



Synthesis and properties of a lithium-organic coordination compound as lithium-inserted material for lithium ion batteries

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ABSTRACT

A lithium-organic coordination compound based on an aromatic carbonyl derivative, $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)]$, was synthesized by the dehydration of $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}]$, and used as a novel lithium-inserted material for lithium ion batteries. The synthesized material has initial discharge capacity of 126 and 115 mAh/g at current densities of 22 and 111 mAh/g, corresponding to the columbic efficiency of 99.2% and 98.3% at the first cycle, and its capacity fading is only 5% and 13% after 50 cycles, respectively, showing that this compound is a promising candidate as lithium-inserted material for lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) are regarded as promising power sources for their applications in electric vehicles because of their longer cycle life and higher energy density than other rechargeable battery systems [1,2]. In recent years, many research groups have devoted their work to the design and synthesis of new lithium-inserted materials for LIBs [3–6]. A variety of inorganic materials as lithium-inserted materials with excellent oxidizing and reducing capabilities, such as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , Co_3O_4 , and Fe_2O_3 , have been successfully developed. However, these inorganic materials are synthesized from limited mineral resources and the synthesis reactions proceed under high temperature. Furthermore, it seems difficult to further increase their capacity without the loss of cycling stability and safety. To avoid the disadvantages of these inorganic materials, a new approach in the development of new lithium-inserted materials is converting from inorganic to organic materials [7–18], including organic sulfide polymers [7–9], lithium-organic compounds [10–15] and other organic materials [16–18]. Recently, some lithium-organic coordination compounds, such as PDBM(Li) (PDBM: Poly(2, 5-dihydroxy-1, 4-benzoquinone-3, 6-methylene)) [10], $[\text{Li}_2(\text{C}_6\text{H}_2\text{O}_4)]$ [11], $[\text{Li}_2(\text{C}_6\text{O}_4\text{Cl}_2)]$ [12], $[\text{Li}_4(\text{C}_6\text{O}_6)]$ [13], $[\text{Li}_2\text{C}_8\text{H}_4\text{O}_4]$ and $[\text{Li}_2\text{C}_6\text{H}_4\text{O}_4]$ [14], have been reported to possess a high lithium-inserted capacity. Gall et al. [10] synthesized PDBM(Li)

with a specific capacity of about 150 mAh/g (theoretical capacity: 705 mAh/g) at a rate of 0.5 C, and its discharge capacity remains at 100 mAh/g after 100 cycles. A discharge capacity of around 176 mAh/g at a current density of 100 mA/g in the first cycle was also reported in coordination polymer $[\text{Li}_2(\text{C}_6\text{H}_2\text{O}_4)]$ (theoretical capacity: 384 mAh/g) [11], but its discharge capacity remains 137 mAh/g after 10 cycles. Armand et al. [14] reported two organic salts, $[\text{Li}_2\text{C}_8\text{H}_4\text{O}_4]$ and $[\text{Li}_2\text{C}_6\text{H}_4\text{O}_4]$, which have initial capacity of 300 and 170 mAh/g, but their discharge capacity remains 78% and 74% of the initial capacities after 50 cycles, respectively. It is obvious that the reported organic materials exhibited lower discharge capacity compared to their theoretical capacity and poor cycling stability.

In this paper, we reported a new lithium-organic coordination compound, $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)]$, as a lithium-inserted material for LIBs. This compound was synthesized by the dehydration of $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}]$ that was obtained through the reaction of an aromatic carbonyl derivative (1,5-dihydroxy anthraquinone) with LiOH. It is found that this compound exhibits a high capacity with good cycling performance.

2. Experimental

2.1. Preparation

$[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}]$ (compound 1) was synthesized from 1,5-dihydroxy anthraquinone (1,5-DHAQ) under N_2 atmosphere to avoid the oxidation of $\text{C}_{14}\text{H}_6\text{O}_4^{2-}$ anion. At 80 °C under stirring, 50 ml of 1.5 mol/L LiOH solution was slowly injected into a 50 ml solution

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prepared by dissolving 0.9 g of 1,5-DHAQ in oxygen-free dry ethanol. A red precipitate was obtained after 48 h, and then the mother liquor was removed by distillation and centrifugation. The as-obtained solid was washed by ethanol and water. Finally, the solid was dried in vacuum at 80 °C for 12 h.

The elemental analysis by a Perkin-Elmer 240 element analyzer indicated that the synthesized $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}]$ consists of 63.05% C and 2.67% H, corresponding to its calculated values: 62.22% C and 2.96% H.

$[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)]$ (compound 2) was obtained by annealing compound 1 at 300 °C for 3 h under N_2 atmosphere. The synthesized $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)]$ consists of 67.33% C and 2.11% H, corresponding to its calculated values: 66.67% C and 2.38% H.

2.2. Characterization

The as-prepared compound 1 and compound 2 were characterized by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) measurements. The morphologies were directly examined by SEM using a JEOL 6700F at an accelerating voltage of 5 kV. The XRD analyses were carried out on a Bruker AXS D8-Advanced diffractom-

eter at 40 kV and 40 mA with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning speed of $0.017^\circ/\text{s}$, the experimental XRD patterns were refined by using Accelrys Materials Studio. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

2.3. Electrochemical measurements

Coin-type cells (size:2016) consisting of a working electrode and a lithium foil counter electrode separated by a Celgard 2300 microporous membrane were assembled in an argon-filled glove-box. The working electrodes were prepared as follows: the prepared sample powders with 15 wt.% acetylene black and 5 wt.% polytetrafluoroethylene binder were mixed, coated and compressed onto an aluminum foil current collector. The electrolyte was $1\text{M LiPF}_6\text{-EC} + \text{EMC} + \text{DMC}$ ($V_{\text{EC}}:V_{\text{EMC}}:V_{\text{DMC}} = 1:1:1$). The charge/discharge experiments were performed by using a LAND cell test system (Land CT 2001A) in the potential range of 1.0–3.8 V versus Li/Li^+ at constant current densities of 22 and 111 mA/g. Cyclic voltammogram was obtained on PGSTAT-30 (Autolab) in the potential range of 1.0–3.8 V at a scanning rate of 0.1 mV/s.

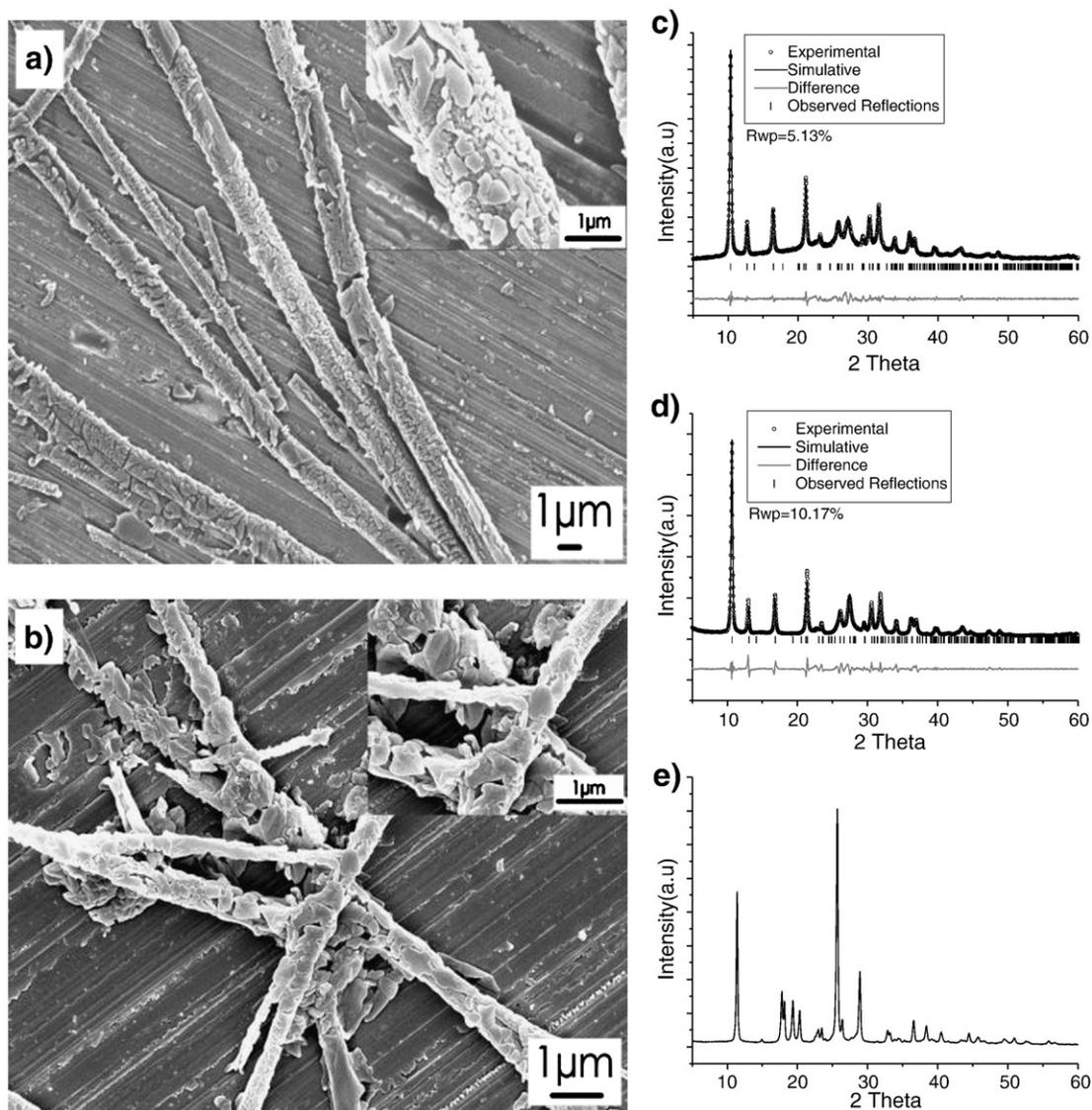


Fig. 1. (a) Low and high magnification (inset) SEM images of the as-prepared compound 1; (b) low and high magnification (inset) SEM images of the compound 2 obtained after annealing the compound 1 at 300 °C for 3 h; (c) and (d) experimental XRD patterns and the Rietveld refined profiles of compound 1 and compound 2; (e) XRD pattern of the 1,5-DHAQ.

3. Results and discussion

The as-prepared compound 1 and compound 2 after thermal treatment were comparatively examined against each other by various techniques. From a low magnification SEM image in Fig. 1a, it can be seen that compound 1 consists of rod structure. The average diameter of these rods is approximately 1.5 μm . The experimental powder X-ray diffraction (XRD) pattern of compound 1 is presented in Fig. 1c. It has the same monoclinic lattice of space group $P2_1/c$ with 1,5-DHAQ (Fig. 1e). However, the lattice constants are different: $a = 6.9325(4) \text{ \AA}$, $b = 17.0193(9) \text{ \AA}$, $c = 4.8411(5) \text{ \AA}$, $\beta = 91.4972(3)^\circ$, and $V = 571.1956(7) \text{ \AA}^3$ for compound 1, but $a = 6.113(0) \text{ \AA}$, $b = 5.375(8) \text{ \AA}$, $c = 16.004(0) \text{ \AA}$, $\beta = 94.11(0)^\circ$, and $V = 525.89(0) \text{ \AA}^3$ for 1,5-DHAQ [19], indicating that the new compound is formed. Thermogravimetric (TG) analysis was conducted to follow thermal treatment of compound 1 and 1,5-DHAQ under a nitrogen atmosphere, the obtained results are shown in Fig. 2. For the compound 1, the gradual weight loss of 5.18% from 40 to 200 $^\circ\text{C}$ can be attributed to the loss of crystal water (Calcd, 6.67%), when the temperature is further increased to 600 $^\circ\text{C}$ the sample start to decompose and the framework collapses. However, the framework of 1,5-DHAQ is stable only at the temperature lower than 280 $^\circ\text{C}$. Upon further heating, the whole framework of 1,5-DHAQ is destroyed and fast weight loss is observed.

After compound 1 was subjected to thermal treatment at 300 $^\circ\text{C}$ for 3 h, the rod structure is conserved but become small and rough, as shown in Fig. 1b. Fig. 1d presents the XRD pattern of compound 2. Compound 2 has the same space group with compound 1 and similar lattice constants: $a = 6.8990(4) \text{ \AA}$, $b = 16.9548(3) \text{ \AA}$, $c = 4.8359(8) \text{ \AA}$, $\beta = 91.5535(2)^\circ$ and $V = 565.6744(9) \text{ \AA}^3$.

The first cyclic voltammogram of the electrode made from compound 2 is shown in Fig. 3. It can be seen from Fig. 3a that two steps for lithium insertion and de-insertion in compound 2 can be separated significantly. The first reduction and oxidation peaks at about 1.7 and 2.1 V correspond to the insertion and de-insertion of one lithium ion, which is accompanying with transformation between lithium enolate and one of the two carbonyl groups. The second reduction and oxidation peaks at about 1.5 and 1.9 V correspond to the insertion and de-insertion of another lithium ion, which is accompanying with transformation between lithium enolate and the other carbonyl groups. The reaction processes can be expressed as Fig. 3b and c [8,11]. This lithium-organic coordination compound, compound 2, comprising of the carbonyl groups makes it possible for lithium enolation, which brings the possibility for Li ions to be inserted or de-inserted reversibly at positions of oxygen atoms when the carbonyl groups are reduced or oxidized, hinting that it could be used as a novel organic energy-storage system in Li-ion batteries [20]. It can be noted that the potentials for the lithium insertion and de-insertion of this compound are between 1.5 and 3.0 V, which is low or high compared to the current cathode or anode materials of lithium ion battery. It should be

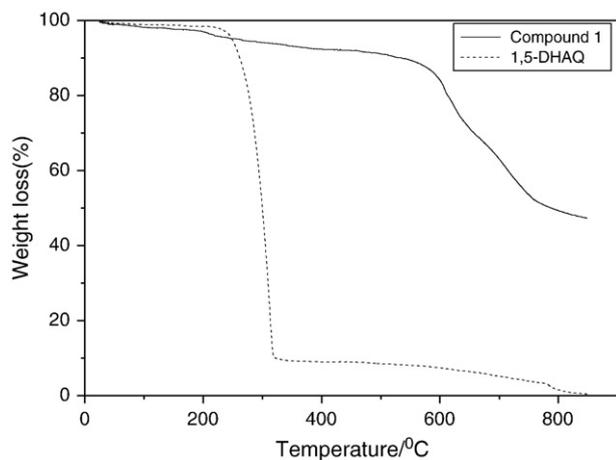


Fig. 2. TGA curves for compound 1 and the 1,5-DHAQ.

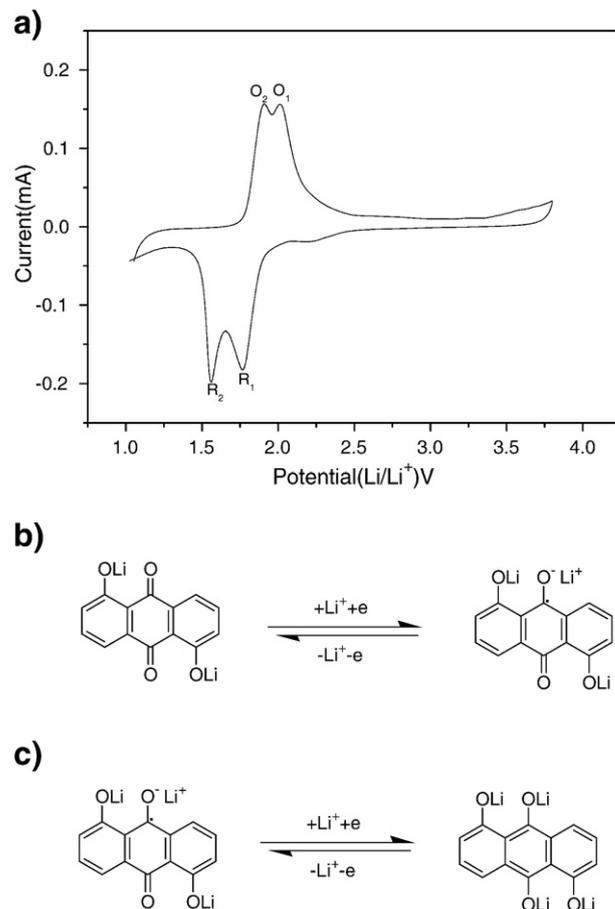


Fig. 3. (a) Cyclic voltammograms of compound 2, scan rate: 0.1 mV/s; (b) and (c) schematic diagram for the proposed reversible Li-ion insertion/de-insertion in 1,5-DHAQ(Li).

possible to enhance or reduce the potential through chemical substitutions of this compound, providing lithium ion batteries with new cathode or anode materials.

The cyclic performance of the electrode made with compound 2 is measured at current densities of 22 and 111 mA/g at room temperature. The obtained results are shown in Fig. 4. It can be seen from the insets of Fig. 4 that compound 2 delivers a good charge/

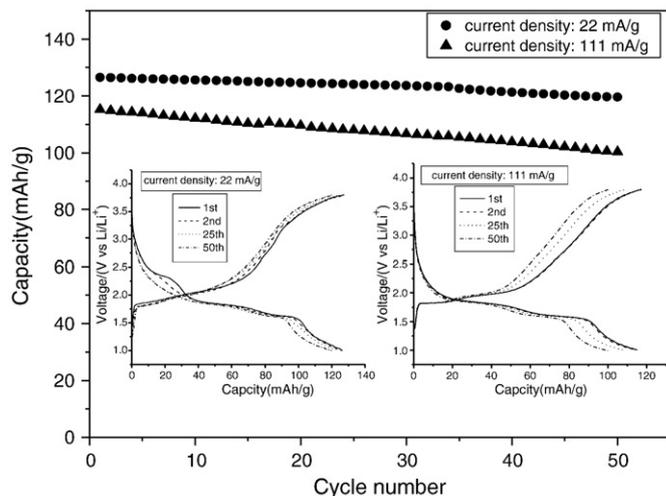


Fig. 4. The discharge capacity retention curves of the compound 2, conditions: cycling current density, 22 mA/g and 111 mA/g; potential limits, 1.0–3.8 V. Inset: the corresponding 1st, 2nd, 25th, and 50th charge and discharge curves.

discharge capacity of 127/126 and 117/115 mAh/g (theoretical capacity = 212 mAh/g), corresponding to the coulombic efficiency of 99.2% and 98.3% in the first cycle, respectively. The initial discharge capacity exceeds a half of theoretical capacity. After 2 and 25 cycles, the discharge capacity keeps 126 and 124 mAh/g, and 115 and 108 mAh/g, respectively. Moreover, after 50 cycles, the discharge capacity still remains at 120 and 100 mAh/g with the capacity fading of only 5% and 13%, respectively (Fig. 4), indicating that compound 2 has good cyclic stability. These performances of the compound 2 are comparable to those of other reported lithium-organic coordination polymers [10–12,14].

4. Conclusions

Our work presents a novel compound based on an aromatic carbonyl derivative, $[\text{Li}_2\text{C}_{14}\text{H}_6\text{O}_4]$, as a lithium-inserted material for lithium ion battery. This compound can be synthesized by the dehydration of $[\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}]$ and exhibits a high initial discharge capacity and good cyclic stability. Although the lithium insertion/de-insertion potential of this compound is low or high compared to the current cathode or anode materials of lithium ion battery, it should be possible to enhance or reduce the potential through chemical substitutions of this compound, providing lithium ion batteries with new cathode or anode materials.

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