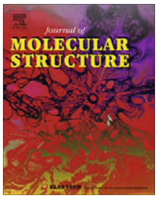
Journal of Molecular Structure 974 (2010) 139–143

Contents lists available at ScienceDirect

Journal of Molecular Structure

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



Characterization of the passivating layer on Li[$Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}$]$O_2$ cathode in the overcharge state

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ARTICLE INFO

Article history:
Received 13 December 2009
Accepted 26 January 2010
Available online 1 February 2010

Keywords:
Solid electrolyte interface
Cathode–electrolyte interface
Overcharge
X-ray photoelectron spectroscopy
2D correlation spectroscopy

ABSTRACT

The passivating layer (also called the solid electrolyte interface, SEI) plays a key role in the performances of Li-ion batteries. In this work, we studied the surface reactions of Li[$Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}$]$O_2$ with the organic electrolyte in the overcharge state by means of FTIR, XPS, XAS, and 2D correlation analysis. The FTIR and XPS results revealed that several types of compounds are formed on the cathode surface. These results also suggest that the organic solvents are decomposed to a greater extent than the Li-salt during the overcharge state. Based on the 2D correlation analysis, we can deduce the following sequence of events: 287.0 (due to C–O) → 290.0 (due to carbonate) → 288.5 (due to C=O) → 291.5 (due to $C-F_x$) → 284.5 eV (due to C–C or C–H).

1. Introduction

Layered $LiCoO_2$ is the most commonly used cathode material in commercial lithium-ion (Li-ion) batteries due to its high theoretical capacity (274 mAh/g) and good electrochemical performance. However, the practically attainable capacity is known to be only ~140 mAh/g in the voltage range of 3.0–4.2 V. Moreover, cobalt has become more expensive nowadays. These limitations have led to intensive studies being conducted to find alternative cathode materials. In this regard, mixed Li–Ni–Mn–Co–O oxides have recently attracted much attention, because of their higher reversible capacity, lower cost, and less toxicity than $LiCoO_2$ [1–3]. Li–Ni–Mn–Co–O oxides also exhibit improved cycleability in the voltage range of 3.0–4.6 V [4,5]. The electrochemical properties of these materials are sensitively dependent on the distribution of the transition metals and the particle morphology. Therefore, various approaches have been adopted to improve their performance, such as the partial substitution of Al, Mg, and Zn for the transition metals and the optimization of the preparation methods [6–9].

The electrochemical reactions at the electrode–electrolyte interface play a key role in the performances of Li-ion batteries. During the charging–discharging process, a passivating layer forms on the electrode surface [10–12]. This passivating layer, also called the solid electrolyte interface (SEI), generally consists of lithium salts, organic solvent-based compounds and, in some cases, polymeric compounds. Under ambient conditions, the composition and morphology of the SEI directly affect the charge–discharge efficiency, cycle life, and irreversible capacity loss [13,14]. In the overcharge state, however, the SEI can produce excessive heat and flammable gas due to its thermal decomposition, thereby leading to thermal runaway and even battery explosion [15,16]. Therefore, an understanding of the composition and structure of the SEI is very important to enhance the performances and safety of the battery. Until recently, because irreversible capacity loss in practical lithium-ion battery systems is strongly correlated with the formation of an SEI on the anode, the investigation of the SEI has mainly focused on the anode electrode using various electrochemical and spectroscopic techniques for different battery systems. There have been few studies of the SEI on mixed Li–Ni–Mn–Co–O oxides.

Generalized 2D correlation spectroscopy has attracted a high level of interest in the analytical science community, as it provides considerable utility and benefit in many fields of spectroscopic study. The 2D correlation spectra are calculated from the dynamic

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doi:10.1016/j.molstruc.2010.01.053

spectra obtained during the measurement of the spectra with an external perturbation. This analytical technology has various advantages, such as the enhancement of the spectral resolution, the establishment of unambiguous assignments and the determination of the sequence of emergence of the spectral peaks. The details of 2D correlation spectroscopy were described previously [17,18].

In this study, we investigated the SEI on the $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$ cathode in the overcharge state by using Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). We also applied 2D correlation spectroscopy to the XPS spectra of the $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$/Li system, in order to obtain detailed information about the composition and structure of the SEI in the overcharge state.

2. Experimental section

The electrochemical behavior of $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$ was investigated by using coin cells (2016 type). Slurries were prepared consisting of 95 wt.% $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$ (Nippon chemical Co., Ltd.) powder, 3 wt.% acetylene black, and 2 wt.% polyvinylidene fluoride (PVdF) dissolved in 1-methyl-2-pyrrolidinone. Cathodes were made by coating the slurry onto an aluminum foil substrate. Test cells were fabricated using these electrodes, as well as metallic Li anodes and polypropylene separators (Celgard 2400) in a glove box filled with Ar gas. The electrolyte used in this study was 1.0 M solution of $LiPF_6$ in ethylene carbonate–diethyl carbonate (EC:DEC = 1:1 by volume) purchased from Merck. Then, the test cells were aged for 4 h at 40 °C in a vacuum oven. Cell performance was evaluated by galvanostatically discharging and charging the cell at a constant current density of 0.2 C-rate at room temperature with a WBCS 3000 battery tester system (Won A Tech Corp., Korea).

The FTIR spectra were recorded at a spectral resolution of $4\ cm^{-1}$ with a FTIR spectrometer (Bomem, FTIR Spectrometer) equipped with a liquid nitrogen-cooled MCT detector under vacuum. A diamond-ATR accessory was used in this study. To ensure a high signal-to-noise ratio, 1024 scans were co-added.

The XPS measurements were performed at the U7 beam line of the Pohang Light Source (PLS). The U7 beam line was designed to provide soft X-rays in the energy range of 50–1500 eV. The XPS data were collected using photon energy of 1265 eV with a photon flux of $\sim 3 \times 10^{10}$ (photons/s/200 mA). The experiment was performed in an ultra-high vacuum (UHV) chamber with a base pressure $\leqslant 5 \times 10^{-10}$. The photoelectrons emitted from the surface of the cathodes were collected and their energy was analyzed with an electron energy analyzer (Physical Electronics: Model PHI 3057 with a 16-channel detector). The analyzer was located at 55° from the surface normal. The binding energy scale is calibrated using the Cu $2p_{3/2}$ feature at 932.62 ± 0.05 eV and Au 4f at 83.96 ± 0.05 eV for known standards. The XPS peak was curve-fitted by Voigt profiles.

The XAS measurement was performed at the U7 beam line of the PLS. The energy resolution was less than 0.20 eV. All spectra were taken in total electron yield mode by recording the sample current at room temperature. The photon energy was calibrated by taking the second peak in the π^* resonance of N_2 gas to be 401.1 eV as a reference. To eliminate the effect of incident beam intensity fluctuations and the monochromator absorption features, all of the spectra were normalized by a reference signal from an Au mesh with 90% transmission. The base pressure of the experimental chamber was in the order of 10^{-8} mbar.

Synchronous and asynchronous 2D correlation spectra were obtained using the same software as those described previously [19,20]. Prior to the 2D correlation calculations, normalization was applied to all of the XPS spectra. In addition, baseline corrections and smoothing of all the XPS spectra were performed before the 2D correlation calculations.

3. Results and discussion

Fig. 1 shows the curves for the second galvanostatical charge (the extraction of Li^+ from the $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$ electrode) in the voltage range of 3.0–4.5 V with a current density of 0.2 C-rate. In this paper, the lithium content is denoted by *x*, as in $Li_{1-x}[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$, where *x* is calculated from the amount of electricity passed. To produce electrodes with various lithium contents for the spectroscopic measurements, we controlled the charging voltage at a constant current density. The values of *x* in the cut-off voltage range of 4.2–4.5 V are 0.50 at 4.2 V, 0.55 at 4.3 V, 0.60 at 4.4 V and 0.62 at 4.5 V.

The FTIR spectra of the pristine $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$ powder and the charged samples are presented in Fig. 2. A typical spectrum of the organic electrolyte is also included in Fig. 2. Before recording the FTIR spectra, the samples were carefully washed with DEC in a glove box filled with Ar gas and then transferred to a vacuum oven to remove the solvent. For the pristine material, the spectrum is nearly featureless in most of the relevant range, except at around 850–600 cm^{-1} (assigned to the M—O vibrations in the layered oxide) [21]. However, the spectra from the charged samples are rich in absorption bands in the range of 1800–1600 cm^{-1} (carbonyl C=O peaks) and many bands appear below 1500 cm^{-1}. The spectral features of the charged samples are also slightly different from those of the organic electrolyte, indicating that the cathode particles are surrounded by some organic/inorganic compounds caused by the electrolyte decomposition reaction as well as the presence of the electrolyte components. It is known that the polarization of the cathode leads to the formation of SEI on the electrode surface, which generally consists of lithium carbonate (Li_2CO_3), lithium oxide (Li_2O), lithium hydroxide (LiOH), lithium fluoride (LiF), lithium alkoxide (ROLi), lithium alkyl carbonate (ROCOOLi), polycarbonate and so on [22–24]. In this study, however, the spectral overlap between these compounds and the electrolyte limits the detailed interpretation of the composition and structure of the SEI in the overcharge state.

To elucidate the nature and composition of the SEI formed on the electrode, XPS data were collected at different charging

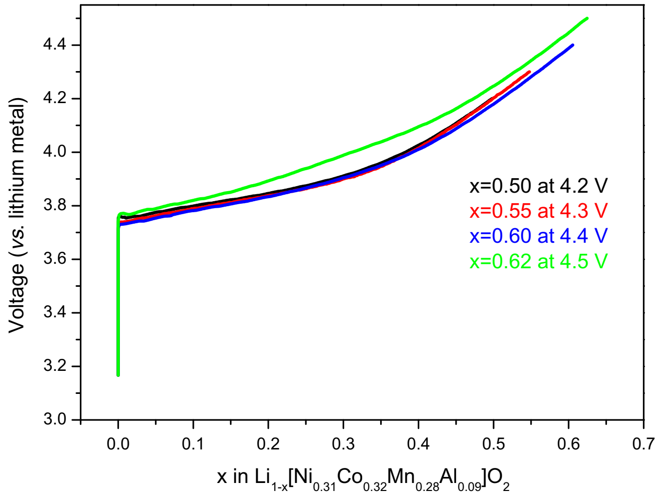

Fig. 1. The second galvanostatical charge curves of the $Li[Ni_{0.31}Co_{0.32}Mn_{0.28}Al_{0.09}]O_2$/Li cell at different charging voltages.