Surface layer formation of LiCoO$_2$ thin film electrodes in non-aqueous electrolyte containing lithium bis(oxalate)borate

Masaki Matsui[a], Kaoru Dokko[b], Yasuhiro Akita[c], Hirokazu Munakata[c], Kiyoshi Kanamura[c,*]

[a] Materials Research Department, Toyota Research Institute of North America, 1555 Woodridge Ave., Ann Arbor, MI 48105, USA
[b] Department of Chemistry & Biotechnology, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[c] Department of Applied Chemistry, Graduate School of Urban Environmental Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

ABSTRACT

Surface layer formation processes on a LiCoO$_2$ thin film electrode in a non-aqueous electrolyte containing lithium bis(oxalate)borate (LiBOB) were investigated using *in situ* FTIR spectroscopy and X-ray photo-electron spectroscopy (XPS). The *in situ* FTIR spectra of the electrolyte solution containing LiBOB showed that the adsorption of BOB anions on the electrode surface occurred during the charge process of the LiCoO$_2$ thin film electrode above 4.0 V. XPS analysis for the LiCoO$_2$ thin film electrode charged in an electrolyte containing LiBOB suggested that the adsorbed BOB anions on the electrode surface prevent the continuous decomposition of hexafluorophosphate (PF$_6$) anions resulting in the formation of a very thin surface layer containing organic species, while the LiCoO$_2$ charged in a LiPF$_6$ solution had a relatively thick surface layer containing organic species and inorganic species.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Numerous R&D related activities for advanced Li-ion batteries are on going for hybrid vehicles (HV), plug-in hybrid vehicles (PHV) and electrical vehicles (EV) these days. Since the average lifetime of a vehicle is much longer than that of consumer electronics devices such as mobile phones or laptop computers, the batteries for vehicle applications require longer cycle life and calendar life Armand and Tarascon [1]. Furthermore, the temperature range of operation for the battery must be wide considering practical driving conditions.

Ethylene carbonate (EC), which is a major component of an electrolyte solution, determines the lower operating temperature limit for a Li-ion cell because of its high melting point of 36.4 °C. Therefore another solvent such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and/or propylene carbonate (PC) needs to be mixed with EC in order to obtain optimum performance [2–4]. On the other hand, the electrolyte salt generally determines the high temperature limit of Li-ion batteries. Since LiPF$_6$, which is used in all the commercial Li-ion cells as an electrolyte salt, decomposes at high temperature resulting in the formation of corrosive species such as PF$_5$ or HF [5], the improvement of the cycle life and the calendar life of Li-ion cell at high

temperature is also a key issue for the implementation of Li-ion batteries in automotive applications.

An alternative electrolyte salt, LiBOB, has been studied because of its unique electrochemical properties and high temperature stability. Reversible lithium intercalation into a graphite negative electrode in a PC-based electrolyte solution containing 1 mol dm^{-3} of LiBOB, was demonstrated by Xu et al. [6]. This result proposed a potential breakthrough for the operation of Li-ion cells at low temperature. Basically it is due to the formation of a stable solid–electrolyte interphase (SEI) at the surface of the graphite negative electrode. As a result of this study, numerous analytical studies of the SEI formation process in electrolyte solutions containing LiBOB were conducted using various analytical techniques such as XPS, FTIR and NMR [7–13].

Xu et al. also reported that a Li-ion cell with an electrolyte solution containing LiBOB improved the cycle performance at high temperature [14]. Amine et al. successfully suppressed the dissolution of manganese from LiMn$_2$O$_4$ at high temperature by using LiBOB as an electrolyte salt [15]. They also reported that the cycle performance of the Li-ion cell was improved by using LiBOB as an additive in the electrolyte solution [16]. These reports suggest that LiBOB suppressed the formation of PF$_5$ and HF in the electrolyte solution resulting in improved thermal stability of the positive electrode materials. On the contrary, Jiang et al. performed a thermal analysis and showed that an electrolyte solution containing LiBOB did not improve the thermal stability of Li$_{0.5}$CoO$_2$, while lithiated graphite negative electrode did show improved thermal

* Corresponding author. Tel.: +81 426 77 2828; fax: +81 426 77 2828.
E-mail addresses: kanamura-kiyoshi@c.metro-u.ac.jp, kanamura@tmu.ac.jp (K. Kanamura).

stability [17]. These results created controversy as to the question whether or not LiBOB improves the thermal stability of positive electrode materials for Li-ion cells. However detailed analytical studies concerning the effect of LiBOB at the interphase of the positive electrode and the electrolyte were not done yet.

In the present study, we analyze the surface layer formation process on a $LiCoO_2$ thin film electrode in an electrolyte solutions containing LiBOB using *in situ* FTIR and XPS and discuss how LiBOB works in the electrolyte solution, especially at the positive electrode–electrolyte interphase.

2. Experimental

In the present study, *in situ* FTIR spectroscopy and XPS were performed using $LiCoO_2$ thin film electrodes. The $LiCoO_2$ thin film electrodes were prepared using an rf-sputtering method (SPK-301, Tokki) on gold substrates (15 mm dia, 2 mm thickness). $LiCoO_2$ powder synthesized by a conventional solid-state synthesis method was used as a sputtering target. The chamber pressure was maintained at 5×10^{-3} Torr with a mixed process gas consisting of argon and oxygen (9:1 by volume). Because the as-sputtered thin film was amorphous, post annealing of the sputtered-film was performed at $700\,^{\circ}$C for 5 h to obtain a crystalline material. The characterization of the thin film was carried out by using X-ray diffraction (XRD) and Raman spectroscopy as reported previously [18]. Three different electrolyte solutions were prepared for the analyses. $LiPF_6$ solution (1 mol dm^{-3} $LiPF_6$ – EC:DEC) and LiBOB solution (0.8 mol dm^{-3} LiBOB – EC:DEC) were purchased from Kishida and Tomiyama respectively. The mixed salt solution (0.5 mol dm^{-3} $LiPF_6$–0.4 mol dm^{-3} LiBOB – EC:DEC) was prepared by mixing these two electrolyte solutions in a 1:1 ratio by volume. *In situ* FTIR spectroscopy (Nicolet 6700, Thermo Electron) was employed to analyze the dynamic behavior of $LiCoO_2$–electrolyte interface during the charging process. The *in situ* spectroelectrochemical cell and the optical set up with the external reflection geometry were used as we reported previously [18,19]. In this study, the *in situ* FTIR spectra were taken using lithium metal as a reference electrode. All the electrode potentials are based on the lithium reference electrode. The *in situ* FTIR spectroscopy was performed using a *p*-polarized IR beam to enhance the signal from adsorbed species on the electrode. A BaF_2 crystal was used as the IR window and the measured wave number region was 900–2200 cm^{-1}. Three hundred scans were collected and averaged for each FTIR spectrum measurement. The $LiCoO_2$ thin film electrode was charged using a potential step method during the *in situ* FTIR spectroscopy measurements. The electrode potential at each step was maintained for 30 min to obtain a uniform electrode potential. The *in situ* FTIR spectra were collected every 0.1 V step of the electrode potential starting from open circuit potential (OCP) up to 5.0 V using the single beam spectrum mode.

Subtractively normalized interfacial FTIR (SNIFTIR) spectra were calculated according to following equation.

$$\triangle R = \frac{R_{n+1} - R_n}{R_n}$$

A SNIFTIR spectrum provides combinations of positive and negative peaks corresponding to vibrations of decreased species and newly formed species, respectively. In the present study, the positive peaks should correspond to the chemical species in the electrolyte solution and the negative peaks correspond to the surface species formed during the charge process.

The XPS analyses on the $LiCoO_2$ thin film electrodes were also conducted in order to analyze the composition and the oxidation state of surface species. The specimens were prepared *via* constant current–constant voltage (CCCV) charging for 24 h by using an automatic charger (TOSCAT-2300, Toyo System Co.). The cut-off
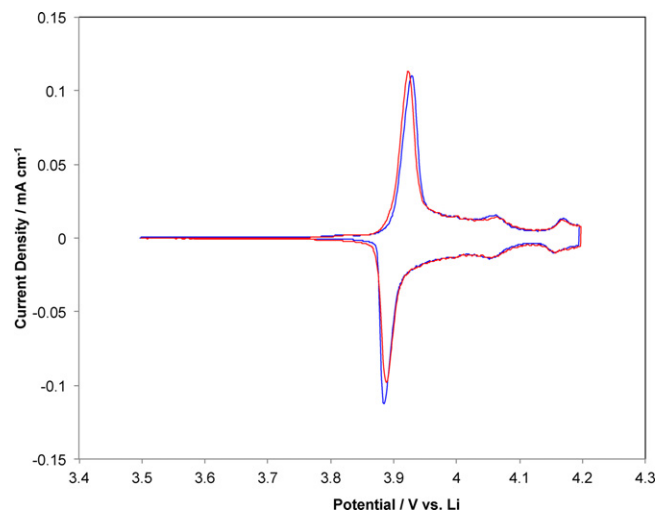

Fig. 1. Cyclic voltammograms of the $LiCoO_2$ thin film electrodes in the $LiPF_6$ solution (red) and the LiBOB solution (blue) taken by using a half-cell and a scan rate = 0.1 mV s^{-1}.

voltage of the CCCV charging was 4.2 V. Half-cells (TJ-AC, Tomcell Japan Ltd.) were fabricated for each electrolyte solution using lithium metal (FMC) as a counter electrode. The electrode surface was carefully rinsed with pure DEC to remove the electrolyte salt from the surface of the electrode. After that, the electrode was dried under high vacuum for 5 h to remove any remaining DEC. The specimens were put into an introduction chamber of the XPS. The sample transfer was carried out in a glove bag filled with dry argon gas. The XPS analyses were performed for these electrodes using a ESCA-3400 (Shimadzu Co.) with Mg Ka X-ray source (emission current: 10 mA, and acceleration voltage: 10 kV). The specimens were sputtered using an Ar-ion sputtering gun (HSE-800 gun controller, Shimadzu Co.) in order to take the depth profiles of C, O, Li, F, P, B and Co. The emission current was 5 mA, and the accelerating voltage was 0.1 kV. The argon-ion etching duration for each sample was 1, 3, 5, 10, 30, 60, 120, 240 and 480 s.

3. Result and discussion

The influence of the choice of the electrolyte on the electrochemical properties of $LiCoO_2$ was investigated by cyclic voltammetry. Fig. 1 shows a comparison of the cyclic voltammograms for the $LiCoO_2$ thin film electrodes in $LiPF_6$ solution (red) and LiBOB (blue) solution. Both of the electrolyte solutions showed very similar electrochemical behavior and no particular peak corresponding to the formation of a surface layer. The higher peak current for the deintercalation of lithium in the $LiPF_6$ solution compared to the LiBOB solution indicates that a slight decomposition of the $LiPF_6$ solution could be simultaneously taking place during the desertion process. However since the cyclic voltammogram does not provide enough evidence for the decomposition of the electrolyte, further analytical studies were performed.

Fig. 2 shows *in situ* FTIR spectra for the $LiPF_6$ solution and the LiBOB solution on a Pt electrode taken during the potential step measurement. The *in situ* FTIR spectra for $LiPF_6$ solution on the platinum electrode during anodic polarization shown in Fig. 2(a) contain several positive peaks and negative peaks. Small positive and negative peaks were observed from the open circuit potential (OCP) up to 4.0 V, however the peak intensity was significantly increased at the more anodic electrode potentials. In the *in situ* FTIR spectrum collected at 4.6 V (referenced to the spectrum at 4.0 V), the positive peaks observed at 1820 cm^{-1} and 1743 cm^{-1} correspond to C=O stretching vibration of EC and DEC respectively.