Valence change by in situ XAS in surface modified LiMn$_2$O$_4$ for Li-ion battery

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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$_2$O$_4$ were examined and probed. Both the LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and Li$_2$O–2B$_2$O$_3$ (LBO)-coated LiMn$_2$O$_4$ 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$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$, exhibiting a well-developed octahedral structure with sharp edges. Nevertheless, from the cross-section view of both LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$, it was observed that the larger particles consisted of many smaller ones in the sub-micrometer range. It was demonstrated that LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$ 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$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ 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.

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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$_2$O$_4$ 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...
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$_2$O$_4$ by HRTEM. Second is to investigate the variation of the oxidation state, electronic configuration, and site symmetry by the in situ X-ray absorption fine structure (EXAFS) during charge and discharge process.

2. Experimental procedure

The LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and Li$_2$O-2B$_2$O$_3$ (LBO)-coated LiMn$_2$O$_4$ 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 bright 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$_2$O < 2 ppm). The stored beam current was in top-up pressure (O$_2$ < 2 ppm) and low moisture (H$_2$O < 2 ppm).

3. Results and discussion

3.1. Microstructure analysis

Figs. 1(a) and (b) show the FESEM image of the cross-section views of LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$, respectively, with the thickness of 900 nm cut by microtome. The particles with the size around 7–8 μm for both LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$ exhibited a well-developed octahedral structure with sharp edges, which was bounded by eight (111) planes. However, from the cross-section view of both LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$, 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$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ and LBO-coated LiMn$_2$O$_4$, 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$_2$O$_4$ particle was clearly observed in Fig. 1(d), which may not influence the valence of Mn in a spinel LiMn$_2$O$_4$. Nevertheless, as shown in Fig. 1(c), Cu diffused into the smaller particles and formed a core-shell LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ particle with LiCu$_x$Mn$_{2-x}$O$_4$ as a shell and LiMn$_2$O$_4$ 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$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ 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$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ revealed apparent facets with (440), (444) and (004) without (222), (222), and (222) at [110] zone. However, no (222), (222), and (222) 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.
According to the above-mentioned phase identification and composition determination, the schematic diagrams for the cross-section view of LBO-coated LiMn$_2$O$_4$ and LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ are revealed in Fig. 3(a) and (b), respectively. In Fig. 3(a), an amorphous LBO glass film was coated on the surface of the LiMn$_2$O$_4$ particles to prevent the side reaction from the interface between the electrode and electrolyte. On the other hand, the concentration gradient of Cu in the smaller primary particles was observed, as demonstrated in Fig. 3(b), which implying the increase of the conductivity and the rate capability of LiMn$_2$O$_4$. In a previous study [27], the plateau potential of LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ was lower than that of the base LiMn$_2$O$_4$ for 50 mV, which can be related to the faster kinetics of the LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ cathode material. In other words, the conductivity of LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ was increased.

Recently, it was demonstrated that the fading rate after 35 cycles for base LiMn$_2$O$_4$ and LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ was 14.18% and 11.93% at 0.2 C rate, respectively [25]. At the rate capability of 0.5 C, the fading rate for base LiMn$_2$O$_4$ and LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ after 35 cycles was 17.14% and 11.98%, respectively, which was significantly decreased by the surface modification. It is apparent that the fading rate of LiMn$_2$O$_4$ at 0.2 C is reduced 2.25% by surface modification. It should be noted that the decrease of fading rate, i.e. 5.16%, was more
evident at higher C rate. For the LBO-coated lithium manganese oxide, the fading rate of 7% for 0.3 wt% LBO-coated LiMn$_2$O$_4$ was lower than that of 16% for the uncoated one [26].

3.2. In situ XAS analysis

A methodical in situ XANES and EXAFS analysis were accomplished to evaluate the change of the electronic and geometric structures of LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ during charge and discharge. For the first cycle of charge and discharge, the coin cell was measured galvanostatically between 3 and 4.5 V at 0.1 C rate, as shown in Fig. 4. The exposure time was 25 min for each spectrum at a specific potential range. The XANES of Cu K-edge spectrum for LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ demonstrated that the valence of Cu was close to Cu$^{2+}$. The Mn K-edge in situ XANES spectra for LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ spinel during cycling at different potentials with reference samples of Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$) are shown in Figs. 5(a) and (b), respectively. The near-edge energy of LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ was found to be lower than MnO$_2$, while higher than Mn$_2$O$_3$ during charge and discharge. It was indicated that Mn was in a mixed oxidation state of Mn$^{3+}$ and Mn$^{4+}$ in LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$. In comparison, the valence of Mn in LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ at 3 V was closer on Mn$^{4+}$ than Mn$^{3+}$, which was a good match for Cu$^{2+}$ in LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$. Furthermore, it was also

![Fig. 3. Schematic diagram for the cross-section view: (a) LBO-coated LiMn$_2$O$_4$ and (b) LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$.](image)

![Fig. 4. Voltage profile for the LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ at the rate of 0.1 C between 3 V and 4.5 V.](image)

![Fig. 5. K-edge XANES spectra for Mn in LiCu$_{x}$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ with the spectra for MnO$_2$ and Mn$_2$O$_3$ at (a) elevated charge voltage and (b) down discharge voltage.](image)
observed that the oxidation state of Mn increased with the elevated potential from 3 V to 4.5 V during charge and was reversible from 4.5 V to 3 V during discharge.

Figs. 6(a) and (b) reveal the Fourier transforms of Mn K-edge EXAFS of LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ during charge and discharge process, respectively. The first peak around 1.9 Å and the second peak around 2.9 Å corresponded to Mn–O interaction and Mn-metal (Mn–Mn or Mn–Cu) interaction, respectively. It was also revealed that the deintercalation of Li ions from spinel resulted in a raise in the amplitude of both Mn–O and Mn-metal peak. All variation in amplitude of both Mn–O and Mn-metal interactions was examined to be reversible during discharge as well. The increase in peak amplitude was due to the transitions in the local structure of Mn from the oxidation of Mn$^{3+}$ to Mn$^{4+}$. In Nakai’s study [19], it was proposed that if the metal ion was not a Jahn–Teller active ion, the metal-oxygen EXAFS would not vary as a function of deintercalation of lithium ions.

The variation of the bonding length for Mn–O and Mn–M (M = Mn or Cu) are plotted in Fig. 7(a) and (b), respectively. Both the bonding length of Mn–O and Mn–M decreased with Li deintercalation during charge, and then increased with Li intercalation during discharge. The bonding length at both 3 V and 4.5 V during charge was identical to that during discharge. It was suggested that the electronic state of Mn was reversible during cycling. In this study, the bonding length of Mn–O was roughly fixed at 1.91 Å from 3 V to 4.5 V, while that of Mn-metal decreased from 2.91 Å to 2.85 Å at the elevated potential from 3 V to 4.5 V, as shown in Fig. 7(a) and (b), respectively. Since Mn$^{4+}$ was not a Jahn–Teller active ion, the oxidation process not only led to an increase in magnitude of Mn–O peak, but reduced the Jahn–Teller effect in a spinel structure.

Fig. 6. Fourier transform spectra for Mn in LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ at (a) elevated charge voltage and (b) down discharge voltage.

Fig. 7. Bonding length for Mn in LiCu$_x$Mn$_{2-x}$O$_4$-coated LiMn$_2$O$_4$ during charge and discharge (a) the 1st shell of Mn–O and (b) the 2nd shell of Mn–M (M = Mn or Cu).
4. Conclusion

In conclusion, from the results of TEM and the corresponding SAD pattern, it was revealed that the Cu\textsuperscript{2+} diffused into the core-shell cathode material, i.e. LiCu\textsubscript{x-}Mn\textsubscript{2-x}O\textsubscript{4} coated LiMn\textsubscript{2}O\textsubscript{4}, located at the 16d site, and the concentration of Cu gradually decreased from the shell to the core. On the contrast, the assembly of a 10–15 nm LBO glass film coated on the surface of LiMn\textsubscript{2}O\textsubscript{4} reduced the fading rate of the base LiMn\textsubscript{2}O\textsubscript{4}. The in situ XAS data exhibited that the bonding state of Cu and Mn was close to Cu\textsuperscript{2+} and Mn\textsuperscript{4+}, respectively, and Mn would transfer toward Mn\textsuperscript{4+} to minimize the Jahn–Teller distortion. From the in situ EXAFS data, the bonding length of both Mn–O and Mn-metal were examined to be reversible during charge and discharge process. In addition, the transition of metal ions during cycling was nearly reversible.

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