Facile synthesis of Co(OH)F micro-rods and its application as anode for lithium ion batteries

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ABSTRACT

Co-based fluoride hydroxide, Co(OH)F was successfully prepared via a facile hydrothermal method. The morphology and size of the as-prepared Co(OH)F were characterized by field emission scanning electron microscopy (FE-SEM), which suggests the Co(OH)F exhibits rod-like morphology with mean diameter and mean length about 200 nm and 3 μm, respectively. The electrochemical performance of the as-prepared Co(OH)F micro-rods as anodes for lithium ion batteries was studied by conventional charge/discharge test, which exhibits clear sloping potential regions in charge and discharge curves, endowing it with potential application in lithium ion batteries.

1. Introduction

Composite materials have always played important roles in the development of lithium ion batteries. Among them, cobalt-based composite materials have received much attention owing to their specific physical and chemical properties, which have been widely used as cathode and/or anode materials for lithium ion batteries. For example, the discovery of LiCoO2 and its application as cathode material for lithium ion batteries promoted the commercialization of lithium ion batteries, which has been becoming one of the main cathode material for commercial lithium ion batteries [1]. Other cobalt-based composite materials such as LiCoPO4, LiCoPO4F, LiCoSO4F, LiCoSO4OH, CoCO3 and Co2SnO4 have also been prepared via different kinds of methods, which show attractive electrochemical performance as cathode and/or anode materials for lithium ion batteries [2–7]. Thus fabricating new sorts of cobalt-based composite materials and studying their electrochemical performance are of great interest.

Here in this article, we report the preparation of Co(OH)F micro-rods via a facile hydrothermal method. Its electrochemical property as anode for lithium ion batteries was studied by conventional charge/discharge test, which shows sloping potential regions in charge and discharge curves, endowing it with potential application in lithium ion batteries. To the best of our knowledge, this is the first report on the fabrication of Co(OH)F micro-rods and its electrochemical property research.

2. Experimental

The chemicals were of analytical grade and purchased from Shanghai Chemical Reagents. Natural graphite was obtained from Yichang Hengda graphite company (99.9%). In a typical process, 0.5 g sodium fluoride, 5 mmol hexamethylenetetramine and 3 mmol cobalt acetate tetrahydrate were dissolved in 30 ml distilled water. After stirring for 20 min, the obtained homogeneous solution was transferred into a 50 ml stainless autoclave, distilled water was subsequently added to 80% of its capacity. The autoclave was then sealed and placed in an oven, heated at 120 °C for 24 h. After the reaction, the resulting products were washed by distilled water and ethanol both four times.

Reference:

http://dx.doi.org/10.1016/j.matlet.2014.10.035
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120 °C for 24 h in vacuum oven. Coin-type cells (2025) of Li/1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/Co(OH)F/natural graphite electrode were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, H₂O < 1.0 ppm, O₂ < 1.0 ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in voltage region 0.02 ~ 3 V with a multichannel battery test system (LAND CT2001A). For evaluating the specific capacity of the electrode, the total weight of natural graphite and Co(OH)F was adopted as the weight of active material.

3. Results and discussion

XRD pattern of the as-synthesized products is shown in Fig. 1. As seen, the diffraction peaks at 20.9°, 32.3°, 33.5°, 34.7°, 35.6°, 38.8°, 39.9°, 43.6°, 51.9°, 52.8°, 56.9°, 59.1° and 61.6° correspond to the (110), (310), (201), (400), (111), (211), (410), (311), (221), (420), (511), (002) and (601) faces of orthorhombic Co(OH)F with lattice constant a = 10.3 Å, b = 4.677 Å and c = 3.126 Å, which are in good agreement with JCPDS, no. 50-0827. Strong and sharp diffraction peaks suggest the as-synthesized Co(OH)F are well crystallized. The formation of Co(OH)F is likely as follows:

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\begin{align*}
\text{C}_2\text{H}_6\text{O}_4 & \rightarrow \text{Co}^{2+} + 2\text{[CH}_3\text{COO]}^- \\
\text{NaF} & \rightarrow \text{Na}^+ + \text{F}^- \\
\text{(CH}_2\text{)}_4\text{N}_4 + 10\text{H}_2\text{O} & \rightarrow 6\text{HCHO} + 4\text{OH}^- + 4\text{[NH}_4]^+ \\
\text{Co}^{2+} + \text{F}^- + \text{OH}^- & \rightarrow \text{Co(OH)}\text{F}
\end{align*}
\]

The excessive NaF in solution can act as a capping agent, inducing the oriented growth of Co(OH)F, which is similar to that of Na₂SO₄ and K₂SO₄ in solution [8,9].

Fig. 2(a) is a low magnification SEM image of the obtained Co(OH)F, which shows a large number of micro-rods. As seen, the morphology, consisting of a large number of micro-flakes, nanoparticles and micro-rods. The micro-flakes and nanoparticles can be attributed to natural graphite and acetylene black, respectively, which are introduced in the electrode preparation process [12]. The micro-rods correspond to the cycled Co(OH)F, which show crooked profile, differing from that of Co(OH)F before cycling. For further studying the morphology of the cycled Co(OH)F, a high magnification SEM image of the cycled electrode is shown in Fig. 4(b).

As seen, the cycled micro-rods show unsmooth surface and irregular top with length about several micrometers. In addition, the mean diameter of the cycled micro-rods is about 300 nm, which is little bigger than that of Co(OH)F before cycling. The morphological variation of the Co(OH)F micro-rods in cycling is similar to that of NiO, which is proposed to be an electrochemical reconstruction [13].

4. Conclusions

In summary, Co(OH)F micro-rods were successfully prepared via a facile hydrothermal method. The electrochemical performance of the as-prepared Co(OH)F as anode for lithium ion batteries was studied by conventional charge/discharge test, which exhibits sloping potential regions, endowing Co(OH)F with
potential application in lithium ion batteries. Further research work on tuning the morphology and size of Co(OH)F may have important effect on its electrochemical performance. In addition, the fabrication method reported here may be useful for fabricating other fluoride hydroxides.

Acknowledgments

We gratefully acknowledge the financial support from Natural Science Foundation of China (NSFC, 51272128, 51302152, 51302153). Moreover, the authors are grateful to Dr. Jianlin Li at Three Gorges University for his kind support to our research.

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