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<th>Deterioration Analysis of Layered Lithium Nickel Oxide Based Cathodes for High Energy Density Lithium-Ion Batteries</th>
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<td>渡邊, 庄一郎</td>
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Deterioration Analysis of Layered Lithium Nickel Oxide Based Cathodes for High Energy Density Lithium-Ion Batteries

(高エネルギー密度リチウムイオン電池用層状リチウムニッケル酸化物系正極の劣化解析)

Shoichiro Watanabe
渡邊 庄一郎

February 2014

Doctoral Thesis at Osaka Prefecture University
Deterioration Analysis of Layered Lithium Nickel Oxide Based Cathodes for High Energy Density Lithium-Ion Batteries

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Chapter 1   General Introduction

1.1 Introduction

Lithium-ion battery is a rechargeable battery with light weight and high energy density. The lithium-ion battery was commercialized in the 1990s and has widely been used in portable devices such as notebook personal computers (PCs), cellular phones and digital still cameras so far. The improvement of energy density has been requested for realizing smaller size and longer operating time. Figure 1-1 shows the progress of gravimetric and volumetric energy density of a standard 18650-size cylindrical lithium-ion battery.

Figure 1-1   The progress of gravimetric and volumetric energy density for a standard 18650-size cylindrical lithium-ion batteries.

*Energy density is calculated with min. capacity and max. dimension
The volumetric energy density of the initial model produced in 1994 was about 250 Wh l\(^{-1}\). In 2012 it exceeds 700 Wh l\(^{-1}\) because of various technical improvements. The achievement of such high energy density is ascribed to the following technological factors.

1. Increase in graphitization and initial charge-discharge efficiency of the graphite anode.
2. Increase in charge voltage up to 4.1 - 4.35 V
3. Increase in density of cathode and anode
4. Introduction of thinner materials (current collector foil, separator, can thickness, etc.)
5. Introduction of Ni-based cathode material

For the above (1) and (2), new electrolytes which could be tolerant to high voltages and additives for electrolyte that could stabilize SEI (Solid Electrolyte Interface) formed at the anode were developed in addition to the improvement of active material. For the above (3), new electrode binders were developed and mass production equipment of electrode was improved. For the above (4), for example, the thickness of separator which was 30 \(\mu\)m in the 1990s was halved by continuous cooperation of battery makers and material makers.

Meanwhile, the uses of lithium-ion batteries are expanded to high-power applications and electric energy storage use because environmental issues become more serious.

For instance, hybrid electric vehicles (HEVs) with an internal combustion engine and a battery system have remarkably improved cost for gasoline consumption and are widespread. Moreover, battery electric vehicles (BEVs) which are operated only by electric power and plug-in hybrid electric vehicles (PHEVs) which are operated by electric power of lithium-ion batteries with high energy density for short distance drives and by the HEV system for long distance uses have been commercialized. In this way, performances required for lithium-ion batteries is highly upgraded and diversified to fit expanded applications.
The requirement for rechargeable batteries of general portable equipments is as follows;

1. High energy density (= discharge voltage × capacity density)
2. High power density
3. Wide temperature range of usage
4. Small self-discharge and good storage characteristics
5. High energy conversion efficiency
6. Easy handling, high safety and high reliability
7. High cost performance

For EV and household electric energy storage applications, battery system units which are composed of many batteries connected in parallels and series are used, and longer calendar life than conventional usages is required. So the following requirements are added.

8. Long-term storage characteristics more than 10 years
9. Charge-discharge cycle performance more than several thousand cycles (stable capacity and impedance)
10. High safety and reliability as a total system

In various types of lithium-ion batteries, the 18650-type cylindrical lithium-ion battery (diameter : 18 mm, total height : 65 mm), which is a standard size for notebook-type PC usage, is widespread as a high cost performance battery which is produced with high-speed production lines. The multi parallel-series system of 18650 batteries is used as accumulation of electricity systems and a vehicle power supplies.
The general features of the multi parallel-series system of small batteries are as follows.

(1) High system redundancy because of a parallel system
(2) High reliability because of inspecting and controlling at a unit of a small capacity cell
(3) Small potential and the current distribution because of the use of small electrodes, causing uniform cell reaction
(4) Use of technology for high energy density because incident events can be controlled at a small unit
(5) No need for new investment because existing mass production lines can be used

For using the multi parallel-series system of small batteries as accumulation of electricity systems and vehicle batteries, it is extremely important to precisely understand deterioration mechanism of the batteries required for establishing the long-term reliability of the system.

I began research and development on lithium-ion batteries in 1990, and then have developed a lot of batteries, improved their performance, and mass-produced them. Especially, I have participated in the LEAD (Li-ion and Excellent Advanced Batteries Development) program by NEDO (New Energy and Industrial Technology Development Organization) since 2008, and focused on Ni-based LiNi_{1-x,y}Co_{x}Al_{y}O_{2} (NCA) as the cathode material in R & D on "High performance electricity system technology for the next generation cars".

In this thesis, I evaluated storage and cycle characteristics requiring long-term reliability for a high capacity cylindrical lithium-ion battery with the LiNi_{1-x,y}Co_{x}Al_{y}O_{2} cathode, and clarified deterioration mechanism of the battery, in particular the cathode.
1. 2 Background of This Study

1. 2. 1 Lithium-ion battery

1. 2. 1. 1 Electrode reactions of lithium-ion battery

The lithium-ion battery is composed of lithium-included metal oxide compounds as a cathode active material, graphite which can reversibly intercalate lithium as a anode active material, organic electrolyte that contains the lithium salt, separator, aluminum foil as a cathode current collector, copper foil as a anode current collector, can and several other parts. Figure 1-2 indicates an electrochemical reaction scheme of a typical lithium-ion battery.

The lithium-ion batteries have a “rocking chair” charge-discharge reaction scheme. Lithium-ions move between the cathode and anode active materials with different host structures in charging and discharging. During the first charging, lithium-ions in the crystal lattices of the cathode active material dissolve with solvation in an electrolyte solution, move to the anode, and intercalate into the crystal lattices of the anode active material. It is well-known that the SEI (solid electrolyte interface) film which lithium-ions can pass through is also formed on the anode surface during the first charging, and suppresses the continuous decomposition reaction of the solvent on the anode surface, leading to high charge-discharge efficiency.
Figure 1-2 An electrochemical reaction scheme of a typical lithium-ion battery.
1. 2. 1. 2  Structure of lithium-ion battery

Figure 1-3 shows the schematic structure of a typical cylindrical lithium-ion battery.

To prepare cathode or anode, the mixture paste of cathode or anode active material, solvent, binder, and conductive compound (mainly carbon material) is thinly coated on an aluminum foil (for cathode) or a copper foil (for anode) as current collector. The cathode, anode and separator are cylindrically winded up. After the winding jerry roll is put into a cylindrical can (nickel-plated iron can) and a tab is welded on the can, electrolyte is put into it. A plastic gasket and a top cap are simultaneously cramped up to the can. Finally the battery is completed by washing, charging-discharging and aging.
The polyolefin porous thin film is used for a separator because the movement of lithium ions is shut down as the battery is heated by short-circuit. Many safety devices such as a Positive Temperature Coefficient (PTC) device which interrupts excessive current on short-circuit, a Current Interrupter Device (CID) which operates automatically as the internal pressure of the battery rises in overcharging and a safety vent which releases the pressurized gas are introduced to lithium-ion batteries.

The long-term reliability tests in this study is performed with 18650 size (cylinder diameter: \( \phi 18 \) mm, total height: 65 mm) lithium-ion batteries.

1.2.1.3 Cathode material for lithium-ion battery

Table 1-1 shows typical cathode materials for the lithium-ion batteries.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Theoretical capacity Ah kg(^{-1})</th>
<th>Experimental rechargeable capacity Ah kg(^{-1})</th>
<th>Average operating voltage V</th>
<th>Density g cm(^{-3})</th>
<th>Energy density Wh kg(^{-1})</th>
<th>Energy density Wh cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_{1-x})CoO(_2)</td>
<td>274</td>
<td>145 (Li(_{0.5})CoO(_2))</td>
<td>3.9</td>
<td>5.05</td>
<td>450</td>
<td>2273</td>
</tr>
<tr>
<td>Li(_{1-x})NiO(_2)</td>
<td>274</td>
<td>192 (Li(_{0.7})NiO(_2))</td>
<td>3.8</td>
<td>4.76</td>
<td>700</td>
<td>3332</td>
</tr>
<tr>
<td>Li(_{1-x})Mn(_2)O(_4)</td>
<td>148</td>
<td>118 (Li(_{0.2})Mn(_2)O(_4))</td>
<td>4</td>
<td>4.28</td>
<td>400</td>
<td>1712</td>
</tr>
<tr>
<td>Li(_{1-x})FePO(_4)</td>
<td>170</td>
<td>160 (Li(_{0.06})FePO(_4))</td>
<td>3.4</td>
<td>3.6</td>
<td>550</td>
<td>1980</td>
</tr>
</tbody>
</table>

LiCoO\(_2\) (LCO) with a hexagonal crystal structure (Fig. 1-4) was widely used as the cathode active material for lithium-ion batteries because of its simple preparation method, high operation voltage of 3.9 V and flat discharge curve.
As shown in Table 1-1, the theoretical capacity for LiCoO\(_2\) is 274 mAh g\(^{-1}\), while the practical capacity is about only a half (145 mAh g\(^{-1}\)), which means low utilization of LiCoO\(_2\). There are two possible approaches for enhancing energy density.

1. Increase in the lithium utilization by increasing the upper limit of voltage in charging
2. Use of LiNiO\(_2\) whose capacity is higher than that of LiCoO\(_2\)

Recently, the increase in energy density by raising the charge voltage from 4.2 to 4.35 V has been realized in most of lithium-ion batteries for cellular phones and note PCs. However, when the charge voltage is raised over 4.3 V, the battery storage characteristic and long-term reliability at high temperatures are lowered due to oxidative dissolution of cathode material, dry out of electrolyte solution and gas evolution which comes from electrolyte oxidation and separator oxidation on the cathode surface. There are many researches on suppression of side reactions, but they have been completely suppressed yet. [1-6]
Ni-based LiNiO₂ has been expected as a promising next generation cathode material because the Ni element has higher capacity, richer resource and lower and stabler price than the Co element.

Lithium metal oxides (LiMO₂ (M= Co, Ni)) are 4 V-class cathode active materials with α-NaFeO₂ type R3m structure discovered by Goodenough [7]. Ohzuku et al. reported basic structure and charge and discharge behaviors of LiNiO₂ in 1993 [8]. LiNiO₂ showed high capacity more than 200mAh g⁻¹ at the charge potential of 4.3 V vs. Li/Li⁺, but it was unstable because the change in crystal structure during charging and discharging was large [8]. The synthesis conditions such as temperature, time and atmosphere strongly affected the capacity of LiNiO₂. The Ni²⁺ mixing into Li layer significantly decreased capacity [9-11]. The doping of foreign metal elements such as Al, Co, Mn, Ti and Fe, etc. to stabilize the crystal structure was investigated at the first stage of development [12-19]. Especially, in LiNi₁₋ₓCoxO₂, Ni could be substituted with Co over the whole Ni content (0 ≤ x ≤ 100), and therefore the cation mixing of Ni²⁺ into Li layer and the large crystal structure change were effectively suppressed, leading to the improvement of cycle characteristics [20-23].

A great deal of effort was put into mass production of LiNi₁₋ₓ₋yCoxAlₜO₂. Basically, LiNiO₂ is prepared by mixing nickel hydroxide with lithium hydroxide and then heat-treating in oxygen atmosphere. On the other hand, LiNi₁₋ₓ₋yCoxAlₜO₂ was prepared by the co-precipitation method. In this method, at first a sodium hydroxide solution is added in an acidic solution containing Ni²⁺, Co²⁺ and Al³⁺ ions with controlling pH to have appropriate particle configuration, resulting in the production of a co-precipitated precursor, Ni₁₋ₓ₋yCoxAlₜ(OH)₂ [24-25]. After that, the precursor was mixed with lithium hydroxide and heat-treated in oxygen atmosphere to prepare the final product LiNi₁₋ₓ₋yCoxAlₜO₂. The resultant LiNi₁₋ₓ₋yCoxAlₜO₂ particles had a spherical configuration which was quite similar to the configuration of the precursor particles. Each LiNi₁₋ₓ₋yCoxAlₜO₂ particle was an aggregate of the primary particles with size of about 10 μm, as shown in Fig. 1-5.
The thermal stability of charged cathode material is important to design batteries with high safety. However, it was a serious problem that the thermal stability of charged LiNiO$_2$ was lower than that of charged LiMn$_2$O$_4$ and LiCoO$_2$ [26].

Since Al has the similar ionic radius to Ni and Co (Ni$^{3+}$=0.0560 nm, Co$^{3+}$=0.0545 nm, Al$^{3+}$=0.0535 nm), substitution of Ni and Co with Al does not change lattice constant. So Al can be uniformly distributed in the Ni and the Co layer of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$. It was reported that the addition of Al in LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ improved thermal stability at the charged states and cycle characteristics, which accelerated the development of Ni-based cathode material [27-31]. Madhavi et al. reported that since the Al-O bond was more ionic than the Co-O bond, the substitution of Co with Al made the Ni-O bond more covalent, leading to the increase in the ionicity of the Li-O bond or the mobility of lithium ions in the Li layer [32]. In 2006, Panasonic Co Ltd. succeeded in mass-production of cylindrical lithium-ion batteries NCR18650 in which NCA was used as a cathode material.
Graphite is usually used as an anode of high-capacity lithium-ion batteries. In this thesis, massive artificial graphite which can be filled with high density is used as an anode material.

Electrolyte for the lithium-ion battery is composed of lithium salt, organic solvent and several kinds of functional additives. Lithium hexafluorophosphate (LiPF₆) was widely used because of its high tolerance for oxidation and reduction, high solubility and high degree of ionization, and so it is used in the present study. Various solvents for lithium-ion batteries are shown in Table 1-2 [33].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical Structure</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
<th>Dielectric constant</th>
<th>Viscosity cP</th>
<th>Exø V vs. Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene carbonate (EC)</td>
<td></td>
<td>37</td>
<td>238</td>
<td>90</td>
<td>1.9(40°C)</td>
<td>6.2</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td></td>
<td>-49</td>
<td>242</td>
<td>65</td>
<td>2.5</td>
<td>6.6</td>
</tr>
<tr>
<td>γ-Butyrolactone (GBL)</td>
<td></td>
<td>-44</td>
<td>204</td>
<td>42</td>
<td>1.7</td>
<td>8.2</td>
</tr>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td></td>
<td>3</td>
<td>90</td>
<td>3.1</td>
<td>0.59</td>
<td>6.7</td>
</tr>
<tr>
<td>Ethyl Methyl carbonate (EMC)</td>
<td></td>
<td>-55</td>
<td>108</td>
<td>2.9</td>
<td>0.65</td>
<td>6.7</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td></td>
<td>-43</td>
<td>127</td>
<td>2.8</td>
<td>0.75</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Since ethylene carbonate (EC) is known to be a solid at room temperature, low viscosity solvents such as chain ester, dimethyl carbonate (DMC), ethylmethyl carbonate (EMC), and diethyl carbonate (DEC) are usually mixed with EC. In this study, a mixed solvent of EC-EMC-DMC was used.

Coating of an inorganic material layer on the polyethylene micro-porous separator has been used for maintaining its insulation properties and shape at high temperatures.
1.2.2 Deterioration analysis

1.2.2.1 Typical deterioration mechanisms of lithium-ion battery

The capacity and charge-discharge performance of lithium-ion battery strongly depend on its charge-discharge mechanism. The reaction of lithium-ion battery that is composed of the carbon anode and lithium metal oxide cathode has the following characteristics;

1. \( \text{Li}^+ \) ions in the charge and discharge reactions are given from the cathode material.
2. The amount of \( \text{Li}^+ \) ions deintercalated from the cathode material is controlled by the charging conditions (charge voltage, charging current and cut-off current).
3. Side reactions at the anode influence capacity.
4. Capacity decreases without deterioration of the battery material when the polarization of the battery is increased.
5. Electrolyte is a medium carrying lithium ions, and does not contribute to the charge and discharge reactions except for side reactions.

The deterioration mechanism of the lithium-ion battery can be classified into three.

1. The amount of \( \text{Li}^+ \) ions which join in charge and discharge reactions is decreased due to chemical changes.
2. The amount of \( \text{Li}^+ \) ions which join in charge and discharge reactions is decreased due to physical changes.
3. The power down and capacity decay occur due to an increase in impedance such as DC, charge-transfer and diffusion resistances.

In practical lithium-ion battery, The above deterioration mechanisms (1) - (3) concurrently proceed, and cause the decrease in capacity and discharge voltage. The proposed mechanism of deterioration is shown in Table 1-4 and the schematic model is shown in Fig. 1-6 [34, 35].
<table>
<thead>
<tr>
<th></th>
<th>Cathode</th>
<th>Cathode surface</th>
<th>separator / electrolyte</th>
<th>Anode surface</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal usage</strong></td>
<td>Changing the Chemicals</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Structural disordering</td>
<td>Oxidation of separator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phase transition</td>
<td>Decomposition of solvent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal dissolution</td>
<td>Decomposition of solute</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microcracking</td>
<td>Surface layer formation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface disordering</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Over Charging</td>
<td>Decomposition of binder</td>
<td>Blocking the hole of separator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxidation of electro conductor</td>
<td>Dry-out of the electrolyte</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isolation from current collector</td>
<td>Decreasing the Li ion conductivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Increasing the</td>
<td>Isolation from each other</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>impedance</td>
<td>Corrosion of current collector</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Over Discharge</td>
<td>Phase transition</td>
<td>Electrolyte decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal dissolution</td>
<td>Gas evolution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abnormal usage</td>
<td>Over Heating (short circuit or</td>
<td>Decomposition of SEI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>outer heating)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Copper deposition</td>
<td>Current collector dissolution</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Ion/nickel deposition</td>
<td>Can iron/nickel dissolution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decomposition of SEI</td>
<td>Shut down of the separator hole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas evolution</td>
<td>Short circuit by separator shrinkage</td>
<td></td>
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<td></td>
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<td>Decomposition of electrolyte</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Dry-up of the electrolyte</td>
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</tbody>
</table>

Table 1-4 The cause of the deterioration of Lithium-ion batteries.
Figure 1-6  Schematic deterioration model of lithium ion battery.
There are a lot of factors that cause the deterioration of the lithium-ion battery as shown in Table 1-4 and Fig. 1-6.

It is very hard to understand the existence and the progress of side reactions because (1) the charge and discharge efficiency of the lithium-ion battery is about 99.9% or more except for initial several cycles, (2) the predominant factor changes with the progress of several concurrent deterioration mechanisms and deterioration progress, and (3) the deterioration mechanism changes when the same batteries are used under different conditions. Therefore, the condition resembling the practical usage pattern should be set in the battery deterioration analysis.

1.2.2 Deterioration analysis of lithium-ion battery

The deterioration analysis method of the lithium-ion battery can be roughly classified as follows.

(1) Battery performance is measured under various acceleration conditions to mathematically predict the lifetime of the battery.

(2) The internal resistance and impedances of charge transfer and diffusion processes with different relaxation times can be separated by AC impedance analysis.

(3) The battery components are taken out of the battery after the deterioration, and analyzed by crystallographic, spectroscopic and chemical methods.

The deterioration behavior of the lithium-ion battery is complex as mentioned above. If two batteries are operated under different acceleration conditions, they will deteriorate in different mechanism. Therefore, it is important to combine the three analysis techniques (1)-(3) to determine deterioration mechanism.
1.2.2.3 Acceleration test of lithium-ion batteries

The acceleration condition for the lithium-ion battery needs to be set depending on applications. For instance, the deterioration mode of lithium-ion batteries for cellular phone and note PC applications in market is quite different. As shown in Fig. 1-7, for cellular phone applications, the battery is charged in the night every day or once in a few days, whereas for note PC application the battery is held in the full-charged and high temperature conditions for a long time because the note PC is often used with connecting to an AC power supply. In the latter, the deterioration mode is dominated by the storage deterioration at high temperature and high state-of charge (SOC).

![Cellular phone usage pattern](image1)

![Note PC usage pattern](image2)

Figure 1-7 Usage pattern of cellular phone and note type personal computer batteries.

Even for on-vehicle use, the SOC range, charge-discharge pattern, and storage condition of batteries for HEV, PHEV and BEV are so different that battery design and acceleration conditions depending on applications need to be modified. The acceleration tests for high capacity lithium-ion battery with Ni-based \( \text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2 \) cathode are preceded. The SAFT team developed lithium-ion batteries for backup and satellite applications.

Brossely et al. in the SAFT team carried out long-term storage tests at 15 – 60 °C after float charging at a certain voltage and periodically measured capacity at 100% DOD (Depth of Discharge).
of Discharge) during charge-discharge cycle tests of 80% DOD range. They found that the corrosion of the SEI film on the anode surface was a predominant factor for deterioration in the storage tests, and the corrosion rate followed the Arrhenius law [36-39].

Argonne National Laboratory (ANL), Sandia National Laboratory (SNL) and Idaho National Engineering and Environmental Laboratory (INEEL) developed the life modeling of lithium-ion batteries in Department of Energy’s Advanced Technology Development (ATD) program for HEV application sponsored by US Department of Energy. In this program, deterioration behavior after storage at several SOCs (40, 60 and 80 %) or charge-discharge cycling at ΔDODs (3, 6 %) at 40 – 70 °C was mathematically discussed. Bloom et al. showed that the increment in impedance depended on $t^{1/2}$ because the rate of SEI formation whose rate-determining step was diffusion was predominant, and the rate of fade in power followed the Arrhenius law [40, 41]. Moreover, they indicated that in the 10% Al-doped cell the time dependence of the impedance rise was composed of two distinct kinetic regimes; the initial portion depended on $t^{1/2}$ and the latter one depended on $t$ [42].

In the lithium-ion battery, it is known that the reaction of the graphite anode with electrolyte to cause the SEI formation is the most active, and the thicker SEI formation at the anode surface is a predominant factor for deterioration.

However, after the carbon material and electrolyte were improved, the predominant factor for deterioration was changed and the deterioration behavior did not follow the conventional lifetime prediction. So the understanding of the predominant deterioration mechanism is an urgent issue. There are a lot of deterioration factors for the lithium-ion batteries as shown in Table 1-4. So it is important to understand the deterioration factors to analyze the deterioration mechanism.
1.2.2.4 Impedance analysis method

The deterioration analysis that uses ac impedance method is effective for to confirm the deterioration factor because of its can divide the resistance element to the factor of electronic, charge transfer and the diffusion resistance. In addition, it is easy to specify the rule factor of deterioration because it is possible to measure by disassemble the deteriorated battery and separating the cathode and anode.

Amine and Chen et al. showed that the impedance rise was dominantly contributed by the increase of charge transfer resistance on the cathode by separating the cathode and anode from disassembling the deteriorated battery. [43, 44] Moreover, Chen and Kondo et al. showed that added Al and Mg, small amount of foreign metal doping in LiNi$_{1-x-y}$Co$_{x}$M$_{y}$O$_{2}$ cathodes significantly stabilizes the cell impedance. [45, 46] Thus, the impedance analysis specifies the factor of the impedance rise, and is important for judging to what to do focus a further analysis.

1.2.2.5 Spectroscopic analysis method

Recently, the deterioration analysis of the lithium-ion battery has dramatically been improved by the progress of spectroscopic technique. Since the spectroscopic technique has resolution of a nanometer level, it is possible to quantitatively analyze the modulations in several nanometers on a specimen surface. Therefore microscopic monitoring of cathode deterioration which was impossible to analyze qualitatively and quantitatively before became possible. Thus the understanding for the deterioration mechanism of the cathode has progressed rapidly.

XPS and FTIR-ATR spectroscopy are effective for the analysis of SEI which generated on the cathode surface by reacting with the electrolyte. Andersson et al. showed in the analysis of the LiNi$_{1-x}$Co$_{x}$O$_{2}$ surface by XPS that lithium carbonate (Li$_{2}$CO$_{3}$) and lithium fluoride
(LiF) had been produced in the preparation of the active material, and they are converted to
the mixture of organic species including polycarbonates, LiF and Li₇PF₅-type and
Li₈PF₇O₂-type compounds during storage in a battery [47].

From the late 1990s, the change in electrode structure with electrochemical reaction was
analyzed by X-ray Absorption Spectroscopy (XAS). Abraham et al. found that there were
oxygen deficiencies at the surface of LiNi₀.₈Co₀.₂O₂ by comparing an oxygen K-edge
spectrum measured by the Total Electron Yield (TEY) method which could analyze from the
electrode material surface to a depth 5 nm with that measured by the Fluorescence Yield (FY)
method which could analyze the bulk of more than 300 nm in depth [48]. High Resolution
transmission Electron Microscopy (HR-TEM) indicated that a NiO-like rock salt (NaCl-type)
structure with 2 – 4 nm in depth was formed in the near-surface region of LiNi₀.₈Co₀.₂O₂,
whereas its bulk had the expected α-NaFeO₂ type layered structure [48].

Ukyo et al. found that the valence of Ni in LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ was converted from Ni³⁺
to Ni⁴⁺ during charging, whereas that of Co was hardly changed although only the local
structure around a Co atom was changed at 60 °C [49]. They showed that Inactive Ni²⁺ atoms
existed on the surface and the average valence of Ni was increased by charge-discharge
cycling and aging. The EELS and HR-TEM revealed that a Ni-O layer with a rock salt
(NaCl)-type structure was formed at the surface of cathode particle during charge-discharge
cycling and aging, causing a rise in cathode impedance [50-52]. Tatsumi et al. proposed a
schematic degradation model of LiNi₁₋ₓ₅ₓCoₓAlₓO₂ based on the above results and the data
obtained by neutron diffractometry and XPS [53-55].
1.3 Objectives of This Study

The main objective of this study was to elucidate the deterioration mechanism of the lithium-ion battery with Lithium Nickel Cobalt Aluminum Oxide (LiNi_{1-x-y}Co_yAl_zO_2, NCA) cathode which has high capacity and high reliability under the acceleration test conditions for charge – discharge cycling and storage, and feed back to practical use.

First, two kinds of commercial lithium-ion batteries with NCA cathode (NCR18650) and LCO cathode (CGR18650E) were compared in terms of long-term reliability, and the key factor of battery deterioration was clarified.

Next, the difference in deterioration mechanism was clarified by testing under several acceleration conditions which seriously influenced battery life using a model cell.

1.4 Outline of This Thesis

This thesis consists of 5 chapters.

In Chapter 1, background on technical development of lithium-ion batteries and analytical method for their deterioration mechanism was described. First, the history on the improvement of energy density was summarized and then technical development of cathode was described. Next, the development of analytical method for deterioration mechanism of lithium-ion batteries was outlined.

In Chapter 2, for two cylindrical lithium-ion batteries, NCR18650 and CGR18650 whose long-term reliability was different, deterioration behavior was analyzed and compared. The accelerated deterioration tests of these batteries were performed with various electrochemical and spectroscopic technique under various conditions. Consequently, it was found that the deterioration mainly came from the cathode and was ascribed to the difference in production rate of a rock salt-type structure at the surface of active material between NCA
and LCO.

In Chapter 3, a model cell with the NCA cathode was fabricated, and the effect of ΔDOD condition on charge and discharge cycling characteristics was investigated. The cycle characteristics in a specific potential region were evaluated. The deterioration of cathode was not accelerated by the cycling in the specific potential region or ΔDOD, but it was accelerated by cycling in the wide ΔDOD range because the generation of microcracks progressed.

In Chapter 4, it was clarified by electrochemical and spectroscopic analyses that deterioration of cycle characteristics was ascribed to the generation of microcracks and the following formation of rock salt-type layer at the surface of active material due to infiltration of electrolyte. The generation of microcracks could be prevented by controlling ΔDOD, and the mechanism which could keep long-term reliability was demonstrated.

In Chapter 5, general conclusions of the results obtained in this study were described.
References


Chapter 2  Comparison analysis between LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ and LiCoO$_2$ cathodes in cylindrical lithium-ion cells during long term storage test

2.1  Introduction

Panasonic Co. launched the highest capacity and light weight lithium-ion battery series with the nickel-based NCA cathode in 2006. The energy density of a cylindrical 18650-type battery were 620 Wh l$^{-1}$ and 230 Wh kg$^{-1}$ or more. In the latest model in 2013, capacity is 3.55Ah and the volumetric energy density exceeds 750Wh l$^{-1}$. These batteries are used as the power supply for PC, power tools, in-vehicle, bicycle and electric energy storage. [1]

Battery packs inside notebook PCs were used under severe conditions like full charge voltages and high temperatures of 40 °C or more because many customers used PCs with connecting the AC power supply as shown in Fig. 1-7. I found that the long term battery life of the NCA-cathode batteries (NCR18650) was several times as long as that of the LCO-cathode batteries (CGR18650E) [2-4]. Probably the difference in long-term reliability between these two commercial lithium-ion batteries is caused by the difference of cathode material.

In this chapter, the change of anode and cathode surface in the two 18650-type cells was investigated by XPS, ICP and TEM-EELS during the long-term storage test simulating actual usage conditions by PC users in the market, and the capacity fade was determined by the reconstructed model cell method. Moreover, the mechanism of deterioration was proposed on the basis of these results.
2. 2  Experimental

2.2.1  Preparation of cylindrical 18650 cells

Two cylindrical battery cells made by Panasonic Co. were used in this study. The NCA and LCO cathode cells are NCR18650 (2900mAh) and CGR18650E (2600mAh).

The nickel-based oxide cathode/graphite cell was composed of nickel-based oxide cathode, graphite anode, electrolyte and micro-porous polyethylene separator. The nickel-based oxide cathode was composed of a mixture of LiNi_{0.8Co0.15Al0.05}O_{2}, carbon black and poly(vinylidene fluoride), and aluminum foil. The cobalt-based oxide cathode/graphite cell was the same as the nickel-based oxide cathode/graphite cell except for the cathode active material. Electrolyte was a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) containing 1 mol L^{-1} (= M) lithium hexafluorophosphate (LiPF_6).
2.2.2  *Accelerated calendar and cycle life tests for cylindrical 18650 cells*

The cycle tests, the storage tests and the interval storage and cycle tests were performed according to protocols in Table 2-1.

<table>
<thead>
<tr>
<th>Test condition</th>
<th>NCR18650</th>
<th>CGR18650E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode material</td>
<td>LiNi0.8Co0.15Al0.05O2</td>
<td>LiCoO2</td>
</tr>
<tr>
<td>Anode material</td>
<td>Graphite</td>
<td>Graphite</td>
</tr>
<tr>
<td>Cell capacity</td>
<td>2.9Ah</td>
<td>2.6Ah</td>
</tr>
</tbody>
</table>

### Cycle test
- **Charge**: 4.2V-cccv, 0.3It-max, 50mA-cutoff
- **Charge rest**: 20min
- **Discharge**: 1.0It-cc, 2.5V-cutoff
- **Discharge rest**: 20min
- **temp.**: 45degC

### Interval storage and cycle test
- **Charge**: 4.2V-cccv, 0.3It-max, 50mA-cutoff
- **Charge rest**: 24h
- **Discharge**: 1.0It-cc, 2.5V-cutoff
- **Discharge rest**: 20min
- **temp.**: 45degC

### Storage test
- **storage temp.**: 45degC
- **charge before storage**: 4.1V-cccv, 0.3It-max, 50mA-cutoff
- **charge for cap. Checking**: 4.2V-cccv, 0.3It-max, 50mA-cutoff
- **discharge for cap. Checking**: 0.2It-cc, 2.5V-cutoff
- **Cap. Checking period**: 90 days

It is thought that the usage pattern that a lot of business uses PC mixed with the (a) continuous charged (b) once a day mobility use as shown in figure 2-2. The protocols for the interval storage and cycle tests imagine user's usage at office in note-type PC. The test environment temperature was 45°C and every charge rest time was 24 h.
Figure 2-2  The typical usage pattern of business uses PC.

(a) Note PC usage pattern
(Continuous charged )

(b) Note PC office usage pattern
(once a day mobility use )
2.2.3 **The model cell and impedance analysis**

In order to determine which electrode was degraded, both the cathode and anode were taken out of each 18650 cell and used for assembling a 2016 coin cell with the lithium metal foil as a counter electrode under Ar atmosphere. An electrolyte and a separator of the coin cell were the same as those of the 18650 cell. Impedance measurements were performed using a Solartron 1260/1286 frequency response analyzer system. The amplitude of the ac signal was 10 mV over the frequency range between 1 MHz and 1 mHz in this study. All measurements were carried out at 25 °C. The capacity fade and impedance change of the cathode and anode were compared with their initial conditions.

2.2.4 **Surface and bulk analysis**

XRD patterns were collected with a Panalytical X’Celerator detector equipped with a Cu target x-ray tube and a diffracted beam monochrometer. Each XRD measurement was performed every 0.05° over a scattering angle range between 2\(\theta\) = 10° and 90° and the counting time was 10 s. SEM images were obtained with a Hitachi S-4500 scanning electron microscope equipped with an energy-dispersive X-ray (EDX) analyzer.

Surface structure of each cathode material was characterized by XPS and scanning transmission microscopy (STEM)-Selected Area Electron Diffraction (SAED)/EELS. XPS analysis was performed with a Perkin–Elmer PHI 560/ESCA-SAM system. XPS spectra were obtained after several times of Ar\(^+\)-sputtering with 4 keV energy ions and a current beam of 0.36 \(\mu\)A cm\(^{-2}\). A sample for the XPS analysis was excited with 1486.6 eV energy AlK\(\alpha\) X-rays. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement was performed using ICPS-7500 in order to quantify the amount of metal deposited on the
anode surface. STEM-SAED/EELS analysis was conducted with a 200 kV JEOL JEM-2100F equipped with a parallel electron energy loss spectrometer (Gatan 863). XRD and SEM were used to study the phase change and microscopic morphology for each active material after storage. For surface and bulk analyses, each cell was charged to a voltage of 4.1V at 0.2It rate and then the voltage was kept until the current was reduced to 0.05It rate. After charging, the cell was disassembled. The samples taken out of the disassembled cells were washed with dry DMC and evaporated at room temperature.
Figure 2-3  Experimental flow chart of analysis for Lithium-ion batteries.
2. 3 Results and Discussion

2.3.1 Performance of 18650 cells

Fig. 2-4 shows cycle performance for an NCR18650 (NCA cathode) and a CGR18650E (LCO cathode) at 45°C. This figure indicates there are only a few differences in cycle performance between both cells. However, as for the interval storage and cycle test performance, the NCR18650 was much superior to the CGR18650E as shown in Fig. 2-5. The life time of the 70% capacity retention for the NCR18650 was twice longer than that for the CGR18650E. These data showed a good correspondence to the difference of reliability in an actual market.
Figure 2-4  Cycle performance of an NCR18650 (NCA cathode) and a CGR18650E (LCO cathode) at 45 °C.

Figure 2-5  Interval storage and cycle test performance of an NCR18650 (NCA cathode) and a CGR18650E (LCO cathode) at 45 °C.
In order to verify the difference, the capacity fade analysis during a long term storage test was performed. Fig. 2-6 shows storage performance at 45°C for the NCR18650 and CGR18650E after they were charged to 4.1 V. The NCR18650 showed better storage performance than the CGR18650E. The NCR18650 maintained about 90% of the initial capacity even after storage for 2 years at 45 °C.

Figure 2-6  Storage performance at 45 °C of an NCR18650 (NCA cathode) and a CGR18650E (LCO cathode) charged to 4.1V.
Fig. 2-7 shows rate performance for the NCR18650 and CGR18650E which were fresh or stored for 2 years at 45 °C after being charged to 4.1 V. As be seen from Fig. 2-7, capacity fade and the polarization of the CGR18650E was remarkably increased during the storage for 2 years.

Figure 2-7 Rate performance of the (a) NCR18650 and (b) CGR18650E fresh and after 2 years storage at 45 °C at 4.1 V. Straight line and closed circles indicate the (—) fresh cell and (●) stored cell, respectively. The cells were charged up to 4.2 V by CVCC until the current reduced to 0.05I mA and discharged at (a) 0.2C, (b) 1C and (c) 2C rate at 25°C.
Fig. 2-8 shows ac impedance spectra of the NCR18650 and CGR18650E which were fresh or stored for 2 years at 45°C after being charged to 4.1 V. Each impedance measurement was performed at 100% SOC and a temperature of 25 °C. The charge transfer resistance ($R_{ct}$) was evaluated from the lower frequency semicircle in each Nyquist plot. The $R_{ct}$ values for the fresh and stored NCR18650 were 0.0262 and 0.0356 Ω, respectively, while those for the fresh and stored CGR18650E were 0.0231 and 0.0407 Ω, respectively. The impedance of both cells was increased during storage, but its increment for the CGR18650E was much larger than that for the NCR18650.
Figure 2-8  Nyquist plots of (a) NCR18650 and (b) CGR18650E which are (○) fresh or (●) stored at 45°C for 2 years after being charged to 4.1 V. Each impedance measurement was performed at 100% SOC and a temperature of 25 °C.
2.3.2 Analysis of disassembled battery

To reassemble a 2016 coin cell, the cathode or anode active materials taken out of the fresh and stored cells were used with a lithium metal counter electrode.

Fig. 2-9 shows discharge curves of each reassembled coin cell operated in the voltage range of 2.5 – 4.3 V or 0.01 – 1.5 V at a constant current of 0.1It at 25 °C. As be seen from Fig. 2-9(a) and (b), in the discharge process no significant capacity fade was observed for the NCA cathode after storage, while 30% capacity fade was observed for the LCO cathode after storage. Moreover, as shown in Fig. 2-9(c) and (d), in the charge process the notable capacity fade was not observed for the graphite anode in both NCR18650 and CGR18650E. These results suggest that the difference in capacity fade of lithium-ion cells during high temperature storage shown in Fig. 2-5 and Fig. 2-6 is ascribed to the degradation of cathode.

ICP analysis confirmed that the lithium composition, 1-x in Li_{1-x}MO_2, of both cathode active materials, NCA and LCO, before and after the storage tests were equal when each cell was charged to a voltage of 4.1V before every analysis below.
Figure 2-9  Discharge curves of (a) NCA cathode of NCR18650, (b) LCO cathode of CGR18650E, (c) graphite anode of NCR18650, (d) graphite anode of CGR18650E; the data of cathode obtained from the (○) fresh cell and (●) stored cell, respectively. Percentage of the initial value of discharge capacity was shown.
Fig. 2-10 and Fig. 2-11 show XRD patterns of the fresh and stored NCA and LCO cathode active materials, respectively. The samples for XRD were prepared by clipping from 4.1V charged cathode and then mixing with the standard reference material (NIST 640c Si). All diffraction lines for fresh and stored cathode active materials were indexed by assuming a hexagonal lattice. All XRD patterns of the fresh and stored NCA and LCO cathode active materials were identical as $\alpha$-NaFeO$_2$ having a space group of R$3m$. Ramadass et al. pointed out that peak intensities of (003), (006), and (104) planes for the LCO changed during the cycle tests at high temperatures [5, 6]. However, as can be seen from Fig. 2-10 and Fig. 2-11, additional diffraction lines and line broadening of each diffraction line were not specifically observed, indicating that the core structure of the cathode materials was not damaged during 2 year storage at 45 °C. The integrated intensity ratio of (003) to (104) lines in each XRD pattern indicates the amount of cobalt or nickel ion mixing into Li layer (cation mixing). There was no significant difference in the intensity ratio between fresh and stored NCA cathode active materials. On the other hand, the intensity ratio between fresh and stored LCO cathode active materials showed a significant change.
Figure 2-10  X-ray diffraction patterns of NCA cathode taken out from the charged NCR18650; (a) fresh cathode material and (b) stored cathode material. Miller indexes and lattice parameters were given by assuming a hexagonal lattice. The lattice parameters were obtained by a least-squares method using nine diffraction lines depending on the number of well-defined diffraction lines.
Figure 2-11  X-ray diffraction patterns of LCO cathode taken out from the charged CGR18650E; (a) fresh cathode material and (b) stored cathode material. Miller indexes and lattice parameters were given by assuming a hexagonal lattice. The lattice parameters were obtained by a least-squares method using nine diffraction lines depending on the number of well-defined diffraction lines.
SEM images of cathode active materials taken out of the disassembled cells are shown in Fig. 2-12. No notable difference in cathode particles morphology between the fresh and stored samples was observed. In addition, we analyzed the electrolyte composition, SEM morphology of the separator and Gurley number which indicated the air permeability of the separator before and after the storage, but there was no substantial change. These results show that the difference in degradation during high temperature long term storage between LCO cathode and NCA cathode is due to the difference of cathode surface. Besides, the influence of cathode surface on battery degradation has been pointed out [7-12].

Figure 2-12  Particles morphology of cathode materials observed by SEM; (a) Fresh NCR18650 cathode, (b) Stored NCR18650 cathode, (c) Fresh CGR18650E cathode and (d) Stored CGR18650E cathode.
2.3.3 Analysis of electrode/electrolyte interface

In order to obtain more information on the cathode/electrolyte interface, the surface of the NCA and LCO cathodes was analyzed by XPS. Fig. 2-13 to 2-17 shows C1s, O1s, Li1s, F1s and P2p core level spectra for the NCA and LCO cathodes before and after 2 year storage at 45 °C.

In the core level spectra of C1s, O1s and Li1s of Fig. 2-13 to 2-15, the peaks of the lithium carbonate and lithium alkyl carbonate were observed before and after storage of NCA and LCO. It is known that the lithium carbonate is generated on the cathode active material surface by the reaction with CO₂ in air as follows [13, 14].

\[
\text{Li(Ni,Co)O}_2 + \frac{x}{2} \text{CO}_2 + \frac{x}{4} \text{O}_2 \rightarrow \text{Li}_{1-x} \text{(Ni,Co)O}_2 + \frac{x}{2} \text{Li}_2 \text{CO}_3 \quad (2-1)
\]

The electrolyte solvents decompose on the cathode surface to form lithium alkyl carbonates [15-16].

\[
\text{LiOOCOCH}_2\text{CH}_2\text{OCOLi} + 2\text{Li}^+ + 2\text{Li}^+ \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}_2 + \text{C}_2\text{H}_4 + 0.5\text{O}_2 \quad (2-4)
\]

\[
\text{LiOOCOCH}_2\text{CH}_2\text{OCOLi} + 2\text{Li}^+ + 2\text{Li}^+ \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 \quad (2-5)
\]
Figure 2-13  C1s core level XPS spectra for cathode surface (a) fresh cathode of NCR18650 (b) fresh cathode of CGR18650 (c) stored cathode of NCR18650 (d) stored cathode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
Figure 2-14 O1s core level XPS spectra for cathode surface (a) fresh cathode of NCR18650 (b) fresh cathode of CGR18650 (c) stored cathode of NCR18650 (d) stored cathode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
Figure 2-15  Li1s core level XPS spectra for cathode surface (a) fresh cathode of NCR18650 (b) fresh cathode of CGR18650 (c) stored cathode of NCR18650 (d) stored cathode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
Figure 2-16  F1s core level XPS spectra for cathode surface (a) fresh cathode of NCR18650 (b) fresh cathode of CGR18650 (c) stored cathode of NCR18650 (d) stored cathode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
Figure 2-17  P2p core level XPS spectra for cathode surface (a) fresh cathode of NCR18650 (b) fresh cathode of CGR18650 (c) stored cathode of NCR18650 (d) stored cathode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
The formation of SEI film which was composed of alkyl carbonates and lithium carbonate was not a dominant factor of deterioration because the growth of the film was not observed during the storage test. Moreover, HF which was generated from LiPF₆ and trace amount of water in an electrolyte reacted with the lithium carbonate and cathode active material to form LiF [18].

\[
\text{Li}_2\text{CO}_3 + 2\text{HF} \rightarrow 2\text{LiF} + \text{H}_2\text{O} + \text{CO}_2 \quad (2-6)
\]

\[
\text{Li(Ni,Co)}_2\text{O}_2(\text{s}) + 2x\text{HF} \rightarrow 2x\text{LiF} + \text{Li}_{1-2x}(\text{Ni,Co})_2\text{O}_{2-x} + x\text{H}_2\text{O} \quad (2-7)
\]

It is thought that the formation of LiF was not a dominant factor of deterioration because the growth of LiF was not observed for stored LCO surface (Fig. 2-16(d)) whose deterioration was larger than that of NCA.

P2p core level spectra (Fig. 2-17) were used for eliminating inappropriate influence of PVdF as a cathode binder. In the P2p core level spectra, peaks at 135.5 and 133.5 eV are assigned to a P-F bond and a P-O bond, respectively. Anderson et al. clarified these two peaks were ascribed to \( \text{Li}_x\text{PF}_y \) and \( \text{Li}_x\text{PF}_y\text{O}_z \) compounds which were formed on the cathode surface [19]. LiPF₆ as an electrolyte often decomposes to PF₅ and LiF (eq. 2-8, 2-9), and PF₅ readily reacts with trace amount of water to form HF as a hydrolysis product (eq. 2-10). Consequently, HF reacts with Li-carbonate compounds to form LiF (eq. 2-11) [20-22].

\[
\text{LiPF}_6 + 2\text{Li}^+ + 2e^- \rightarrow \text{LiF} + \text{Li}_x\text{PF}_y \quad (2-8)
\]

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5 \quad (2-9)
\]

\[
\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} \quad (2-10)
\]

\[
\text{POF}_3 + 2x\text{Li}^+ + 2xe^- \rightarrow \text{Li}_x\text{PF}_{3-x}\text{O} + x\text{LiF} \quad (2-11)
\]
The thickness of the surface layer for the NCA cathode scarcely increased during the long-term storage, while that for the LCO cathode increased by only several nanometer. So the formation of surface layer does not seem to be a predominant factor for the deterioration of cathode performance.

Fig. 2-18 shows F1s core level spectra for the anode surface of NCR18650 and CGR18650E before and after 2 years storage at 45 °C. In the F1s core level spectra, peaks at 688 and 686 eV are assigned to P-F and Li-F, respectively. In each spectrum these two peaks were observed, suggesting the formation of the anode surface layer or SEI with LiF and hydrolysis products such as LiPOF$_3$ and Li$_n$PO$_y$F$_z$ compounds as shown in eq. (2-8) to eq. (2-11). The anode surface layer after the long-term storage for the NCR18650 had thickness close to that for the CGR18650E strongly suggesting that the formation of SEI on the anode surface also did not seem to be a predominant factor for the deterioration of cathode performance.
Figure 2-18  F1s core level XPS spectra for anode surface (a) fresh anode of NCR18650
(b) fresh anode of CGR18650 (c) stored anode of NCR18650 (d) stored anode of CGR18650, the storage condition was 4.1V charged state at 45°C for 2 years.
Fig. 2-19 shows the amount of Ni and Co components in deposits on the anode surface of NCR18650 and CGR18650E before and after 2 years storage at 45 °C. The amount of the Ni and Co components was quantified by ICP-AES. Fig. 2-19 clearly indicated that in both cases Co and Ni dissolved from the cathode were deposited on the graphite anode surface. Amatucci et al. reported that there was a linear correlation between the capacity loss of the LiCoO₂ cathode during high voltage cycling tests and the amount of Co deposited on the anode [23]. In the present study, the amount of Ni dissolved from the NCA cathode during the long-term storage was less than half that of Co dissolved from the LCO cathode. This implies that the amount of Co and Ni dissolved from cathode material can be related to the change in surface crystal and electronic structures of the nickel-based and the cobalt-based oxide cathodes.
2.3.4 Analysis of local structure of cathode active material

STEM-EELS was used in order to investigate the changes in the local structure and the electronic structure of active material before and after storage at 45 °C for 2 years. Fig. 2-20 and Fig. 2-21 show the Ni-L2,3 energy-loss and the Co-L2,3 energy-loss near-edge structure (ELNES) spectra for the NCA and LCO cathode materials in the 18650 cells before and after storage at 45 °C for 2 years. Fig. 2-22 summarized the Ni- and Co-L2,3 ELNES peak depth profiles of cathode particle before and after storage.

The Ni-L2,3 ELNES spectra were acquired in a depth range from the surface to 100 nm for a selected NCA cathode material particle. The NiO powder as the standard has a peak at 854.5 eV, indicating that it is assigned to divalent nickel. In contrast, the peak at 856.5 eV is assigned to trivalent nickel. The Ni-L2,3 ELNES spectra after storage exhibited that the peak at 856.5 eV in a depth range of 6 to 10 nm was shifted to 855.5 eV during the storage test, suggesting that the surface layer composed of oxygen deficient NiO became thick. It was reported that the Ni4+ ions which existed in the charged state could be transformed into Ni2+ with the oxidation of the electrolyte and solvents at the cathode/electrolyte interface, and the structure change into rock-salt type and oxygen loss also occurred simultaneously [24,25]. In this study, the charged NCA oxidized the electrolyte with oxygen loss to form the nano-order surface layer of lithium/oxygen-deficient Li(Ni,Co)O2 with the rock-salt structure at the cathode/electrolyte interface as follows [26]:

\[
\text{Li}_{1-x}(\text{Ni,Co})^{3+/4+}\text{O}_2 ^+ (\text{delithiation state}) \rightarrow \text{Li}_{1-x}(\text{Ni,Co})^{3+/2+}\text{O}_{2-\delta} ^- (\text{oxygen loss}) \quad (2-12)
\]
Figure 2-20  Cross section TEM images and Ni-L2,3 ELNES spectra from NCA cathode material taken out from the charged NCR18650; (a) fresh cathode material and (b) stored cathode material. Dash lines show the Ni(II) peak positions of Ni-L2,3 ELNES spectrum from the NiO powder.
The Co-L2,3 ELNES spectra for the LCO cathode material in the CGR18650E before and after storage are shown in Fig. 2-21. The peak positions of CoO powder for the standard of divalent cobalt are shown in Fig. 2-21 and Fig. 2-22. Before storage the peak at 782.5 eV assigned to trivalent cobalt was observed underneath the surface layer with thickness of around 10 nm, but after storage it shifted to 781 eV as shown in Fig. 2-21. The crystal structure of the surface layer can be identified as a CoO-like rock-salt structure by selected area electron diffraction (SAD) analysis, as discussed by some groups [12, 27-28].

Fig.2-23 to Fig.2-26 show high resolution TEM images and experimental electron diffraction patterns for surface and bulk of active materials after storage at 45 °C for 2 years. Fig.2-23 and Fig.2-24 show the image of stored NCA bulk-surface with two micro diffraction patterns layer. Fig. 2-23 and Fig. 2-25 exhibited that the surface layer of NCA and LCO had about several nanometers in thickness and a cubic rock salt-type NiO and CoO structures. In the case of stored LCO particle, three types of micro diffraction layers were observed in Fig. 2-25. The thickness of the surface cubic rock-salt layer was about 9 nm which was thicker than that of the NCA particle. Moreover, a partially layered structure which was composed of the α-NaFeO2-type R3m and cubic rock-salt structures was formed underneath the LCO surface layer, and its thickness was about 20 nm. The lithium nickel/cobalt oxide layer with rock-salt structure formed on the NCA/LCO surface can bring low lithium ion conductivity and low electric conductivity, which caused an increase in cathode impedance.
Figure 2-21  Cross section TEM images and Co-L2,3 ELNES spectra from the LCO cathode material taken out from the charged CGR18650E; (a) fresh cathode material and (b) stored cathode material. Dash lines show the peak positions of Co-L2,3 ELNES spectrum from the CoO powder.
Figure 2-22  The Ni- and Co-L\textsubscript{2,3} EELS peak position changes from surface of charged cathode particle. (○)Ni-L\textsubscript{2,3} of NCA before storage, (●)Ni-L\textsubscript{2,3} of NCA after storage, (◇)Co-L\textsubscript{2,3} of LCO before storage, (◆)Co-L\textsubscript{2,3} of LCO after storage.
Figure 2-23  The high resolution image and convergent beam electron diffraction patterns of NCA cathode material taken out from stored NCR18650. Storage condition was charged state 45°C 2years.

Figure 2-24  Experimental electron diffraction patterns exhibiting only fundamental reflections collected from stored NCA cathode material taken out from the charged NCR18650, (a) surface area which is indexed to the [1-10] zone axis ((111) d=0.238), (b) Bulk area which is indexed to the [100] zone axis. ((003) d=0.472).
Figure 2-25  The high resolution image and convergent beam electron diffraction patterns of LCO cathode material taken out from stored CGR18650E. Storage condition was charged state 45°C 2years.

Figure 2-26  Experimental electron diffraction patterns exhibiting only fundamental reflections collected from stored LCO cathode material taken out from the charged NCGR18650E, (a) surface area which is indexed to the [1-10] zone axis ((111) d=0.240nm) , (b) Bulk area which is indexed to the [100] zone axis. ((003) d=0.466nm).
Fig. 2-27 indicates the R₃m layered structure is changed to the partially layered structure and rock salt structure. The partially layered structure is formed by disordering Li⁺ ions and partially introducing Ni²⁺ or Co²⁺ ions into Li⁺ layers. The growth of the rock-salt type surface layer for LCO was much faster than that for NCA. The difference of growth rate of the rock-salt type surface layer may be due to the difference in amount of Ni and Co dissolution in Fig. 2-19. This is responsible for a big difference in storage characteristics between LCO and NCA.

Fig. 2-27  Schematic model for the change from R₃m layered structure to partially layered structure and rock salt structure.
The schematic representation of crystal structure changes as Ni\textsuperscript{2+} and Co\textsuperscript{2+} is introduced into the Li layer is shown in Fig. 2-28. Both pure NiO and CoO are electronic and ionic insulators. So it is apparent that only the oxide surface contained Li\textsuperscript{+} ions to form LixNi\textsubscript{1-x}O or LixCo\textsubscript{1-x}O. Small amounts of Li\textsuperscript{+} ions can increase the electronic conductivity of LixNi\textsubscript{1-x}O or LixCo\textsubscript{1-x}O by several orders of magnitude [29, 30]. However, the Li\textsuperscript{+} conductivity is strongly influenced by crystal structure depending on the content of Li\textsuperscript{+}.

The Lix\textsuperscript{+}Ni\textsubscript{3-x}Ni\textsubscript{2-2x}O and Lix\textsuperscript{+}Co\textsubscript{3-x}Co\textsubscript{2-2x}O solid solutions are formed over a wide lithium concentration range of 0 to 0.5 [26, 31-32]. To increase the content of Li\textsuperscript{+} or the x value, Ni\textsuperscript{2+} or Co\textsuperscript{2+} is partially converted to Ni\textsuperscript{3+} or Co\textsuperscript{3+} ions due to charge compensation. The crystal structure of solid solutions changes with the content of Li\textsuperscript{+} or the x value (see Fig. 2-28). For 0 < x \leq 0.3, the Li and Ni or Co ions are randomly distributed in the octahedral positions of the close-packed oxygen lattice (NaCl-type structure). For 0.3 < x < 0.5, the ordering of the Li and Ni or Co ions starts in alternate cubic (1 1 1) planes, and at x = 0.5 the layered LiNiO\textsubscript{2} or LiCoO\textsubscript{2} (\alpha-\text{NaFeO\textsubscript{2}} structure) is formed. The Li\textsuperscript{+} diffusion through the layered structure (x=0.5) is much faster than that through the rock-salt structure.
Figure 2-28 The schematic representation of crystal structure change as Ni^{2+} and Co^{2+} are introduced into the Li^{+} layer.
2.4. Conclusion

In this chapter, capacity fade of NCR18650 (NCA cathode) during long-term storage tests was investigated and compared with CGR18650E (LCO cathode) in order to verify good long life reliability of the NCR18650. The findings obtained in this chapter are summarized as follows;

(1) NCR18650 was greatly superior to CGR18650E in the storage characteristics.
(2) The increase in impedance and capacity fade was mainly attributed to the degradation of the cathode, and the deterioration of LCO cathode was larger than that of NCA cathode.
(3) SEI on NCA and LCO cathode surface analyzed by XPS was composed of almost same elements and had same thickness level, suggesting that SEI was not the main factor of the difference in degradation behavior between NCA and LCO cathodes.
(4) Change in the surface crystal / electronic structures and the cation mixing of NCA cathode material during the long-term storage at high temperature was much smaller than that of LCO cathode material, indicating that NCA had excellent storage characteristics.
References


[16] D. Aurbach, Y. Ein-Eli, B. Markovsky, A. Zaban, S. Luski, Y. Carmeli, and H. Yamin, 


[18] D. Aurbach, K. Gamolsky, B. Markovsky, G. Salitra, Y. Gofer, U. Heider, 


1885.


3809.


[26] D.P. Abraham, R.D. Twesten, M. Balasubramanian, I. Petrov, J. McBreen, K. Amine, 


[29] J.B. Wagner Jr., in: N.M. Tallan (Ed.), Electrical Conductivity in Ceramics and Glass, 
4.3.2 Surface and cross section analysis of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ particle

4.4 Conclusion

the NCA cathode
Chapter 3  Effect of ΔDOD in charge-discharge cycling on the suppression of the micro-crack generation of LiNi_{1-x-y}Co_xAl_yO_2 particle

3.1  Introduction

In Chapter 2, it was clarified from the deterioration analysis of the lithium-ion battery using NCA as a cathode active material with long-term storage that the change in the surface structure of NCA from R3m layered structure to the rock-salt type structure was a dominant factor. In the development of rechargeable battery, the charge-discharge cycle characteristics are as important as the storage characteristics for practical use, especially, for eco-vehicle application. Typical charge-discharge patterns on state of charge (SOC) for HEV (hybrid electric vehicle), PHEV (plug-in hybrid electric vehicle) and BEV (battery electric vehicle) are summarized in Fig. 3-1.
Figure 3-1  Typical schematic usage patterns of rechargeable batteries for ECO drive systems.
The pulse-charge and discharge due to the driver’s acceleration and braking are frequently given to the rechargeable battery for the HEV system. Therefore, it needs to be tolerance to large pulse-shape charge-discharge current. The battery is not discharged to SOC = 0 % or depth of discharge (DOD) = 100 %, and the DOD is controlled in the middle DOD region of 30 – 70 %. On the other hand, the battery is kept at full charged state before log-range driving, and 100 % discharge is not carried out for BEV application. Moreover, PHEV is an intermediate system of HEV and BEV, and the battery for PHEV is kept at full charged state like BHV. After discharging to prescribed DOD, the pulse-charge and discharge in the middle DOD region are repeated like HEV. Thus, the required characteristics of the battery depend on vehicle system. The high capacity lithium rechargeable battery with the NCA cathode is the most suitable for BEV application. For introducing the small, lightweight and high capacity lithium-ion batteries to BEV, the battery space in the car should be reduced, and BEV must be valuable.

In recent literatures, there are many studies on the deterioration of NCA cathode lithium-ion batteries. Broussely et al. investigated long-term stability of the Lithium-ion batteries with the Ni-based oxide cathode for satellite or standby applications, and found they exhibited outstanding stability on cycling and storage [1-3].

On the other hand, when the Lithium-ion batteries with LiNi_{1-x,y}Co_{x}Al_{y}O_{2} cathode were subjected to charge-discharge cycle tests in large ΔDOD conditions at high temperatures such as 40 - 70 °C, serious capacity fading and power loss due to the increase in impedance at the cathode/electrolyte interface have been reported [4-8]. It was found that aluminum doping was very effective to suppress the cell impedance rise by the suppression of the charge-transfer impedance rise at the cathode [9-13]. Moreover, it was reported that cycle characteristics remarkably depended on ΔDOD [14]. The ΔDOD influenced the capacity fading and power loss in LiNi_{1-x,y}Co_{x}Al_{y}O_{2}/Graphite cells. From a comparison between cells cycled in ΔDOD conditions of 0 - 100 % and 0 - 70 %, the capacity of the former faded much
faster than that of the latter.

Ukyo et al. reported that the morphology of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles changed during charge-discharge cycling [15-16]. They suggested that the growth of microcracks formed at grain boundaries of the LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles as spherical secondary ones which consist of small primary particles was responsible for the increase in cell resistance because of the interruption of electronic and ionic conduction. Moreover, they showed the surface of the microcracks turned from an ordered layer structure (α-NaFeO$_2$-type) to a partially ordered structure and then to a disordered rock-salt structure during the first charge-discharge cycle [17-18]. ΔDOD and temperature also induced the increase in cell resistance. However, it has not been elucidated why the larger ΔDOD accelerated increase in cell resistance. In this regard, there are two possibilities: (1) Deterioration of active materials occurred in a specific potential region; (2) Crystal structure of active materials was destroyed in larger ΔDOD conditions. It is significant to clarify the reason for improving battery performance.

In this chapter, the effect of microcracks on battery performance, in particular cell resistance, of the Lithium-ion batteries with the NCA cathode was investigated by charge-discharge tests in various ΔDOD conditions.
3.2 Experimental

3.2.1 Cycle tests in different ΔDOD conditions for cylindrical model cells

A cylindrical model cell with capacity of 400mAh which was composed of a lithium nickel cobalt aluminum oxide cathode which consisted of a mixture of NCA, carbon black and poly vinylidene fluoride, a graphite anode, electrolyte and a microporous polyethylene separator was used in this investigation. Electrolyte was a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) with lithium hexafluorophosphate (LiPF₆).

Charge-discharge cycle tests were executed by two series. First series were performed with two ΔDOD conditions (DOD 0-100% and DOD 10-70%) at 25 and 60 °C. These tests were operated at a current rate of 1It (400mA). Capacity checking test was performed at every 50 cycles during 0-500 cycles and at every 500 cycles during 500-2500cycles to compare discharge capacity in the voltage region of 4.2-2.5V among four conditions.

Second series were performed at 25°C in four ΔDODs which were 0 – 60 % (4.2 - 3.54 V), 10 – 70 % (4.05 - 3.48 V), 40 – 100 % (3.78 - 2.5V) and 0 – 100 % (4.2V – 2.5V). The charge-discharge cycle tests were operated at a current rate of 2It (800mA). The charge condition was CC-CV, and CV cut current value was 20mA (0.05It mA). Discharge capacity checking test was performed in the voltage region of 4.2 - 2.5 V at every 500 cycle. The detail test conditions are summarized in Table 3-1.
3.2.2 Impedance analysis of coin-type model cells

In order to investigate the increase in impedance and capacity deteriorations for the cathode and anode, cylindrical cells were disassembled to take out the cathode and anode, and each was rinsed by DMC, and then used to assemble a coin-type cell with a Li metal as a counter electrode under dry air atmosphere. The deterioration capacity was measured by charge-discharge tests and compared with a fresh electrode. The change in cell impedance was measured by a Solartron 1260/1286 frequency response analyzer system.
3.2.3 Surface and bulk analyses

In X-ray diffraction (XRD) patterns were collected with a Panalytical X’Celerator detector equipped with a Cu target x-ray tube and a diffracted beam monochromator. Each XRD measurement was performed every 0.05° over a scattering angle region between $2\theta = 10$ and $90°$ and the counting time was 10 s. Rietveld refinement was performed by using HighScore (plus) software package. Scanning electron microscopy (SEM) was carried out to observe a cross section of an NCA particle after being treated by cross section polisher. SEM images were taken with a scanning electron microscope Hitachi S-4500 equipped with an energy-dispersive X-ray (EDX) analyzer.

XRD and SEM were used to study the phase change and microscopic morphology for active materials after cycling. For surface and bulk analyses, each cell was discharged to a voltage of 2.5V at 1It rate and then disassembled. The samples taken out of the disassembled cells were washed with dry DMC and evaporated at room temperature. Other experimental conditions are given in the next section.
3. 3 Results and Discussion

3.3.1 Cycle performance of cylindrical model cells in the different ΔDOD conditions and characteristics of disassembled cathodes

Figure 3-2 shows charge-discharge cycle performance for NCA cathode/graphite anode cylindrical model cells in two ΔDOD conditions at 25 and 60 °C. The vertical axis or relative capacity is defined as the ratio of discharge capacity at a certain cycle to the initial one. In the ΔDOD condition of 0 – 100 %, significant capacity fading was observed, and the capacity deteriorated more rapidly at the higher temperature. On the other hand, in the ΔDOD condition of 10 – 70 %, cycle performance was greatly improved even at 60°C. These results indicate that the mechanism for capacity deterioration of Lithium-ion batteries with the NCA cathode was not simple.

![Graph showing cycle performance](image)

Figure 3-2 Cycle performance of NCA cathode/graphite anode model cells in two ΔDOD conditions at 25 and 60 °C; (●) 10 – 70 % DOD at 25 °C, (○) 10 – 70 % DOD at 60 °C, (▲) 0-100 % DOD at 25 °C and (△) 0 - 100 % DOD at 60 °C.
Furthermore, in the program of the advanced technology development (ATD), lithium-ion cells with NCA cathode were pulse–tested with a high-power profile at high temperatures in very narrow $\Delta$DOD range of 3 or 6%. It was found that the capacity fading of these cells was small but the rise in cell impedance during cycling was large [6-8]. The capacity fading mechanism in the $\Delta$DOD condition of 0 – 100 % was different from that in the narrow $\Delta$DOD cycling.

The NCA cathode or graphite anode after cycle tests was reassembled into 2016-type coin cells with Li metal as a counter electrode. Cell impedance for each coin-type cell is shown in Fig. 3-3. The cell impedance was measured at 70 % DOD at 25 °C and the resistance was evaluated from the lower frequency semicircle in each Nyquist plot. The resistance of the NCA cathode before 10 – 70 % DOD cycle test was 14.07 $\Omega$, and that after cycle test was 11.03 $\Omega$ at 25°C and 21.30 $\Omega$ at 60°C, respectively. On the other hand, the resistance after 0 – 100% DOD cycle test was 230.80 $\Omega$ at 60°C. In this way, the resistance significantly increased only for the cell with the NCA cathode after the cycle test in the $\Delta$DOD of 0 – 100 %, while the resistance change was not observed for the cells with the NCA cathode after the cycle test in the $\Delta$DOD of 10 – 70 %. As for the cell with the graphite anode, the resistance was almost equal irrespective of $\Delta$DOD cycle test condition and operating temperature (Fig. 3-3 (b)). The impedances for cathode and anode in the $\Delta$DOD of 0 – 100 % were similar to the previous ones [4, 12, 13]. Zhang et al. showed that the resistance in equivalent circuit was composed of ohmic resistance ($R_{\text{ohm}}$), charge-transfer resistance ($R_{\text{ct}}$) and resistance of SEI layer ($R_{\text{SEI}}$), and the dominant resistance for the increased impedance was $R_{\text{SEI}}$ [13]. Therefore, in this study, it was assumed that the increase of the resistance for the lower frequency semicircle in the $\Delta$DOD of 0 – 100 % was ascribed to $R_{\text{SEI}}$. The surface structure change will be analyzed by XPS and TEM-EELS in Chapter 4. On the other hand, it was not clarified why $R_{\text{SEI}}$ is increased during 0 – 100% $\Delta$DOD cycle test.
Figure 3-3 Nyquist plots of coin cells before and after cycle tests; (a) NCA cathode / Li metal cell (○) initial, (●) 10 – 70 % DOD at 25 °C, 2500 cycle, (■) 10 – 70 % DOD at 60 °C, 2500 cycle, (▲) 0 – 100 % DOD at 60 °C, 350 cycle, (b) Graphite anode / Li metal cell (○) initial, (●) 10 – 70 % DOD at 25 °C, 2500 cycle, (■) 10 – 70 % DOD at 60 °C, 2500 cycle, (▲) 0 – 100 % DOD at 60 °C, 350 cycle.
Figure 3-4 shows discharge curves of the reassembled coin-type cells operated in a voltage region of 4.3 - 2.5 V for NCA cathode or of 1.0 - 0.01 V for graphite anode at a constant current of 0.1It at 25 and 60 °C. After cycle tests in the ΔDOD of 0 – 100 %, capacity loss for the cell with the NCA cathode was 33.5 % at 25°C and 45.2 % at 60°C, while that for the cell with the graphite anode was about 10 %. These results suggest that the capacity loss is mainly ascribed to the deterioration of the NCA cathode which is influenced by ΔDOD cycle test condition and temperature. On the other hand, after cycle tests in the ΔDOD of 10 – 70 %, capacity loss for the cell with the NCA cathode was 1.5 % at 25°C and 9.9 % at 60°C, These results indicate that the capacity loss is strongly affected by ΔDOD cycle test condition and test temperature.

In order to investigate the cause of deterioration of the NCA cathode accelerated by cell tests in the ΔDOD of 0 – 100 % at 25 and 60 °C, the cathode and anode disassembled before and after cycle tests were characterized by XRD and SEM. Figure 3-5 shows XRD patterns of the NCA cathode before and after cycle tests. Neither new diffraction peaks nor significant peak shift were observed after cycle tests, suggesting that crystal structure of NCA bulk did not suffer serious damage during cycle tests, suggesting that this is not the cause of capacity loss. Shim et al. and Striebel et al. studied XRD, Raman and current-sensing atomic force microscopy (CSAFM) for deteriorated cathode after cycling in the ΔDOD of 0 – 100 % at 60 °C. Their XRD patterns were almost same as those in this study, and they suggested capacity loss occurs due to a rise in the impedance of the cathode caused by loss of the conductive carbon at the surface and/or by an organic film on the cathode surface [9, 14]. Therefore, we analyzed the structure of cathode surface and bulk in detail.
Figure 3-4  Discharge curves of the cells with (a) NCA cathode electrode and (b) graphite anode electrode before and after cycle tests. Each curve was obtained from (---) a fresh cell and cycled cells with the conditions of (●) 10 – 70 % DOD 25 °C, 2500 cycle, (■) 10 – 70 % DOD 60 °C, 2500 cycle, (◆) 0 – 100 % DOD at 25 °C, 2000 cycle and (▲) 0 – 100 % DOD 60°C, 350 cycle.
Figure 3-5  XRD patterns of the NCA cathode taken out of the model cell (a) before cycle tests, and after cycle tests with the conditions of (b) 10 – 70 % DOD 25°C, 2500 cycle, (c) 10 – 70 % DOD 60 °C, 2500 cycle, (d) 0 – 100 % DOD 25°C, 2000 cycle and (e) 0 – 100 % DOD 60 °C, 350 cycle.
3.3.2 Change in morphology and electrochemical properties of LiNi$_{1-x-y}$Co$_{x}$Al$_{y}$O$_{2}$ particles with charge-discharge cycling in different ΔDOD conditions and temperatures

There was no significant change in crystal structure of NCA. We also analyzed the surface of the SEI film on the cathode by XPS. The thickness of the SEI film was not increased during charge-discharge cycling. In addition, we analyzed the morphology change of the NCA cathode by the cross sectional analysis by SEM.

Figure 3-6 shows cross sectional SEM images (Fig. 3-6 (a)-(e)) of NCA particles before and after cycle tests. After each cycle test, many microcracks in NCA particles were observed after 2000 cycles at 25 °C and 350 cycles at 60 °C in the ΔDOD of 0 – 100 %. In order to quantify the microcrack generation, each SEM image were converted to black areas due to microcracks and original pores and white ones due to NCA domains by image processing (Fig. 3-6 (f) – (j)), and then area ratio of black to white was calculated and given in converted images. It was revealed that the microcrack generation was accelerated at 60 °C in the ΔDOD of 0 – 100 %, while in the ΔDOD of 10 – 70 % it was small even at 60 °C and there was little difference in black/white area ratio between 25 and 60 °C. These results indicate that the microcrack generation in the NCA particles is one of the main deterioration factors of NCA cathode.

The BET surface area of the NCA cathode before and after cycle tests is also shown in Fig. 3-6. When the cells were cycled in the ΔDOD of 0 – 100 %, BET surface area has increased by 100 % or more because of the increase in initial surface to contact with infiltrated electrolyte along the microcracks. Ukyo et al. found that the formation of microcrack was observed even after the first cycle and the structure of microcrack surface gradually changed from an ordered layer structure (α-NaFeO$_2$-type) to a partially ordered structure and then to a disordered rock-salt structure [17, 18]. It was thought that in addition to the decrease in electronic conductivity with microcrack generation the new disordered layers could be formed.
on the surface of the grain boundary, which would increase the impedance of the cathode. Figure 3-7 shows the temperature dependence of electrolyte conductivity and viscosity. The viscosity of electrolyte decreased from 0.023 P at 25 °C to 0.012 P at 60 °C. This would accelerate the infiltration of electrolyte into the clefts of microcrack, leading to intense deterioration at 60 °C.

The deterioration phenomena of LiNi₀.₇₄Co₀.₁₆Al₀.₁O₂ cathode was consistent with that of LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ cathode during charge-discharge cycling in the ΔDOD of 0 – 100 % which was reported by Striebel et al. and Ukyo et al. [14, 15]. However, the difference in cycling characteristic between ΔDOD 0 - 100% and ΔDOD 10 - 70% could not be explained by the proposed deterioration mechanism. Ukyo et al. studied the relationship between the rate of cell resistance rise and initial capacity obtained by charge-discharge cycling in different potential ranges [15]. The initial capacity was 154 and 98 mAh g⁻¹ for the potential ranges of 4.1 – 2.5 V and 4.1 – 3.0 V, respectively. In contrast, the rate of cell resistance rise for the narrower potential range was one third of that for the wider potential range, indicating that the wider the potential range, the larger the rise in cell resistance. The volume change of positive material seems to cause the rise in resistance. Moreover, Ukyo et al. showed the many cracks occurred on Li₁₋ₓNi₀.₈Co₀.₁₅Al₀.₀₅O₂ as it was charged to x = 0.6 which was the distortion point of the crystal lattice [15]. Therefore, they set the upper limit of charge-discharge potential range at 4.1 V because no cracks were formed at this potential.

There are two possibilities for different cycling characteristics between the ΔDOD 0 – 100 % and ΔDOD 10 – 70 %: (1) Deterioration of active materials occurred in a specific potential region, (2) Crystal structure of active materials was destroyed more intensely in the larger ΔDOD condition. Therefore, we investigated the influence of ΔDOD on the deterioration of battery.
Figure 3-6  Cross sectional SEM images (a-e) and corresponding images that microcracks and pore converted to black points and NCA converted to white points (f-j) of NCA cathode particles (a) before cycle test, and after (b) 10 – 70 % DOD 25° C, 2500 cycle, (c) 10 – 70 % DOD 60° C, 2500 cycle, (d) 0 – 100 % DOD 25° C, 2000 cycle and (e) 0 – 100 % DOD 60° C, 350 cycle. Inserted numbers in converted images indicate the ratio of area of crack or pore to the BET surface area of cathode electrode.
Figure 3-7  The temperature dependence of electrolyte characteristics; conductivity (◆) and viscosity (●).
3.3.3 Change in morphology and electrochemical properties of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ particles with charge-discharge cycling in restricted ΔDODs

A remarkable suppression effect on the microcrack generation of NCA particles was observed by charge-discharge cycling in the restricted ΔDOD, suggesting that the deterioration occurred in a specific potential range. In order to verify our hypothesis, charge-discharge cycle tests were performed at 25 °C in four ΔDOD conditions which were 0 – 60 % (4.2 - 3.54 V), 10 – 70 % (4.05 - 3.48 V), 40 – 100 % (3.78 - 2.5 V) and 0 – 100 % (4.2 - 2.5 V) as shown in Figure 3-8.

![Figure 3-8](image_url)  
Figure 3-8  ΔDOD conditions for charge-discharge cycle tests; (a) 0 – 60 %, (b) 10 – 70 %, (c) 40 – 100 % and (d) 0 – 100 %.
Figure 3-9 shows the change in unit cell volume and lattice parameters of NCA with x value in Li$_{1-x}$Ni$_{0.74}$Co$_{0.16}$Al$_{0.1}$O$_2$ and DOD. The large crystal lattice distortion was observed in the $\Delta$DOD range of 0 – 60 % (4.2 - 3.54 V, Fig. 3-9 (a)), while there was no significant change in unit cell volume and lattice parameters of NCA in the $\Delta$DOD range of 40 – 100 % (3.78 - 2.5V, Fig. 3-9 (c)), indicating that the deterioration occurred in a specific potential range. The capacity in the $\Delta$DOD range of 0 – 100 % (4.2V – 2.5V, Fig. 3-9 (d)) was 185 mAh g$^{-1}$ which was higher than that reported by Ukyo et al (155mAh g$^{-1}$). [15].

![Figure 3-9](image-url)

Figure 3-9  Change in unit cell volume and lattice parameters of NCA with x value in Li$_{1-x}$Ni$_{0.76}$Co$_{0.14}$Al$_{0.1}$O$_2$ and DOD.
Figure 3-10 shows cycle performance of NCA cathode/graphite model cells at 25 °C in four ΔDOD conditions. The capacity fading in the ΔDOD of 0 – 100 % was significantly large compared to that in the other restricted ΔDOD conditions. There was little difference in degradation behavior of discharge capacity among the three restricted ΔDOD conditions. These results suggest that the deterioration behavior during cycle tests depends on not the lower or upper limit of DOD but ΔDOD.

![Graph showing cycle performance of model cells under four ΔDOD conditions at 25 °C;](image)

Figure 3-10  Cycle performance of model cells under four ΔDOD conditions at 25 °C;

(●) 0 – 60 %, (◆) 10 – 70 %, (■) 40 – 100 % and (▲) 0 – 100 %. 
In order to investigate why deterioration was accelerated in wider ΔDOD, model cells were disassembled before and after cycle tests and then the cathode and anode electrodes were taken out for analysis. First, the NCA cathode was reassembled into 2016 coin cells with lithium metal electrode as a counter electrode. Figure 3-11 shows the discharge curves of the reassembled coin-type cells operated in the voltage region of 4.2 - 2.5 V for the NCA cathode at a constant current of 0.1It at 25 °C. After 1500 times cycle tests in the ΔDOD of 0 – 100 %, capacity deterioration of the NCA cathode was 35 %, while there was no significant deterioration for the other cycle conditions even in after 2500 times cycled.

Change in the impedance of the NCA cathode/Li metal coin-type cells after cycle tests in different ΔDOD conditions was shown in Figure 3-12. The cell impedance was measured at 70% DOD at 25 °C. As shown in Figure 3-12, the impedance after 2500 times cycled was hardly changed in the ΔDOD conditions of 0 – 60 %, 10 – 70 % and 40 – 100 % which have the difference in DOD of 60 %. In contrast, the impedance was greatly increased after the 1500 times cycled in the ΔDOD of 0 – 100 %. These results indicates that the impedance of NCA cathode can maintain stable in each potential region even in cycled 2500 times when the ΔDOD restriction at 60%. The potential range (a) 0 – 60 % (4.2 - 3.54 V) and (c) 40 – 100 % (3.78 - 2.5V) were not in a specific potential range of deterioration.

From the above results, it is obvious that the capacity fading mainly comes from the deterioration of the NCA cathode which was closely dependent upon not upper or lower limit of operation voltage but ΔDOD. Therefore, operations at wider ΔDOD and higher temperature can accelerate cycle life deterioration of the NCA cell.
Figure 3-11   Discharge curves of (a) NCA cathode electrodes before (---) and after cycle tests under the ΔDOD conditions of (●) 0 – 60 %, (◆) 10 – 70 %, (■) 40 – 100 % (after 2500 cycle) and (▲) 0 – 100 % (after 1500 cycle).

Figure 3-12   Nyquist plots of NCA cathode/Li metal coin cells fabricated using NCA cathodes taken out of model cells after cycle tests in the ΔDOD conditions of (●) 0 – 60 %, (◆) 10 – 70 %, (■) 40 – 100 % (after 2500 cycle) and (▲) 0 – 100 % (after 1500 cycle).
Figure 3-13 shows cross-sectional SEM images of NCA particles before and after cycle tests in the ΔDOD conditions of 0 – 60 %, 10 – 70 % and 40 – 100 % of 2500 cycles and in the ΔDOD of 0 – 100 % of 1500 cycles. As shown in Fig. 3-13, many microcracks were observed after the cycle test in the ΔDOD of 0 – 100 %. In order to quantify microcrack generation, each SEM image was converted to black areas due to microcracks and pores and the other white areas, and then the percentage of black areas was calculated with the same way as Fig. 3-6. The converted images were displayed in Fig. 3-13. From the comparison of these images, it was revealed that the microcrack generation was accelerated in the ΔDOD of 0 – 100 % while it was suppressed in the ΔDOD conditions of 0 – 60 %, 10 – 70 % and 40 – 100 % and there was little difference among three conditions.
Figure 3-13  Cross-sectional SEM images (a-e) and their converted images (f-j) of NCA cathode particles obtained from model cells (a, f) before cycle test, and after cycle test in the ΔDOD conditions of (b, g) 0 – 60 %, (c, h) 10 – 70 %, (d, i) 40 – 100 % of 2500 cycles and (e, j) 0 – 100 % of 1500 cycles. Inserted number in each converted image indicates the percentage of black areas.
The cross-sectional analysis for ΔDOD 0 – 60 % (4.2 - 3.54 V, Fig. 3-13 (b)) showed the crystal lattice distortion did not cause microcrack generation even after 2500 cycles. Ukyo et al. have reported that crystal lattice of Li$_{1-x}$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles was distorted and many cracks and clearance were formed at their grain boundary during the initial charging to $x=0.6$, and were pulverized for 800 cycles although the upper limit voltage was 4.1 V [15]. In this study, when the Li$_{1-x}$Ni$_{0.74}$Co$_{0.16}$Al$_{0.1}$O$_2$ electrode was charged to 4.2 V, the $x$ value was 0.76. The connection between the NCA primary particles is probably stronger than that between the Li$_{1-x}$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles used by Ukyo et al., which can inhibit microcrack generation. Amine et al. have reported that the Al doping suppressed the cell impedance rise during the aging test because the added Al reduces the oxidation of electrolyte [11]. The Al content in the Li$_{1-x}$Ni$_{0.74}$Co$_{0.16}$Al$_{0.1}$O$_2$ in this study was twice as large as that in the Li$_{1-x}$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ used by Ukyo et al. From these results, the improved cycle characteristics at 60°C in the ΔDOD range of 60 % in this study can be ascribed to stronger connection between the primary particles and higher Al content of the NCA.

The NCA has a hexagonal crystal structure which belongs to a R3m space group. When DOD become lower or Li ions are deintercalated from Li sites in NCA, its unit cells are monotonically contracted. Therefore it is expected that the larger ΔDOD cause larger volume change of NCA during charge-discharge cycling, which can induce microcrack generation in NCA particles. Therefore, microcracks in NCA particles after cycle test in the ΔDOD of 0 – 100 % are more than those after cycle tests in the three restricted ΔDODs whose width is all 60%. Further analysis for the microcrack surface and deterioration mechanism will be examined in detail in Chapter 4.
3.4. Conclusion

In this chapter, in order to verify the mechanism of the cycle life deterioration for NCA cathode Lithium-ion batteries, its capacity fading and the increase in cell resistance for LiNi_{0.76}Co_{0.14}Al_{0.10}O_2 cathode/graphite anode cylindrical model cells during charge-discharge cycle tests were investigated. The following findings were obtained.

(1) The capacity fading and the increase in cell resistance were dependent upon ΔDOD and test temperature. They were effectively suppressed even in 60°C when ΔDOD was restricted to 0 – 60 %. On the other hand, large deterioration was observed when ΔDOD was 100% (4.2V – 2.5V) especially at high temperature.

(2) The cell deterioration came from not the specific voltage region such as high voltage (4.0 - 4.2 V) and low voltage (2.5 - 3.0V) but the wide region of ΔDOD.

(3) The cell deterioration was caused by the NCA cathode. The change in macro crystal structure of NCA and SEI film growth onto the NCA surface were not observed by XRD and XPS analysis. The micro-crack generation was responsible for the NCA cathode deterioration.
References


Chapter 4  Surface analysis of LiNi_{1-x-y}Co_xAl_yO_2 cathode after cycle tests in restricted DOD ranges

4.1 Introduction

In Chapter 3, it was found that the capacity fading and the increase in cell resistance were dependent upon ΔDOD and test temperature. The micro-crack generation was one of the main factors for the NCA cathode deterioration. In order to clarify the deterioration mechanism and understand the rise in cell impedance, the analysis of microcrack/electrolyte interface is important. The deterioration mechanism of the NCA cathode has been clarified by the recent researches with various spectroscopic methods such as X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FT-IR), attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR), high resolution hard XPS and so on.

Abraham et al. found that the deterioration of the NCA cathode mainly contributed to the rise in cell impedance, and the cathode surface film was a mixture of polycarbonates, LiF and Li_xPF_y –type and Li_xPF_yO_z –type compounds by XPS [3-4].

Kostecki et al. reported that a thin and nonuniform SEI film which was decomposition products of electrolyte such as LiF, Li_xPF_y –type and Li_xPF_yO_z –type compounds did not inhibit lithium-ion transport through the interface of cathode/electrolyte, and the loss of electric contacts caused cathode deterioration. They demonstrated electric conductivity of the cathode surface was significantly diminished after a cycle test in the ΔDOD of 0 – 100 % by using CSAFM imaging. [5]. Abraham et al. proposed that an oxygen-deficient surface layer was formed on a LiNiCoO_2 cathode due to oxygen-transfer reactions with the electrolyte by using X-ray absorption spectroscopy (XAS), the electron energy loss spectroscopy (EELS)
The cathode surface was turned to a Li$_{x}$Ni$_{1-x}$O type (NaCl-type) structure which was believed to contribute to impedance rise of the cathode.

Tatsumi et al. proposed a schematic degradation model of LiNi$_{1-x-y}$Co$_{x}$Al$_{y}$O$_{2}$ by combining spectroscopic methods such as X-ray absorption near-edge structure (XANES), X-ray photoemission spectroscopic (PES) and high-resolution hard X-ray photoemission spectroscopy (HX-PES) [8-10]. In their deterioration model of NCA, the Li$_{x}$Ni$_{0.73}$Co$_{0.17}$Al$_{0.10}$O$_{2}$ surface was a multilayer of Li deficient cubic phase layer and surface films which were composed of Li$_2$CO$_3$, hydrocarbons, ROCO$_2$Li, polycarbonate-type compounds, P-O containing compounds and LiF.

Zheng et al. used STEM and EELS to clarify that the extended grain boundary layers were formed and increased during the first charge-discharge cycle [11,12]. The structure of grain boundary was continuously changed from interior to the surface, from the layered structure to a disordered rock-salt structure via a partially ordered structure. They suggested that the microstructure change was primarily responsible for the irreversible capacity at the first cycle.

The results of storage test in chapter 2 were consistent with these proposed deterioration models. However, the difference in deterioration mechanism between the cycle test conditions of ΔDOD 0 – 100 % and the restricted ΔDOD has not been clarified yet.

In this chapter, deterioration mechanism of Lithium-ion batteries with the NCA cathode during charge-discharge cycle tests in restricted ΔDODs was investigated by XPS, STEM, and TEM-EELS.
4.2 Experimental

4.2.1 Cycle tests in restricted $\Delta$DODs for cylindrical model cells

The cylindrical model cells with capacity of 400mAh were used. These cells were composed of the NCA cathode which consisted of NCA, carbon black, and polyvinylidene fluoride, the graphite anode, electrolyte and micro-porous polyethylene separator. Electrolyte was a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) containing lithium hexafluorophosphate (LiPF$_6$).

Charge-discharge cycle tests were performed at 25 and 60 °C with two $\Delta$DOD conditions (0 – 100 % and 10 – 70 %). The charge-discharge cycle tests were operated at a current rate of 1It (400mA). Capacity checking test was inserted at every 50 cycle during the initial 500 cycles and at every 500 cycle during 500 – 2500 cycles to compare discharge capacity in the voltage region of 4.2-2.5V among four conditions.

4.2.2 Surface and bulk analyses

Surface structure of each cathode was observed by XPS and scanning transmission microscopy (STEM)-EELS. The XPS analysis was performed with a Perkin–Elmer PHI 560/ESCA-SAM system. XPS spectra were obtained after several times of Ar$^+$-sputtering with 4 keV energy ions and a current beam of 0.36 $\mu$A cm$^{-2}$. A sample for the XPS analysis was excited with 1486.6 eV energy AlK$_\alpha$ X-rays. STEM-EELS analysis was conducted with a 200 kV JEM-2100F equipped with a parallel electron energy loss (EEL) spectrometer (Gatan 863). XRD and SEM were used to study the phase change and microscopic morphology for active materials after cycling. For surface and bulk analyses, each cell was
discharged to a voltage of 2.5V at 1It rate and then disassembled. The samples taken out of the disassembled cells were washed with dry DMC and evaporated at room temperature. Other experimental conditions are given in the next section.

4. 3  Results and Discussion

4.3.1  Cycle performance of cylindrical model cells after cycle tests in the controlled $\Delta$DODs and cross-sectional SEM images of the NCA cathode

Figure 4-1 shows charge-discharge cycle performance at 25 and 60°C in two $\Delta$DOD conditions for NCA cathode/graphite model cylindrical cells and the cross-sectional SEM images of the NCA cathode after cycle tests that were described in chapter 3. The vertical axis or relative capacity is defined as the ratio of discharge capacity at a certain cycle to the initial one. In the $\Delta$DOD condition of 0 – 100 %, significant capacity fading and the growth of microcracks were observed, and the capacity deterioration was faster at higher temperature. On the other hand, in the $\Delta$DOD condition of 10 – 70 %, cycle performance was greatly improved even at 60°C, and microcracks were scarcely observed.
Figure 4-1  Cycle performance of cylindrical model cells and cross-sectional SEM images of the NCA cathode in two ΔDOD conditions at 25 and 60 °C;

(●) 10 – 70 % at 25 °C, (○) 10 – 70 % at 60 °C, (▲) 0 – 100 % at 25 °C and (△) 0 – 100 % at 60 °C.
4.3.2 Surface and cross section analysis of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ particle

In the macro structure analysis by XRD, there was not a large change between NCA cathodes before and after cycle tests irrespective of $\Delta$DOD and temperature [2]. For surface and cross-sectional analyses by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), a NCA cathode was disassembled from a completely discharged cell and then washed with dry DMC and evaporated at room temperature. After that, the cathode was sliced by focused ion beam (FIB) method.

Figure 4-2 shows the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and maps of C and F atoms for an NCA particle after 350 cycles in the $\Delta$DOD of 0 – 100 % at 60°C. The C and F atoms which were ascribed to electrolyte mainly distributed in the microcracks of an NCA secondary particle. This suggests that the electrolyte infiltrated into the NCA particle through the microcracks. New SEI films are surely formed on the primary particle surface of NCA along the microcracks and the ionic/electric conductivity of the NCA particle would become worse remarkably.

![Figure 4-2. HAADF-STEM images and maps of C and F atoms for an NCA particle after 350 cycles in the $\Delta$DOD of 0 – 100 % at 60 °C.](image)

Figure 4-2. HAADF-STEM images and maps of C and F atoms for an NCA particle after 350 cycles in the $\Delta$DOD of 0 – 100 % at 60 °C.
Figure 4-3  (a, f) C1s, (b, g) O1s, (c, h) F1s, (d, i) Li1s and (e, j) P2p core level spectra of NCA cathode (a – e) before and (f – j) after cycle tests of 350 cycles in the ΔDOD of 0 – 100 % at 60°C. The numerical values in each figure indicate the distance from the surface.
Figure 4-3 indicates C1s, O1s, F1s, Li1s and P2p core level spectra of NCA cathode before and after cycle tests of 350 cycles in the ΔDOD of 0 – 100 % at 60 °C. There was no obvious change between spectra before and after cycle test for all elements although there was a little change in the O1s spectrum and P2p at the surface. The O1s spectrum after the cycle test was deconvoluted to that of ROCO2Li, Li2CO3 and NCA (LiMO2) as shown in Fig. 4-4.

![Figure 4-4](image)

Figure 4-4  O1s core level spectrum of NCA cathode after 350 cycles in the ΔDOD of 0 – 100 % at 60 °C, ROCO2Li, Li2CO3 and NCA (LiMO2).

The ROCO2Li and Li2CO3 are included in an SEI film formed by electrolyte decomposition. The relative peak intensity of ROCO2Li or Li2CO3 to NCA (LiMO2) (IROCO2Li/I_{NCA (LiMO2)} or ILi2CO3/I_{NCA (LiMO2)} ) before and after cycle tests in various conditions are summarized in Fig. 4-5. The relative peak intensity of ROCO2Li, which was an oxidation product of electrolyte decomposition materials, after cycle tests at 60 °C became high, while that of Li2CO3 was relatively similar regardless of the condition of cycle test.
Figure 4-5  Ratios of peak intensity of ROCO₂Li or Li₂CO₃ to NCA (LiMO₂) in O₁s core level spectra before and after cycle tests in various conditions. (a) before cycle test, (b) 10 – 70 % ΔDOD, 25 °C, 2500 cycles, (c) 10 – 70 % ΔDOD, 60 °C, 2500 cycles, (d) 0 – 100 % ΔDOD, 25 °C, 2000 cycles and (e) 0 – 100 % ΔDOD, 60 °C, 350 cycles.
The mechanism of the electrolyte decomposition reaction is proposed as follows [13-15].

\[
EC + e^- \rightarrow EC^- \text{ (radical anion)} \quad (4-1)
\]

\[
2EC^- \text{ (radical anion)} \rightarrow \text{ethylene} + \text{CH}_2(\text{OCO}_2)^- + \text{CH}_2(\text{OCO}_2)^- \quad (4-2)
\]

\[
\text{CH}_2(\text{OCO}_2)^- + \text{CH}_2(\text{OCO}_2)^- + 2\text{Li}^+ \rightarrow \text{CH}_2(\text{OCO}_2\text{Li})_n \text{CH}_2(\text{OCO}_2\text{Li})(s) \quad (4-3)
\]

\[
\text{DMC(CH}_3\text{OCO}_2\text{CH}_3) + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OCO}_2\text{Li} + \text{CH}_3^* \quad (4-4)
\]

\[
\text{EMC (CH}_3\text{CH}_2\text{OCO}_2\text{CH}_3) + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{CH}_2\text{OCO}_2\text{Li} + \text{CH}_3^* \quad (4-5)
\]

or

\[
\text{EMC (CH}_3\text{CH}_2\text{OCO}_2\text{CH}_3) + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OCO}_2\text{Li} + \text{CH}_3\text{CH}_2^* \quad (4-6)
\]

CH\text{\textbullet} or CH\text{\textbullet}CH\text{\textbullet} radical was converted to ether (CH\text{\textbullet}CH\text{\textbullet}, CH\text{\textbullet}CH\text{\textbullet}OCH\text{\textbullet}CH\text{\textbullet} and, CH\text{\textbullet}CH\text{\textbullet}OCH\text{\textbullet}CH\text{\textbullet}) and alkyl carbonate (CH\text{\textbullet}OCO\text{\textbullet}CH\text{\textbullet}, CH\text{\textbullet}CH\text{\textbullet}OCO\text{\textbullet}CH\text{\textbullet} and CH\text{\textbullet}CH\text{\textbullet}OCO\text{\textbullet}CH\text{\textbullet}CH\text{\textbullet})

In the P2p core level spectra, the peaks at 135.5 and 133.5 eV are assigned to a P-F bond and a P-O bond, respectively. These peaks can be ascribed to Li\text{\textk}PF\text{\texty} and Li\text{\textk}PF\text{\texty}O\text{\textz} compounds formed on the cathode surface as shown in chapter 2. LiPF\text{\text6} as an electrolyte often decomposes to PF\text{\text5} and LiF (eq. 4-7, 4-8), and PF\text{\text5} readily reacts with trace amount of water to form HF as a hydrolysis product (eq. 4-9). Consequently, HF reacts with Li-carbonate compounds to form LiF (eq. 2-11) [16-19].

\[
\text{LiPF}_6 + 2e^- + 2\text{Li}^+ \rightarrow \text{LiF} + \text{Li}_x\text{PF}_y \quad (4-7)
\]

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5 \quad (4-8)
\]

\[
\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} \quad (4-9)
\]

\[
\text{POF}_3 + 2x\text{Li}^+ + 2x\text{e}^- \rightarrow \text{Li}_x\text{PF}_{3-x}\text{O} + x\text{LiF} \quad (4-10)
\]
Depth analysis of the O1s peak after the cycle test (Fig. 4-3 (g)) exhibited the thickness of ROCO$_2$Li film was about 4 nm. The relative peak intensity of ROCO$_2$Li for the condition of 0 – 100 % ΔDOD, 60 °C and 350 cycles which showed the largest capacity loss was smaller than that for the condition of 10 – 70 % ΔDOD, 60 °C, 2500 cycles, indicating that the generation of ROCO$_2$Li was not a dominant factor of deterioration. The relative peak intensity of ROCO$_2$Li depended on test temperature and the elapsed time. The growth of SEI film was also affected by temperature and the elapsed time, but the SEI film with about several nanometers in thickness did not influence any electrochemical performance. The SEI formation mechanism at the cathode is summarized in Fig. 4-6. The SEI at the cathode is composed of organic and inorganic thin layers. The thicknesses of these layers are several nanometers.

Figure 4-6  Schematic representation for SEI formation mechanism at the cathode.
The contact of fresh NCA surface with new electrolyte due to the growth of microcracks led to deterioration in battery performance. Therefore we investigated the change of the interface in the grain boundary of NCA by TEM and EELS analysis.

Figure 4-7 shows TEM images and the corresponding selected area electron diffraction (SAED) patterns of NCA particles before and after cycle tests of 350 cycles in the ΔDOD of 0 – 100 % at 60 °C. Before the cycle test, there were no cracks in NCA particles and the electron diffraction pattern (Fig. 4-7(f)) exhibited that the surface of a primary particle had R3̅ m crystal structure. On the other hand, after the cycle test, many cracks were observed in a secondary particle. The R3m structure was maintained at the surface of a primary particle faced on neighbor one (Fig. 4-7(g)), but a Fm3m rock salt like structure was formed at a primary particle faced on microcrack(Fig. 4-7(h)).

This seems to be a NiO-like layer, as reported previously [6, 7, 11, 12]. NiO is known to have poor conductivities of lithium-ions and electrons, so the resistance layer formed inside secondary particles would contribute to the rise in impedance.
Figure 4-7. Cross section TEM images (a, b), their magnifications (c-e) and corresponding SAED patterns (f-h) of NCA cathodes before (a, c, f) and after (b, d, e, g, h) cycle tests in the ΔDOD of 0 - 100 %. SAED patterns (f, g) were obtained from edge (A and B) of a primary particle faced on the neighbor particle. SAED patterns (h) was obtained from a primary particle (C) faced on microcrack.
In order to examine why the resistance layer was formed only at vicinity of microcracks, STEM-EELS analyses were performed.

Figure 4-8 shows STEM-ADF images and Ni-L edge EELS spectra for the surface of a primary particle of NCA cathode before immersion to electrolyte and after immersion and then the first charge-discharge cycle. Before immersion, no peak shift was observed in the EELS spectra (Fig. 4-8(c)). However, after immersion and the first charge-discharge cycle, peak shifts in the low energy direction were detected at around 4 nm in depth from the primary particle surface (shown by arrows in Fig. 4-8(d)). The shifted peak position was identical to that of NiO as shown in Figure 4-8(d), suggesting that the NiO-like layer was formed at the interface between electrolyte and NCA particles during the first charge-discharge cycle. These results are agreement with the recent investigation by Ukyo et al. [11, 12]. From these results, the microcrack generation would be accompanied by penetration of electrolyte into NCA secondary particles to form a new NiO-like layer.
Figure 4-8  STEM-ADF images (a, b) and Ni-L edge EELS spectra (c, d) for the surface of a primary particle of NCA cathode. (a, c) Before and (b, d) after immersion and then first charge-discharge cycle.
Figures 4-9 and 4-10 show cross-sectional TEM images and depth profiles of Ni-L edge EELS spectra for the NCA particle surface after 5000 cycles in the ΔDOD of 10 – 70 % at 25 and 60°C. No microcracks evolved even after 5000 cycles at both temperatures. The generation rate of NiO-like layer was increased with increasing the cycle test temperature. The thickness of NiO-like layer was increased to 8 nm at 25 °C and 25 nm at 60 °C. Therefore, the growth of NiO-like layer on the secondary particle surface can be suppressed even after 5000 cycles at 60 °C as long as ΔDOD is restricted to 10 – 70 %. On the other hand, the NiO-like layer was formed on most of the primary particle surface after charge-discharge cycling in the ΔDOD condition of 0 – 100 %. So the infiltration of electrolyte can cause the formation of surface film and the NiO-like interface layer. Lack of contact between primary particles and the increase in resistance layer are caused by microcrack generation, which leads to capacity fading and impedance increase. It is important to suppress the microcrack generation to achieve excellent cycle life.
Figure 4-9  Cross-sectional TEM images and depth profiles of STEM-EELS for NCA surface after cycle test of 5000 cycles in the ΔDOD of 10 – 70 % at 25 °C.
Figure 4-10  Cross-sectional TEM images and depth profiles of STEM-EELS for NCA surface after cycle test of 5000 cycles in the ΔDOD of 10 – 70 % at 60°C.
A schematic model for the deterioration of NCA particle during cycle test is shown in Fig. 4-11. For the cycle test in the ΔDOD of 0 – 100 %, microcracks easily generate in the secondary particles because of the stress with shrinkage and expansion of NCA crystal lattices is larger compared with the cycle test in the restricted ΔDOD. The electrolyte infiltrates into the microcracks and causes the formation of the surface SEI film and the NiO-like interface layer. The NiO-like layer with the rock salt-type crystal structure shows low lithium ion conductivity and low electric conductivity, which would cause lack of electric contact between the primary particles and the inhibition of lithium ion transport into the surface layer. Consequently, this leads to capacity fading and rise in impedance. At higher operation temperatures, the formation rate of the NiO-like layer in microcrack regions is increased and the deterioration of the cell capacity is accelerated. In contrast, for the cycle test in the ΔDOD of 10 – 70 %, the generation of microcracks is effectively prevented and the formation of NiO-like layer is also limited near the surface of the secondary particle surface, not the primary particle surface.
Figure 4-11  A schematic model for the deterioration of NCA particle during cycle test.
4.4. Conclusion

In chapter 4, the mechanism of cycle life deterioration for Lithium-ion batteries with the NCA cathode was investigated by analyzing the LiNi_{0.76}Co_{0.14}Al_{0.10}O\textsubscript{2} cathode after cycle tests in different ΔDOD conditions using some spectroscopic methods such as XPS, HAADF-STEM and STEM-EELS. The following findings were obtained.

(1) The residual capacity depended on ΔDOD and temperature. When ΔDOD was restricted to 10 – 70 %, cycle life at 25 °C was maintained even at 60 °C, while the generation and growth of microcracks were often observed especially at 60 °C as the ΔDOD was 0 – 100 % (4.2V – 2.5V).

(2) The growth of SEI film on the NCA surface was hardly detected by XPS.

(3) The electrolyte infiltrated into the NCA secondary particles with the generation of microcracks, and the NiO-like structure layer was formed on the primary particle surfaces, causing the rise in impedance.

(4) The formation rate of the NiO-like layer was accelerated in the cycle test at 60 °C and the impedance rise was further accelerated.

(5) The microcrack generation and the growth of the NiO-like structure layer on the primary particle surface were the main reason of the NCA cathode deterioration.
References


Chapter 5  General Conclusions

In this thesis, the deterioration mechanism for cylindrical Lithium-ion batteries with the Ni-based LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ (NCA) cathode were investigated in detail. The dominant factor of deterioration during high temperature storage test was clarified by comparison analysis of NCR18650 (NCA cathode) and CGR18650E (LCO cathode). Moreover, cycle deterioration of Lithium-ion batteries with the NCA cathode has been remarkably improved by controlling ΔDOD and temperature. The deterioration mechanism was clarified by spectroscopic surface analysis and electrochemical technique. The conclusions obtained in this study are summarized as follows.

(1) The increase in impedance and capacity fade during high temperature storage tests was mainly attributed to the degradation of the cathode, and the deterioration of LCO cathode was larger than that of NCA cathode. SEI on NCA and LCO cathode surface analyzed by XPS was composed of almost same elements and had similar thickness, suggesting that SEI was not the main factor of the difference in degradation behavior between NCA and LCO cathodes. Change in the surface crystal/electronic structures and the cation mixing of cathode material were the dominant factors of deterioration. The macrocrystal structure of cathode materials maintained the α-NaFeO$_2$-type layered structure, but the structure of several nanometer depth from the surface changed to NaCl-like rock-salt structure and partially layered structure. The depth analysis of surface layer structure on NCA and LCO cathodes by TEM-EELS exhibited that the change of NCA cathode material during the long-term storage at high temperature was much smaller than that of LCO cathode material, indicating that NCA had excellent storage characteristics.
(2) The capacity fading and the rise in cell resistance of Lithium-ion batteries with the NCA cathode during the cycle test were dependent upon ΔDOD and test temperature. They were effectively suppressed even in 60 °C as ΔDOD was restricted to 60 %. On the other hand, large deterioration was observed as ΔDOD was 100% (4.2V – 2.5V) especially at high temperature. The cell deterioration could be ascribed to not the specific voltage region such as high voltage (4.0 - 4.2 V) and low voltage (2.5 - 3.0V) but the wide region of ΔDOD. The cell deterioration was caused by the NCA cathode. The change in macrocrystal structure of NCA was not observed by XRD analysis. The microcrack generation was responsible for the NCA cathode deterioration. The synergy effect among the microcrack generation accelerated by expanding ΔDOD, the electrolyte infiltration into microcracks accelerated by decreasing the viscosity of electrolyte, and the deterioration rate accelerated by the temperature rise caused the rapid deterioration.

(3) The growth of microcracks is accelerated in wide ΔDOD ranges. The electrolyte infiltrated into the NCA secondary particles with the generation of microcracks, and the NiO-like structure layer was formed on the primary particle surfaces, causing the rise in impedance. The formation rate of the NiO-like layer was accelerated in the cycle test at 60 °C and the impedance rise was further accelerated. The microcrack generation and the growth of the NiO-like structure layer on the primary particle surface were the main reason of the NCA cathode cycle deterioration.
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List of Publications

1. Comparison of the Surface Changes on Cathode during Long Term Storage Testing of High Energy Density Cylindrical Lithium-Ion Cells
   S. Watanabe, M. Kinoshita and K. Nakura

2. Capacity Fade of LiNi_{1-x-y}Co_xAl_yO_2 Cathode for Lithium-Ion Batteries during Accelerated Calendar and Cycle Life Test.
   I. Comparison Analysis between LiNi_{1-x-y}Co_xAl_yO_2 and LiCoO_2 Cathodes in Cylindrical Lithium-Ion Cells during Long Term Storage Test
   S. Watanabe, M. Kinoshita and K. Nakura

3. Prevention of the Micro Cracks Generation in LiNiCoAlO_2 Cathode by the Restriction of $\Delta$DOD
   S. Watanabe, T. Hosokawa, K. Morigaki, M. Kinoshita and K. Nakura

4. Capacity Fade of LiNi_{1-x-y}Co_xAl_yO_2 Cathode for Lithium-Ion Batteries during Accelerated Calendar and Cycle Life Tests
   II. Effect of $\Delta$DOD in Charge Discharge Cycling on the Suppression of the Microcrack Generation of LiNi_{1-x-y}Co_xAl_yO_2 particle.
   S. Watanabe, T. Hosokawa, K. Morigaki, M. Kinoshita and K. Nakura
   J. Power Sources Submitted.
5. Capacity Fade of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ Cathode for Lithium-Ion Batteries during Accelerated Calendar and Cycle Life Tests

III. Surface Analysis of LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ Cathode after Cycle Tests in Restricted DOD Ranges

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J. Power Sources Submitted.