Short communication

X-ray absorption near-edge structure study on positive electrodes of degraded lithium-ion battery

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ABSTRACT

18650-type cylindrical cells using $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) and hard carbon as positive and negative electrode material, respectively, were fabricated and degraded by cycle tests. The capacity of the cells remained more than 95% and 85% after cycle tests at 25 and 50 °C, respectively. After the cycle tests, Li-deficient cubic phase was observed on the surface of NMC. This phenomenon should be related to the degradation mechanism of this type of cell.

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1. Introduction

Lithium-ion batteries are a promising option for the nickel metal hydride batteries used in hybrid electric vehicles (HEVs). Therefore, for next-generation vehicles, such as plug-in HEVs, lithium-ion batteries are a key technology to obtain the required high power output and energy density. In previous work in AIST, we focused on lithium nickel oxide ($LiNiO_2$)-based materials, which are promising for positive electrode material for high-power lithium-ion cells because of the high power-to-energy ratio [1–5]. X-ray photo-electron spectroscopic (XPS) [3,6] and attenuated total reflection infrared spectroscopic (ATR-IR) [4] studies showed that positive electrode laminate surfaces contain a mixture of organic species, lithium carbonates (Li_2CO_3) and lithium fluoride (LiF). However, this laminate has a supporting role in power-fade mechanism because the solid electrolyte interphase (SEI) on the negative electrode is much thicker and contains similar species. It was concluded that power-fade of the lithium batteries resulted from degradation of positive electrode [1–3]. The crystal structure of $LiNiO_2$-based materials near the surface is changed to a cubic structure from a layered rock-salt structure, and then charge transfer resistance between the positive electrode and the electrolyte increases.

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) [7] is another candidate for positive electrode material for high-power lithium-ion cells. In this study, we prepared cylindrical cells (18650-type) using NMC and conducted cycle tests to investigate the degradation mechanism of lithium-ion cells of this material. In order to obtain information on the surface of the positive electrodes, X-ray absorption near-edge structure (XANES) analysis in total electron yield (TEY) mode was used [1,8]. The relationship between degradation of the cells and the surface state of the positive electrode will be discussed.

2. Experimental

Cylindrical cells with a capacity of ca. 420 mAh, designed to have a rate capability of more than 5 C, were used in this study. The cells were constructed from pressed double-side-coated electrodes using a high-power design; the positive electrode was comprised of NMC (Nippon Chemical Industrial), acetylene black, and poly(vinyldene fluoride) (PVDF) binder, and the negative electrode consisted of non-graphitizable carbon (hard carbon: Carbotron®, Kureha) and PVDF binder. 1 mol dm^{-3} of $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio 1:2) was used as electrolyte.

The cells were degraded by carrying out cycle tests, in which the charge–discharge current was 420 mA with a voltage range between 3.0 and 4.2 V at 25 and 50 °C and the rest time was 30 min. The capacity of cells before/after cycle tests was examined at 25 °C under the same conditions as the cycle test. After completion of

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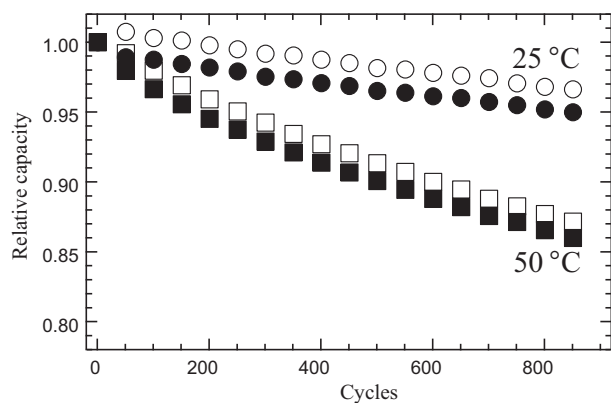E-mail address: shikano.masahiro@aist.go.jp (M. Shikano).

Fig. 1. Capacity fade as a function of charge–discharge cycle at 25 (circles) and 50 °C (squares). Closed and open symbols show the charge and discharge capacity, respectively.

the cycle tests, the state of charge (SOC) of the cells was adjusted to 0% or 100% immediately before disassembling them since the chemical and physical properties of the active materials are influenced by the SOC. All cells were disassembled in dry box filled with argon gas in which the dew point was <−50 °C. After disassembly of the SOC-adjusted cells, the surface of the positive electrode was examined by XANES and XPS in order to study the surface of the active material. XANES measurements were carried out at SPring-8/BL27SU and UVSOR/BL4B. PHI Versa Prob™ (ULVAC-PHI) system was used for XPS measurement.

3. Results and discussion

Fig. 1 shows relative discharge capacity as a function of charge–discharge cycle. After 850 cycles, the capacity retention of the cells was more than 95% in the case of the test at 25 °C and 85% in the case of the test at 50 °C. The cycle test was performed continuously for almost three months. Degradation behavior was accelerated by a higher temperature.

Fig. 2 shows charge–discharge profiles of model cells before/after cycle tests at 25 and 50 °C. After the test at 25 °C, charge–discharge profiles of the cells were very similar to that before the test. On the other hand, after the test at 50 °C, polarization was enhanced in the whole range of the charge–discharge profile, that is, DC resistance of the cell should be increased.

XPS measurements showed laminate surfaces containing a mixture of carbonate compounds such as polycarbonate and lithium
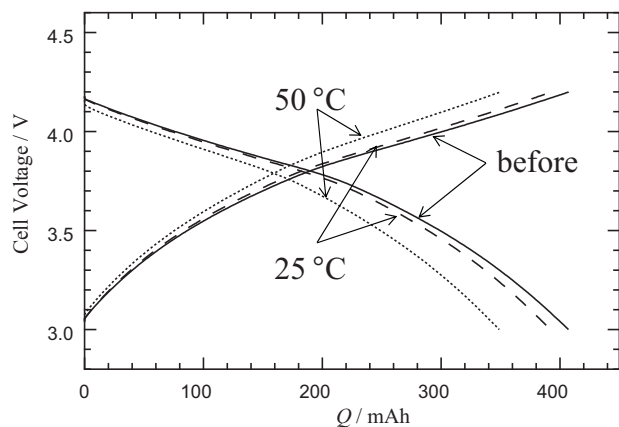

Fig. 2. Charge–discharge profiles of model cells before/after cycle tests at 25 and 50 °C. Solid lines, broken lines and dotted lines show the profiles before the test, and after the tests at 25 and 50 °C, respectively.
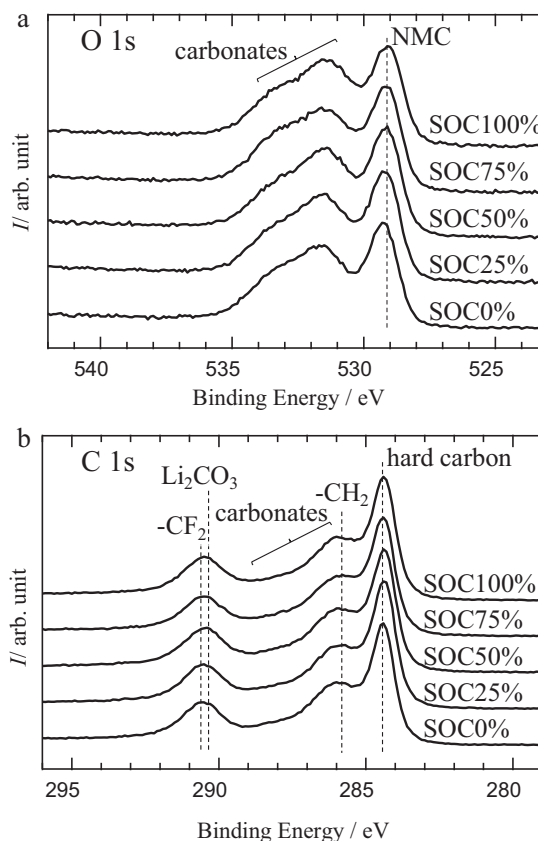

Fig. 3. XPS spectra of positive electrodes from cells before cycle tests at various SOC: (a) O 1s and (b) C 1s core level.
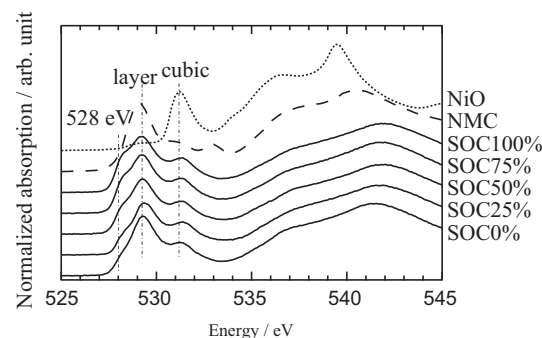

Fig. 4. O K-edge TEY spectra of positive electrodes before cycle tests at various SOC, and reference materials: NiO and NMC (SPring-8/BL27SU).
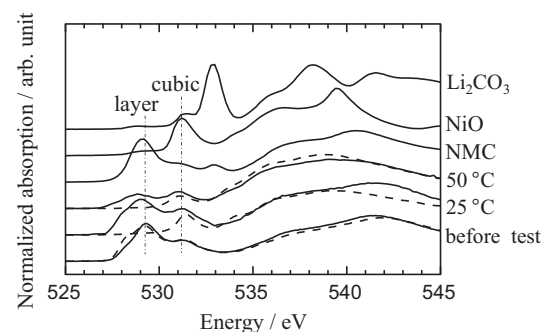

Fig. 5. O K-edge TEY spectra of positive electrodes before and after cycle tests at 25 and 50 °C, and reference materials: Li_2CO_3, NiO and NMC. Solid lines and broken lines show SOC 0% and 100%, respectively (SPring-8/BL27SU and UVSOR/BL4B).
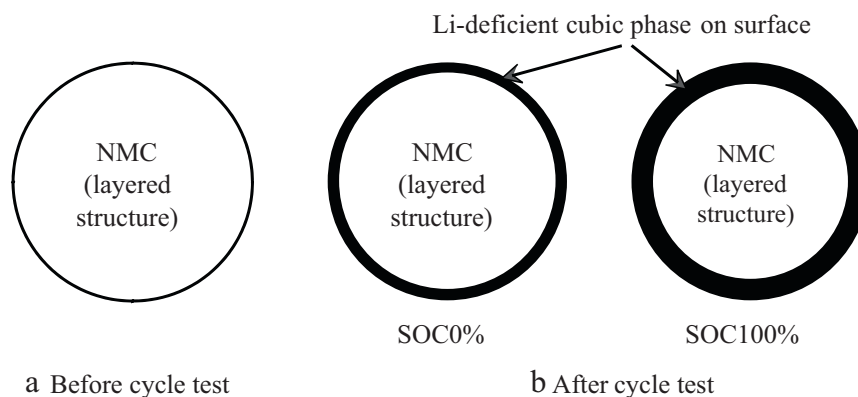
Li-deficient cubic phase on surface

Fig. 6. Schematic representation of the surface structure of the NMC positive electrode (a) before and (b) after cycle tests.

alkyl carbonates ($ROCO_2Li$), Li_2CO_3, on the positive electrode (Fig. 3). In our previous work [3,4], $LiNiO_2$-based material of positive electrodes also had similar laminate surfaces, and the amount of Li_2CO_3 decreased with an increase of SOC. On the other hand, in the case of NMC, the laminate surface condition seemed to be independent of SOC. In order to obtain more information on the surface of the NMC positive electrode, O K-edge XANES spectra in TEY mode were measured using soft X-rays at synchrotron facilities. Fig. 4 shows the O K-edge XANES spectra of 0%, 25%, 50%, 75% and 100% SOC samples before the cycle test. The spectra of nickel monoxide (NiO), Li_2CO_3 and NMC powder are also shown as references. All spectra of the samples are very similar to that of NMC; therefore, the environment of oxide ions in positive electrodes remained the same as that in the initial material, NMC. Around 528 eV, a shoulder, which was enhanced with an increase of SOC, can be observed in the pre-edge structure. In the case of $LiNiO_2$-based material, such a shoulder did not occur. The shoulder should be related to change of Mn–O bonding by charge. The scattering peak around 541–542 eV shifted to a higher energy with an increase of SOC because distances between transition metal and oxide ions should shrink by oxidation of transition metal ions. To resolve the detail of these phenomena, theoretical calculation should be undertaken.

The O K-edge XANES spectra of 0% and 100% SOC samples before/after the cycle test are shown in Fig. 5. As a result of calculations using FEFF8.40, NiO and $(Ni_{1/3}Mn_{1/3}Co_{1/3})O$ with cubic rock-salt structure and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})_2O_4$ with cubic spinel structure show a scattering peak around 531 eV. Therefore, peaks around 529 and 531 eV are assigned to oxide ions in layered and cubic structures, respectively [1,8–10]. After the cycle tests, in the case of SOC = 100%, the peak of layered structure disappeared, while the peak was observed in the case of SOC = 0%. A schematic representation of the surface structure of the NMC is given in Fig. 6. After the cycle test, cubic phase appeared on the surface of NMC. In the case of SOC = 100%, the thickness of the cubic phase was greater than that in the case of 0%. Therefore, the cubic phase was formed by Li deficiency of the layered structure of NMC [1–3,8,9]. Before the cycle test, the layered structure of NMC was maintained as mentioned above. This cubic phase should increase the DC resistance of the cell because of disordering in cationic coordination. The scattering peak shown in Fig. 4 shifted to a lower energy after the cycle tests, which also indicates the change of surface structure around oxide ion. After the cycle test at 25 °C, a shoulder around 528 eV

was observed in the case of SOC = 0%; therefore, Li content of NMC decreased compared with that before the cycle test. That is, capacity imbalance between positive and negative electrodes occurred. One can consider that this imbalance is a reason for the capacity fade. And also, the enhancement of the polarization is another reason of the capacity fade. These phenomena should be related to the degradation mechanism of the cells.

4. Conclusion

18650-type cylindrical cells using NMC and hard carbon as positive and negative electrode material, respectively, were fabricated and degraded by carrying out cycle tests. The capacity of the cells remained more than 95% and 85% after the cycle tests at 25 and 50 °C, respectively. After the cycle tests, Li-deficient cubic phase and decrease of Li content were observed on the surface of NMC. These phenomena should be related to the degradation mechanism of this type of cell.

Acknowledgements

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