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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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Keywords: Organic cathode material, lithium ion battery, long cycle-life, polymerization.

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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, $\nu(^1H)$=500 MHz).