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Electrochemistry Communications 8 (2006) 1731–1736
electrochemistry communications
www.elsevier.com/locate/elecom

Valence change by in situ XAS in surface modified $LiMn_2O_4$ for Li-ion battery

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Received 13 July 2006; received in revised form 25 July 2006; accepted 26 July 2006

Abstract

The surface-modified cathode material in Li-ion battery was synthesized to decrease the side reactions at the interface between the cathode electrode and electrolyte. It is aimed to reduce the fading rate and to enhance the electrochemical performance, particularly at high C rate. In this study, microstructure, valence change and variation of bonding state in the surface-modified $LiMn_2O_4$ were examined and probed. Both the $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and $Li_2O–2B_2O_3$ (LBO)-coated $LiMn_2O_4$ were synthesized by chemical solution method in this study. Field-emission SEM plan-view observation revealed the particles with the size of 7–8 μm for both $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$, exhibiting a well-developed octahedral structure with sharp edges. Nevertheless, from the cross-section view of both $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$, it was observed that the lager particles consisted of many smaller ones in the sub-micrometer range. It was demonstrated that $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$ exhibited two distinct types of surface modification on the basis of the detailed analysis of FESEM and HRTEM. The XANES of Cu and Mn K-edge spectrum for $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ showed that the valence of Cu and Mn was close to Cu^{2+} and Mn^{4+}. Furthermore, the oxidation state of Mn was reversibly increased and decreased during charge. It was further revealed in this study that the trend of the variation for the bonding length of Mn–O and Mn–M (M = Mn or Cu) was in agreement with the oxidation state of Mn, which was decreased with Li deintercalation while increased with Li intercalation during cycling. On the basis of the in situ XAS data, it was evidenced that Mn transferred toward Mn^{4+} to minimize the Jahn–Teller distortion, and thus the electrochemical property was improved.

Keywords: Cathode material; Spinel $LiMn_2O_4$; Surface modification; In situ XAS; Li-ion battery

1. Introduction

Since the “eye ball” trend was proposed in the 39th Consumer Electronics Show (CES) at the beginning of 2006, the amounts of the requirement of portable electronics will be larger and larger. In a portable electronic device, rechargeable lithium ion battery function as the power source plays a critical role. In the near future, there are plenty of opportunities for the electric vehicle (EV) and hybrid electric vehicle (HEV) with the rechargeable battery as power source to substitute the traditional vehicle. The requests of the rechargeable lithium ion battery are nothing more than low cost, long life, high energy density and green.

Among all candidate cathode materials, $LiMn_2O_4$ is proposed to satisfy the field-use requirements and becomes the promising cathode material for commercial usage. However, there are some drawbacks such as Jahn–Teller distortion [1] and manganese dissolution and electrolyte decomposition [2]. The first factor could be significantly improved by partial substitution of manganese cations Mn^{3+} with transition metals [3–8] and substitution of oxygen with fluorine [9,10]. The dissolution of manganese and

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doi:10.1016/j.elecom.2006.07.038

the electrolyte decomposition could be overcome by altering the surface chemistry of the cathode electrode particles by inorganic materials and metal oxide [11–17]. Recently, X-ray absorption spectroscopy (XAS) motivates researchers to investigate the variation of the local atomic and electronic structure surrounding the absorbing atom [18–24].

In this study, two interesting aspects are addressed to better understanding the mechanism of surface modification during cycling. First is to precisely evaluate the film thickness coated on the surface of cathode powders as well as to confirm the phase for both the coating layer and base spinel $LiMn_2O_4$ by HRTEM. Second is to investigate the variation of the oxidation state, electronic configuration, and site symmetry by the in situ X-ray absorption near edge structure (XANES) and interatomic distance by the in situ extended X-ray absorption fine structure (EXAFS) during charge and discharge process.

2. Experimental procedure

The $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and $Li_2O–2B_2O_3$ (LBO)-coated $LiMn_2O_4$ were synthesized by solution method in previous works [25,26]. The weight percent of Cu and LBO glass in a surface modified lithium manganese oxide was 1 wt% and 0–0.5 wt%, respectively. The particles were mounted in the epoxy with a weight ratio of ERL-4206:DER-736:NSA:DMAE = 5:3:13:0.1. After cured at 70 °C for 8 h, the epoxy with particles was cut to a trapezoid shape with various thickness of 900–90 nm by microtome. High resolution transmission electron microscope (HRTEM, JEM-4000EX, JEOL, Japan) was further utilized to observe the bight field image and the corresponding SAD pattern. The particle morphology and particle size were examined using a field scanning electron microscope (FESEM, JSM-6500F, JEOL, Japan) at an accelerating voltage of 15 kV. The cathode was manufactured by mixing active material, KS6 graphite, and polyvinylidene fluoride (PVDF) binder at a weight ratio of 85:10:5 in *N*-methyl-2-pyrrolidinone (NMP). The 2016 coin cell with cathode, Li foil as anode and an electrolyte of 1M $LiPF_6$ in a 1:1 (volume ratio) mixture of EC/DMC was fabricated in a specially designed chamber with low oxygen pressure ($O_2 < 2$ ppm) and low moisture ($H_2O < 2$ ppm). For passing through the cathode electrode by synchrotron radiation light, the upper cover, bottom cover and Ni spacer of the 2016 coin cell were drilled with a hole of 4 mm in diameter and then sealed by a Kapton film.

In situ XAS experiments of Mn K-edge were performed in transmission mode at beam line BL-17C at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan. The stored beam current was in top-up mode, which was initially maintained at 200 mA with approximately 0.6 mA per current bin and photon stability in the range of 10^{-3}–10^{-4}. The energy selection was actualized by a Si (1 1 1) double crystal monochromator. The Mn foil was employed for energy calibration in each scan simultaneously. To analyze the in situ XAS data, all raw absorption spectra were normalized to compare the regions of pre-edge, near-edge and post-edge. The *k* space ranging from 3.6 to 13.75 Å was Fourier transformed (FT) to *r* space by separating the EXAFS contributions according to different coordination shells. All fitting procedure and parameters including the coordination number (*N*) and the Debye–Waller factor were executed by the UWXAFS 3.0 software package.

3. Results and discussion

3.1. Microstructure analysis

Figs. 1(a) and (b) show the FESEM image of the cross-section views of $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$, respectively, with the thickness of 900 nm cut by microtome. The particles with the size around 7–8 μm for both $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$ exhibited a well-developed octahedral structure with sharp edges, which was bounded by eight (1 1 1) planes. However, from the cross-section view of both $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$, it was demonstrated that the lager particles consisted of many smaller ones in sub-micrometer range. Composition and phase analysis inside the particles were evaluated by EDS and HRTEM, respectively. Figs. 1(c) and (d) reveal the bright field image of the cross-section views of $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ and LBO-coated $LiMn_2O_4$, respectively, with the thickness of 90 nm cut by microtome. An amorphous LBO film with the thickness of 10–15 nm coated on the surface of $LiMn_2O_4$ particle was clearly observed in Fig. 1(d), which may not influence the valence of Mn in a spinel $LiMn_2O_4$. Nevertheless, as shown in Fig. 1(c), Cu diffused into the smaller particles and formed a core-shell $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ particle with $LiCu_xMn_{2-x}O_4$ as a shell and $LiMn_2O_4$ as a core. The amount of Cu in a core-shell particle decreased gradually from 5.61 wt% at the shell down to zero in the core.

Since Cu diffusion into the spinel structure was evidenced, the next task was to realize where the Cu occupied in the spinel. More detailed lattice image for 90 nm $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ cut by microtome is displayed in Fig. 2 along with the corresponding SAD pattern at the left corner. The SAD pattern at the right bottom corner was created by the program CaRIne Crystallography 3.1, by which the Cu atom at the 16c site in a spinel structure was simulated. As compared with the simulated one, the SAD pattern of $LiCu_xMn_{2-x}O_4$-coated $LiMn_2O_4$ revealed apparent facets with $(4\bar{4}0)$, $(4\bar{4}4)$ and (004) without $(2\bar{2}\bar{2})$, $(2\bar{2}2)$, $(\bar{2}22)$ and $(\bar{2}2\bar{2})$ at [1 1 0] zone. However, no $(2\bar{2}\bar{2})$, $(2\bar{2}2)$, $(\bar{2}22)$ and $(\bar{2}2\bar{2})$ were ever found, which was in accordance with the simulated SAD pattern assuming Cu at the 16d site in a spinel structure at the right top corner in Fig. 2. This suggested that Cu was located at the 16d site rather than the 16c site, since no diffraction facet from the 16c site was detected.