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High resolution in situ Li depth profiling of thin films stacked Li ion batteries under charging conditions by means of TERD and RBS techniques with 5 MeV He^{+2} ion beam

K. Morita[a,*], B. Tsuchiya[b], J. Oonishi[c], N. Mitsukuchi[c], T. Yamamoto[c], Y. Iriyama[c], H. Tsuchida[d], T. Majima[d]

[a] Nagoya Industrial Science Research Institute, Yotsuya-tori, Chikusa-ku, 464-0819 Nagoya, Japan
[b] Department of General Education, Meijo Univ., Tenpaku-ku, 468-8052 Nagoya, Japan
[c] Department of Materials Design Innovation Eng., Nagoya Univ., Chikusa-ku, 464-8602 Nagoya, Japan
[d] Quantum Energy Sci. and Eng. Education and Research Center, Kyoto Univ., 611-0011 Uji, Japan

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ABSTRACT

The experimental results are reported on Ni/Si/LiPON/LCO/Pt/Ti and Au/Si/LiPON/LCO/Au batteries prepared on SiN and Al self-supporting films (LiPON = $Li_{3.3}PO_{3.8}N_{0.2}$, LCO = $LiCoO_2$) which have been in situ measured simultaneously by Transmission ERD and RBS techniques with 5 MeV He^{+2} ion beam, in order to understand Li transport from positive electrode (LCO) to negative electrode (Si) under charging and over-charging. It has been found on over-charging that for the former battery Li ions over-flowed out of Si reacts with Ni electrode in the follow direction, whereas for the latter battery Li once charged in Si returns back through LiPON to LCO in the counter direction and reacts with Al through intermediate Au. Quite different two transport phenomena of Li on over-charging are discussed in terms of transport process of Li through LiPON, the difference in Fermi energies of the metal electrodes at both sides of LCO/LiPON/Si and in contact potentials of Si with the metal electrodes.

1. Introduction

The present commercially available Li-ion batteries utilize an electrolyte of solution which might ignite at over charging and over load. Thus, all solid state Li-ion batteries of no combustible have been newly developing to further safer way, as well as for high power capacity and micro-fabrication [1–6]. For its realization it is essentially important to understand dynamic transport of Li from anode through solid electrolyte to cathode and their interfaces of the Li-ion battery, as Li is so reactive with metal. In this study, for the first time, Li depth profiles in metal/electrolyte/metal capacitors under biasing and Au/LCO/LATP/Pt (LATP = $Li_{3.1}Al_{0.86}Ti_{1.14}Ge_{1.27}P_{1.73}O_{12}$) battery under charging condition have been in situ measured by means of conventional Reflection ERD and RBS techniques with 9 MeV O^{+4} ions to understand transport process of Li in the battery [7,8]. It was found for the capacitors that the Li concentration in the electrolyte was depleted at the interface with metal biased positively and it was enriched at the interface with metal biased negatively and that the amounts of Li depleted and enriched at the same voltage were not equal with each other, but asymmetric, although the capacitor was itself symmetric. It was shown, for the first time, from analysis of the Li depth profiles that the transport fraction of Li ion in electrolyte by biasing was less than unity [7]. It was also found for the battery that the Li composition in LCO was reduced uniformly over the whole depth by charging.

The Transmission ERD (TERD) technique with the self-supporting specimen of capacitors and batteries has been developed [9], in order to obtain total Li depth profiles over the whole battery simultaneously. It could be found that Li was leaked from the capacitors and batteries into the Al substrate, because of very high reactivity of Li with Al. However, we could not determine directly the interfaces since the TERD spectra of Li recoils were so broad, because of large straggling of incident O ions transmitting through the specimen and their Li recoils doing through Al absorber. Thus, the interfaces were successfully evaluated using thickness of constituent films determined from RBS data with O and He ions. Very recently, it has been demonstrated by means of the newly developed TERD technique with 5 MeV He^{+2} ions with no absorber that the Li composition and thickness of each constituent film and their interfaces of the capacitor and battery can be determined directly from highly resolved and clear step-wise TERD spectra [10].

* Corresponding author.
E-mail address: rse51151@nifty.com (K. Morita).

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In this paper, described are the experimental results on Ni/Si/LiPON/LCO/Pt/Ti/SiN battery, in comparison with Au/Si/LiPON/LCO/Au/Al battery in the previous paper [10], which have been in situ measured under charging and over-charging by means of the TERD and RBS techniques with 5 MeV He^{+2} ions. Although it has been found for the latter battery that Li once charged from LCO to Si under over-charging returns back in the counter direction and reacts with Al substrate through intermediate Au film, in the former battery Li reacts with Ni film in the follow direction. The difference in both results is discussed in terms of the difference in Fermi level energies of top and bottom metal electrodes at both sides of the Si/LiPON/LCO battery: E_F (Au) < E_F (Au/Al) and E_F (Ni) > E_F (Pt/Ti) and that of top metal electrode (Au:Ni) and negative electrode (Si) and in contact potentials of Si with Au and Ni.

2. Experimental

The experiment was carried out using the B1 beam-line of 2 MeV Tandem Accelerator at Micro Beam Facilities of Kyoto University. Specimens used were Ni/Si/LiPON/LCO/Pt/Ti and Au/Si/LiPON/LCO/Au batteries prepared on self-supporting SiN and Al substrates, respectively. The constituent films were deposited with a magnetron sputter method, except of LCO deposited with a laser ablation method in an O_2 atmosphere [11]. Thickness of each film was controlled by keeping the deposition time, without thickness monitor.

In experiments, 5 MeV He^{+2} ion beam was incident on to the SiN substrate and Li and He ions recoiled and scattered at a forward angle of 40° and He ions scattered at a backward angle of 165° from the incident direction were simultaneously measured with two solid state detectors, as shown schematically in Fig. 1. The ion beam analysis was performed after applying negative DC step voltage to the to Ni electrode against the bottom Pt/Ti electrode for 10 min at earth potential and keeping it open. On each measurement, the specimen was always shifted to the incident beam so that its spot was not overlapped with each other, in order to minimize radiation effects of probing He ions [7].

3. Experimental results

3.1. Ni/Si/LiPON/LCO/Pt/Ti/SiN battery

The ion beam analysis was performed for two specimens. Their constituent films were deposited simultaneously deposited except of LCO deposited separately. However, as shown later, the amounts of Li up-taken into Si via diffusion, due to heating by magnetron plasma, during their deposition were different. Firstly, are described the results for the No. 1 specimen, where Li was observed to be not fully up-taken. The RBS spectra and TERD spectra of 4.5 MeV He^{+2} ions from Ni/Si/LiPON/LCO/Pt/Ti/SiN battery biased at 0, 2.0 and 3.8 V and the corresponding TERD spectra at 2.0 and 3.8 V are shown in Figs. 2 and 3. In Fig. 2 of RBS spectra, energies of He ions scattered from Si at the SiN surface, Ti and Pt films, Co in LCO and Ni at the interface of Ni and Si films are indicated by arrows. In Fig. 3 of TERD spectra energies of Li recoiled at the surface of Ni film and at the interfaces of Si/LiPON/LCO and from films of SiN/Ti/Pt and those of recoils from Si film, N, O and P

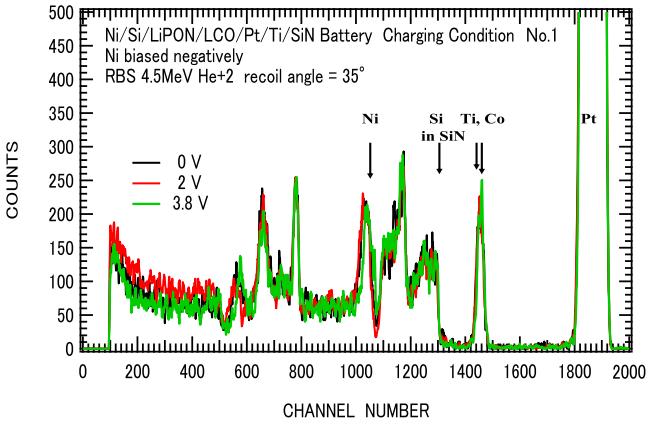

Fig. 2. RBS spectra of 4.5 MeV He^{+2} ions from Ni/Si/LiPON/LCO/Pt/Ti/SiN (No. 1) biased at 0, 2.0 and 3.8 V.

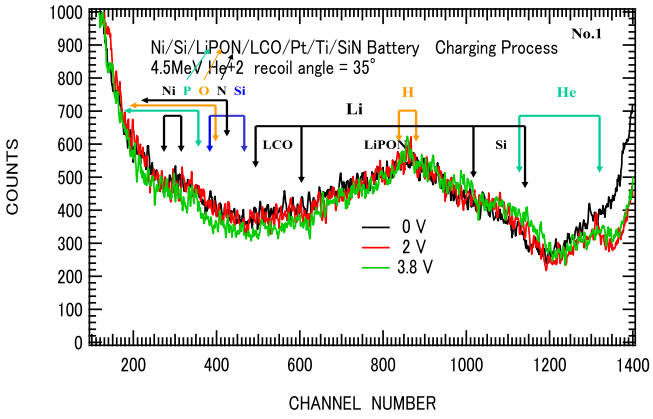

Fig. 3. TERD spectra of 4.5 MeV He^{+2} ions from Ni/Si/LiPON/LCO/Pt/Ti/SiN (No. 1) biased at 0, 2.0 and 3.8 V.

from LiPON film and Ni from Ni film are also indicated by arrows. The other recoils except Li are so-called background, which may be reduced by inserting of Al absorber of ~1 μm thick front of the silicon detector, although the energy resolution would be degraded a little bits. Thickness of each constituent film estimated consistently using both RBS and TERD spectra are inserted in units of nm in Fig. 1

It is seen from Fig. 2 of RBS spectra that the energy of Ni peak at 3.8 V only shifts towards the higher energy against those of Pt, Ti, Co and Si in SiN, which are overlapped with each other. This result indicates that the stopping power of Si/LiPON/LCO was reduced by raise up of the bias voltage from 0 and 2 V to 3.8 V, which means the leakage of Li from there. This point is discussed with TERD spectra in Fig. 3.

It is seen also from Fig. 3 of TERD spectra that as the bias voltage increases the Li yields from LCO deceases and those from Si increases, which means that ordinary charging of Li takes place from LCO (cathode) to Si (anode).

In order to inspect change in Li yields over the whole battery, TERD

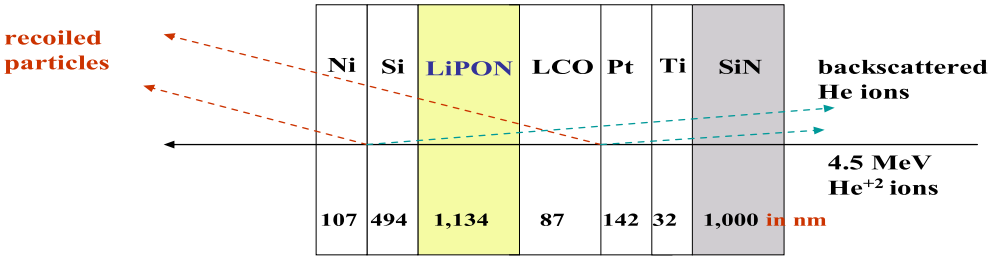

Fig. 1. Schematics of a self-supporting specimen of Ni/Si/LiPON/LCO/Pt/Ti/SiN and transmission ERD and RBS experiments.