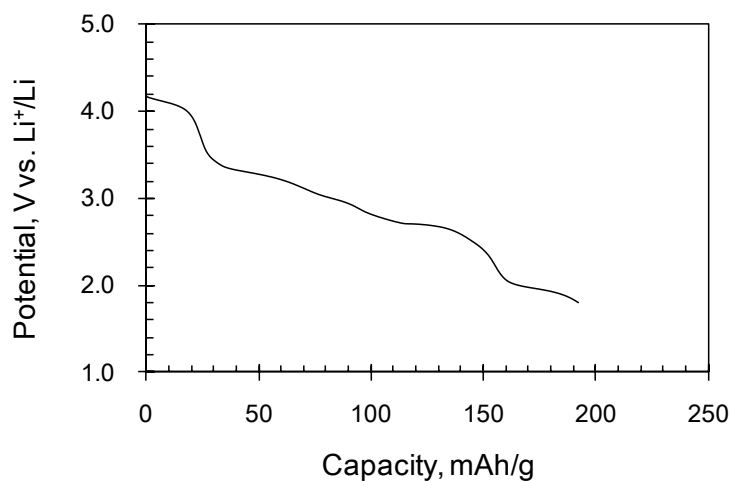

Fig. 2. Initial discharge curve of the DHNQ-electrode. Current density: 20 mA/g, Potential range: 1.8–4.5V vs. Li⁺/Li.
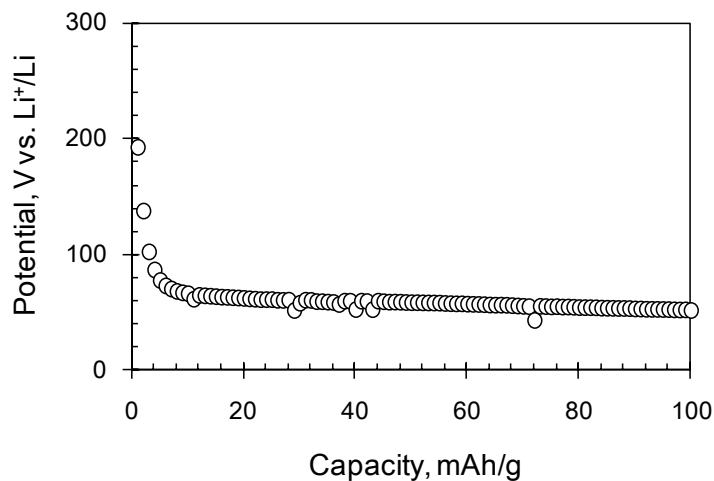

Fig. 3. Cycle-life performance of the DHNQ-electrode. Current density: 20 mA/g, Potential range: 1.8–4.5V vs. Li⁺/Li.

The cycle-life of the DHNQ-electrode is shown in Fig. 3. After a quick decay during the initial cycles, the discharge capacity of the DHNQ-electrode became stable, maintaining 56 mAh/g after 100 cycles. The observed cycle-life behavior is typical for low-molecular-weight organic active materials [5–11].

To analyze the reason for the capacity decay, the inside of the cell was examined by disassembling the cell after cycling. Fig. 4 compares the appearance of the glass filter separators that had absorbed the electrolyte solution taken out of the cell before and after cycling . The separator before the cycle-test is already reddish due to the considerable

dissolution of the DHNQ in the electrolyte solution. After 100 cycles, the color deepened, indicating a further dissolution. This observation implies that the dissolution of the organic compound during cycling is one of the major factors for the capacity decay.
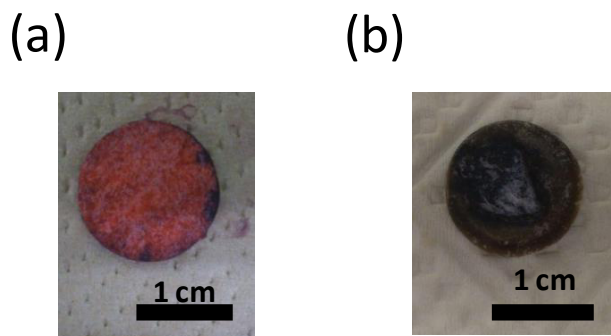

Fig. 4. Color change of the separator used for the cells incorporating the DHNQ-electrode. (a) Before the cycle-test and (b) after 100 cycles

3.2. Polymer synthesis

To suppress the dissolution of the DHNQ-based redox active moiety into the electrolyte solution, we synthesized the polymer, PDHNQ, carrying the DHNQ skeleton as shown in Fig. 5. The solubility in the ordinary organic solvents successfully decreased by the polymerization as shown in Fig. 6.

Soluble in neither water nor organic solvents, PDHNQ defied a further solution-based characterization. We instead characterized its lithium salt, PDHNQ-Li (§2.3), a fraction of which is soluble in water, allowing the GPC and ^{1}H-NMR measurements.

The result of the GPC analysis is as follows: the number average molecular weight $M_n=9.1\times10^5$ g/mol; the weight average molecular weight $M_w=9.6\times10^5$ g/mol; and $M_w/M_n=1.1$, indicated that the polymerization was successful by the applied methods and its molecular weight is monodispersed and high enough. By considering the water-insoluble residue in PDHNQ-Li, the true average molecular weight should be higher than the observed values.

A ^{1}H-NMR spectrum of PDNQ-Li measured in deuterium oxide (D$_2$O) has broad peaks at 6.8 and 3.8 ppm as shown in Fig. 7. These peaks are considered to reflect the aromatic hydrogen nucleus of the naphthoquinone skeleton and the bridging methylene hydrogen nucleus, respectively, which supports the synthesized material as having thea desired structure as depicted in Fig. 5.
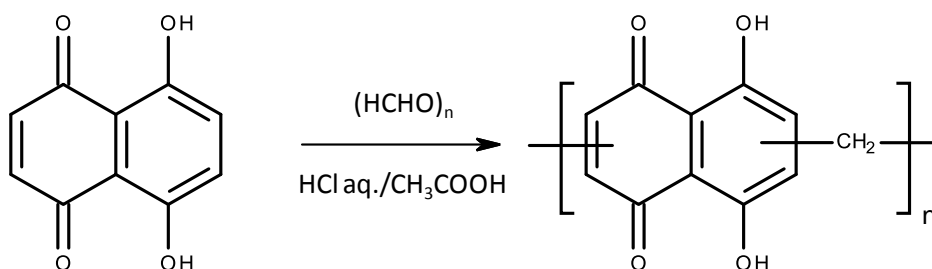

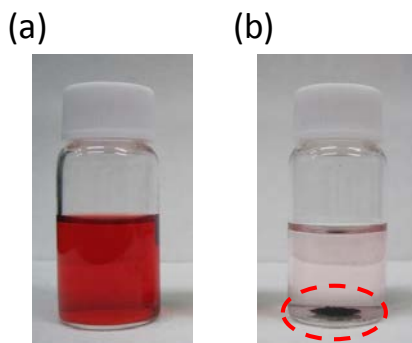Fig. 5. Synthetic procedure for PDHNQ.

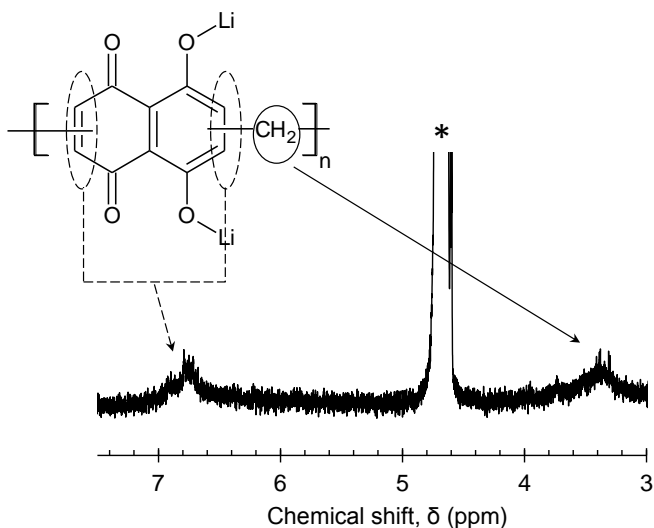Fig. 6. Solubility comparison of (a) DHNQ to (b) PDHNQ in propylene carbonate.

Fig.7. ^{1}H-NMR spectrum of PDHNQ-Li in D$_2$O and the peak assignment. The peak marked with * reflects the light water contaminant.

3.3. Battery performance of the polymer

Fig. 8 shows the discharge curve of the PDHNQ-electrode after the first charge. The shape of the discharge curve of PDHNQ is simple compared to that of DHNQ in Fig. 2. The initial discharge capacity of 256 mAh/g is higher than that of the monomer; however, this value is still much lower than the theoretical value of 532 mAh/g. The average potential of 2.7 V vs. Li$^+$/Li is 0.2 V lower than that of the monomer. Such phenomena are often observed for polymeric compounds [4–6,8,12–15]. Especially, for the issue concerning its low utilization ratio, we address it in §4.

The result of the cycle-life performance of the PDNQ-electrode is shown in Fig. 9. The capacity quickly decays during the first several cycles; however, it settles to a steady value of about 150 mAh/g after about 10 cycles. The electrode maintains 133 mAh/g even after 100 cycles. The observed cycle-life performance is much better than the behavior of the monomer-electrode, Fig. 3.

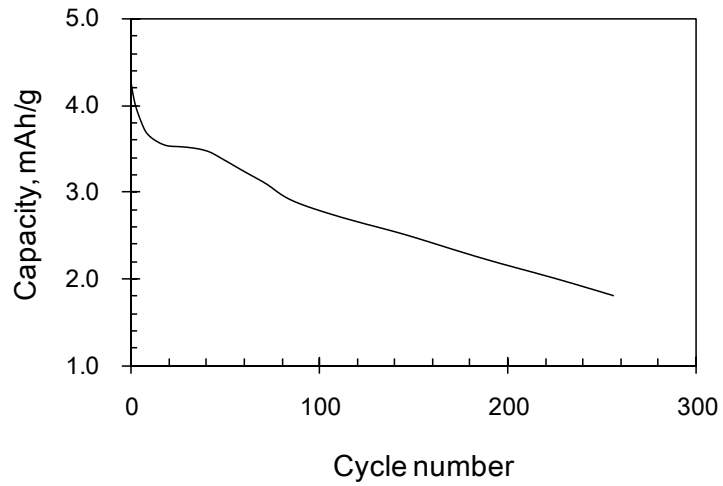Fig. 8. Initial discharge curve of the PDHNQ-electrode. Current density: 20 mA/g, Potential range: 1.8–4.5V vs. Li$^+$/Li.
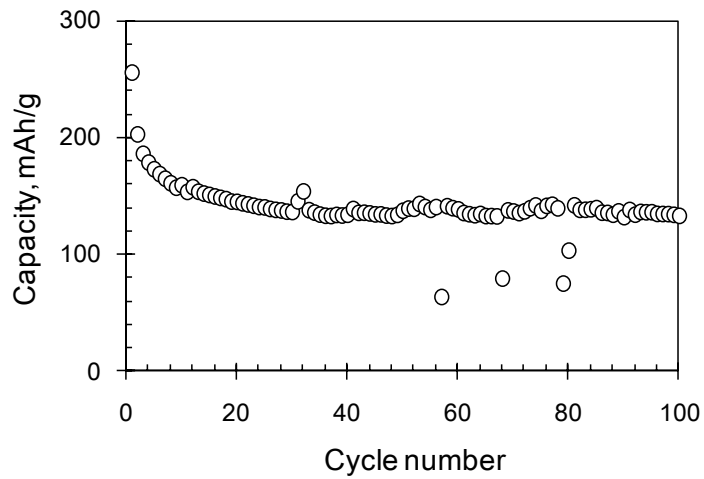

Fig. 9. Cycle-life performance of the PDHNQ-electrode. Current density: 20 mA/g, Potential range: 1.8–4.5V vs. Li$^+$/Li.

Fig.10 shows the appearance of the glass filter separator in the cell containing PDHNQ after cycling. During the cell assembling process, no noticeable dissolution was observed for this cell. After 100 cycles, a color change in the separator was observed; however, its degree is far less than that of the monomer-based cell (Fig. 4b). This observation implies that the dissolution of the organic compound during cycling is suppressed by the polymerization of the redox active sites.
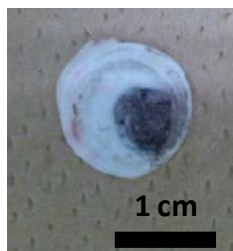

Fig. 10. Separator used for the cell incorporating the PDHNQ-electrode after 100 cycles.

4. Discussion

Several papers have reported the battery performance of polymers containing the benzoquinone skeleton; however, the desired two-electron redox reaction per quinone unit has not yet been realized in these polymers [12,13]. In contrast, polymers carrying an anthracene skeleton or a pyrene compound with quinone-type carbonyl moieties show high discharge capacities which are close to the theoretical values [14,19]. The difference in the size of their molecular planes is considered to affect the battery behavior. In the present study, we focused on the naphthoquinone skeleton, which has a medium size plane compared to those of the above mentioned derivatives. There is a report about the charge/discharge behavior of a naphthoquinone-based polymer which was synthesized in a different way from ours [15]. The previously reported naphthoquinone-polymer shows a discharge capacity of only about 60 mAh/g during cycling, although its cycle-life is fair. On the other hand, our sample shows relatively high capacities. We also examined the effect of the polymer synthesis temperature on the battery performance, and found that there is an optimum at around 100°C at which PDHNQ that we describe in this paper was synthesized. The degree of polymerization or polymeric structure is considered to affect the battery performance. What results in the limited utilization ratios for the naphthoquinone polymers is not clear. One possible reason for this can be related to the amorphous nature of the polymer that hinders the ionic and/or electronic conductions. Polymers carrying a large planar redox site might tend to have a crystalline phase. To improve the utilization of the naphthoquinone polymers, further optimization of the synthetic conditions or another molecular design will be needed.

5. Conclusions

In this study, to suppress the dissolution of the active material during cycling, a reason for the capacity decay, the redox active sites were polymerized using a 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) skeleton, which potentially undergoes a four-electron transfer redox reaction. The solubility of the synthesized polymeric material (PDHNQ) was successfully decreased and the cycle-stability was improved by the polymerization, although the utilization of the redox active sites was not high enough. These results indicated that polymerization can be an effective way to improve the cycle-life performance of naphthoquinone-based active materials; however, the synthesis method has a profound effect on their discharge capacities. Further optimization of the synthesis conditions is necessary to improve the battery properties.

Acknowledgements

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