Materials Letters 194 (2017) 189–192

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Cobalt-based layered metal compound nanoplatelets for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 20 December 2016
Received in revised form 13 February 2017
Accepted 16 February 2017
Available online 20 February 2017

Keywords:
Electrical properties
Transition metal compounds
Nanoplatelets
Lithium-ion battery
Energy storage and conversion

ABSTRACT

Cobalt-based layered metal compound ($Co(OH)(OCH_3)$) nanoplatelets synthesized by a facile solvothermal method were systemically characterized and investigated as an anode material for Li-ion batteries for the first time. It can deliver a high capacity of 1150 mA h g^{-1} at 100 mA g^{-1} and stay stable even after 160 cycles. It also shows high rate performance and reversibility. Its good electrochemical performance might be attributed to the unique layered structure with large layer spacing, 2D nanoplatelet-like morphology, and the void space between the nanoplatelets. The present synthesis strategy develops a potential candidate for anode materials with good performance for lithium-ion batteries.

1. Introduction

Technological improvements in high-energy-density lithium ion batteries (LIBs) are recently being driven by an ever-increasing demand for wearable electronics, long-range electric vehicles, and grid-scale energy storage [1]. As far as the current commercial LIBs using graphite anodes are concerned, the reversible capacity is poor due to its intercalation-type mechanism. Therefore, it is urgent to explore low-cost and high-capacity electrode materials for LIBs [2]. Recent efforts in this realm have focused on high-capacity anode materials such as alloys, metal oxides, or transition-metal dichalcogenide [3–5].

Some of us have reported a new class of layered metal compounds with a general formula of $M(OH)(OCH_3)$ (where M is Co or Mg), which was used as an important intermediate for the preparation of metal oxides covered by Tasker III type (1 1 1) facets [6,7]. $M(OH)(OCH_3)$ possesses a two-dimensional (2D) platelet morphology, which could provide large accessible surfaces as well as short Li^+ diffusion paths [8–10].

In this paper, we explore the possibility to employ the new layered metal compound $Co(OH)(OCH_3)$ for anode materials, with the finding that $Co(OH)(OCH_3)$ maps out as a promising candidate of anode materials in LIBs. 2D $Co(OH)(OCH_3)$ nanoplatelets was synthesized with a facile solvothermal method and it can deliver a highly stable and reversible capacity and exhibit good cyclability and rate capability.

2. Experimental

To prepare $Co(OH)(OCH_3)$, cobalt acetate tetrahydrate (Sinopharmacy, 98%) was dissolved in anhydrous methanol (Sinopharmacy, 99.5%) under stirring. The resultant mixture was further stirred for 1 h to form a 0.02 M solution. The 100 mL pink solution was charged into a 200-mL Teflon-lined autoclave, which was subsequently heated in an oven at 180 °C for 48 h. The prepared educt was filtered and washed with methanol, and dried in an oven at 60 °C for 24 h. $Ni(OH)(OCH_3)$ and $Mn(OH)(OCH_3)$ were synthesized following the same procedure. Details on characterization and electrochemical measurements of the as-prepared samples were described in the Supplementary Information (SI).

3. Results and discussion

As previously reported, during the solvothermal process, the cobalt acetate is reacted with methanol to afford $Co(OH)(OCH_3)$ as follows [11]:

$$Co(CH_3CO_2)_2 + 3CH_3OH \rightarrow Co(OH)(OCH_3) + 2CH_3CO_2CH_3 + H_2O \quad (1)$$

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http://dx.doi.org/10.1016/j.matlet.2017.02.052
0167-577X/

Fig. 1 shows the XRD pattern of the as-synthesized sample, which resembles that of $Mg(OH)(OCH_3)$ (JCPDS No. 22-1788) or $Ni(OH)(OCH_3)$ (JCPDS No. 38-0715) [6,12]. It can be indexed to a *R-3m* (space group no. 166) structure with a lattice parameter of $a = 0.316$ nm and $c = 2.317$ nm. In $Co(OH)(OCH_3)$, the c axis is extraordinarily longer than the a axis.

According to the Gibbs-Wulff theorem on thermally stable crystalline shapes, $Co(OH)(OCH_3)$ tends to possess a platelet-like morphology enclosed by (001) facets owing to an anisotropic nature of the crystalline structure. The SEM observation in Figs. 2a and S1a–b reveals that the as-prepared product consists of irregularly shaped platelets with a lateral size of hundreds of nanometers to several micrometers and thickness of 20–50 nm. As shown in Figs. 2b and S1c–d, TEM images further disclose its 2D platelet-like micro-structure. The corresponding electronic diffraction (ED) spots (Fig. S1d) can be indexed also to a *R-3m* structure, and the platelet is found to be projected along the [001] axis, which

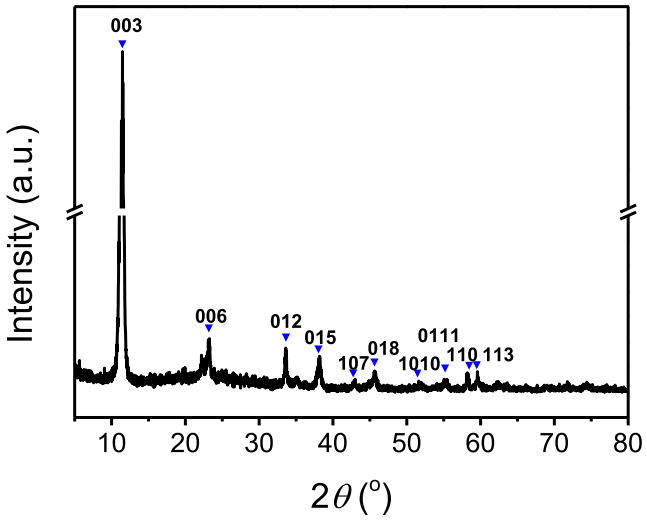

Fig. 1. XRD pattern of $Co(OH)(OCH_3)$.

is in line with the XRD result. Notably, part of $Co(OH)(OCH_3)$ has been transformed into cobalt oxides with a rocksalt structure (ED shown in small red letters in the inset of Fig. S1d) when they are exposed for a prolonged period [11]. In addition, from the energy-dispersive X-ray spectroscopy mapping (Fig. 2c) and XPS survey spectrum (Fig. S2a), it is confirmed that cobalt, carbon, and oxide elements are present and uniformly distributed in the platelets.

XPS analysis and FTIR spectroscopy were carried out to determine the elemental composition of the sample and their chemical states, and the detailed discussion is provided in the SI. The Co 2p core line suggests that the Co(II) oxidation state dominates in the compound (Fig. S2b). The FTIR spectrum discloses the presence of hydroxyl, methoxyl, Co–O, and water molecules in the sample, indicating that hydroxyl and methoxyl groups are covalently bonded to cobalt (Fig. S2c). This is further proven by the high resolution XPS spectra of C 1s and O 1s (Fig. S2d–e).

Motivated by the unique structural and micro-structure features, $Co(OH)(OCH_3)$ was used to fabricate a new anode material for LIBs. The cycling performance of $Co(OH)(OCH_3)$ is exhibited in Fig. 3a at a current density of 100 mA g^{-1}. It can be seen that the capacity of $Co(OH)(OCH_3)$ shows a slight decrease in the initial few cycles, while continues to increase to a plateau as high as ~1150 mA h g^{-1}. Such a high reversible capacity of $Co(OH)(OCH_3)$ is competitive with some of the previously reported Co_3O_4-based anodes. This result suggests the potential of this new layered compound to be used as a future anode material. It should be pointed out that the capacity-rise phenomenon here may be ascribed to the formation of a polymer/gel-like organic layer and the activation of the active material, which has been observed for many anodes [13]. The CE of $Co(OH)(OCH_3)$ was maintained at as high as ~99.19% (Fig. 3a) after the 3rd cycle, suggesting high charge/discharge reversibility and good cycling stability of the material.

Fig. 3b presents the typical galvanostatic discharge-charge (GCD) curves of the $Co(OH)(OCH_3)$ electrode. Remarkably, the initial discharge curve exhibits a well-defined voltage plateau at about 0.8 V, followed by a sloping curve down to the voltage of 0.01 V. Meanwhile, a poorly defined plateau is observed in the

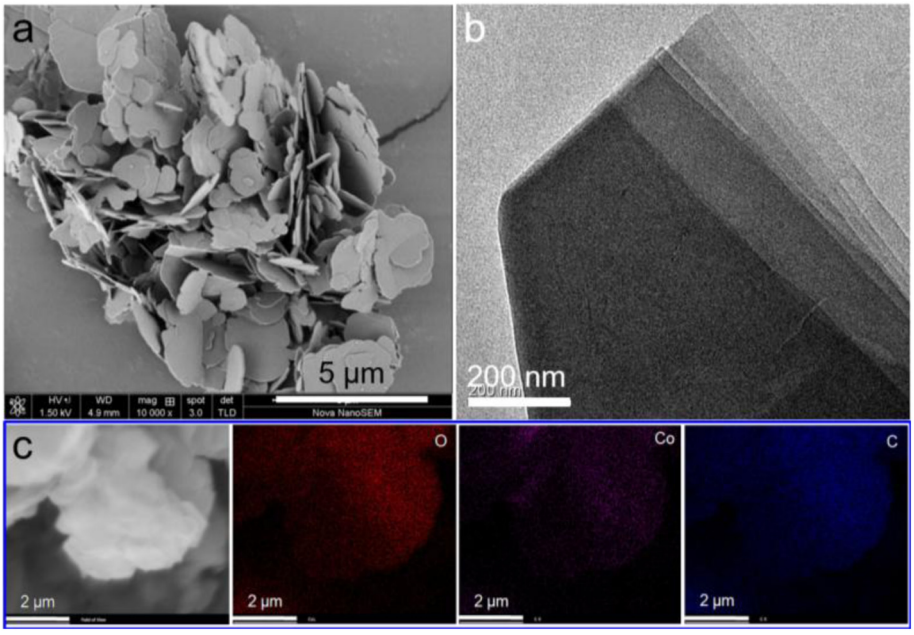

Fig. 2. (a) SEM and (b) TEM images of $Co(OH)(OCH_3)$. (c) An SEM image with the corresponding EDS elemental mapping images for oxygen, cobalt, and carbon.