Influence of surface modification on structure and electrochemical performance of LiNi$_{0.5}$Co$_{0.5}$VO$_4$

L.-Q. Mai, W. Chen*, Q. Xu, Q.-Y. Zhu, C.-H. Han, W.-L. Guo

Institute of Materials Science and Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan 430070, PR China

Received 3 January 2003; received in revised form 17 July 2003; accepted 22 July 2003

Abstract

The electrochemical stability of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ is improved by sol–gel coating with an amorphous SiO$_2$ film. This limits direct contact between LiNi$_{0.5}$Co$_{0.5}$VO$_4$ and electrolyte, and thus, effectively provides the structural stability for the electrochemically active intercalation compound LiNi$_{0.5}$Co$_{0.5}$VO$_4$, resulting in improved specific capacity and cycling performance.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Secondary lithium batteries; LiNi$_{0.5}$Co$_{0.5}$VO$_4$; Surface modification

1. Introduction

Li ion batteries belong to a rapidly growing field as rechargeable power sources for room temperature consumer applications, since the commercialization of Sony’s lithium-ion cell in 1990 [1–7]. However, harmful interactions between the active positive materials and the electrolyte in lithium secondary batteries deteriorate the performance of the cathode materials and the batteries [8–10]. In order to limit these harmful interactions, interest in surface-modified cathodes has increased due to their improved electrochemical behavior [8–11]. It is reported that thin film oxide coating (Al$_2$O$_3$, ZrO$_2$, MgO, etc.) on the powder surface has improved the electrochemical performance of the electrochemically active intercalation compound (LiCoO$_2$, LiNiO$_2$, LiMnO$_2$, etc.) [9–13]. LiNi$_{0.5}$Co$_{0.5}$VO$_4$, a high-voltage cathode candidate, also suffers from harmful interaction at the surface [14,15]. In the present work, a SiO$_2$ film has been coated onto the surface of the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ cathode material by the sol–gel method using Si(OCH$_2$CH$_3$)$_4$. The influence of surface modification on electrochemical performance of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ is reported.

2. Experimental

LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders were prepared first by dissolving stoichiometric quantities of Li$_2$CO$_3$, Ni$_2$(OH)$_2$CO$_3$, Co(OAc)$_2$ and NH$_4$VO$_3$ in de-ionized water. Under vigorous stirring, saturated citric acid solution and polyethylene glycol solution were added and a brown xerogel was obtained after being heated...
at 80–100 °C. The as-obtained xerogel was heated at 450 °C for 4 h and brown powders were attained.

The sol–gel coating of SiO$_2$ on the powders was carried out as follows: 0.5 mol LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders were added to the mixed solution of 100 ml Si(OCH$_2$CH$_3$)$_4$ and 0.01 mol ethanol under vigorous stirring and ultrasonic treatment at 40 °C, and then exposed in the air. After 3 days, the products obtained were heated at 600 °C for 10 h; this ultimately gave a yellowish powder.

X-ray diffraction (XRD) experiments were performed on a D/MAX-III X-ray diffractrometer with Cu K$_\alpha$ radiation and a graphite monochrometer. Transmission electron microscopy (TEM) images were attained using a JEM-100CX II scanning electron microscope at 80 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using an ESCALAB MK II multi-technique electron spectrometer. The data were obtained at room temperature; typically, the operating pressure in the analysis chamber was below 1 × 10$^{-8}$ Pa. The cathode preparation and the test cell were similar to as described in Ref. [14]. Ni metal was used as the anode. The test cells containing 1 M LiPF$_6$-EC-DEC (1:1 volume ratio) were usually charged to 4.9 V and discharged to 2.8 V at a 0.15 C rate.

3. Results and discussion

The XRD patterns for uncoated and coated LiNi$_{0.5}$Co$_{0.5}$VO$_4$ are shown in Fig. 1. They are dominated by the (311) Bragg peak at 2$\theta$ = 36°. Both of the XRD patterns display a weak (111) peak and a strong (220) peak, which indicate the predominant inverse spinel structure of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ [14]. The presence of vanadium atoms on the tetrahedrally coordinated 8a site leads to the increase of the (220) intensity at the expense of the (111) peak [14,15]. The XRD pattern of coated LiNi$_{0.5}$Co$_{0.5}$VO$_4$ shows no any secondary phase, indicating that SiO$_2$ exits in an amorphous state, or can react with LiNi$_{0.5}$Co$_{0.5}$VO$_4$ to give concentration gradients at the particle surface. The lattice constant $a$ of the coated samples ($a = 8.220 \pm 0.002$ Å) show no change compared to the uncoated one ($a = 8.220 \pm 0.002$ Å), indicating that Si does not enter the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ lattice.

The TEM images of uncoated and coated LiNi$_{0.5}$Co$_{0.5}$VO$_4$ are shown in Fig. 2. Spherical grains of uncoated LiNi$_{0.5}$Co$_{0.5}$VO$_4$ are clear, with little impurity on their surface (Fig. 2a). In contrast, there is some deposit on the surface of spherical grains of
coated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> (Fig. 2b). Surface composition of uncoated and coated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> were analyzed by XPS [16] and summarized in Table 1. Surface composition of uncoated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> is very near to the stoichiometric ratio of the elements in LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub>, but the content of Li, Ni and Co on the surface of coated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> decreases and a concentration of silicon (21.52 at.%) appears. There is only one chemical state for Si with a binding energy of 102.99 eV, corresponding to SiO<sub>2</sub> [16]. A significant amount of Si atoms is thus distributed at the surface in the form of SiO<sub>2</sub>, and Si atoms do not enter LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> in the form of a solid solution; this supports the result of the XRD, but is different from the solid solution forming on the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> material [11,13] or on the ZrO<sub>2</sub>-coated LiNiO<sub>2</sub> material [12].

The first charge-discharge curves and the capacity of the first ten cycles for uncoated and coated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> are shown in Figs. 3 and 4, respectively. The first-charge capacity of uncoated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> is 90 mAh/g; it decreases to 38.7 mAh/g after ten cycles, where the cycling efficiency is 43%. However, the first-charge capacity of coated LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> is 100 mAh/g, decreasing to 87 mAh/g after ten cycles; its cycling efficiency is 87%. It is shown that the specific capacity and cycling performance of LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> are improved significantly. The reason for this can be that contact area and side reactions between LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> and the electrolyte are effectively reduced through the surface modification by SiO<sub>2</sub>. The structural stability of the electrochemically active intercalation compound LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> can thus effectively be engineered by the artificial formation of a thin SiO<sub>2</sub> coating; the mechanism causing this improved performance needs to be further identified.

4. Conclusions

An amorphous SiO<sub>2</sub> film has been coated onto the surface of LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> cathode particles by the sol–gel method using Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>. This surface modification improves specific capacity and cycling performance by the SiO<sub>2</sub> layer reducing the contact area and side reactions between LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> and the electrolyte, thus providing structural stability of electrochemically active intercalation compound LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub>.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 50172036),
the Teaching and Research Award Program for Outstanding Young Professors in Higher Education Institute, MOE, P.R. China and the Science Fund for Distinguished Young Scholars of Hubei Province.

References