Hard X-ray Photoelectron Spectroscopy Analysis of Surface Chemistry of Spray Pyrolyzed $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Positive Electrode Coated with Lithium Boron Oxide

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ABSTRACT

It is known that the deterioration of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is suppressed by inhibiting direct contact between the cathodes and the electrolyte by surface coating. In order to evaluate the influence of the electrode/electrolyte interface degradation, it is necessary to eliminate the influence of particle cracking. In this study, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ particles with a small size (500 nm to 1 μm) without crack formation after charge-discharge cycling were synthesized by a spray pyrolysis method. Hard X-ray photoelectron spectroscopy was used to investigate the structural changes of the cathode. It was revealed that the cathode coated with lithium boron oxide (LBO) by an antisolvent precipitation method had high durability against the surface structure changes by the reduction of transition metal ions. The formation and dissolution of NiO occurred in the uncoated sample during cycling, but the formation of NiO was suppressed in the LBO-coated sample. It was considered that the structural changes of the active material surface during cycling led to an increase in surface resistance of the uncoated sample, which is the main reason for the capacity fading of the spray pyrolyzed $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode particles.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used not only in portable electronic devices, but also in automobiles including plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs) due to their high energy density. The development of electrode materials with high energy density is indispensable to meet a variety of demands such as high specific capacity, low cost, and long cycle life.¹ Layered lithium transition metal oxide $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ has attractive electrochemical properties as a cathode, which can be varied with the composition of Ni, Co and Mn in the structure. Although increasing the content of Ni raises the specific capacity, it deteriorates the capacity retention and the thermal stability.² High cost Co also affects the capacity and offers an increased electronic conductivity, whereas Mn contributes to the structural stability and thereby safety. The most well-known composition is $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, which has been already used in commercially available LIBs because it has well-balanced charge/discharge properties as a cathode with a capacity of around 150 mAh g⁻¹.³

Recently Ni-rich layered lithium transition metal oxide $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ has attracted much attention for further increasing that capacity. $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is considered one of the most promising cathodes because it offers a high capacity of around 200 mAh g⁻¹ by raising the cut-off potential to 4.5–4.6 V vs. Li⁺/Li on charging.⁴ However, the high Ni content and the high cut-off potential result in poor cycle performance. Many studies have been reported on the degradation factors for the capacity fading of the Ni-rich layered materials, which include the decomposition of electrolytes and the irreversible structural transformations to the spinel and rock salt phases on the particle surface.^{4–7} The dissolution

of transition metal ions from active materials is also considered as a degradation factor.^{7,8} Moreover, crack formation inside the secondary particles has been recently recognized as a severe degradation factor, which is caused by a volume change of the material upon lithium ion extraction and re-insertion.^{9–12} The layered cathode materials are usually granulated to reduce the surface area and to improve the packing density of the electrode. The size of commercially available cathode materials is typically around 10 μm .^{7,12} However, the large expansion and shrinkage of the primary particles during charge and discharge cycling cause a high stress to the granular secondary particles, resulting in severe crack formation of the Ni-rich cathode materials after cycling. The cracks disconnect the electrical pathway among the grains in a secondary particle. In addition, the irreversible reactions of electrolyte decomposition should occur within the cracks, and as a result they accelerate the deterioration of the charge/discharge properties.

In this study, the layered $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was synthesized by a spray pyrolysis method. The particles prepared by spray pyrolysis have some advantages such as narrow particle size distribution, high purity, and easy control in composition and morphology of multi-component metal oxides.¹³ Moreover, since spray pyrolyzed particles are small in the range of 100 nm–2 μm , it is expected that the crack formation is less likely to occur due to a lower stress induced inside the secondary particles. On the other hand, the surface of small particles needs to be protected because of their large surface area. In order to mitigate the electrode/electrolyte interface deterioration, coating of the surface of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ with oxides has been investigated.^{14–17} Wang et al. reported that $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ coated with lithium boron oxide (LBO), which has a lithium-ion conductivity, is effective for protecting the surface

of the cathode particles and reducing the increase in overpotential upon cycling.¹⁸ The use of small spray pyrolyzed particles eliminates the crack formation as a degradation factor, and the analysis of the electrode/electrolyte interface will give us useful insights on the effects of LBO on other surface originating degradation factors. In this study, the cathodes at the charged and discharged states after the charge-discharge tests were analyzed by synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES) to obtain information on the structural transformations and the decomposition of the electrolyte as degradation factors.

2. Experimental

2.1 Preparation of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ particles by spray pyrolysis

Stoichiometric amounts of lithium nitrate (99.9%, Wako Pure Chemical Industries, Ltd.), manganese nitrate hexahydrate (99.9%, Wako Pure Chemical Industries, Ltd.), nickel nitrate hexahydrate (99.9%, Wako Pure Chemical Industries, Ltd.) and cobalt nitrate hexahydrate (99.0%, Wako Pure Chemical Industries, Ltd.) were weighed to prepare 0.25 mol of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and were dissolved in 1 L of deionized water and used for spray pyrolysis. The apparatus of spray pyrolysis was described elsewhere.¹⁹ The solution was atomized using ultrasonic vibrators with an oscillation frequency of 1.65 MHz in an atomizing vessel. Because the ultrasonic vibrators raise the temperature of the solution during atomizing, cold water was circulated around the atomizing vessel to keep the temperature of the solutions lower than 30°C. This is because atomization at a high temperature tends to give inhomogeneous droplets. The reaction furnace consisted of four independent heating zones, whose temperatures were set at 200, 400, 800, and 800°C from the inlet to the outlet. The atomized mists were flown into an alumina tube in the furnace area with 1 L min⁻¹ of air. The droplets including lithium and the transition metal ions were dried, decomposed, reacted, and sintered when passing through the reaction furnace. The powder was collected using a membrane filter and was heat-treated at 850°C for 8 h in air.

2.2 Coating procedure of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ with lithium boron oxide

LBO was coated on the surface of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ powder via an antisolvent precipitation method.²⁰ Lithium metaborate LiBO_2 (Wako Pure Chemical Industries, Ltd.) was added to ultra-pure water so as to be 2 or 5 wt% with respect to $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. This suspension was allowed to stand overnight at 45°C and LiBO_2 was completely dissolved in aqueous solution. $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ powder prepared by spray pyrolysis was added to the solution followed by stirring at 50°C. Then ethanol as an antisolvent was added dropwisely to the suspension with vigorous stirring. LBO was precipitated out on the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ by a poor solubility in ethanol. The precipitate was filtered and dried at 60°C for 12 h. Then, the powder was annealed at 500°C for 8 h to obtain lithium borate-coated $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. The 2 and 5 wt% coated samples were hereafter referred to as 2 and 5 wt% LBO-NCM, respectively.

2.3 Cell fabrication and charge/discharge tests

A cathode slurry was prepared by mixing the oxide powder (80 wt%), an acetylene black conductor (Denka Co., Ltd., 10 wt%), a polyvinylidene difluoride binder (PVdF, Kureha Corp., 10 wt%) using 1-methyl-2-pyrrolidinone (Wako Pure Chemical Industries, Ltd.) as a solvent. The slurry was cast by the doctor blade method on an Al foil current collector (20 µm thickness), and then dried at 80°C for 18 h under vacuum. The sheet was punched into circular disks of 13 mm in diameter as cathodes. The loading of the cathode was typically 2.0 mg cm⁻².

Charge and discharge tests were carried out using two electrode cells, which were assembled in an Ar-filled glove box (Miwa Manufacturing Co., Ltd., MDB-1NKP-DS). Li metal foil (Honjo Metal) was used as a counter electrode, and a microporous polypropylene monolayer membrane (Celgard® 2400) was used as a separator. The electrolyte solution was 1 M LiPF_6 dissolved in a 1:2 (by volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Kishida Chemical Co., Ltd., Battery Grade). The charge and discharge tests were performed galvanostatically at a 1 C rate (1 C = 200 mAh g⁻¹) between 2.5 and 4.5 V at 30°C using a TOSCAT-3100 battery test system (TOYO SYSTEM CO., LTD.). The rate capability tests were performed in the voltage range of 2.5–4.5 V at 0.1, 0.2, 0.5, 1 and 2 C for three cycles each.

2.4 Characterization

The morphology of the oxide particles was observed with a scanning electron microscope (SEM, JSM-7001FD). The crystal structure of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ powders uncoated and coated with LBO was investigated by X-ray diffraction (XRD, Shimadzu XRD-6000) using a $\text{CuK}\alpha$ radiation. Elemental distribution was investigated by Auger electron spectroscopy (AES, PHI710). The oxide particles were embedded in a polymer resin, and samples for SEM observation were prepared by a cross-section polisher (CP, SM-09010DM). After disassembled the cell, the Li metal foil was soaked in ultra-pure water, and the amounts of dissolved transition metal ions were measured by inductively coupled plasma emission spectroscopy (ICP, iCAP 6000 SERIES). HAXPES measurements were carried out at the BL16XU beam line at SPring-8 in Japan. The excitation energy was 7947 eV and the pass energy was set to 200 eV. The binding energies of the HAXPES spectra were calibrated by the carbon binding energy (284.6 eV) and the peak intensities were normalized by the intensity of the main peak of each element.

3. Results and Discussion

3.1 Structure and morphology of LBO-NCM prepared by spray pyrolysis

Figures 1(a)–(c) show SEM images of uncoated, 2 wt% and 5 wt% LBO-NCM, respectively. The particles were not agglomerated and their diameter was distributed in the range of 500 nm to 1 µm for each sample. The secondary particles consisted of primary particles of about 100 nm in diameter. The particle shape and size were not appreciably changed by LBO coating. The spray pyrolysis method usually gives spherical particles with a void inside; however, void-free non-spherical particles were obtained in the present study. When the concentration of the solution for spray pyrolysis was low, dense and non-spherical particles tend to be formed. The dense structure of the particles is favorable because the cathode/electrolyte interfaces are protected effectively by the LBO coating. XRD patterns of uncoated NCM, 2 wt% LBO-NCM and 5 wt% LBO-NCM prepared by spray pyrolysis are shown in Fig. 1(d). The XRD pattern of each sample was typical of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ layered structure. The diffraction peak intensity ratio R of the 003 to the 104 peak is known to be a measure of the cation mixing.²¹ The R values of uncoated NCM, 2 wt% LBO-NCM and 5 wt% LBO-NCM were 0.91, 0.86 and 0.86, respectively. The R value decreased by the coating of LBO. This may be due to partial occupation of small-sized boron ions in lithium positions within the layered structure.²¹ From the peak indexing, the a -axis lattice parameters of all the three samples were almost identical with each other within a range of 2.8725–2.8742 Å; however, the c -axis lattice parameters of the LBO-coated samples (14.274 Å and 14.25 Å for 2 and 5 wt% LBO-NCM, respectively) were slightly shorter than 14.286 Å for the uncoated NCM. This suggests that a small amount of boron may be substituted with lithium in NCM. It was also considered that part of

Figure 1. SEM images of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ particles coated with (a) 0 wt%, (b) 2 wt% and (c) 5 wt% LBO. (d) X-ray diffraction patterns of spray pyrolyzed $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ particles coated with 0, 2 and 5 wt% LBO by an antisolvent precipitation method.

Li ions in $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was consumed to form LBO. On the other hand, crystalline borates were not detected by XRD. One possible reason is that LBO compounds may exist as amorphous states. However, we synthesized the coating material only using the antisolvent precipitation method in a previous study, and confirmed the formation of the LiBO_2 phase after calcined at 500°C .²² Therefore, another possible reason is that the amount of the crystalline phase is too small to be detected.

In order to confirm the formation of LBO at the surface of the particles, AES maps of 5 wt% LBO-NCM were obtained and are shown in Fig. 2. It was seen that boron and nickel are uniformly distributed on the 5 wt% LBO-NCM particle surface, which clearly confirmed the presence of the LBO coating on the particle surface. Moreover, the coating layer on the surface of 5 wt% LBO-NCM was thin and uniform.

3.2 Charge and discharge properties

Figures 3(a)–(c) compare the charge-discharge curves during charge/discharge cycling tests for uncoated and 2 wt%, and 5 wt% LBO-NCM. The discharge capacity of the uncoated sample declined rapidly. The capacity retentions at the 50th cycle of uncoated, 2 wt% and 5 wt% LBO-NCM were 53.8%, 82.5% and 85.6%, respectively, which shows that the capacity retention was highly improved by LBO coating. The coulombic efficiency of both LBO-coated samples was 99.6% at 50 cycle, which was higher than that of uncoated sample (98.9%). These data show that the lithium borate coating is effective for improving the cycleability of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. The discharge curves at various rates for uncoated, 2 wt% and 5 wt% LBO-NCM are shown in Figs. 3(d)–(f). All samples provided discharge capacities higher than 190 mAh g^{-1} at 0.1 C between 2.5 and 4.5 V, which are typical values for the layered lithium transition-metal oxide $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathodes. However, for the uncoated sample, the overpotential increased remarkably after cycling. The discharge capacity of the uncoated sample rapidly decreased with increasing the discharge rate, whereas the LBO-coated samples were capable of maintaining a higher

discharge capacity. These results suggest that the inactivation of the particle surface was suppressed by the LBO coating. In this study, it was found that the deterioration was larger during cycling at lower rates. This is because the cathode was exposed to high potentials for a longer time at lower rates. At high potentials such as 4.5 V, the deterioration by electrolyte decomposition and formation of unstable delithiated layered structures becomes more seriously. Therefore, the discharge capacity of the three samples rapidly decreased during cycling at lower rates in this study.

The effect of the LBO-coating on the dissolution of transition metal ions into the electrolyte was investigated. Charge and discharge tests of the uncoated, 2 wt% and 5 wt% LBO-NCM were performed between 2.5 and 4.5 V at 1 C at 30°C . After 30 cycles, the cells were disassembled, and the amount of transition metal ions deposited on the Li counter electrode was measured by ICP. The amounts of dissolved Mn ions from uncoated NCM, 2 wt% LBO-NCM and 5 wt% LBO-NCM were 0.33 ± 0.02 , 0.20 ± 0.03 and $0.22 \pm 0.01\%$, respectively. The amounts of dissolved Ni ions were 0.69 ± 0.10 , 0.67 ± 0.09 and $0.55 \pm 0.10\%$, respectively, and those of dissolved Co ions were 0.23 ± 0.05 , 0.08 ± 0.03 and $0.12 \pm 0.01\%$, respectively. These results showed that the LBO coating is effective for the suppression of transition metal ions dissolution during cycling.

The cross-sectional SEM images of uncoated and 5 wt% LBO-NCM after 50 cycles are shown in Figs. 4(a) and (b), respectively. Crack-free cross sections were maintained for both samples after 50 cycles. These results indicated that the suppression of crack formation is less likely to be the reason why the LBO coating improved the cycleability and rate capability shown in Fig. 3. This is reasonable because the spray pyrolyzed particles are less than $1 \mu\text{m}$ in the present study. Consequently, the crack formation can be excluded from the major degradation factor of spray pyrolyzed NCM prepared in the present study, though it is an important degradation factor of commercially available NCM cathode materials with a larger particle diameter.²⁰

Figure 2. SEM image (a) and AES (b) B and Ni, (c) B, and (d) Ni elemental maps of 5 wt% LBO-NCM.

Figure 3. Charge-discharge curves (a, b, c) at 1 C between 2.5–4.5 V and discharge curves (d, e, f) at various C-rates between 2.5–4.5 V for (a, d) uncoated NCM, (b, e) 2 wt% LBO-NCM, and (c, f) 5 wt% LBO-NCM in 1 M LiPF₆/EC+DMC (1:2) at 30°C.

3.3 Hard X-ray photoelectron spectroscopy

In order to investigate the cathode surface chemistry, HAXPES spectra were measured for uncoated and 5 wt% LBO-NCM. HAXPES C 1s, O 1s and F 1s spectra obtained at the 4.5 V charged state after the 1st and 50th charge-discharge cycle are displayed in Fig. 5. B 1s and P 2s spectra were also measured, but are not shown

here because the peaks were overlapped and the P 2p peaks were very weak. In the C 1s spectra of the uncoated sample, a peak at 284.6 eV characteristic of conductive carbon and another peak at 290.4 eV assigned to the PVdF binder were observed.²³ In the O 1s spectra, a peak at 529.1 eV is characteristic of lattice oxygen, and a broad peak at 531.5–533.5 eV is assigned to lithium carbonate.²⁴ It

Figure 4. Cross-sectional SEM images of (a) uncoated and (b) 5 wt% LBO-NCM after 50 cycles.

Figure 5. HAXPES (a) C 1s, (b) O 1s and (c) F 1s spectra of uncoated and 5 wt% LBO-NCM at the 4.5 V charged state after the 1st and 50th cycle.

was confirmed that the peak at 529.1 eV was shifted to a lower binding energy when charging to a higher potential (Fig. S1). It was reported that hole doping causes a shift of the O 1s to a lower binding energy.²⁵ The contribution of oxygen redox in charge and discharge reactions was confirmed in LiCoO_2 by XAS analysis,²⁶ and it is suggested that oxygen redox also contributes to the charge compensation in $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. In this study, it was considered that part of the active material particle surface remained uncharged after cycling even when it was fully charged (to 4.5 V) due to increased overpotentials. As a result, the O 1s peak of the uncoated samples after 50 cycles was shifted to a higher binding energy. The broad peak at 531.5–533.5 eV is assigned to C–O and C=O species on the surface of the cathode particles, which is consistent with electrolyte decomposition products formed on the particle surface.

In the F 1s spectra, a peak assigned to LiF and a peak assigned to PVdF and LiPF_6 species were observed at 685.0 and 687.5 eV, respectively.²⁴ In the case of the uncoated sample, the peak intensity of LiF strongly increased after 50 cycles, while the increase was slightly suppressed for 5 wt% LBO-NCM. These results suggest that the LBO coating suppressed the formation of LiF, which originates from oxidative decomposition of the electrolyte salts during cycling. From these results, it is concluded that the LBO coating is effective for suppressing oxidative decomposition of the solvents and electrolyte though the effect is not so remarkable.

HAXPES Ni 2p and Co 2p spectra for uncoated NCM and 5 wt% LBO-NCM are displayed in Figs. 6 and 7, respectively. Any appreciable shifts and the reduction were not observed in the Mn spectra (not shown) during 50 cycling. Figure 6(a) showed Ni 2p HAXPES spectra for uncoated NCM and 5 wt% LBO-NCM at 4.5 V in the charging process after the 1st and 50th charge-discharge cycle. The spectra of Ni $2p_{3/2}$ showed that the oxidation state of Ni was a mixture of Ni^{2+} , Ni^{3+} and Ni^{4+} for all samples.²⁷ Shimoda et al. reported that the chemical shifts for the trivalent and tetravalent Ni

references were very close to each other although the Ni^{4+} peak should appear at a higher binding energy than the Ni^{2+} and Ni^{3+} peaks.²⁸ In this study, the Ni^{3+} and Ni^{4+} peaks were not separated, either. The shoulders of Ni $2p_{3/2}$ at the lower valence side increased in intensity after cycling. This fact indicated that part of the active material particle surface remained at an uncharged state even when it was fully charged (to 4.5 V) due to an increased overpotential upon cycling as shown in Fig. 3. The increase of Ni^{2+} after 50 cycles may suggest the formation of the reduced species such as NiO rock-salt phase; however, the effect of an increase in overpotential cannot be eliminated in this figure.

Figure 6(b) showed Ni 2p HAXPES spectra for uncoated NCM and 5 wt% LBO-NCM at 2.5 V in the discharging process after the 1st and 50th charge-discharge cycle. No obvious changes were observed in the Ni $2p_{2/3}$ spectra for both samples after 50 cycles. It showed that Ni was divalent at the active material surface in the discharged $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ at 2.5 V.

In order to eliminate the influence of overpotential, the samples after 1st and 50th cycle were charged to 4.0 V at a constant current (CC) of a C/2 rate, and then constant voltage (CV) charging (until 1 μA) was performed. As shown in Fig. 6(c), a peak shift towards the lower binding energy was observed in the uncoated sample after 50 cycles. On the other hand, no peak shift was observed in 5 wt% LBO after 50 cycles as shown in Fig. 6(d). The presence of low-valence Ni in the uncoated sample suggested the formation of a reduced phase such as the rock-salt NiO phase during cycling, which deteriorated the cycleability and rate capability. Moreover, both samples after 50th cycle were charged to 4.5 V, then constant voltage charging was performed (4.5 V/CV). After constant voltage charging at 4.5 V, there was almost no difference between the two samples. This point is discussed in a later section.

Figures 7(a) and (b) showed Co 2p HAXPES spectra for uncoated and 5 wt% LBO-NCM obtained at 4.5 V and 2.5 V, respectively, after the 1st and 50th charge-discharge cycling.

Figure 6. HAXPES Ni 2p spectra of uncoated and 5 wt% LBO-NCM at the (a) 4.5 V charged state and (b) 2.5 V discharged state after the 1st and 50th cycle. Ni 2p spectra of (c) uncoated and (d) 5 wt% LBO-NCM after constant voltage charging at 4.0 and 4.5 V.

Figure 7. HAXPES Co 2p spectra of uncoated and 5 wt% LBO-NCM at the (a) 4.5 V charged state and (b) 2.5 V discharged state after the 1st and 50th cycle. Co 2p spectra of (c) uncoated and (d) 5 wt% LBO-NCM after constant voltage charging at 4.0 and 4.5 V.

Compared with Figs. 6(a) and (b), it was revealed that the Co binding energy (BE) shifted to a lower energy slightly upon charging. The shift to a lower energy seems unusual; however, it was reported that the higher BE and lower BE of Co $2p_{3/2}$ peak are attributed to lower valence and higher valence of Co, respectively,^{29–34} and therefore, we judged that the shift to a lower binding energy on charging means an increase in high-valence state of Co. As shown in Fig. 7(a), high energy shoulders slightly appeared in Co $2p_{3/2}$ spectra after 50 cycles for the uncoated sample, which supported the fact that part of the particle surface remained at an uncharged state due to an increased overpotential. As shown in Fig. 7(b), high energy shoulders slightly appeared in Co $2p_{3/2}$ spectra for the uncoated sample after 50 cycles while the shoulders were not observed for 5 wt% LBO-NCM after 50 cycles. The oxidation state of Co can be used to investigate the formation of reduced phases on the surface of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ in the discharged state.¹⁸ Therefore the change of the Co $2p_{3/2}$ spectra in Fig. 7(b) indicates that 5 wt% LBO-NCM had an enhanced durability against the surface structural transformations caused by the reduction of surface Co. The presence of Co^{2+} may suggest the formation of a reduced phase, such as the rock-salt CoO phase, during cycling, which deteriorates the cycleability and rate capability. As shown in Figs. 7(c) and (d), no obvious changes were observed in the Co $2p_{2/3}$ spectra for both samples at 4.0 and 4.5 V, which suggested that the valence of cobalt did not change in the high voltage region (>4.0 V) during charging.

As Wang et al. pointed out, the LBO coating protected $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ from HF corrosion and thereby, the electrochemical performances of the cathode materials was enhanced dramatically.¹⁸ As the cycling test goes on, the highly acid HF may corrode the bare active materials, which will lead to the surface corrosion and the dissolution of transition metal ions. These results were confirmed by the suppression of transition metals dissolution in this study. In addition to the above mechanism, we also found a change in the valence of the uncoated and LBO-coated cathode materials in HAXPES measurements in this study. After constant voltage charging at 4.0 V after the 50th cycle, a shift of the Ni $2p_{3/2}$ peak toward the lower binding energy was observed in the uncoated sample in Fig. 6(c). This suggests the formation of a reduced phase in the uncoated samples. On the other hand, after constant voltage charging at 4.5 V after the 50th cycle, there was almost no difference between the uncoated and 5 wt% LBO-coated samples in Fig. 6(c, d). From these results, it was speculated that the reduced NiO phase was leached out when charged to a high potential of 4.5 V. The potential dependence of the dissolution reaction of NiO has been investigated.³⁵ Although it was measured at 95°C in sulfuric acid, NiO was dissolved significantly at a high potential of 1.68 V (vs. SHE). Moreover, it was reported that NiO is formed on the surface by immersing a NCM electrode in an EC-based electrolyte without charging or discharging.⁵ In addition, it was reported that resistive Co_3O_4 is electrochemically leached out from the surface of LiCoO_2 during cycling.³⁶ The generation and dissolution of NiO during cycling between 2.5–4.5 V in the uncoated sample may cause surface damage of the cathode particles due to the structural changes. As a result, it was considered that the surface resistance of the uncoated sample greatly increased and led to the observed capacity decrease.

4. Conclusions

A highly uniform LBO layer was coated on the surface of spray pyrolyzed NCM particles by an antisolvent precipitation method. The capacity retention up to 50 cycles was significantly improved by the LBO coating. The discharge capacity of the uncoated sample rapidly decreased with an increase in the charge/discharge rate, whereas the LBO-NCM samples were capable of maintaining higher

discharge capacities at high rates. Crack formation during cycling was not observed for both uncoated NCM and LBO-NCM prepared by the spray pyrolysis. We investigated the chemical changes of the surface of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ after constant voltage charging at 4.0 and 4.5 V after 50 cycles by HAXPES. After constant voltage charging at 4.0 V, a peak shift in Ni $2p_{3/2}$ spectra toward a lower binding energy was observed in the uncoated sample. This suggested the formation of a reduced phase in the sample. On the other hand, after constant voltage charging at 4.5 V, there was almost no difference between the two samples. From these results, it was speculated that the reduced phase was leached out when constant voltage charging at a high voltage of 4.5 V. It should be noted that the formation and dissolution of NiO were occurred in the uncoated sample, whereas the formation of NiO was suppressed in the LBO-coated sample. Therefore, it was suggested that the structural changes on the active material surface due to charge-discharge cycling led to an increase in resistance, which is a major factor of the capacity fading for the spray pyrolyzed NCM particles in this study.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.19-00022>.

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