Degradation Mechanism of Lithium-ion Battery in Charge and Discharge Cycling Tests

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1. Introduction

Lithium-ion batteries have been widely used in mobile phone and notebook personal computer (PC). Recently they are being used as batteries for hybrid electric vehicle (HEV) and electric vehicle (EV). In order to develop novel battery materials, it is important to investigate the degradation mechanism of battery as well as the characteristics of battery materials. In this study, we carried out charge and discharge cycling tests of a lithium-ion battery for notebook PC and investigated its degradation mechanism by using several techniques that we developed[1].

2. Experimental

Commercial 18650-type lithium-ion battery for notebook PC with a capacity of 3100 mAh was used in this study. The battery contained $LiNi_{1-y-z}Co_yAl_zO_2$ (NCA)-based positive electrode and graphite-based negative electrode. Cycling tests were carried out at a voltage between 2.5 and 4.2V at 25℃ with a charge condition of 0.3C or 1.0C rate and with a discharge condition of 1.0C rate until capacity fades became under 60% against a fresh battery. Following these tests, the lithium-ion batteries were discharged to a voltage lower than 2.5V and the battery was disassembled to pick up a positive electrode in a dry room at a dew point lower than -30 ℃. We assembled coin-cells with the picked up positive electrode and fresh battery materials except positive electrode. We examined the influences of the positive electrode on the cycling degradation by measuring capacities of the assembled coin-cells. We analyzed the degradation mechanism of the positive electrode by X-ray diffraction (XRD), spherical-aberration corrected scanning transmission electron microscopy (Cs-STEM), electron energy loss spectroscopy (EELS) and hard X-ray photoemission spectroscopy (HX-PES).

3. Results and Discussion

Fig. 1 shows capacities of coin-cells assembled with the picked up positive electrodes before and after cycling tests and with other fresh battery materials. When cycling test at 1.0C charging rate was carried out, capacity was nearly zero with carbon negative electrode but capacity recovered to almost at the same level as before cycling test with lithium negative electrode. This result suggested that the positive electrode was in a normal state and the cycling characteristic degraded by the influence of degradation of other battery materials such as negative electrode and separator. On the other hand, when we carried out cycling test at 0.3C charging rate, the capacity was about half as compared with before cycling test, which suggested that the positive electrode itself degraded. We observed the cross section of positive active material

to investigate the degradation mechanism of positive electrode after cycling test at 0.3C charging rate. In the particle surface (A of Fig. 2), lithium absent cation mixing layer was clearly observed, which indicated that crystal structure was disordered in this part. The thickness of this layer was about 70nm from the surface. On the other hand, the particle bulk (B of Fig. 2) showed that transition metal elements were arrayed in layered $LiNiO_2$ structure and the structure was in a normal state. Analysis of the cation mixing layer by EELS showed that the structure of this region was not altered in NiO by deintercalating lithium in excess, but was at a state of disordered layer structure such as a random distribution of atoms on the 3a(Li) and 3b(Ni) sites of the $LiNiO_2$ structure. Analysis of positive electrode before and after cycling test by HX-PES revealed that the cation mixing layer contained many Ni oxide compounds of low valence and it was confirmed that this region was inactive against charge and discharge reactions. No such change was observed in crystal structures before and after cycling tests by XRD. The results of our study suggested that the degradation of positive electrode during cycling test was caused by alternation of crystal structures in the surface of positive active material.
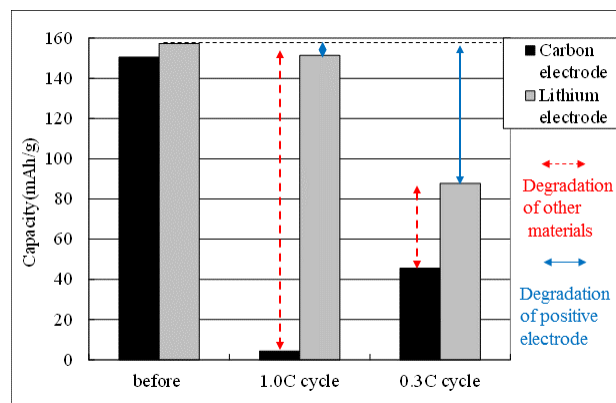

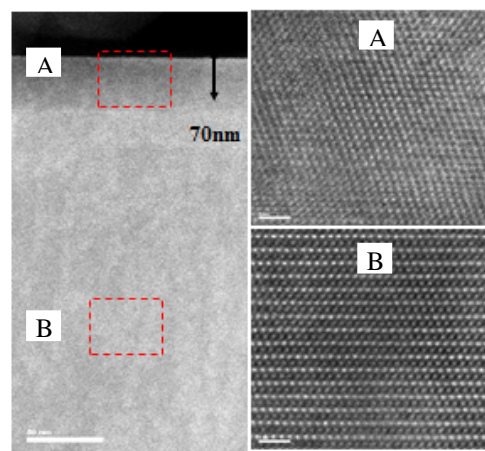Fig. 1.Capacities of assembled coin-cells before and after cycling tests.

Fig. 2.Cs-STEM images of the cross section of NCA primary particle after cycling test at 0.3C charging rate.

4. Reference

1) T.Hayashi and M.Kondo et al, The Electrochemical Society of Japan 80th Meeting 1G04 (2013).