High Energy Density Lithium-Ion Batteries

Consisting of Graphite and Lithium Nickel Oxide

March 2015

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General Introduction

Lithium-ion batteries have already spread among people in a modern world. The batteries, however, cannot be seen in their bare cells because the batteries are always inside the electronic devices, such as mobile phones, laptop computers, or recent smart phones. Among secondary batteries, a lithium-ion battery is quite new compared with a lead-acid battery or nickel-cadmium alkaline battery [1-4]. A lithium-ion cell consists of two lithium insertion materials having different chemical species and composition. A freshly fabricated lithium-ion cell does not deliver electricity. After charging, the cell stores and then delivers electricity, meaning the secondary source of electricity, so that lithium-ion batteries are classified as secondary batteries. On charge for a freshly fabricated lithium-ion cell, a positive-electrode material is oxidized and a negative-electrode material is reduced forming oxidation and reduction products, respectively, at positive and negative electrodes and consequently generating electric potential in a few or several volts depending on the combination of lithium insertion materials. Although “anode” and “cathode” are commonly or customarily used in the battery community, “anode” and “cathode” do not mean any polarity [5]. In this thesis, “positive” and “negative” are used substituting for “anode” and “cathode” in order to avoid possible confusion due to terminology [6]. During charge and discharge of a lithium-ion battery, lithium ions and electrons are inserted into and extracted from the solid matrixes of lithium insertion materials at the positive and negative electrodes without a destructive change in core structures, so-called topotactic reactions [7]. In other words, lithium ions shuttle between the positive and negative electrodes on storing and delivering electricity, named lithium-ion (shuttlecock) batteries.

As has been briefly described above, lithium insertion materials are the keys to lithium-ion batteries. According to the basic concept on lithium insertion materials based on the hard sphere model [8], the volumetric specific capacity in Ah cm\(^{-3}\) is shown to be maximized when a reaction of \(\text{LiMO}_2 \rightarrow □\text{MO}_2 + \text{Li}^+ + \text{e}^-\) reversibly proceeds in a topotactic manner, in which M indicates a 3d-transition metal element and □ denotes a vacant site for a lithium ion. The maximum values are calculated to be 1.43 Ah cm\(^{-3}\) for LiMO\(_2\) and 1.56 Ah cm\(^{-3}\) for □MO\(_2\). The basic concept is applicable for both positive- and negative-electrode materials.
because they are the same except their polarity relative to a counter electrode. For example, when LiM_{1}O_{2} is used as a positive-electrode material and □M_{11}O_{2} is used as a negative-electrode material, LiM_{1}O_{2} is oxidized to □M_{11}O_{2} on charge, i.e.,

$$\text{LiM}_{1}\text{O}_{2} \rightarrow □\text{M}_{1}\text{O}_{2} + \text{Li}^{+} + e^{-} \quad (1),$$

and □M_{11}O_{2} is reduced to LiM_{11}O_{2}, i.e.,

$$□\text{M}_{11}\text{O}_{2} + \text{Li}^{+} + e^{-} \rightarrow \text{LiM}_{11}\text{O}_{2} \quad (2).$$

Consequently, the overall cell reaction on charge is given by

$$\text{LiM}_{1}\text{O}_{2} + □\text{M}_{11}\text{O}_{2} \rightarrow □\text{M}_{1}\text{O}_{2} + \text{LiM}_{11}\text{O}_{2} \quad (3).$$

(18.76 cm^{3} mol^{-1}) (17.15 cm^{3} mol^{-1}) (17.15 cm^{3} mol^{-1}) (18.76 cm^{3} mol^{-1})

Because reactions (1) and (2) proceed at different potential, the combination of LiM_{1}O_{2} and □M_{11}O_{2} gives a lithium-ion battery whose overall cell reaction is given by equation (3). A volume of 35.91 cm^{3} is theoretically required to store and deliver an electricity of one faraday. There is no volume change during charge and discharge in this case. The theoretical volumetric specific capacity of a lithium-ion cell (3) is calculated to be 750 mAh cm^{-3}, which is the maximum value within a framework of lithium insertion materials under consideration. During the past 30 years, almost every material has been examined in non-aqueous lithium cells along the lines mentioned above [8-10]. The operating potentials of LiM_{1}O_{2} or □M_{11}O_{2} range from 0.5 to 5 V against a lithium metal electrode. Therefore, lithium transition metal oxides have been extensively examined as positive-electrode materials for lithium-ion batteries, such as LiCoO_{2} [11-17], LiNiO_{2} [18-24], LiCoO_{2}-LiNiO_{2} [13, 25-30], LiMn_{2}O_{4} [31-34], LiAlO_{2}-LiNiO_{2} [35-41], etc., as will be discussed later.

Energy density is a common measure in evaluating batteries. Energy stored in a battery is measured by discharging a battery at an appropriate current. The energy in watt-hour (Wh) is the product of average operating voltage in volt (V) and discharge capacity in ampere-hour (Ah). Accordingly higher operating voltage
and larger capacity give higher energy density. The operating voltage is the derivative of the Gibbs free energy change for a cell reaction. The discharge capacity follows the Faraday’s law. The voltage (intensive quantity) and capacity (extensive quantity) are independent of each other and not interchangeable. For practical batteries the cell dimensions are specified, so that space rather than weight is limited in designing batteries. This is the reason why the volumetric specific capacity has been first described. Apart from the specific volumetric capacity of lithium insertion materials, operating voltage of a lithium-ion battery is discussed.

It is very simple to make high-voltage lithium-ion batteries. The combination of a high-voltage positive electrode and a low-voltage negative electrode gives high-voltage lithium-ion batteries. “High” and “low” are arbitrary. Among the possible negative-electrode materials, graphite shows the lowest operating voltage of ca. 0.1 V against a lithium metal electrode and the reaction mechanism of a graphite-negative electrode is well understood [42]. The characteristic feature of lithium-graphite intercalation compounds is the staging phenomenon, which is characterized by periodic sequence of lithium layers between graphite layers. The first stage compound of LiC₆ consists of lithium layers which arranged between every graphite layers, which is golden yellow in color. In general, the n-th stage compound consists of lithium layers arranging between every n graphite layer. Lithium metal has 2.06 Ah cm⁻³ of volumetric specific capacity. The volumetric capacity calculated for the first stage compound (LiC₆) is 0.75 Ah cm⁻³, which is about one third of that for a lithium metal. However, the graphite-negative electrode cycles well compared to a lithium metal electrode while the change in dimension of the graphite-negative electrode is remarkable as will be described in Chapter 1. At present, graphite is the best negative-electrode material among other materials reported so far. Therefore, graphite is used as the negative-electrode material in developing high energy density lithium-ion batteries.

The electrode reaction of graphite at the negative electrode is represented as

\[
\square C_6 + Li^+ + e^- \rightarrow LiC_6 \quad (4),
\]

so that cell reaction (3) is re-written as
As clearly seen in cell reaction (5), a volume of 50.65 cm$^3$ in the discharged state expands to 53.06 cm$^3$ in the charged state when one mole of electrons is stored in the lithium-ion battery consisting of graphite and LiMO$_2$.

Fig. 1 XRD patterns of LiCoO$_2$ prepared by heating a reaction mixture of Li$_2$CO$_3$ and CoCO$_3$ at (a) 700, (b) 800, (c) 900, (d) 950, and (e) 1000ºC for 12 h in air. These samples were identified as a layered structure with a space group of R3m. The hexagonal lattice parameters determined by a least squares method using 11 diffraction lines are (a) $a = 2.815\,\text{Å}$, $c = 14.047\,\text{Å}$, (b) $a = 2.814\,\text{Å}$, $c = 14.041\,\text{Å}$, (c) $a = 2.815\,\text{Å}$, $c = 14.051\,\text{Å}$, (d) $a = 2.814\,\text{Å}$, $c = 14.040\,\text{Å}$, and (e) $a = 2.818\,\text{Å}$, $c = 14.060\,\text{Å}$. 
The above arguments are still an ideal case because LiMO$_2$ is not specified. Among LiMO$_2$ (M = Ti, V, Cr, Mn, Fe, Co, and Ni) examined so far, the research on LiCoO$_2$ is more advanced than other materials because LiCoO$_2$ combined with non-graphitized carbon is first applied to lithium-ion batteries. The electrochemistry and structural chemistry of LiCoO$_2$ have been described in a sophisticated manner, which is quite unique in terms of solid state electrochemistry [14-17]. Researchers have learned a lot from the preparation and characterization of LiCoO$_2$. The preparation of LiCoO$_2$ is easy. Anybody can prepare battery-active LiCoO$_2$ because it easily crystallizes at any temperature ranging from 700 to 1000°C in air. Powder X-ray diffraction patterns of LiCoO$_2$ do not change as are illustrated in Fig. 1. The shape of diffraction line is sharp and well defined, indicating that the crystallite size is well developed, more than 0.1 μm. The lattice constants determined for LiCoO$_2$ prepared at several temperatures of 700 - 1000°C are the same within an experimental error. This clearly shows that XRD cannot distinguish the character of each sample. Particle morphology clearly shows that LiCoO$_2$ prepared at higher temperature than 900°C is single crystalline form. Some of them contain a crystal habit with smooth (0001) facets, as seen in Fig. 2. Primary particles are single crystals of LiCoO$_2$, resulting in small irreversible capacity, large rechargeable capacity, low polarization, and stable steady-state charge and discharge curves, as are illustrated in Figs. 3 and 4. Highly-crystallized LiCoO$_2$ gives clear signals due to phase transitions in their differential chronopotentiograms as are illustrated in Fig. 5. Striking features on the highly-crystallized LiCoO$_2$ are capacity retention and rate-capability, as are depicted in Figs. 6 and 7. As clearly seen in Fig. 6, the highly-crystallized LiCoO$_2$ prepared at 950 and 1000°C works very well during charge and discharge of Li / LiCoO$_2$ cells operated in voltage ranging from 2.6 to 4.2 V. It is usually said that the transportation of lithium ions in a solid matrix is slower than that in the viscous liquid of an electrolyte solution, so that fine powders or nano-particles of lithium insertion materials are preferred to large particles. Experimental facts shown in Fig. 7 are just the reverse. They clearly show that lithium-ion migration and diffusion in an ordered solid matrix of large single crystalline LiCoO$_2$ are faster than those in an electrolyte solution.
Fig. 2  Particle morphology observed by SEM for LiCoO$_2$ prepared by heating a reaction mixture of Li$_2$CO$_3$ and CoCO$_3$ at (a) 800, (b) 900, (c) 950, and (d) 1000ºC for 12 h in air.

Fig. 3  Charge and discharge curves of Li cells with LiCoO$_2$ prepared by heating a reaction mixture of Li$_2$CO$_3$ and CoCO$_3$ at (a) 700, (b) 800, (c) 900, (d) 950, and (e) 1000ºC for 12 h in air. These samples are the same as described in Figs. 1 and 2. The cells were operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. Electrode weights are (a) 45.3, (b) 51.8, (c) 45.3, (d) 60.1, and (e) 43.6 mg. The 1st to 5th cycles are shown in these figures.
Fig. 4  (a) Discharge capacity and (b) irreversible capacity of LiCoO$_2$ as a function of heating temperatures. The cells were operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. Discharge capacity observed for 5 cycles is shown. These cells are the same as described in Fig. 3. A dashed line indicates the theoretical capacity under upper voltage limit of 4.2 V against Li.

Fig. 5  Differential chronopotentiograms calculated from the second cycle of charge and discharge curves of Li cells with LiCoO$_2$ prepared by heating a reaction mixture of Li$_2$CO$_3$ and CoCO$_3$ at (a) 700, (b) 800, (c) 900, and (d) 1000°C for 12 h in air.
Fig. 6 Discharge capacity as a function of cycle number for lithium cells with LiCoO₂ prepared by heating a reaction mixture of Li₂CO₃ and CoCO₃ at (a) 700, (b) 800, (c) 900, (d) 950, and (e) 1000ºC for 12 h in air. The cells were operated at a rate of 0.17 mA cm⁻² in voltage of 2.6 to 4.2 V.

Fig. 7 Rate-capability tests on lithium cells with LiCoO₂ prepared by heating a reaction mixture of Li₂CO₃ and CoCO₃ at (a) 900 and (b) 1000ºC for 12 h in air. The cells were charged to 4.2 V at a rate of 0.17 mA cm⁻² then hold for 30 minutes (CCCV charging mode). Discharge current densities are described in these figures. The cells were operated in voltage of 2.6 to 4.2 V. Electrode weights are (a) 42.6 and (b) 42.7 mg.
The charge-end voltage of lithium-ion batteries consisting of graphite and LiCoO$_2$ is determined to be 4.2 V because of the instability of LiCoO$_2$ combined with an electrolyte, leading to thermal runaway [43]. The potential curve of Li$_{1-x}$CoO$_2$ has been already known, which determines the maximum rechargeable capacity as shown in Fig. 8 [16]. When LiCoO$_2$ is charged to 4.2 V vs. Li, a capacity of 147 mAh g$^{-1}$ based on the weight of LiCoO$_2$ is expected to be stored and delivered electricity. Higher upper voltage gives larger capacity while it gives less reliable performance in terms of capacity retention and safety [44]. As clearly seen in Fig. 8, the rechargeable capacity increases 17 mAh g$^{-1}$, when the charge-end voltage is raised from 4.2 to 4.3 V. Such a trial on the extension of rechargeable capacity by raising charge-end voltage has already been done. Some of typical results are illustrated in Fig. 9. Higher charge-end voltage gives larger capacity while it spoils some characters associated with capacity retention together with thermal stability. According to basic data widely accepted in Fig. 9 combined with Fig. 8, the maximum rechargeable capacity of LiCoO$_2$ is shown to be 140 mAh g$^{-1}$ examined in voltage ranging from 2.5 to 4.2 V against a lithium metal electrode.

![Fig. 8](image)

*Fig. 8* The open-circuit voltages of Li$_{1-x}$CoO$_2$ as a function of the capacity in mAh g$^{-1}$ based on LiCoO$_2$ sample weight. The lithium cells were operated at a rate of 0.17 mA cm$^{-2}$ at 30ºC. Open-circuit voltages were recorded 1 h after the current was switched off. Detailed open-circuit voltages in capacity ranging from 140 to 200 mAh g$^{-1}$ are shown in the inset.
The reaction mechanism of LiCoO$_2$ has already been known to be a topotactic reaction over an entire range from layered cobalt dioxide to LiCoO$_2$ with varying the interlayer distance [14-17]. When the Li / LiCoO$_2$ cell is cycled over the limited composition range of $0 < x < 1/2$ in Li$_{1-x}$CoO$_2$, rechargeability is excellent. However, the rechargeable capacity fades during deep charge / discharge cycles for $x > 1/2$ in Li$_{1-x}$CoO$_2$. A critical composition in terms of cycle life failure seems to be at about $x = 1/2$ in Li$_{1-x}$CoO$_2$, at which a monoclinic phase is observed, consistent with the potential curve of Li$_{1-x}$CoO$_2$ in Figs. 8 and 9 together with the differential chronopotentiograms in Fig. 5 [16]. Coexistence of two phases is also proved by in-situ and ex-situ XRD examinations for the flat portions in $0 < x < 1/4$ and $3/4 < x < 1$ in Li$_{1-x}$CoO$_2$ in the potential curve in Fig. 8. A crystallographic description of what happened in a topotactic electrochemical reaction is highly advanced through the research on solid state electrochemistry of LiCoO$_2$. Thus the lithium insertion material of LiCoO$_2$ stands as a landmark in electrochemical science or a revolution...
in the secondary battery field.

As have been described above, LiCoO\(_2\) is used as a positive-electrode material. The electrode reaction of LiCoO\(_2\) at the positive electrode is represented as

\[
\text{LiCoO}_2 \rightarrow \square_{1/2}\text{Li}_{1/2}\text{CoO}_2 + 1/2\text{Li}^+ + 1/2\text{e}^- \quad (6).
\]

(19.43 cm\(^3\) mol\(^{-1}\)) \quad (19.42 cm\(^3\) mol\(^{-1}\))

The combination of a graphite-negative electrode and a LiCoO\(_2\)-positive electrode gives a lithium-ion battery. The balanced cell reaction is given by

\[
\square_{\text{C}_6} + 2\text{LiCoO}_2 \rightarrow \text{LiC}_6 + 2\square_{1/2}\text{Li}_{1/2}\text{CoO}_2 \quad (7).
\]

(31.89 cm\(^3\)) \quad (38.86 cm\(^3\)) \quad (35.91 cm\(^3\)) \quad (38.84 cm\(^3\))

Therefore, theoretical capacity and energy density can be calculated from equation (7) using the basic data widely accepted on graphite and LiCoO\(_2\). It should be noted that theoretical values are based on the weight and volume of active materials, so that these are ultimate values. One can approach the theoretical values by improving engineering aspects, but never reach the values. To make lithium-ion batteries, one needs conductive additive, binder, separator, electrolyte solution, current feeder, cell case, etc., in addition to active materials. They do not produce any electrical energy, so that they should be minimized in designing lithium-ion batteries. A brief history of lithium-ion batteries tells the importance of engineering aspects.

In 1991, Sony announced new batteries, called lithium-ion batteries, consisting of LiCoO\(_2\) and non-graphitized carbon, which strongly impacted the battery community all over the world because of their high operating voltage. The nominal capacity of 18650-cylindrical cell (18 mm in diameter and 65.0 mm in height), as is illustrated in Fig. 10, was 750 mAh at that time [45]. In 1993-1994, the nominal capacity increased to 1250 mAh by introducing graphitized carbon substituting for non-graphitized carbon and raising the charge-end voltage from 4.1 to 4.2 V. In the latter half of the 1990s, the nominal capacity of 18650-cylindrical cell increased every year. The energy density of 18650 lithium-ion batteries was approximately 390 Wh dm\(^{-3}\) in 2000 and reached 500 Wh dm\(^{-3}\) in 2005, approached a
critical limit as far as the energy density of lithium-ion batteries consisting of LiCoO₂ and graphitized carbon was concerned. Figure 11 shows a brief history of secondary batteries in terms of volumetric energy density in Wh dm⁻³. As clearly seen in Fig. 11, even if the cell design of specific batteries is optimized, the volumetric energy density in Wh dm⁻³ reaches a saturated or critical value unless the innovation of cell chemistry has been performed. For examples, the volumetric energy density of the nickel-cadmium alkaline batteries has reached 160 Wh dm⁻³ for a sintered type and 200 Wh dm⁻³ for a foamed type. The nickel-metal hydride alkaline battery has already shown its critical value of 350 Wh dm⁻³. The volumetric energy density of lithium-ion batteries consisting of graphite-negative and LiCoO₂-positive electrodes has approached its critical value around 500 Wh dm⁻³. Because the lithium-ion batteries do not depend on specific chemistry, such as cadmium, nickel, or metal hydride for alkaline secondary batteries, materials innovation may help breakthrough the critical limit of volumetric energy density.

Fig. 10 Schematic illustration of cylindrical lithium-ion battery. “Anode” and “cathode” are conventionally used worldwide in the battery community. “Anode” is the negative electrode and “cathode” is the positive electrode in the strict sense of the technical term because “anode” and “cathode” do not mean any polarity in electrochemical science.
Fig. 11  Increase in volumetric energy density in Wh dm$^{-3}$ for secondary batteries since 1980. During the past 30 years the volumetric energy density increases about 7 times.

Fig. 12  Brief history of rechargeable batteries and their applications. Recent demands for storage and power applications stimulate the research and development of high energy density batteries. ICT stands for “Information and Communication Technology”. UPS and ESS denote “Uninterruptible Power Supply” and “Energy Storage System”, respectively.
Lithium-ion batteries are expected to next high-power applications, such as electric vehicle and domestic/general industrial electric energy storage uses. The uses suitable for lithium-ion batteries are illustrated in Fig. 12. Lithium batteries have been developed as high-energy density batteries, and they have grown side by side with advanced electronic devices, such as digital watches in the 1970s, automatic cameras in the 1980s, mobile phones in the 1990s, and laptop computers, especially during 2000–2005. New demands usually stimulate the development of new batteries and consequently accelerate the researches on new lithium insertion materials. Recent market demands for advanced lithium-ion batteries emphasize not only high-energy density but also very high-power density for both charge and discharge, especially for power tools, electric vehicle (EV) and hybrid electric vehicle (HEV) applications. Development of advanced lithium-ion batteries for these applications will require basic and applied research on lithium insertion materials for both positive and negative electrodes. New concepts and approaches from quite different angles become more important than has been previously recognized.

In this thesis, the research on high energy density lithium-ion batteries beyond a critical limit of 500 Wh dm\(^{-3}\) has been summarized, which has mainly been done in the academic years of 1991-1992 and 2009-2011.

In Chapter 1, a precision dilatometer is described. In designing high energy density batteries, all the cell parts have to be filled in a cell body in a compact way. A usual device does not change in its dimension, but lithium-ion batteries expand and contract during charge and discharge because the volume of lithium insertion materials in positive and negative electrodes changes during a cell reaction. Backing of an electrode bobbin and swelling of a cell are usually observed, so that the hundreds of prototype cells are pre-fabricated in order not to fail the development of new lithium-ion batteries. Such a prototype stage is a time-consuming step. In order to measure a change in electrode thickness in a submicron level in advance of the prototype stage, a precision dilatometer is designed and fabricated by a trial-and-error method and a new concept of area-specific deformation is proposed.

In Chapter 2, a new lithium insertion material of lithium nickel manganese
oxide is described. It potentially has the rechargeable capacity more than 300 mAh g\(^{-1}\), which is the highest gravimetric specific capacity reported so far. The material is stably cycles in lithium cells operated in voltage ranging from 2.5 to 5.0 V even at 55°C. It seems to be quite promising positive-electrode material for the next-generation high energy lithium-ion batteries. Discussion will be given as to whether or not the material opens new window toward the innovation of lithium insertion materials for advanced lithium-ion batteries.

In Chapter 3, lithium insertion materials of the solid solution between LiCoO\(_2\) and LiNiO\(_2\) prepared at optimum temperature are described. Among the samples prepared in a series of trials, some of them show the rechargeable capacity more than 200 mAh g\(^{-1}\) obtained from lithium cells examined in voltage ranging from 2.5 to 4.2 V. Because the rechargeable capacity of LiCoO\(_2\) is 140 mAh g\(^{-1}\) currently used in lithium-ion batteries, high-capacity lithium insertion materials will be intensively discussed in the same constraint as exerted in current lithium-ion batteries.

In Chapter 4, the 18650-cylindrical batteries (18 mm in diameter and 65.0 mm in height) consisting of lithium nickel oxide and graphitized carbon are fabricated and examined in order to verify the results and discussion described in the previous chapters. The nominal capacity is 2750 mAh and the energy density exceeds a critical limit of 500 Wh dm\(^{-3}\) for the lithium-ion batteries consisting of graphite and LiCoO\(_2\). The detailed battery performance including rate capability, temperature dependence of capacity, cycle life, etc., will be given and the possibility of further developments on high energy density batteries will be discussed therefrom.

References

Chapter 1

Characterization of Lithium Insertion Electrodes by Precision Dilatometer: Area-Specific Deformation of Single Electrode

1.1 Introduction

As has been described in General Introduction, lithium insertion materials change in their lattice volume during charge and discharge. Consequently, the lithium insertion electrodes expand or contact during the operation of lithium-ion batteries, resulting in electrode backing or swelling of batteries, which usually cause serious problems. In order to avoid such problems due to backing or swelling, the hundreds of prototype cells are fabricated and examined, which are time-consuming or not efficient way. In order to measure such a change in an electrode level, a precision dilatometer is designed and fabricated.

In this chapter, a dilatometric method to characterize the electrodes in lithium and lithium-ion batteries is described in terms of the deformation of electrodes. A precision dilatometer consists of a main body and a flexible bag cell, in which a counter electrode is selected to be the zero-strain insertion electrode of lithium titanium oxide (LTO: Li[Li_{1/3}Ti_{5/3}]O_4). Change in thickness of the cell consisting of a target electrode and an LTO electrode is measured in a sub-micron scale as a function of area-specific capacity stored or delivered electricity in mAh cm\(^{-2}\), and the area-specific deformation in μm / (mAh cm\(^{-2}\)) is defined as a common measure to evaluate the deformation or swelling of the electrodes. The method is applied to the electrodes of lithium metal, LTO, LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2, LiCoO_2, and graphite, and a basic concept of the area-specific deformation is discussed in designing high energy density lithium-ion batteries.

1.2 Experimental
1. 2. 1 A framework of dilatometer

Figure 1. 1 shows the main body of a dilatometer originally designed and fabricated. Because the dilatometer previously designed did not have enough sensitivity and stability to measure change in electrode thickness as a function of time during the electrochemical reaction of a lithium insertion electrode [1], a dilatometer has been improved again and again in order to measure change in thickness in a proper manner that a dilatometric signal reflects a character of lithium insertion electrodes one needs to know. A dilatometer in Fig. 1. 1 consists of a main body and a flexible bag cell. The change in thickness of the cell is transmitted via a spindle to a linear voltage displacement transducer (AT2-51, Keyence Co. Ltd., Japan) tightly fixed to the main body on the top of a spindle. The transducer connected to an amplifier (AT2-301, Keyence Co. Ltd.) converts a displacement signal in \( \mu m \) to a voltage signal in mV. A range of displacement to be able to record is ±0.5 mm corresponding to ±5 V in voltage output with a zero-shift allowance of ±25 mV. In order to calibrate a full system, a voltage signal from the amplifier is measured by inserting a stainless steel sheet or plate accurately measured by a micrometer. The determined value is that one-micron displacement corresponds to 10 mV, i.e., 0.1 \( \mu m \text{ mV}^{-1} \).

![Fig. 1. 1 A schematic illustration of a dilatometer consisting of (a) a displacement transducer, (b) a spring, (c) a spindle, and (d) a flexible bag cell.](image-url)
1. Electrodes and Electrochemical cells

Active materials used in this study are lithium titanium oxide (LTO) of \( \text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4 \) (LT-855-17C, Ishihara Sangyo Co. Ltd., Japan), \( \text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2 \) [2, 3], \( \text{LiCoO}_2 \) [4], lithium aluminum manganese oxide (LAMO: \( \text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4 \) [5], lithium nickel manganese oxide (LiNiMO: \( \text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4 \) [6], and graphite (NG-7, The Kansai Coke and Chemicals Co. Ltd., Japan) [7]. \( \text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2 \), LAMO, and LiNiMO are prepared by the same methods as described in refs. 10, 12, and 13, respectively. \( \text{LiCoO}_2 \) was prepared by heating a reaction mixture of CoO and \( \text{Li}_2\text{CO}_3 \) at 850°C for 12 h in air. In preparing the electrodes, polyvinylidene fluoride (PVdF; Kureha Co. Ltd., Japan) dissolved in N-methyl-2-pyrrolidone (NMP) solution is used as a binder. Viscous slurry consisting of 88 weight percent (wt%) active material except graphite, 6wt% acetylene black (Denki Kagaku Kogyo Co. Ltd., Japan), and 6wt% PVdF is cast on aluminum foil with a blade. A graphite electrode consists of 95wt% graphite and 5wt% PVdF on copper foil. NMP is evaporated at 60°C for 30 min and then dried under vacuum for 1 h. Finally, the electrodes are dried under vacuum at 150°C overnight. Then the electrodes are punched out into a disk (16 mm of diameter, 2 cm²). Lithium electrodes are prepared by cutting a piece from a lithium rod, rolling it into a sheet, and pressing it onto a stainless steel sheet. The electrolyte used is 1 M LiPF\(_6\) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) solution obtained from Kishida Chemical Co. Ltd., Japan.

Two types of electrochemical cells are used in this study. One is a hard stainless steel case [8] and the other is a flexible bag cell. An electrochemical cell consists of sample-positive and lithium-negative electrodes separated by a separator, which are placed in a cavity of a container. Apparent electrode area is 2 cm². A container consists of two stainless steel plates (5 mm thick) separated by a Teflon spacer (2 mm thick) in which a ca. 25 × 35 mm² window is made. In fabricating flexible bag cells for dilatometry, an aluminum laminate film obtained from Showa Denko K. K., Japan, is used. After a 2.0-cm² disk electrode and a counter electrode separated by a diaphragm are placed inside a bag made with an aluminum laminate film by a heat-sealing method, 0.2 cm³ of the electrolyte are introduced by
using a 1-cm³ glass syringe, and then the flexible bag cell is heat-sealed in an argon-filled glove box. A diaphragm is either a polypropylene microporous membrane (Celgard 2500) or polypropylene non-woven cloth 44 μm thick. Other sets of experimental conditions are described in the results and discussion section.

1.3 Results and Discussion

1.3.1 Li / LTO cells

There have been several trials on dilatometry to measure electrode thickness [1, 9-17], mainly to examine negative electrodes for lithium-ion batteries. One of the difficulties in designing an in-situ electrochemical cell or developing an in-situ technique associated with lithium insertion materials is reliability and reproducibility in terms of the one-to-one correspondence between new information and electrochemical data. The electrochemical data widely accepted are usually charge and discharge curves in the E / V vs. Q / mAh g⁻¹ plots for lithium insertion materials, so that a new electrochemical cell is verified by showing that the charge and discharge curves observed for an in-situ technique is the same as those previously reported and confirmed by others in the E / V vs. Q / mAh g⁻¹ plots. In order to examine whether or not a dilatometer works well, an LTO electrode is combined with a lithium metal electrode in a flexible bag cell and the change in cell thickness during charge and discharge is measured by using a dilatometer with monitoring cell voltage.

Figure 1.2 shows the charge and discharge curves of a Li/LTO flexible bag cell operated at 0.25 mA cm⁻² in voltage ranging from 1.0 to 3.0 V. The cell is fixed under spindle (c) in Fig. 1.1. The first discharge curve in Fig. 1.2 is different from subsequent curves due to an external electrical short sometimes happens in making a flexible bag cell flat and setting it to the dilatometer. The horizontal axis on the top is the area-specific capacity (ASC) in mAh cm⁻² of the LTO electrode. As clearly seen in Fig. 1.2, the flexible bag cell gives the same charge and discharge curves as those examined in a hard cell case [18]. The LTO electrode shows the steady-state charge and discharge curves with the rechargeable
capacity of 160 mAh g\(^{-1}\) based on the weight of LTO or the area-specific capacity of 2.96 mAh cm\(^{-2}\) in this case.

![Graph showing charge and discharge curves of a Li/LTO cell](image)

**Fig. 1.2** Charge and discharge curves of a Li/LTO cell fabricated in a flexible bag. The cell is operated at 0.25 mA cm\(^{-2}\) in voltage ranging from 1.0 to 3.0 V. A 42.8-mg LTO-electrode mix 161.8 μm thick is used in the lithium cell. A sheet of Celgard 2500 is used as a separator.

![Graph showing charge and discharge curves of a Li/LTO cell](image)

**Fig. 1.3** Charge and discharge curves of a Li/LTO cell; (a) cell voltage as a function of time and (b) the change in cell thickness concurrently measured by a dilatometer. The charge and discharge curves have already been shown in Fig. 1.2 in order to verify a cell operation.
Figure 1.3 shows the dilatometric signal together with the cell voltage as a function of time during the charge and discharge of a Li/LTO cell operated at 0.25 mA cm$^{-2}$ in voltage ranging from 1.0 to 3.0 V. The vertical axis on the left is cell voltage in V and that on the right is a dilatometric signal in μm with respect to a starting point, i.e., zero at $t = 0$. The charge and discharge curves have already been shown in the E/V vs. Q/mAh g$^{-1}$ plots in Fig. 1.2. The dilatometric signal corresponds to a change in thickness of the Li/LTO cell. An algebraic sign in the axis on the right side indicates that “plus” means increase in thickness and “minus” decrease. According to the dilatometric trace in Fig. 1.3, a thickness of the Li/LTO cell almost linearly decreases on discharge and increases on charge, and it seems to increase cycle by cycle. Because the LTO is the zero-strain lithium insertion material, it is hard to imagine that the dilatometric signals in Fig. 1.3 are due to the LTO electrode. At the lithium-negative electrode in a Li/LTO cell, a lithium metal is dissolved on discharge and deposited on charge, which seemingly results in the dilatometric signals in Fig. 1.3. To discuss whether or not this is true, the volume change of a lithium metal during charge and discharge is considered [19]. An atomic weight of lithium is 6.94 g mol$^{-1}$ and its density is 0.534 g cm$^{-3}$. Therefore, a molar volume of lithium is 13.00 cm$^{3}$, meaning that a volume of 0.48 cm$^{3}$ is needed to store or deliver electricity of 1 Ah. The characterization of an electrode is usually performed on a per cm$^{2}$ basis in electrochemistry by considering an active electrode area, giving area-specific deformation (ASD). A unit of area-specific deformation is selected to be μm / (mAh cm$^{-2}$) in this chapter, because one is familiar with a length in μm and an area-specific capacity in mAh cm$^{-2}$ and also because it is easy to imagine its physical meaning. For a lithium metal electrode, area-specific deformation is calculated to be ±4.85 μm / (mAh cm$^{-2}$), suggesting that the thickness of lithium metal changes by 14.3 μm when a dilatometer works properly for a Li/LTO cell operated in a fashion that the area-specific capacity of 2.96 mAh cm$^{-2}$ is stored and delivered on charge and discharge, respectively. According to Fig. 1.3, the dilatometric signal increases by 13 – 17 μm on charge and decreases by 12 – 13 μm on discharge. The degree of elongation on charge is always larger than that of contraction.

Figure 1.4 shows the area-specific deformation (ASD) for a Li/LTO cell
together with the cell voltage as a function of time. The area-specific deformation is calculated from $\partial \Delta d / \partial Q$ with the dilatometric signal $\Delta d$ in $\mu m$ and the area-specific capacity $Q$ in $mA h \ cm^{-2}$ in Figs. 1.2 and 1.3. When the lithium metal in a Li/LTO cell is uniformly dissolved and deposited respectively on discharge and charge, the ASD, i.e., $\partial \Delta d / \partial Q$, is independent of time and should follow a line at $\pm 4.85 \ \mu m / (mA h \ cm^{-2})$. However, the result in Fig. 1.4 does not show such an ideal behavior. On first discharge the ASD follows just above a line at $-4.85 \ \mu m / (mA h \ cm^{-2})$, suggesting that a dilatometer works moderately well to follow the change in cell thickness. On subsequent charge the ASD sharply increases to above a line at $+4.85 \ \mu m / (mA h \ cm^{-2})$ and then decreases to below the line drawing a hump. The curves are asymmetric, indicative of the non-uniform deposition and dissolution of a lithium metal on the negative electrode during charge and discharge of a Li/LTO cell. As clearly seen in Fig. 1.3, the cell thickness increases cycle by cycle. In order to examine whether or not this type of swelling is only limited to the electrochemical charge and discharge of a Li/LTO cell, lithium cells with LAMO, LiNiMO, and LiCoO$_2$ are fabricated and examined by a dilatometer. Results are shown in Fig. 1.5. The cells are cycled until the cell capacity fades. The number of cycles with its duration is 80 cycles with 320 h for a Li/LTO cell, 100 cycles with 368 h for a Li/LAMO cell, 40 cycles with 276 h for a Li/LiNiMO cell, or 150 cycles with 707 h for a Li/LiCoO$_2$ cell. As clearly seen in Fig. 1.5, a tendency to increase in cell thickness is the same among these lithium cells, as had already been discussed in terms of “dead lithium”, “stack pressure”, or “the figure of merit” [20-23]. After the cycle tests, the cells were disassembled in an argon-filled glove box and visually inspected. There was a rise at the active-electrode region while there were still metallic luster outside the active region. In order to measure a height of the rise, a thickness of the electrode on the active and non-active regions was measured at several points by a micrometer and the height of the rise was calculated by averaging the observed values. The height of the rise observed by a micrometer is 127.5 $\mu m$ while the dilatometric signal indicates 124.9 $\mu m$ for a Li/LTO cell in Fig. 1.5 (a). Similarly, these values obtained by both methods are; 128.6 $\mu m$ by a micrometer versus 128.4 $\mu m$ by a dilatometer for a Li/LAMO cell in Fig. 1.5 (b), 153.0 $\mu m$ versus 160.7 $\mu m$ for a Li/LiNiMO cell in
Fig. 1. 5 (c), and 273.9 μm versus 267.4 μm for a Li/LiCoO₂ cell in Fig. 1. 5(d). The values obtained by a micrometer agree well with the dilatometric signals, indicating that a dilatometer properly follows the change in cell thickness within an experimental error of 5%.

The area-specific deformation in μm / (mAh cm⁻²) calculated from ∂(Δd) / ∂Q with Δd in μm and Q in mAh cm⁻² in Fig. 1. 3 for a Li / LTO cell: (a) the area-specific deformation and (b) cell voltage as a function of time. The theoretical value of area-specific deformation for a lithium metal electrode is ±4.85 μm / (mAh cm⁻²).

All the cells are operated at 0.50 mA cm⁻² until cell capacity fades. A 42.8-mg LTO-electrode mix 161.8 μm thick, 36.3-mg LAMO-electrode mix 107.8 μm thick, 41.8-mg LiNiMO-electrode mix 144.8 μm thick, and 29.4-mg LiCoO₂-electrode mix 116.8 μm are used in flexible bag cells.
1.3.2 Zero-volt lithium-ion cell of LTO

It is difficult to show that the area-specific deformation of an LTO electrode is zero directly by experiments, so that an indirect way by using zero-volt lithium-ion cell of LTO is selected. Figure 1.6 shows the charge and discharge curves of a zero-volt lithium-ion cell consisting of two identical LTO electrodes. In fabricating the zero-volt lithium-ion cell, two identical LTO electrodes are prepared in non-aqueous lithium cells. One is a 24.1-mg electrode 100 μm thick and the other is a 25.2-mg electrode 103 μm thick. The charge and discharge curves are the same as those illustrated in Fig. 1.2 except cell capacity. In examining the LTO electrodes in lithium cells, two sheets of a microporous membrane of Celgard 2500 are used in order to prevent a loose short during charge and discharge and to make it easy to remove an electrode. After five cycles in lithium cells, one is charged to 3 V and the other is discharged to 1 V. After a one-hour rest, both cells are disassembled in an argon-filled glove box, and the one LTO electrode is combined with the other LTO electrode in a flexible bag cell. As can be seen in Fig. 1.6, the rechargeable capacity of the zero-volt lithium-ion cell operated at 0.25 mA cm\(^{-2}\) in voltage ranging from –0.5 to +0.5 V is observed to be 160 mAh g\(^{-1}\) based on the weight of LTO, indicating that a zero-volt lithium-ion cell of LTO works well in a flexible bag cell for dilatometry.

![Figure 1.6 Charge and discharge curves of a zero-volt lithium-ion cell of LTO operated at 0.25 mA cm\(^{-2}\) in voltage ranging from –0.5 to +0.5 V. A 24.1-mg LTO-electrode mix 100 μm thick and a 25.2-mg LTO-electrode mix 103 μm thick are combined in a flexible bag cell with a symmetric parallel-plate electrode configuration.](image)
Dilatometric data obtained for a zero-volt lithium-ion cell operated at 0.25 mA cm\(^{-2}\) in voltage ranging from –0.5 to +0.5 V: (a) cell voltage in V, (b) change in cell thickness in \(\mu\text{m}\), and (c) the area-specific deformation in \(\mu\text{m} / (\text{mAh cm}^{-2})\) calculated from the change in thickness in \(\mu\text{m}\) and the area-specific capacity in mAh cm\(^{-2}\) as a function of time. The cell is the same as that shown in Fig. 1.6.

Figure 1.7 shows the dilatometric data simultaneously recorded with the charge and discharge curves of the zero-volt lithium-ion cell of LTO. Figure 1.7(a) is the operating voltage as a function of time for the same data as those already shown in Fig. 1.6, so that the dilatometric signals in Fig. 1.7(b) properly correspond to the electrochemical data. As seen in Fig. 1.7(b), the cell thickness gradually decreases in an initial few cycles and then stays at a constant value. One micron out of 203 \(\mu\text{m}\) in thickness of the electrode mix decreases during initial cycles in Fig. 1.7. This may be a reason why the area-specific deformation of Li does not reach –4.85 \(\mu\text{m} / (\text{mAh cm}^{-2})\) on first discharge for a Li/LTO cell shown in Fig. 1.4. Although a ripple is observed every 5 h in this case, a possible origin is not known yet. Ripples are sometimes observed in the dilatometric signal versus
time plots, especially for such a case that a change in dilatometric signals is small. For practical lithium or lithium-ion batteries, gassing inside the batteries increases internal pressure and consequently it deforms or swells the batteries. However, gassing in the flexible bag cell does not affect the dilatometric signals because the gas evolved in an electrolyte/electrode interface under pressure due to spindle (d) easily escapes from the pressurized region. No general rules can be found for the occurrence of the ripples in this stage of our investigation. The ripple, however, does not correlate to the sharp increase or decrease in voltage, as seen in Fig. 1.7(a) and (b). During charge and discharge, the dilatometric signals seem to be unchanged. Figure 1.7(c) shows the area-specific deformation calculated from  $\frac{\partial \Delta d}{\partial Q}$ for a zero-volt lithium-ion cell of LTO. Although the values are fluctuated due to ripples, the area-specific deformation of LTO is almost zero $\mu$m / (mAh cm$^{-2}$), indicating that the LTO electrode can be used as a common counter electrode for the dilatometry of lithium insertion electrodes or more generally the electrodes associated with lithium and lithium-ion batteries.

1.3.3 LTO / LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell

In previous sections, the LTO electrode is shown to be a possible common counter electrode for the dilatometry of lithium insertion electrodes. A new technique is applied to the measurements of the area-specific deformation of lithium nickel manganese cobalt oxide (LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, abbreviated NMC hereafter), because the solid-state chemistry and electrochemistry of NMC are known [3, 24, 25]. Figure 1.8 shows the charge and discharge curves of an LTO/NMC cell examined at 0.25 mA cm$^{-2}$ in voltage ranging from 1.0 to 3.1 V in a flexible bag. An LTO/NMC cell consists of a 49.1-mg NMC-electrode mix 129 $\mu$m thick and a 70.9-mg LTO-electrode mix 255 $\mu$m thick separated by two sheets of nonwoven cloth. The area-specific capacity loaded on the LTO electrode is 5 mAh cm$^{-2}$ while that of NMC is 4.65 mAh cm$^{-2}$ for an assumed charge capacity of 215 mAh g$^{-1}$. Therefore, the NMC electrode determines the cell capacity. As seen in Fig. 1.8, the first charge capacity is 215 mAh g$^{-1}$ based on the weight of NMC and the first discharge capacity is 195 mAh g$^{-1}$. A 20-mAh g$^{-1}$ irreversible capacity and a 195 mAh g$^{-1}$
rechargeable capacity well agree with the previous results [25]. Figure 1. 9 shows the dilatometric data during the charge and discharge of an LTO/NMC cell in Fig. 1. 8. Although a base line of dilatometric signal $\Delta d$ linearly decreases, $\Delta d$ does not change in voltage ranging from 1.0 to 2.6 V. Above 2.6 V the cell thickness decreases on charge and increases on discharge as clearly seen in Fig. 1. 9(b). Consequently, the area-specific deformation of the NMC electrode is almost zero $\mu m^2/(mAh \ cm^{-2})$ in operating voltage ranging from 1.0 to 2.6 V, as seen in Fig. 1. 9(c). Because the LTO electrode stays at 1.55 V vs. Li, the NMC electrode operates in voltage ranging from 2.55 to 4.15 V vs. Li. In other words, the LTO/NMC cell is dimensionally highly stable when the cell is operated under an upper restriction of 2.6 V, which is consistent with the analytical results on the solid-state electrochemistry of NMC [3, 24, 25] combined with that of the zero-strain lithium insertion material of LTO [18, 26]. Such a dimensional stability is one of the reasons why the LTO/NMC cells show a tough nature and extraordinarily long cycle life [27-29].

![Figure 1. 8 Charge and discharge curves of an LTO / LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell operated at 0.25 mA cm$^{-2}$ in voltage ranging from 1.0 to 3.1 V. The cell consists of a 49.1-mg LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$-electrode mix 129.3 $\mu$m thick and a 70.9-mg LTO-electrode mix 254.8 $\mu$m thick separated by two sheets of non-woven cloth in a flexible bag.](image_url)
Fig. 1.9 Dilatometric data obtained for an LTO/LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell operated at 0.25 mA cm$^{-2}$ in voltage ranging from 1.0 to 3.1 V; (a) cell voltage, (b) change in cell thickness, and (c) the area-specific deformation of a LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrode as a function of time. The cell is the same as that shown in Fig. 1.8.

Fig. 1.10 A LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrode characterized by a dilatometer; (a) cell voltage and (b) the area-specific deformation as a function of Q in both mAh cm$^{-2}$ and mAh g$^{-1}$ based on the weight of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. 
Figure 1. 10 shows the charge and discharge curves of an LTO/NMC cell, illustrated in the E vs. Q plots together with the area-specific deformation of NMC vs. Q plots. Data are taken from 2nd to 4th cycles in Fig. 1. 9. As clearly seen in this figure, the area-specific deformation of NMC in μm / (mAh cm\(^{-2}\)) is correlated with the electrochemical data. Thus a lithium insertion electrode of NMC has been characterized by dilatometry.

1. 3. 4 LTO / LiCoO\(_2\) cell

The dilatometric technique established in this work is applied to the measurement of a LiCoO\(_2\)-positive electrode, which has been used in current lithium-ion batteries. Figure 1. 11 shows the charge and discharge curves of an LTO/LiCoO\(_2\) cell operated at 0.25 mA cm\(^{-2}\) in voltage ranging from 1.5 to 2.7 V in a flexible bag. The cell consists of a 27.3-mg LiCoO\(_2\)-electrode mix 89.3 μm thick and a 27.6-mg LTO-electrode mix 107.7 μm thick separated by a separator of 30-μm nonwoven cloth. The area-specific capacity loaded on the LiCoO\(_2\) electrode is 3.36 mAh cm\(^{-2}\) for the rechargeable capacity of 140 mAh g\(^{-1}\) while that of LTO is 3.89 mAh cm\(^{-2}\) for the capacity of 160 mAh g\(^{-1}\), so that the cell capacity is determined by the LiCoO\(_2\)-positive electrode. This means that the cell voltage ranging from 1.5 to 2.7 V corresponds to 3.05 to 4.25 V vs. Li for the LiCoO\(_2\) electrode.

As seen in Fig. 1. 11, the cell thickness increases slightly on charge and decreases on discharge by 0.1 to 0.2 μm. The general drift of a dilatometric signal in Fig. 1. 11(b) is toward decrease in thickness as a function of time. The change in thickness is quite small as seen in Fig. 1. 11. Therefore, the area-specific deformation in μm / (mAh cm\(^{-2}\)) in Fig. 1. 11(c) is almost featureless, looks like an LTO/LTO cell in Fig. 1. 7 or an LTO/NMC cell in Fig. 1. 9. The change in the area-specific deformation is below ±0.2 μm / (mAh cm\(^{-2}\)) during charge and discharge for the LiCoO\(_2\) electrode.

1. 3. 5 LTO / Graphite cell
Fig. 1.11 Dilatometric data obtained for an LTO / LiCoO$_2$ cell operated at 0.25 mA cm$^{-2}$ in voltage ranging from 1.5 to 2.7 V; (a) cell voltage, (b) change in cell thickness, and (c) the area-specific deformation of a LiCoO$_2$ electrodes. The cell consists of a 27.3-mg LiCoO$_2$-electrode mix 89.3 $\mu$m thick and a 27.6-mg LTO-electrode mix 107.5 $\mu$m thick separated by 30-$\mu$m nonwoven cloth in a flexible bag.

Fig. 1.12 Dilatometric data obtained for an LTO / graphite cell operated at 0.25 mA cm$^{-2}$ in voltage ranging from 0 to 0.59 V vs. Li; (a) cell voltage, (b) change in cell thickness, and (c) the area-specific deformation of a graphite electrodes. The cell consists of a 12.4-mg graphite-electrode mix 92.5 $\mu$m thick and a 44.8-mg LTO-electrode mix 168.3 $\mu$m thick separated by 44-$\mu$m nonwoven cloth in a flexible bag. The reduced form of LTO and fresh graphite are combined in a bag, so that the cell voltage is referred to LTO, i.e., 1.55 V vs. Li.
Figure 1.12 shows dilatometric data obtained for an LTO/graphite cell operated at 0.25 mA cm\(^{-2}\) in voltage ranging from –1.55 to –0.96 V, corresponding to 0 to 0.59 V vs. Li for a graphite electrode. Because LTO and graphite cannot be combined in a form of lithium-ion cells, LTO is reduced in a non-aqueous lithium cell. An LTO electrode is a 44.8 mg with 168.3 μm thick, giving an area-specific capacity of 6.31 mAh cm\(^{-2}\). A 12.4-mg graphite electrode 92.5 μm thick to be combined with a reduced form of the LTO electrode gives an area-specific capacity of 4.24 mAh cm\(^{-2}\). When a reduced form of the LTO electrode is combined with a fresh graphite electrode in a flexible bag cell, the potential of the LTO electrode always stays at 1.55 V against a lithium electrode and that of graphite operates in voltage ranging from 0 to 0.5 V against a lithium electrode. Therefore, the cell potential varies from –1.55 to –0.96 V with respect to the LTO electrode. In illustrating Fig. 1.12, the cell potential is offset by 1.55 V in order to show how the graphite electrode works with respect to a lithium electrode in a flexible bag cell. As clearly seen in Fig. 1.12, the graphite electrode works well in voltage ranging from 0 to 0.59 V vs. Li. On first charge of the graphite-negative electrode, the graphite electrode 92.5 μm thick expands by ca. 5 μm and it gradually increases cycle by cycle. The area-specific deformation of a graphite-negative electrode obtained clearly shows the expansion on charge and contraction on discharge. The change in the area-specific deformation is ± 4 μm / (mAh cm\(^{-2}\)) during charge and discharge for the graphite electrode, which is almost the same as that of a lithium metal electrode in Fig. 1.4. The difference between a graphite and lithium electrode is the morphological stability together with reactivity toward organic solvents during charge and discharge. The graphite is never decomposed in lithium-ion batteries while a lithium metal electrode is decomposed in several ways [27-30].

The graphite-negative electrode has already been used in lithium-ion batteries. The dimensional instability of the lithium-ion batteries during charge and discharge has already been adjusted in an engineering aspect during the past 20 years, resulting in long-life lithium-ion batteries consisting of LiCoO\(_2\) and graphite.

1.3.6 Long-term operation of a dilatometer
A long-term operation of the dilatometer has already been shown in Fig. 1.5. However, it is hard to decide whether or not the dilatometer stably works for a long-term examination of lithium insertion materials because of capacity failure together with continuous elongation in cell thickness in Fig. 1.5.

![Graph showing dilatometric signals](image)

Fig. 1.13. Long-term dilatometric traces of lithium-ion cells consisting of lithium insertion electrodes; (a) an LTO/LiNiMO cell consisting of a 38.0-mg LiNiMO-electrode mix 119.0 μm thick and 30.3-mg LTO-electrode mix 105.5 μm thick, operated in voltage ranging from 1.5 to 3.6 V, (b) an LTO/LAMO cell consisting of a 43.6-mg LAMO-electrode mix 151.0 μm thick and 37.4-mg LTO-electrode mix 143.8 μm thick, operated in 1.5 – 3.0 V, and (c) a graphite/LiCoO2 cell consisting of a 47.2-mg LiCoO2-electrode mix 128.5 μm thick and 15.7-mg graphite-electrode mix 102.3 μm thick, operated in 2.5 – 4.1 V. A current of 0.25 mA cm\(^{-2}\) is applied to these cells, in which a sheet of non-woven cloth 44 μm thick is used as a separator. In drawing the figure, (a) is offset upward by 35 μm and (b) by 20 μm in order to avoid the overlap of each curve.

In order to examine a long-term operation of the dilatometer, LTO/LAMO, LTO/LiNiMO, and graphite/LiCoO2 cells are fabricated and continuously examined at 0.25 mA cm\(^{-2}\) in voltage between upper and lower constraints for 500 h. Dilatometric signal Δd in μm as a function of time is shown in Fig. 1.13. Dilatometric signals observed for an LTO/LiNiMO and LTO/LAMO cell decrease while those for a graphite/LiCoO2 cell increase in an initial stage of operation.
anomalous expansion observed during the first charge of a graphite/LiCoO₂ cell is due to a graphite electrode as was reported previously [1]. After a broken-in period, these cells stably cycle between upper and lower values of Δd. The extent of deformation depends on the combination of lithium insertion electrodes. A graphite/LiCoO₂ cell has already been used in practical lithium-ion batteries. As seen in Fig. 1.13, it is evident that a dilatometer stably operates for a period long enough to reach steady state cycling.

1.4 Summary

In this chapter, the dilatometric method to characterize lithium insertion electrodes has been described. As have been described, the area-specific deformation (ASD) in μm/(mAh cm⁻²) is one of the most important parametric factors to characterize not only lithium insertion electrodes but also the electrodes associated with lithium and lithium-ion batteries. The ASD of a lithium insertion electrode is adjustable somewhat by improving the composition of an electrode mix, selecting particle of an active material together with a carbon additive and a binder, and adjusting a forming pressure if needed. In designing the batteries consisting of lithium insertion electrodes, if the ASD as a function of the state of charge (SOC) of the electrode in % combined with the area-specific capacity in mAh cm⁻² for both positive and negative electrodes is known, one can calculate the deformation of the electrodes during a cell operation and consequently predict a mechanical cell failure in advance of making a prototype battery.

References


Chapter 2  
High-Capacity Lithium Insertion Materials of Lithium Nickel Manganese Oxides for Advanced Lithium-Ion Batteries; Toward Rechargeable Capacity More Than 300 mAh g⁻¹

2.1 Introduction

During the past 25 years, systematic researches on the positive- and negative-electrode materials for high-energy density lithium batteries have been done under a framework of lithium insertion materials. According to a hard sphere model [1], the maximum volumetric capacity is given when a solid-state redox reaction of Me³⁺ and Me⁴⁺ concurrent with lithium-ion insertion and extraction, i.e.,

\[
\begin{align*}
\mathrm{\Box} \mathrm{Me}^{4+} \mathrm{O}_2 + \mathrm{Li}^{+} + \mathrm{e}^{-} & \leftrightarrow \mathrm{LiMe}^{3+} \mathrm{O}_2 \quad (1), \\
\text{(oct)} \text{(oct)} \text{(cp)} & \text{(oct)} \text{(oct)} \text{(cp)}
\end{align*}
\]

occurs in a topotactic manner. In equation (1) (cp) and (oct) indicate the close(st) packing of oxygen ions and octahedral sites, respectively, \(\Box\) denotes vacant octahedral sites, and Me indicates transition metal ions. The specific volumetric capacity is calculated using Shannon ionic radii to be 1.56 Ah cm⁻³ for \(\Box\mathrm{MeO}_2\) or 1.43 Ah cm⁻³ for LiMeO₂. No exception can be found in volumetric capacity of lithium insertion materials [2-7]. In other words, the volumetric capacity is limited to below 1.4 Ah cm⁻³. The gravimetric capacity is also an important parametric factor in evaluating materials for high-energy density batteries. To increase gravimetric capacity of lithium insertion materials, a light element is better than heavy elements among chemical species listed in the periodic table. Consequently, lithium 3d-transition metal dioxides have been extensively examined in terms of solid solution or superlattice, leading to lithium aluminum cobalt nickel
dioxides [8, 9], lithium nickel manganese dioxides with or without cobalt [5], and superstructural lithium nickel manganese dioxide [10], specifically LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ currently used in lithium-ion batteries. The theoretical gravimetric capacity ranges from 275 mAh g$^{-1}$ for LiNiO$_2$ to 310 mAh g$^{-1}$ for hypothetical LiTiO$_2$, or, from 295 mAh g$^{-1}$ for □NiO$_2$ to 335 mAh g$^{-1}$ for □TiO$_2$. The rechargeable capacity attained in laboratory cells is around 200 mAh g$^{-1}$ out of ca. 300 mAh g$^{-1}$ of theoretical capacity.

An introduction of scrap-and-built-type reactions substituting for lithium insertion reactions is an option to break such limitations of volumetric and gravimetric capacities. Scrap-and-built-type reactions include lithium metal, lithium metal alloys, and “conversion” electrodes [11, 12]. These electrodes, however, are usually poor in cycle-ability compared to lithium insertion electrodes.

As were briefly described above, rechargeable capacity in both volumetric and gravimetric capacities will saturate soon if a concept of lithium insertion materials based on equation (1) is only way to systematically study materials for high-energy density lithium-ion batteries. An innovative concept is necessary to break through such a limitation. To establish a new concept, one needs anomalous experimental facts that one cannot explain by the previous concept on lithium insertion materials based on equation (1). In this chapter, a material showing rechargeable capacity more than a critical limit of 300 mAh g$^{-1}$ is described and discussion as to whether or not the material opens new window toward innovation of lithium insertion materials for advanced batteries is given.

2.2 Experimental

Lithium nickel manganese oxides were prepared from nickel manganese double hydroxides of MX-114: (Ni / Mn = 0.99 / 1.01 in molar ratio; Tanaka Chemical Corp. Ltd.), MX-005-1 (Ni / Mn = 1.00 / 2.00) and MX-003-1 (Ni / Mn = 1.04 / 2.96). To prepare a lithium nickel manganese oxide at Ni / Mn = 1 / 1 with Li / (Ni + Mn) = 5 / 4, the powder with the molar ratio of LiOH / NiMnO$_3$ = 5 / 2 was well mixed with mortar and pestle by hand. The reaction mixture was pressed into pellet and heated at 1000$^\circ$C for 12 h in air. NiMnO$_3$ was prepared by heating
MX-114 at 600°C for 4 h. To prepare lithium nickel manganese oxides at Ni / Mn = 1 / 2 or 1 / 3 respectively with Li / (Ni + Mn) = 4 / 3 or 3 / 2, a reaction mixture of lithium hydroxide and MX-005-1 or MX-003-1 was heated at 500°C for 12 h and then at 1000°C for 12 h in air. Heating and cooling rates were approximately 5°C min⁻¹. The reaction products were characterized by powder X-ray diffraction using X-ray diffractometer (XRD-6100, Shimadzu, Co. Ltd., Japan) with FeKα radiation, equipped with a graphite monochromater. Tube voltage and current applied were 40 kV and 15 mA, respectively. The XRD data were recorded from 10° to 104° in 2θ at a scan rate of 0.5° min⁻¹. Lattice constants of reaction products were calculated by a least squares method using X-ray diffraction lines. FT-IR spectra of the samples were obtained by a KBr method by using a Fourier-transform infrared spectrometer (FT-IR 8300, Shimadzu, Co. Ltd., Japan). A KBr crystal was freshly crushed, grounded and granulated, and then about 3 mg of the sample was well mixed with ca. 200 mg of the KBr. The KBr pellet was prepared by pressing the mixture under vacuum for 5 minutes. FT-IR spectra were recorded in wavenumber between 400 and 2000 cm⁻¹.

An electrochemical cell is the same as described in Chapter 1. The separator used is two sheets of porous membrane (Celgard 2500 or 2320, Hoechst Celanese Co. Ltd., USA). Apparent electrode area is 2 cm². A container consists of two stainless steel plates (5 mm thick) separated by a Teflon spacer (2 mm thick) in which a ca. 25 × 35 mm² window is made. To prepare positive electrodes, black viscous slurry was cast onto aluminum foil with a blade, which consisted of 88 wt% sample, 6 wt% acetylene black, 6 wt% polivinylidene fluoride dissolved in N-methyl-2-pyrolidone (NMP). NMP was evaporated at 60°C for 1 h under vacuum, and finally the electrodes were dried under vacuum at 140°C for at least 12 h. Lithium-negative electrode was prepared by pressing a lithium foil onto a stainless steel plate. The lithium foil was freshly rolled a lithium chip cut out from a lithium rod (purity 99 % Rare Metallic Co. Ltd., Japan). The electrolyte used was 1 M LiPF₆ dissolved in ethylene carbonate (EC) / dimethyl carbonate (DMC) (3/7 by volume) solution (Kishida Chemical Co. Ltd., Japan). In fabricating cells, all materials except the electrolyte and lithium metal were dried at 40°C for at least 2 h under vacuum to avoid possible contamination with water.
The cells were assembled in an argon filled glove box. After the electrodes and a separator were placed in the cavity, ca. 0.15 ml of electrolyte was injected with a syringe. Other sets of experimental conditions are given in results and discussion section.

2.3 Results and Discussion

2.3.1 Characterization of samples

Figure 2.1 shows the XRD patterns of lithium nickel manganese oxides together with Li$_2$MnO$_3$. All XRD patterns of lithium nickel manganese oxides are similar to those of α-NaFeO$_2$-structural type. All main diffraction lines of lithium nickel manganese oxides (a), (b), and (c) in Fig. 2.1 are indexed in hexagonal setting. Although Li$_2$MnO$_3$ (d) is indexed in monoclinic setting, XRD patterns of these four samples are quite similar. Differences are selective line broadening and diffraction lines observed in 25 - 35° in 2θ. As seen in Fig. 2.1, selective line broadening of (110) line is seen in (a) while a split due to K$_{α1}$ and K$_{α2}$ is seen in (d). Weak diffraction lines at 26°, 27°, 30°, and 35° in 2θ are seen in Fig. 2.1(b) and (c).

Millar indexes for these diffraction lines can be given as (1/3, 1/3, 0), (1/3, 1/3, 1), (1/3, 1/3, 2), and (1/3, 1/3, 3). The extra diffraction lines are quite similar to those of (020), (110), (11-1), and (021) in Fig. 1(d) for Li$_2$MnO$_3$ resulting from one-to-two cation ordering of lithium and manganese ions in a transition metal layer, forming a $\sqrt{3} \times \sqrt{3}$R30° superlattice based on a basal net in Wood notation. The extra diffraction lines in Fig. 2.1(b) and (c) suggest such a cation ordering in the transition metal layer.

The hexagonal lattice parameters of a-axis, c-axis, and c/a-ratio as a function of Ni / (Ni+Mn) are shown in Fig. 2.2. In drawing Fig. 2.2, the monoclinic lattice parameters of Li$_2$MnO$_3$ are converted to approximate hexagonal lattice parameters using equations

$$a_h = (a_m / \sqrt{3} + b_m) / 2 \quad \text{and} \quad c_h = 3c_m \sin \beta,$$

where $a_m$, $b_m$, $c_m$, and $β$ are monoclinic lattice parameters, and, $a_h$ and $c_h$ are the approximate hexagonal lattice parameters. The a-axis linearly increases from 2.84
to 2.89 Å and c-axis also linearly increases from 14.23 to 14.29 Å with increasing the Ni content. The c/a value decreases with increasing the Ni content. This clearly indicates that these samples follow a Vegard’s rule. The end member at Ni/Mn = 0 with Li/Mn = 2 is Li₂MnO₃ or alternatively Li[Li₁/₃Mn₂/₃]O₂ and that prepared at Ni/Mn = 1/1 with Li/(Ni + Mn) = 1/1 is LiNi₁/₂Mn₁/₂O₂ [13].

![XRD patterns of lithium nickel manganese oxides](image)

Fig. 2. 1 XRD patterns of lithium nickel manganese oxides with Ni/Mn = (a) 1/1 (LiOH/NiMnO₃ = 2.5), (b) 1/2 (Li/Me = 4/3), (c) 1/3 (Li/Me = 3/2), and (d) Li₂MnO₃. Miller indexes and lattice parameters are given by assuming a hexagonal lattice for (a), (b), and (c), and a monoclinic lattice for (d). Lattice parameters are (a) a = 2.883 Å, c = 14.268 Å, (b) a = 2.869 Å, c = 14.270 Å, (c) a = 2.863 Å, c = 14.267 Å, and (d) a = 4.930 Å, b = 8.518 Å, c = 5.021 Å, and β = 109.28°.

Therefore, the sample prepared at Ni/Mn = 1/2 with Li/(Ni + Mn) = 4/3 is represented as Li[Li₁/₇Ni₂/₇Mn₄/₇]O₂, which is one-to-two mixture of Li[Li₁/₃Mn₂/₃]O₂ and LiNi₁/₂Mn₁/₂O₂. The sample at Ni/Mn = 1/3 with Li/(Ni + Mn) = 3/2 is the one-to-one mixture, represented as Li[Li₁/₅Ni₁/₅Mn₃/₅]O₂ hereafter. Sample notation to describe a series of solid solution between Li₂MnO₃
and LiNi$_{1/2}$Mn$_{1/2}$O$_2$ will be described in later section. In order to characterize the samples, the FT-IR spectra are measured and shown in Fig. 2.3. Absorption bands in wavenumber ranging from 400 to 800 cm$^{-1}$ are commonly observed among these samples. Some of fine structures are seen in Fig. 3(d) for Li$_2$MnO$_3$ although LiNi$_{1/2}$Mn$_{1/2}$O$_2$ shows rounded and ill-defined two absorption bands overlapped at 520 and 575 cm$^{-1}$ in Fig. 2.3(a). IR spectra in Fig. 2.3(b) and (c) contain absorption bands at about 445, 530, and 620 cm$^{-1}$, which may be a sum of the intensities of the absorption bands in Fig. 2.3(a) and (d) in the molar ratio of one to two for (b) and one to one for (c).

Fig. 2.2 The hexagonal lattice parameters of (a) a-axis, (b) c-axis, and (c) c/a as a function of the molar ratio of Ni / (Ni + Mn). Open circles indicate lattice parameters of lithium nickel manganese oxides with Ni / Mn = 1 / 1, 1 / 2 and 1 / 3 were prepared with the molar ratio of Li / Me = 1 / 1, 4 / 3 and 3 / 2, respectively. Closed circles indicate lattice parameters of lithium nickel manganese oxides with Ni / Mn = 1 / 1 prepared with the molar ratio of LiOH / NiMnO$_3$ = 2.5.
2.3.2 Electrochemical charge and discharge at room temperature

Figure 2.4 shows the charge and discharge curves of LiNi\(_{1/2}\)Mn\(_{1/2}\)O\(_2\), Li[Li\(_{1/7}\)Ni\(_{2/7}\)Mn\(_{4/7}\)]O\(_2\) and Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\) examined in lithium cells at room temperature (ca. 25°C). The operating voltage of the first charging curve of LiNi\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) monotonously increases from 3.7 to 4.7 V, as shown in Fig. 2.4(a). The operating voltages in the first charging curves of Li[Li\(_{1/7}\)Ni\(_{2/7}\)Mn\(_{4/7}\)]O\(_2\) and Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\) almost linearly increase up to an inflection point at 4.5 V, and then it follows a plateau at 4.5 V. At plateau voltage of 4.5 V in Fig. 2.4, the charge capacities of LiNi\(_{1/2}\)Mn\(_{1/2}\)O\(_2\), Li[Li\(_{1/7}\)Ni\(_{2/7}\)Mn\(_{4/7}\)]O\(_2\) and Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\)
are observed to be ca. 40, 120, and 150 mAh g\(^{-1}\), respectively. When the Mn content increases, charge capacity in voltage below 4.5 V decrease although the capacity at 4.5 V increases. For subsequent cycles, all samples exhibit stable cycle behaviors as shown in Fig. 2. 4. The rechargeable capacities are 205 mAh g\(^{-1}\) for LiNi\(_{1/2}\)Mn\(_{1/2}\)O\(_2\), 220 mAh g\(^{-1}\) for Li[Li\(_{1/7}\)Ni\(_{2/7}\)Mn\(_{4/7}\)]O\(_2\), and 240 mAh g\(^{-1}\) for Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\) at room temperature. A crossing point between charge and discharge curves for each sample is 95, 80, and 75 mAh g\(^{-1}\), respectively, for (a), (b), and (c) in Fig. 2. 4, suggesting the increase in polarization. This is better illustrated in Fig. 2. 5.

Fig. 2. 4 Charge and discharge curves of lithium cell with lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO\(_3\) = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), (c) 1 / 3 (Li / Me = 3 / 2). The electrode mix consisted of 88 wt% lithium nickel manganese oxides, 6 wt% acetylene black, and 6 wt% PVdF. The cells were operated at a rate of (a) 0.17 mA cm\(^{-2}\) (11.3 mA g\(^{-1}\)) in voltage of 2.5 to 5.0 V or (b) (8.6 mA g\(^{-1}\)) and (c) 0.10 mA cm\(^{-2}\) (7.2 mA g\(^{-1}\)) in voltage of 2.0 to 5.0 V at room temperature (ca. 25°C). Electrode weight and thickness are (a) 44.4 mg with 129 µm, (b) 35.1 mg with 97.6 µm, and (c) 41.5 mg with 104.6 µm. The 1st to 5th cycles are shown in this figure.
The charge and discharge curves observed from 2nd to 5th cycles are shown in Fig. 2.5. All curves merge in steady-state charge and discharge curves, drawing a hysteresis loop. The difference in voltage between the charge and discharge curves at a midpoint of rechargeable capacity is 65 mV at 100 mAh g\(^{-1}\) for LiNi\(_{1/2}\)Mn\(_{1/2}\)O\(_2\), 190 mV at 105 mAh g\(^{-1}\) for Li[Li\(_{1/7}\)Ni\(_{2/7}\)Mn\(_{4/7}\)]O\(_2\), and 380 mV at 120 mAh g\(^{-1}\) for Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\). Since polarization is defined by a difference between voltage at current applied and that at zero current [14], so-called open circuit voltage, one can say that polarization increases together with rechargeable capacity, as clearly seen in Fig. 2.5.

Fig. 2.5 Charge and discharge curves of lithium cell with lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO\(_3\) = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), and (c) 1 / 3 (Li / Me = 3 / 2). The data are the same as (a) to (c) in Fig. 2.4. The 2nd to 5th cycles are shown in these figure.
Fig. 2.6 Differential chronopotentiograms for lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO$_3$ = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), and (c) 1 / 3 (Li / Me = 3 / 2). Differential chronopotentiograms were calculated from the charge and discharge curves of lithium cells at the 2nd cycle shown in Fig. 2.5.

In order to examine the solid-state redox reactions in lithium nickel manganese oxides, $dQ/dE$ are calculated from numerical data observed in steady-state charge and discharge curves in Fig. 2.5 and the $dQ/dE$ vs. $E$ plots are illustrated in Fig. 2.6. LiNi$_{1/2}$Mn$_{1/2}$O$_2$ shows two well-defined oxidation peaks at 3.77 and 4.37 V. The reduction peaks corresponding to oxidation peaks are also observed at 3.74 and 4.34 V, indicating that the reactions are reversible. If we define mid-point voltage between them as redox potential, the electrochemical reaction of LiNi$_{1/2}$Mn$_{1/2}$O$_2$ consists of two solid-state redox reactions characterized by 3.75 and 4.35 V of redox potential. Shapes of oxidation and reduction peaks in Fig. 2.6(a) indicate that the reaction proceeds in homogeneous or one phase. Li[Li$_{1/7}$Ni$_{2/7}$Mn$_{4/7}$]O$_2$ and Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$ show some oxidation and reduction peaks, but the shape is rounded and ill-defined. Oxidation and reduction peaks around 3.75 and 4.35 V may be due to the solid-state redox reactions observed for LiNi$_{1/2}$Mn$_{1/2}$O$_2$. The reduction peak at 3.28 V and the oxidation peak at ca. 3.62 V
cannot be seen in Fig. 2. 6 for LiNi_{1/2}Mn_{1/2}O_2. These oxidation and reduction peaks in voltage below ca. 3.7 V are characteristic of Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2 and Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2. If we use the electrochemical terms of “reversible” and “irreversible” [15] are used, the electrochemical reaction of LiNi_{1/2}Mn_{1/2}O_2 is a reversible reaction and those of Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2 and Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 are irreversible because of a kinetic effect resulting in oxidation and reduction peaks far apart. As clearly seen in Fig. 2. 6 with Figs. 2. 4 and 2. 5, these three electrodes are rechargeable in non-aqueous lithium cells.

2.3.3 Electrochemical charge and discharge at 55°C

As described in the previous section, Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2 and Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 show some of kinetic problems. Polarization, such as resistance, concentration, or activation, usually decreases when an electrochemical system is heated [14]. In order to examine the effect of temperature upon the electrochemistry of LiNi_{1/2}Mn_{1/2}O_2, Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2 and Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2, the cells are operated at 55°C and the results are compared to those at room temperature.

Figure 2. 7 shows the charge and discharge curves of the samples examined in lithium cells at 55°C. Because all history is needed from the first cycle to that approaching steady-state charge and discharge curves, raw data observed at 55°C are shown in Fig. 2. 7, corresponding to Fig. 2. 4 at room temperature. At plateau voltage of 4.5 V, charge capacities are 60 mAh g^{-1} for LiNi_{1/2}Mn_{1/2}O_2, 140 mAh g^{-1} for Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2, and 200 mAh g^{-1} for Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2, which are larger than those examined at room temperature, as seen in Fig. 2. 4. Rechargeable capacities observed at 55°C are 235 mAh g^{-1} for LiNi_{1/2}Mn_{1/2}O_2, 270 mAh g^{-1} for Li[Li_{1/7}Ni_{2/7}Mn_{4/7}]O_2, and 310 mAh g^{-1} for Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2. The rechargeable capacities increase by heating especially for Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2. It shows the rechargeable capacity more than 300 mAh g^{-1}.

To show the effect of temperature upon polarization and solid-state redox potential, data in Fig. 2. 7 are re-plotted in Figs. 2. 8 and 2. 9. The differences in voltage between the charge and discharge curves at a midpoint of rechargeable
capacity are 120 mV at 120 mAh g\textsuperscript{-1} for LiNi\textsubscript{1/2}Mn\textsubscript{1/2}O\textsubscript{2}, 370 mV at 145 mAh g\textsuperscript{-1} for Li[Li\textsubscript{1/7}Ni\textsubscript{2/7}Mn\textsubscript{4/7}]O\textsubscript{2}, and 535 mV at 155 mAh g\textsuperscript{-1} for Li[Li\textsubscript{1/5}Ni\textsubscript{1/5}Mn\textsubscript{3/5}]O\textsubscript{2}.

**Fig. 2.7** Charge and discharge curves of lithium cells with lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO\textsubscript{3} = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), and (c) 1 / 3 (Li / Me = 3 / 2). The cells were operated at a rate of (a) 0.17 mA cm\textsuperscript{-2} (10.9 mA g\textsuperscript{-1}) in voltage of 2.5 to 5.0 V or (b) (6.6 mA g\textsuperscript{-1}) and (c) 0.10 mA cm\textsuperscript{-2} (8.2 mA g\textsuperscript{-1}) in voltage of 2.0 to 5.0 V at 55°C. Electrode weights and thickness are (a) 46.1 mg with 127.8 µm, (b) 45.2 mg with 128.2 µm, and (c) 36.6 mg with 102.6 µm. The 1st to 5th cycles are shown in these figure.

Polarization usually decreases when the cells are examined at high temperature. However, polarization largely increases in this case, as clearly seen when data at 55°C in Fig. 2.8 are compared to those at room temperature in Fig. 2.5. This suggests that observed polarization is not the same as listed in electrochemical
systems previously examined [14]. General observations on solid-state redox potentials in Fig. 2. 9 are the same as described in Fig. 2. 6 except shape of peak and its height. At 55°C, all of oxidation and reduction peaks are shaped up nearly well-defined peaks compared to those at room temperature in Fig. 2. 6. The biggest difference between data in Figs. 2. 6 and 2. 9 is the reduction peak at 3.28 V for Li[Li$_{1/7}$Ni$_{2/7}$Mn$_{4/7}$]O$_2$ and Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$. A peak potential at 3.28 V is insensitive to temperature, but their values in dQ/dE at 55°C are about two times larger than those at room temperature. Increase in dQ/dE at 3.28 V is derived from the increase in discharge capacity in voltage below 3.5 V in Figs. 2. 7 and 2. 8, resulting in lower operating voltage compared to LiNi$_{1/2}$Mn$_{1/2}$O$_2$, although the rechargeable capacity of Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$ is 70 mAh g$^{-1}$ larger than that of LiNi$_{1/2}$Mn$_{1/2}$O$_2$.

![Graphs](attachment:graph.png)

**Fig. 2. 8** Charge and discharge curves of lithium cells with lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO$_3$ = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), or (c) 1 / 3 (Li / Me = 3 / 2). The data are the same as (a) to (c) in Fig. 2. 7. The 2nd to 5th cycles are shown in these figure.
Fig. 2. 9  Differential chronopotentiograms for lithium nickel manganese oxides with Ni / Mn = (a) 1 / 1 (LiOH / NiMnO$_3$ = 2.5), (b) 1 / 2 (Li / Me = 4 / 3), or (c) 1 / 3 (Li / Me = 3 / 2). Differential chronopotentiograms were calculated from the charge and discharge curves of lithium cells at the 2nd cycle shown in Fig. 2. 8.

2. 3. 4 Electrochemistry of Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$

Rechargeable capacity more than 300 mAh g$^{-1}$ is the highest value reported so far for a series of lithium insertion materials, which is very attractive for advanced lithium-ion batteries. However, the voltage shape at the first charge is quite different from that for subsequent cycles. Consequently, irreversible capacity seems to be large compared to that of LiCoO$_2$. In order to examine whether or not Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$ can be used as a positive-electrode material for lithium-ion batteries, the irreversible loss of capacity during the first cycle and cycling behavior during subsequent cycles are studies in detail at room temperature and 55°C. Figure 2. 10 shows the charge and discharge curves of a Li / Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$ cell examined at room temperature (ca. 25°C). On first charge, operating voltage linearly increases to 4.45 V until charge capacity reaches 115 mAh g$^{-1}$ and then stayed at 4.5 V until charge capacity reaches 260 mAh g$^{-1}$, drawing 4.5 V plateau.
On first discharge, operating voltage linearly decreases from 4.4 to 3.1 V, and the cell cycles mainly in voltage ranging from 3.0 to 4.5 V. As clearly seen in Fig. 2.10, the loss of capacity during the first cycle is observed to be ca. 70 mAh g\(^{-1}\) and the rechargeable capacity is 230 mAh g\(^{-1}\) at room temperature.

![Charge and discharge curves of Li/Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\) cell operated at a rate of 0.15 mA cm\(^{-2}\) (7.7 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at room temperature (ca. 25°C). The electrode weight and thickness are 39.1 mg with 100 μm. The 1st to 10th cycles are shown in the figure.](image)

In order to examine electrochemical reactions at 4.5 V plateau, Li/Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]O\(_2\) cell is cycled in such a window-opening condition that charge capacity increases by 25 mAh g\(^{-1}\) every cycle until the voltage reaches 5.0 V. The result is shown in Fig. 2.11. In capacity ranging from 0 to 110 mAh g\(^{-1}\), discharge voltage follows just below charging curves. The irreversible capacity is observed to be ca. 10 mAh g\(^{-1}\) in this range. At 4.5 V plateau in 110 to 280 mAh g\(^{-1}\), the irreversible capacity increases cycle by cycle from 10 to 70 mAh g\(^{-1}\) and then it stays at that value even when the cell cycles in voltage ranging from 2 to 5 V, i.e., the rechargeable capacity of 250 mAh g\(^{-1}\) and irreversible capacity of 70 mAh g\(^{-1}\). As seen in Fig. 2.11, a 4.5 V plateau is always observed unless the capacity at 4.5 V plateau is consumed.
Fig. 2.11 Charge and discharge curves of Li/Li[Li_{1/3}Ni_{1/3}Mn_{3/5}]O_2 cell operated at a rate of 0.15 mA cm^{-2} (8.7 mA g^{-1}) in voltages of 2.0 to 5.0 V at room temperature (ca. 25°C). The charge capacity is increased by 25 mAh g^{-1} every cycle until the voltage reaches 5 V. The electrode is 34.5 mg with 94 μm thick.

Figures 2.12 and 2.13 show the results at 55°C. General observations are the same as those at room temperature, except their values. The irreversible capacity observed at 55°C is 40 mAh g^{-1}, which is 30 mAh g^{-1} smaller than that at room temperature. The rechargeable capacity at 55°C is 300 mAh g^{-1}, which is 70 mAh g^{-1} larger than that at room temperature. A long plateau at 4.5 V, specifically from 4.43 to 4.54 V in capacity ranging from 120 to 300 mAh g^{-1} in Fig. 2.12, is 180 mAh g^{-1} at 55°C, which is longer than that at room temperature. The window-opening experiment at 55°C in Fig. 2.13 also supports the above observations. Figure 2.13 combined with Fig. 2.12 illustrates how the steady-state charge and discharge of rechargeable capacity more than 300 mAh g^{-1} develop from the material of Li[Li_{1/3}Ni_{1/3}Mn_{3/5}]O_2. As clearly seen in Fig. 2.13, one has to charge Li[Li_{1/3}Ni_{1/3}Mn_{3/5}]O_2 once to the voltage above 4.5 V with respect to Li to have the attractive rechargeable capacity.
Fig. 2. 12 Charge and discharge curves of Li/Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 cell operated at a rate of 0.15 mA cm\(^{-2}\) (8.9 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at 55°C. The electrode is 33.9 mg with 94 μm thick. The 1st to 10th cycles are shown in the figure.

Fig. 2. 13 Charge and discharge curves of Li/Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 cell operated at a rate of 0.15 mA cm\(^{-2}\) (7.7 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at 55°C. The charge capacity is increased by 25 mAh g\(^{-1}\) every cycle until the voltage reaches 5 V. The electrode weight and thickness are 38.9 mg with 119 μm.
2. 3. 5 Twenty-cycle test of Li / Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_{2} cell at 55°C

Although an electrochemical reaction at 4.5 V plateau is specifically not known yet, it is interesting to know whether or not the rechargeable capacity more than 300 mAh g\(^{-1}\) is sustainable at 55°C. The cycle test of a Li / Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_{2} cell at 55°C is carried out. Results are shown in Figs. 2.14 and 2.15. The cell is operated at a rate of 0.15 mA cm\(^{-2}\) or 10.1 mA g\(^{-1}\) based on the weight of Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_{2} in voltage ranging from 2.0 to 5.0 V at 55°C. The sample shows the rechargeable capacity more than 300 mAh g\(^{-1}\) during 20 cycles, as is expected. Almost all discharge curves converge at two points of 3.85 V with 70 mAh g\(^{-1}\) and 2.91 V with 295 mAh g\(^{-1}\). Before the first crossing point in 0 – 70 mAh g\(^{-1}\), the operating voltage increases by cycling. Conversely, the operating voltage on discharge between two crossing points, i.e., 70 – 295 mAh g\(^{-1}\), decreases.

![Charge and discharge curves of Li / Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_{2} cell operated at a rate of 0.15 mA cm\(^{-2}\) (8.8 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at 55°C for 20 cycles. The electrode is 33.9 mg with 94 μm thick.](image)

Fig. 2.14 Charge and discharge curves of Li / Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_{2} cell operated at a rate of 0.15 mA cm\(^{-2}\) (8.8 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at 55°C for 20 cycles. The electrode is 33.9 mg with 94 μm thick.
After the second crossing point, the capacity increases after 4th cycle. The operating voltage on charge decreases by cycling. Charge and discharge capacity in mAh g⁻¹ together with coulombic efficiency in % as a function of cycle number are shown in Fig. 2. 15. The capacities decrease from 310 mAh g⁻¹ at 1st discharge to 300 mAh g⁻¹ at 6th and then almost linearly increase as a function of cycle number. The charge and discharge coulombic efficiencies are more than 99% except 90% for the 1st cycle. The average efficiency is calculated to be 99.75% from the values observed from 2nd to 20th cycle. These results suggest that reactions associated with high rechargeable capacity are still changing by cycling at 55°C in addition to irreversible change at 4.5 V plateau observed at 1st charge. 

Fig. 2. 15  (a) Charge and discharge capacities and (b) coulombic efficiency as a function of cycle number for a Li / Li[Li₁/₅Ni₁/₅Mn₃/₅]O₂ cell operated at a rate of 0.15 mA cm⁻² (8.8 mA g⁻¹) in voltages of 2.0 to 5.0 V at 55°C. The electrode is 33.9 mg with 94 μm thick.
order to examine whether or not such a change in electrochemical reaction is involved, the differential chronopotentiograms are calculated from numerical data obtained at 2nd, 10th and 20th cycles and shown in Fig. 2.16. The differential chronopotentiogram at 2nd cycle in Fig. 2.16(a) is consistent with that shown in Fig. 2.9, indicating that data is highly reproducible in spite of the irreversible change at the 1st cycle. As clearly seen in Fig. 2.16, the reduction peak shifts toward a cathodic direction, specifically 3.28 to 3.02 V via 3.12 V, while \(\frac{dQ}{dE}\) values are almost the same. A striking feature is that the oxidation peaks at 3.04 and 3.18 V develop by cycling in return for the decrease in oxidation peaks at 3.90 and 4.40 V. These two oxidation peaks at 3.04 and 3.18 V are not observed at all in initial cycles. Because the reduction peak at ca. 3.02 V and oxidation peaks at 3.04 and 3.18 V seem to relate each other, the redox reactions characterized by these reduction and oxidation peaks around 3.1 V may be new redox reactions developed during cycling at 55°C.

![Graph showing differential chronopotentiograms](image)

Fig. 2.16 Differential chronopotentiograms for a \(\text{Li} / \text{Li}[\text{Li}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2\) cell at (a) 2nd, (b) 10th, and (c) 20th cycle. Differential chronopotentiograms were calculated from the charge and discharge curves shown in Fig. 2.14.
2.3.6 Toward the rechargeable capacity more than 300 mAh g\(^{-1}\)

The rechargeable capacity of Li\([Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2\) remarkably increases by heating. Although there are some limiting factors in experiments, such as stability of electrolyte, side reactions during charge and discharge, etc., we would like to know maximum rechargeable capacity observable for Li\([Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2\). The maximum rechargeable capacity observed in a series of trials is 350 mAh g\(^{-1}\). The result is shown in Fig. 2.17. The irreversible capacity observed at 85 °C is 40 mAh g\(^{-1}\). The steady-state charge and discharge curves are hardly observed when the cell is operated at 85 °C. However, it is clear that Li\([Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2\) potentially has the rechargeable capacity of ca. 350 mAh g\(^{-1}\).

Fig. 2. 1.7 Charge and discharge curves of Li / Li\([Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2\) cell operated at a rate of 0.15 mA cm\(^{-2}\) (8.6 mA g\(^{-1}\)) in voltages of 2.0 to 5.0 V at 85 °C. The electrode is 34.8 mg with 98 μm thick. The 1st to 7th cycles are shows in this figure.

As stated above, the rechargeable capacity increases up to 350 mAh g\(^{-1}\) by heating. Such an effect of temperature upon the rechargeable capacity strongly suggests that the electrochemical reactions determining rechargeable capacity are
under a kinetic control. If this is true, the rechargeable capacity more than 300 mAh g\(^{-1}\) could be observed even at room temperature when the current is reduced to small value. Figure 2. 18 shows the discharge curves of Li[Li\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{3/5}\)]O\(_2\) examined at several current at room temperature. The cell was charged at 0.15 mA cm\(^{-2}\) up to 5 V and then held at 5 V until the current decreased to 0.025 mA cm\(^{-2}\), so-called CCCV mode. As clearly seen in Fig. 2. 18, the rechargeable capacity approaches 300 mAh g\(^{-1}\) when the current reduces from 1.65 to 0.075 mA cm\(^{-2}\) or 106.5 to 4.8 mA g\(^{-1}\). The electrochemistry of Li[Li\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{3/5}\)]O\(_2\) suffers kinetic problems which appear as polarization, hysteresis loop in charge and discharge curves, and variation of rechargeable capacity depending on current drain together with temperature.

![Figure 2. 18](image)

**Fig. 2. 18** The effect of current density upon discharge capacity of Li[Li\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{3/5}\)]O\(_2\) examined in a lithium cell. The cell was charged to 5 V at constant current of 0.15 mA cm\(^{-2}\) (8.6 mA g\(^{-1}\)) and then stayed until current decreased to 0.025 mA cm\(^{-2}\) at each charge-end voltages (CCCV charging mode). Discharge current densities are (a) 1.65, (b) 1.05, (c) 0.3, (d) 0.15, and (e) 0.075 mA cm\(^{-2}\). The electrode mix used is 35.2 mg with 101 \(\mu\)m thick.
2. 3. 7 The reaction mechanism of Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 showing the rechargeable capacity more than 300 mAh g^{-1}

Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 shows the rechargeable capacity more than 300 mAh g^{-1} and stably cycles with an average coulombic efficiency of 99.75% even at 55°C except the 1st cycle. The efficiency observed at the 1st cycle is 90%, which is usually observed for lithium insertion materials, such as LiCo_{x}Ni_{1-x}O_2 (0 < x < 1), LiAl_{0.05}Co_{0.15}Ni_{0.8}O_2, etc. The charge and discharge curve at the 1st cycle is quite different from those observed for lithium insertion materials.

High-capacity positive-electrode materials based on lithium manganese oxides have already been reported and discussed possible mechanism as to a long voltage plateau at 4.5 V and large specific capacity in mAh g^{-1} [16-32]. To describe the composition under consideration, there seems to be two notations. One is Dahn’s layered notation of Li[Ni_{x}Li_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2 [17], where 0 ≤ x ≤ 1/2, and the other is Thackeray’s composite description in two-component notation of \( y \) Li_2MnO_3 • \( (1 - y) \) LiNi_{1/2}Mn_{1/2}O_2 [22], where 0 ≤ y ≤ 1. In these notations, the end members are LiNi_{1/2}Mn_{1/2}O_2 [13] and Li_2MnO_3 (Li[Li_{1/3}Mn_{2/3}])O_2. Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 used in this study is equivalent to Dahn’s notation with x = 1/5 and Thackeray’s notation with y = 1/2.

Among literatures there seem to be general agreements that (1) Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 consists of divalent nickel and tetravalent manganese ions in a cubic-close packed oxygen array forming a layered structure, (2) a long voltage plateau at 4.5 V is observed in the first charging process, which is irreversible, and (3) the material shows considerably greater rechargeable capacity compared to LiCoO_2. We agree with these observations as have been described in previous sections.

A long voltage plateau at 4.5 V is usually explained in terms of irreversible loss of oxygen [17] together with lithium removal evolving O_2 [33, 34] and reorganizing structure. According to a proposed mechanism [31], the electrochemical extraction of lithium from Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2 or alternatively 1/2Li_2MnO_3 •1/2LiNi_{1/2}Mn_{1/2}O_2 occurs in two steps, i.e.,
$$\frac{1}{2}\text{Li}_2\text{Mn}^{4+}\text{O}_3\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2$$

$$\rightarrow \frac{1}{2}\text{Li}_2\text{Mn}^{4+}\text{O}_3\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2 + \frac{1}{2}\text{Li}^+ + \frac{1}{2}\text{e}^- \quad (2)$$

and

$$\frac{1}{2}\text{Li}_2\text{Mn}^{4+}\text{O}_3\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2$$

$$\rightarrow \frac{1}{2}\text{Li}\text{Mn}^{3+}\text{O}_2\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2 + \text{Li}^+ + \frac{1}{4}\text{O}_2 + \text{e}^- \quad (3).$$

Reaction (2) is reversible in voltage below 4.5 V and reaction (3) is irreversible at 4.5 V plateau. The theoretical capacity calculated from equation (2) based on the sample weight is 126 mAh g$^{-1}$, which well agrees with experimental results in Figs. 2. 11 and 2. 13. The irreversible capacity due to reaction (3) is calculated to be 252 mAh g$^{-1}$ to form new active material of $\frac{1}{2}\text{Mn}^{4+}\text{O}_2\cdot\frac{1}{2}\text{Ni}^{4+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2$ in a long plateau at 4.5 V. The observed values range from 180 mAh g$^{-1}$ at room temperature in Fig. 2. 10 to 270 mAh g$^{-1}$ at 85°C in Fig. 2. 17. These values may be explained by the above argument based on equation (3) if possible side reactions above 4.5 V at high temperature are taken into account.

After first charging to 5 V, $\frac{1}{2}\text{Mn}^{4+}\text{O}_2\cdot\frac{1}{2}\text{Ni}^{4+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2$ is presumably new active material for subsequent cycles, i.e.,

$$\frac{1}{2}\text{Mn}^{4+}\text{O}_2\cdot\frac{1}{2}\text{Ni}^{4+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2 + \text{Li}^+ + \text{e}^-$$

$$\rightarrow \frac{1}{2}\text{Li}\text{Mn}^{3+}\text{O}_2\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2 \quad (4).$$

The rechargeable capacity calculated from equation (4) is 252 mAh g$^{-1}$ based on the weight of starting material of $\frac{1}{2}\text{Li}_2\text{Mn}^{4+}\text{O}_3\cdot\frac{1}{2}\text{Li}\text{Ni}^{2+}\frac{1}{2}\text{Mn}^{4+}\frac{1}{2}\text{O}_2$. Therefore, the first charging capacity is expected to be 378 mAh g$^{-1}$ and the rechargeable capacity is 252 mAh g$^{-1}$. In other words, the irreversible capacity is once observed to be 126 mAh g$^{-1}$ and then the rechargeable capacity of 252 mAh g$^{-1}$ is observed for the subsequent cycles. Our results, however, hardly support such a mechanism. So-called irreversible capacity observed is 70 mAh g$^{-1}$ at room temperature, as seen in Figs. 2. 10 and 2. 11, or 40 mAh g$^{-1}$ at 55°C in Figs. 2. 12 and 2. 13, which are too small compared to the expected irreversible capacity of 126 mAh g$^{-1}$. The irreversible capacity observed at 55°C is smaller than that at room temperature, suggesting that kinetic problems associated with lithium insertion
reactions involve in a system under consideration. In addition to the irreversible capacity, the rechargeable capacity is also deviated from the expected value of 252 mAh g\(^{-1}\) based on equation (4). The rechargeable capacity observed in this study is 230 mAh g\(^{-1}\) at room temperature, which may be explained because it is below the expected rechargeable capacity of 252 mAh g\(^{-1}\). However, the rechargeable capacities observed at 55 and 85°C are respectively 300 and 350 mAh g\(^{-1}\), which are larger than the expected value of 252 mAh g\(^{-1}\). The irreversible capacity smaller than 100 mAh g\(^{-1}\) and the rechargeable capacity larger than 250 mAh g\(^{-1}\) cannot be explained using equations (3) and (4).

Oxygen evolution in equation (3) supposedly occurs at the solid / electrolyte interface and consequently the surface composition changes reorganizing structure [31, 32]. Such a change in composition and structure at the solid / electrolyte interface reflects upon the electrode potential. Transition metal ions may diffuse from the surface to bulk, changing the surface composition and consequently the electrode potential. Such a kinetic process is sensitive to the previous electrode history. According to a results on window-opening experiments in Figs. 2.11 and 2.13, a 4.5 V plateau is insensitive to previous history. When charging voltage reaches 4.5 V, the voltage always stays at that value until a reaction at 4.5 V is completed. It should be noted here that the first charge and discharge curves in Figs. 2.10 and 2.12 superimpose upon circumscribed curves in Figs. 2.11 and 2.13, respectively. Then, question arises as to the irreversible loss of oxygen from Li[Li\(_{1/5}\)Ni\(_{1/5}\)Mn\(_{3/5}\)]\(_2\).O\(_2\).

The irreversible loss of oxygen is first proposed by Lu and Dahn [17] in their electrochemical and structural study of Li[Ni\(_x\)Li\(_{(1/3-2x/3)}\)Mn\(_{(2/3-x/3)}\)]\(_2\)O\(_2\) for x = 1/6, 1/4, 1/3, 5/12, and 1/2. To find one-to-one correspondence between electrochemical and structural data before and after a long voltage plateau, they use electrochemical data to calculate the composition of lithium ions in their samples, and then its composition is fixed in analyzing in-situ XRD results while oxygen positional parameter and the occupation of the oxygen ions are set to be variable. They find that the best fit is obtained when the occupation of the oxygen sites is below 100% for electrodes at 4.8 V, resulting in the description on the loss of oxygen. The ex-situ XRD results examined using Fe K\(_{\alpha}\)-radiation are consistent with their
observations. After first charge to 5 V, the lattice volume contracts below the original lattice volume. During subsequent charge and discharge, the lattice volume expands on discharge and contracts on charge. After the first cycle, the lattice volume is irreversibly expanded to larger value than that of original one. The a-axis shrinks on charge and elongates on discharge. The c-axis elongates on charge until it reaches a certain value and then shrinks a little. The reverse direction is on discharge. XRD observations are quite similar to those of LiCo$_x$Ni$_{1-x}$O$_2$ [35, 36]. As clearly seen in Figs. 2.4 and 2.7 combined with in-situ XRD observation in ref. 17, the electrochemical reactions of a series of Li[Ni$_x$Li$_{(1/3-2x/3)}$Mn$_{(2/3-x/3)}$]O$_2$ seemingly proceed in a topotactic manner. No dramatic change in XRD and neutron diffraction [33] and the voltage during charge and discharge monotonously changes as a function of the degree of reaction, so that the reactions are classified as homogeneous phase reaction or one-phase reaction under the framework of lithium insertion electrodes.

Flat operating voltage on first charge reminds us the case for LiVO$_2$ [37] or LT-LiMnO$_2$ [38-40]. The original crystal lattices are entirely destroyed at flat operation voltage, which is conventional two-phase reaction. LiVO$_2$ is converted to an inactive layered material and LiMnO$_2$ is converted to an ill-defined spinel phase, which is active for subsequent cycles with small irreversible capacity. Hysteresis loops observed during charge and discharge in Figs. 2.5, 2.8, 2.10, 2.12, and 2.13 are similar to that of ill-defined spinel phase derived from LiMnO$_2$ [38-41]. A hysteresis loop may be explained in terms of a kinetic effect, such as slow lithium diffusion and migration in a solid matrix. Such a slow process is usually accelerated when an electrode system is heated. However, a hysteresis loop observed at 55°C in Fig. 2.8 is larger than that at room temperature in Fig. 2.5. Therefore, a hysteresis loop observed in this study is not the same kind of kinetic problems. One needs to find another possible explanation for a series of mysterious phenomena observed for Li[Ni$_x$Li$_{(1/3-2x/3)}$Mn$_{(2/3-x/3)}$]O$_2$, especially Li[Li$_{1/5}$Ni$_{1/5}$Mn$_{3/5}$]O$_2$.

If one assumes penta-valent manganese ions surrounded by six or four oxygen ions, a solid state redox reaction of Mn$^{4+}$ / Mn$^{5+}$, specifically MnO$_6^{8-}$ / MnO$_6^{7-}$ or MnO$_6^{8-}$ / MnO$_4^{3-}$ in a local environment, may participate in the reaction under
consideration, i.e.,

$$\text{Li}[\text{Li}_{1/5}\text{Ni}^{2+}_{1/5}\text{Mn}^{4+}_{3/5}]\text{O}_2$$

$$\rightarrow \Box_{2/5} \text{Li}_{3/5}[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{4+}_{3/5}]\text{O}_2 + 2/5 e^- + 2/5 \text{Li}^+$$  \hspace{1cm} (5),

which is another expression of a reversible reaction (2), and then

$$\Box_{2/5} \text{Li}_{3/5}[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{4+}_{3/5}]\text{O}_2$$

$$\rightarrow \Box[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{5+}_{3/5}]\text{O}_2 + 3/5 e^- + 3/5 \text{Li}^+$$  \hspace{1cm} (6).

The theoretical capacities based on equations (5) and (6) are respectively 126 and 189 mAh g\(^{-1}\). Totally 315 mAh g\(^{-1}\) is expected for the one-electron transfer based on the original sample of Li[Li\(_{1/5}\)Ni\(_{2+}\)\(_{1/5}\)Mn\(_{4+}\)\(_{3/5}\)]O\(_2\). Further oxidation is possible if we assume the formation of Mn\(_{6+}\) surrounded by four oxygen ions, MnO\(_4^{2-}\), because lithium ions to be removed are available in equation (6). Then, an addition capacity is calculated to be 63 mAh g\(^{-1}\) by

$$\Box[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{5+}_{3/5}]\text{O}_2$$

$$\rightarrow \Box[\Box_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{5+}_{2/5}\text{Mn}^{6+}_{1/5}]\text{O}_2 + 1/5 e^- + 1/5 \text{Li}^+$$  \hspace{1cm} (7).

If we account for equation (7), totally 378 mAh g\(^{-1}\) is expected. Chemical species of manganese ions having higher oxidation number than 4+ are known as green manganate ions of MnO\(_4^{2-}\) and purple permanganate ion of MnO\(_4^{-}\). Blue manganese ion may be oxidation number of 5+ [42]. These species are observed in strong acid or base under an oxidative condition, such as concentrated H\(_2\)SO\(_4\) or KOH under O\(_2\).

Another possibility is an anion redox reaction in a solid matrix. If we assume a redox reaction of 2O\(^{2-}\) / O\(_2\)\(^{2-}\) substituting for equation (6), the reaction is represented by

$$\Box_{2/5}\text{Li}_{13/5}[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{4+}_{3/5}]\text{O}_2$$

$$\rightarrow \Box[\text{Li}_{1/5}\text{Ni}^{4+}_{1/5}\text{Mn}^{4+}_{3/5}] (2\text{O}^{2-})_{7/10}(\text{O}_2^{2-})_{3/10} + 3/5 e^- + 3/5 \text{Li}^+$$  \hspace{1cm} (8),

and it is further oxidized by
The theoretical capacities based on equations (8) and (9) are the same as previously calculated using equations (6) and (7) because the number of electrons transferred per a formula unit of \( \text{Li}_{1/5}\text{Ni}_{1/5}\text{Mn}_{3/5}\text{O}_2 \) is the same. Peroxide ions in a solid matrix are seen in \( \text{Na}_2\text{O}_2 \), which is a reaction product of sodium oxidation with dry oxygen, and also in \( \text{ZnO}_2 \) consisting of \( \text{Zn}^{2+} \) and \( \text{O}_2^{2-} \). They are stable in non-aqueous environment. An anion redox reaction in a solid matrix is not known for oxygen but known for sulfur. Pyrite \( \text{FeS}_2 \) consisting of \( \text{Fe}^{2+} \) and \( \text{S}_2^{2-} \) is reduced to \( \text{Li}_2\text{FeS}_2 \) consisting of \( \text{Li}^+ \), \( \text{Fe}^{2+} \) and \( 2\text{S}_2^{2-} \). The reaction is reversible. The theoretical capacity is calculated to be 447 mAh g\(^{-1}\), which is two times larger than that calculated for \( \text{LiMeS}_2 \leftrightarrow \text{□MeS}_2 + \text{Li}^+ + \text{e}^- \) because of two-electron redox reaction of anions, i.e., \( \text{S}_2^{2-} + 2 \text{e}^- \rightarrow 2\text{S}_2^{2-} \) [43].

The above arguments are based on “cation” or “anion” redox reaction in a solid matrix. This is exaggerated ionic character of each chemical species. Such an elementary step of reaction based on oxidation number does not hold in a solid-state redox reaction, as was discussed previously [5]. During an oxidation of \( \text{LiMeO}_2 \), electrons are removed from oxygen ions rearranging electron distribution between anions and cations, and consequently transition metal ions are sometimes reduced in spite of the oxidation of \( \text{LiMeO}_2 \). This makes the problem difficult to directly show which is probable, cation or anion redox reaction, by experiments.

2.4 Summary

In this chapter, high-capacity lithium nickel manganese dioxides are described. The layered material of \( \text{Li}[\text{Li}_{1/5}\text{Ni}_{1/5}\text{Mn}_{3/5}]\text{O}_2 \) potentially has the rechargeable capacity of 350 mAh g\(^{-1}\), which clearly exceeds a critical limit of 300 mAh g\(^{-1}\) with respect to the previous concept of lithium insertion materials based on a topotactic reaction of \( \text{LiMeO}_2 \leftrightarrow \text{Li}^+ + \text{e}^- + \text{□MeO}_2 \). Although the irreversible reaction at plateau voltage of 4.5 V observed at first charge is still a debatable subject, all of
experimental results can be explained in terms of lithium insertion materials. Understanding of solid-state chemistry and electrochemistry underlying such a high rechargeable capacity more than 300 mAh g\(^{-1}\) will open a new window toward an innovative concept on lithium insertion materials for advanced lithium-ion batteries. The experimental facts described in this chapter will help break through a conventional limit of concept on lithium insertion materials in near future.

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Chapter 3
High-Capacity Lithium Insertion Materials Examined under Upper-Voltage Constraint of 4.2 V against Lithium: Toward the Rechargeable Capacity of 200 mAh g⁻¹

3.1 Introduction

As has been described in General Introduction, highly crystallized materials are a preferable form for long-life high-capacity lithium-ion batteries. Although highly crystallized LiCoO₂ shows steady-state charge and discharge curves, rechargeable capacity is limited to the capacity below 145 mAh g⁻¹ under an upper voltage limit of 4.2 V. According to basic data on LiNiO₂, it should have larger rechargeable capacity than that of LiCoO₂ [1-3]. However, no one has succeeded to replace LiCoO₂ by LiNiO₂, because it is very difficult to prepare battery-active LiNiO₂ superior to LiCoO₂ in terms of all the aspects on battery performance. Many trials to extend the rechargeable capacity of a positive-electrode material have already been done, such as LiNiO₂ [1, 4, 5], LiCoₓNi₁₋ₓO₂ [6-10], LiAl₁/₄Ni₃/₄O₂ [11-13], LiCo₁/₃Ni₁/₃Mn₁/₃O₂ [14-21], LiNi₁/₂Mn₁/₂O₂ [22, 23], etc., in addition to the high-capacity lithium insertion materials described in Chapter 2. However, no material shows superior property to LiCoO₂ when the materials examine in voltage ranging from 2.5 to 4.2 V. In order to apply a new material substituting for LiCoO₂ in lithium-ion batteries, rechargeable capacity at least more than 175 mAh g⁻¹, hopefully 200 mAh g⁻¹, is required in an appropriate operating voltage under the same voltage constraint as imposed to the current lithium-ion batteries, i.e., upper voltage limit of 4.2 V.

In this chapter, a solid solution of LiNiO₂ and LiCoO₂ is re-examined in order to assess research results on a series of reports on LiNiO₂, LiCoO₂, and their mixture in a unit cell level. The synthetic methods to prepare battery-active lithium cobalt nickel oxides are optimized mainly at x = 1/4, 1/2, and 3/4 in LiCoₓNi₁₋ₓO₂ and the electrochemical reactivity in non-aqueous lithium cells is examined in a current method differed from that used in 1990s. New findings on high-capacity lithium insertion materials whose rechargeable capacities are
more than 200 mAh g\(^{-1}\) in voltage ranging from 2.5 to 4.2 V are also highlighted.

3.2 Experimental

3.2.1 Preparation of Solid Solution of LiNiO\(_2\) and LiCoO\(_2\)

LiNiO\(_2\) was prepared from LiNO\(_3\) (Kishida Chemical Co. Ltd., Japan) and NiCO\(_3\) (Kishida Chemical Co. Ltd., Japan). LiNO\(_3\) and NiCO\(_3\) were weighed to obtain about 3 g LiNiO\(_2\). Three-percent excess lithium, Li / Co = 1.03, was loaded to compensate for lithium loss during a preparation at high temperature in an electric furnace. The samples were mixed well with mortar and pestle and then dissolved in distilled water. After stirring, the solution was dried at 80°C for 12 h in air. The reaction mixture dried was pressed into pellets 23 mm dia. The pellets were preheated at 650°C for 5 h in O\(_2\) and then cooled to room temperature. The pellets were crushed into powder and pressed into pellets 23 mm dia. again. The pellets were heated at several temperatures for 12 h in O\(_2\) and then cooled to room temperature. Heating and cooling rates were approximately 4 and 5 °C min\(^{-1}\), respectively.

LiCo\(_x\)Ni\(_{1-x}\)O\(_2\) (\(1/4 \leq x \leq 3/4\)) were prepared from LiNO\(_3\) (Kishida Chemical Co. Ltd., Japan), CoCO\(_3\) (Wako Pure Chemical Industries, Ltd., Japan), and NiCO\(_3\) (Kishida Chemical Co. Ltd., Japan), in which NiCO\(_3\) is a basic nickel carbonate (2NiCO\(_3\) 3Ni(OH)\(_2\) 4H\(_2\)O). LiNO\(_3\), CoCO\(_3\), and NiCO\(_3\) were weighed to obtain about 3 g LiCo\(_x\)Ni\(_{1-x}\)O\(_2\) (\(1/4 \leq x \leq 3/4\)) as a final reaction product. Three-percent excess lithium, Li / Co = 1.03, was loaded to compensate for lithium loss. The samples were mixed well with mortar and pestle and then the reaction mixture was pressed into pellets 23 mm dia. The pellets were preheated at 650°C for 5 h in O\(_2\) and then cooled to room temperature. The pellets were crushed into powder and again pressed into pellets 23 mm dia. The pellets were heated at several temperatures ranging from 700 to 1050 °C for 12 h in O\(_2\) and then cooled to room temperature. All the reaction products were crushed into powder and stored in a desiccator over blue silica-gel before use.

3.2.2 Characterization of lithium cobalt nickel oxides
The samples of lithium cobalt nickel oxides were characterized by XRD, Fourier-transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM), and examined in non-aqueous lithium cells. The characterization techniques are the same methods as have already been described in Section 2.2. The other sets of experimental conditions are given in results and discussion section.

3.3 Results and Discussion

3.3.1 Characterization of LiNiO₂

Figure 3.1 shows the XRD patterns of LiNiO₂ prepared by heating at several temperatures ranging from 750 to 900°C. All the diffraction lines are identified as a layered structure with space group symmetry of R̅3m [1]. As seen in Fig. 3.1, all samples show well-defined diffraction lines. Of these, LiNiO₂ prepared by heating the reaction mixture at 750°C in an oxygen stream shows a clear split of diffraction lines due to Kα₁ and Kα₂. In other words, LiNiO₂ is prepared in the large crystallite size when the sample is prepared at 750°C. The hexagonal lattice parameters are determined by a least squares method using 10 diffraction lines. The a-axis and c-axis dimensions correspond to metal-metal and inter-layer distance, respectively, so that the ratio of c to a is a parameter to characterize a layer structure. Cubic lattice parameter (aₜ) can be converted to hexagonal lattice parameter (aₕ and cₕ) by using the equations of

\[ aₕ = \frac{1}{\sqrt{2}} \times aₜ, \quad \text{and} \quad cₕ = 2\sqrt{3} \times aₜ. \]

Consequently, \( cₕ / aₕ = 4.90 \) is geometrically equivalent to a cubic lattice. When LiNiO₂ is prepared at higher temperature than 750°C, the value of \( cₕ / aₕ \) approaches 4.90, i.e., 4.933 at 750°C, 4.929 at 800°C, 4.927 at 850°C, and 4.920 at 900°C, suggesting that LiNiO₂ prepared at higher temperature than 750°C approaches cubic, which agrees with the previous results reported [1, 4, 5].

Figure 3.2 shows particle morphology observed by SEM for LiNiO₂ prepared at 750, 775, 800, and 900°C. The samples of LiNiO₂ prepared at 750 or 775°C show finely grained particles with ca. 1 μm of particle size without any crystal habits in their particle morphology. Particle morphology of LiNiO₂ prepared at 900°C is obviously once melted, whose secondary
particle is more than 50 µm in size. Particle morphology observed for LiNiO₂ is quite different from that for LiCoO₂ briefly highlighted in general Introduction. Ideal structures of LiCoO₂ and LiNiO₂ are the same as those classified as α-NaFeO₂-structural type [1, 2], so that they crystallize as a graphite-like layer structure with smooth (0001) facets as seen in Fig. 2(d) in General Introduction. It should be noted that a maximum crystallite size can be determined by XRD is 0.1 µm, which is a fine particle size in a sub-micron scale for particle morphology observed by SEM.

![XRD patterns of LiNiO₂](image)

Fig. 3. 1 XRD patterns of LiNiO₂ prepared by heating a reaction mixture of LiNO₃ and NiCO₃ at 650°C for 5 h in O₂ and then at (a) 750, (b) 775, (c) 800, (d) 850, and (e) 900°C for 12 h in O₂. These samples were identified as a layered structure with space group symmetry of R3m. The hexagonal lattice parameters determined by a least squares method using 10 diffraction lines are (a) \( a = 2.878 \) Å, \( c = 14.198 \) Å, (b) \( a = 2.878 \) Å, \( c = 14.188 \) Å, (c) \( a = 2.875 \) Å, \( c = 14.172 \) Å, (d) \( a = 2.882 \) Å, \( c = 14.200 \) Å, and (e) \( a = 2.890 \) Å, \( c = 14.219 \) Å.
Fig. 3. 2 Particle morphology observed by SEM for LiNiO₂ prepared by heating a reaction mixture of LiNO₃ and NiCO₃ at 650°C for 5 h in O₂ and at (a) 750, (b) 775, (c) 800, and (d) 900°C for 12 h in O₂.

Figure 3. 3 shows the FT-IR spectra of LiNiO₂ prepared by heating at temperatures ranging from 750 to 900°C. Infrared spectra are sensitive to the local environment of oxygen coordination around the transition metal ions in a solid matrix. As seen in Fig. 3. 3, two absorption bands are observed for LiNiO₂ prepared at temperature below 775°C. Two absorption bands, however, are not clearly split for LiNiO₂ prepared at higher temperature than 800 °C, forming a broad band. Absorption bands at about 850, 1440, and 1500 cm⁻¹ probably derived from Li₂CO₃ became apparent as heating temperature to prepare LiNiO₂ rises, which are not observed for LiCoO₂ [8]. The absorption bands at about 1500, 1440, and 850 cm⁻¹ are characteristic of LiNiO₂.

As has been described above, LiNiO₂ prepared at 750°C is characterized by well-defined diffraction lines in XRD, finely grained primary particles by SEM, and well-defined two absorption bands at ca. 500 and 560 cm⁻¹ in FT-IR.
3. 3. 2 Electrochemical reactivity of LiNiO₂ in non-aqueous lithium cells

Figure 3. 4 shows the charge and discharge curves of Li / LiNiO₂ cells operated at a rate of 0.17 mA cm⁻² in voltage ranging from 2.6 to 4.2 V at room temperature. The samples of LiNiO₂ tested are the same as those in Figs. 3. 1 to 3. 3. The first charge capacity of LiNiO₂ prepared at 750°C is 225 mAh g⁻¹ based on the weight of sample while that prepared at 900°C is 140 mAh g⁻¹. The sample prepared at 775°C shows the smallest irreversible capacity while its rechargeable capacity is smaller than that prepared at 750°C because the first charge capacity is 200 mAh g⁻¹. As clearly seen in Fig. 3. 4, the samples of LiNiO₂
prepared at temperature ranging from 750 to 900ºC are characterized in the charge and discharge curves in terms of the irreversible capacity, the rechargeable capacity, and polarization. The irreversible capacity is the difference between the first charge capacity and discharge capacity. As seen in Fig. 3.4, the irreversible capacity is 40 mAh g⁻¹ for the sample prepared at 750ºC, and it is 70 mAh g⁻¹ at 900ºC. Higher heating temperature gives larger irreversible capacity. The smallest irreversible capacity is observed to be 30 mAh g⁻¹ for the sample prepared at 775 ºC.

![Graph of charge and discharge curves](image)

Fig. 3.4 Charge and discharge curves of the Li / LiNiO₂ cells operated at a rate of 0.17 mA cm⁻² in voltage of 2.6 to 4.2 V. The samples are prepared by heating a reaction mixture of LiNO₃ and NiCO₃ at 650ºC for 5 h in O₂ and then at (a) 750, (b) 775, (c) 800, (d) 850, and (e) 900ºC for 12 h in O₂.
The rechargeable capacity is simply the discharge capacity when the sample is cycled well in non-aqueous lithium cells. Figure 3.5 shows the discharge capacity together with “polarization” as a function of temperature at which LiNiO$_2$ is prepared. The term of polarization is generally defined as the difference between the electrode potential at finite current and the zero current potential in electrochemistry [24]. The “polarization” in this chapter is defined as the voltage difference between charge and discharge at 50 and 100 mAh g$^{-1}$ of charge capacity at the fifth cycle in order to evaluate a series of samples in terms of polarization. As seen in Fig. 3.5, the discharge capacity decreases with increasing heating temperature to prepare LiNiO$_2$. When heating temperature rises from 750 to 900°C, the discharge capacity dramatically decreases from ca. 175 mAh g$^{-1}$ to 55 mAh g$^{-1}$ together with an increase in polarization from ca. 45 to 315 mV, indicating that the optimum temperature to prepare the battery-active LiNiO$_2$ is 750°C as has already been reported in 1991-1993 [1, 25, 26]. In contrast to LiCoO$_2$, high temperature synthesis of LiNiO$_2$ does not give good results in terms of polarization, irreversible capacity, and rechargeable capacity.

Fig. 3.5 Summary in terms of (a) rechargeable capacity together with (b) polarization observed for LiNiO$_2$ as a function of heating temperatures to prepare LiNiO$_2$. The Li / LiNiO$_2$ cells are examined at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. Discharge capacity observed for 5 cycles is shown, i.e., rechargeable capacity. The polarization was defined by the voltage difference between charge and discharge at 50 mAh g$^{-1}$ (closed triangles) and 100 mAh g$^{-1}$ (open triangles) of charge capacity at the 5th cycle.
3.3.3 Characterization of LiCo$_{1/4}$Ni$_{3/4}$O$_2$, LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and LiCo$_{3/4}$Ni$_{1/4}$O$_2$

It is well known that LiCoO$_2$ and LiNiO$_2$ form a solid solution in an entire range [8]. In order to examine whether or not a series of solid solution is properly prepared, LiCo$_{3/4}$Ni$_{1/4}$O$_2$, LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and LiCo$_{1/4}$Ni$_{3/4}$O$_2$ are prepared at temperature ranging from 750 to 1000ºC. All the samples prepared are identified as a layered structure with space group symmetry of R3m, so that the XRD patterns are identical with those of LiCoO$_2$ in Fig. 1 or LiNiO$_2$ in Fig. 3.1. The hexagonal lattice parameters obtained by a least squares method using 10 or 11 diffraction lines are summarized in Table 3.1 for LiCo$_{3/4}$Ni$_{1/4}$O$_2$, Table 3.2 for LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and Table 3.3 for LiCo$_{1/4}$Ni$_{3/4}$O$_2$. The hexagonal lattice parameters of each sample are almost the same regardless of heating temperatures to prepare the samples except LiCo$_{1/2}$Ni$_{1/2}$O$_2$ prepared at 1000ºC. LiCo$_{1/2}$Ni$_{1/2}$O$_2$ prepared at 1000ºC shows larger c-axis dimension compared to that prepared at lower temperature.

**Table 3.1** The hexagonal lattice parameters for LiCo$_{3/4}$Ni$_{1/4}$O$_2$ prepared at temperatures ranging from 750 to 900ºC.

<table>
<thead>
<tr>
<th>Heating temperature / ºC</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>875</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal lattice parameters</td>
<td>a / Å</td>
<td>2.819</td>
<td>2.821</td>
<td>2.825</td>
<td>2.827</td>
</tr>
</tbody>
</table>

**Table 3.2** The hexagonal lattice parameters for LiCo$_{1/2}$Ni$_{1/2}$O$_2$ prepared at temperatures ranging from 750 to 1000ºC.

<table>
<thead>
<tr>
<th>Heating temperature / ºC</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>875</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal lattice parameters</td>
<td>a / Å</td>
<td>2.847</td>
<td>2.840</td>
<td>2.843</td>
<td>2.845</td>
<td>2.845</td>
</tr>
</tbody>
</table>

**Table 3.3** The hexagonal lattice parameters for LiCo$_{1/4}$Ni$_{3/4}$O$_2$ prepared at temperature ranging from 750 to 900ºC.

<table>
<thead>
<tr>
<th>Heating temperature / ºC</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal lattice parameters</td>
<td>a / Å</td>
<td>2.860</td>
<td>2.860</td>
<td>2.860</td>
</tr>
</tbody>
</table>
Fig. 3.6 Charge and discharge curves of lithium cells with (a) LiCo$_{3/4}$Ni$_{1/4}$O$_2$, (b) LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and (c) LiCo$_{1/4}$Ni$_{3/4}$O$_2$ prepared by heating a reaction mixture of LiNO$_3$, CoCO$_3$, and NiCO$_3$ at 650°C for 5 h in O$_2$ and then at temperature described in the figure for 12 h in O$_2$. The cells are operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. The 1st to 5th cycles are shown in figures.
Fig. 3. Summary on the rechargeable capacity together with irreversible capacity for (a) LiCo_{0.4}Ni_{0.6}O_2, (b) LiCo_{0.5}Ni_{0.5}O_2, and (c) LiCo_{0.25}Ni_{0.75}O_2 as a function of heating temperatures. The cells are operated at a rate of 0.17 mA cm^{-2} in voltage of 2.6 to 4.2 V. The 1st to 5th cycles are shown in figures.
Figure 3.6 shows the charge and discharge curves of LiCo$_{3/4}$Ni$_{1/4}$O$_2$, LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and LiCo$_{1/4}$Ni$_{3/4}$O$_2$ examined in non-aqueous lithium cells. The cells are operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V at room temperature. LiCo$_{3/4}$Ni$_{1/4}$O$_2$ shows ca. 150 mAh g$^{-1}$ of the first charge capacity regardless of the synthesis temperature. Irreversible capacity of LiCo$_{3/4}$Ni$_{1/4}$O$_2$ decreases as heating temperature rises from 750ºC to 875ºC. However, the irreversible capacity of LiCo$_{3/4}$Ni$_{1/4}$O$_2$ prepared at 900ºC is larger than that of the sample prepared at temperature below 875ºC. As seen in Fig. 3.6, LiCo$_{3/4}$Ni$_{1/4}$O$_2$ prepared at 875ºC is the best among samples prepared at temperature ranging from 750 to 900ºC. Similarly, LiCo$_{1/2}$Ni$_{1/2}$O$_2$ prepared at 825ºC and LiCo$_{1/4}$Ni$_{3/4}$O$_2$ prepared at 800ºC are better than other samples. This is better illustrated in Fig. 3.7. Relation between the irreversible capacity and rechargeable capacity can be seen for LiCo$_{3/4}$Ni$_{1/4}$O$_2$, LiCo$_{1/2}$Ni$_{1/2}$O$_2$, and LiCo$_{1/4}$Ni$_{3/4}$O$_2$. Both appear to be parabolic curves in the discharge capacity or irreversible capacity vs. heating temperature plots. Maximum discharge capacity is always observed at the minimum irreversible capacity, so that the optimum temperature can be determined from Fig. 3.7. The optimum temperature determined is 875ºC for LiCo$_{3/4}$Ni$_{1/4}$O$_2$, 825ºC for LiCo$_{1/2}$Ni$_{1/2}$O$_2$, or 800ºC for LiCo$_{1/4}$Ni$_{3/4}$O$_2$, which are visually inspected from Fig. 3.6. The rechargeable capacity of the sample prepared at the optimum temperature is 140 mAh g$^{-1}$ for LiCo$_{3/4}$Ni$_{1/4}$O$_2$, 160 mAh g$^{-1}$ for LiCo$_{1/2}$Ni$_{1/2}$O$_2$, or 180 mAh g$^{-1}$ for LiCo$_{1/4}$Ni$_{3/4}$O$_2$. Because the rechargeable capacity of highly crystallized LiCoO$_2$ is 140 mAh g$^{-1}$ and the potential curves ranges from 3.9 to 4.2 V, LiCo$_{3/4}$Ni$_{1/4}$O$_2$ and LiCo$_{1/2}$Ni$_{1/2}$O$_2$ are less attractive compared to LiCo$_{1/4}$Ni$_{3/4}$O$_2$ showing the rechargeable capacity more than 175 mAh g$^{-1}$. Particle morphology of these samples is shown in Figs. 3.8 to 3.10. General observation is the same as that for either LiNiO$_2$ or LiCoO$_2$. LiCo$_{3/4}$Ni$_{1/4}$O$_2$ and LiCo$_{1/2}$Ni$_{1/2}$O$_2$ show a crystal habit of a layered structure in their particle morphology when the samples are prepared at 850ºC, 875ºC, and 900ºC, as seen in Fig. 3.8 (d) and Fig. 3.9 (d), & (e). However, when LiCo$_{1/2}$Ni$_{1/2}$O$_2$ is prepared at 1000ºC, particles are seemingly once melted and developed their particle size more than 10 µm as observed for LiNiO$_2$ prepared at temperature above 800ºC in Fig. 3.2. Similarly, the particles of LiCo$_{1/4}$Ni$_{3/4}$O$_2$ shown in Fig. 3.10 are seemingly once melted and they show large particle size when LiCo$_{1/4}$Ni$_{3/4}$O$_2$ is prepared at temperature above 850ºC.

As have been described above, the character of LiCo$_{3/4}$Ni$_{1/4}$O$_2$ is closely related to LiCoO$_2$, and LiCo$_{1/4}$Ni$_{3/4}$O$_2$ resembles LiNiO$_2$. LiCo$_{1/2}$Ni$_{1/2}$O$_2$ is one-to-one mixture of
LiNiO$_2$ and LiCoO$_2$ in a unit cell level, so that the character of LiCo$_{1/2}$Ni$_{1/2}$O$_2$ comes from both LiNiO$_2$ and LiCoO$_2$. Consequently, the optimum temperature to prepare LiCo$_x$Ni$_{1-x}$O$_2$ shifts from 750ºC for LiNiO$_2$ to 1000ºC for LiCoO$_2$. The optimum temperature determined to prepare the battery-active LiCo$_x$Ni$_{1-x}$O$_2$ is summarized in Table 3.4.

Table 3.4 The summary of the optimum temperature determined to prepare LiCo$_x$Ni$_{1-x}$O$_2$

<table>
<thead>
<tr>
<th>x in LiCo$_{1-x}$Ni$_x$O$_2$</th>
<th>0</th>
<th>1/4</th>
<th>1/2</th>
<th>3/4</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>LiCoO$_2$</td>
<td>LiCo$<em>{3/4}$Ni$</em>{1/4}$O$_2$</td>
<td>LiCo$<em>{1/2}$Ni$</em>{1/2}$O$_2$</td>
<td>LiCo$<em>{1/4}$Ni$</em>{3/4}$O$_2$</td>
<td>LiNiO$_2$</td>
</tr>
<tr>
<td>Optimum temperature / ºC</td>
<td>1000</td>
<td>875</td>
<td>825</td>
<td>800</td>
<td>750</td>
</tr>
</tbody>
</table>

Fig. 3.8 Particle morphology observed by SEM for LiCo$_{3/4}$Ni$_{1/4}$O$_2$ prepared by heating a reaction mixture of LiNO$_3$, CoCO$_3$, and NiCO$_3$ at 650ºC for 5 h in O$_2$ and then at (a) 750, (b) 800, (c) 850, and (d) 875ºC for 12 h in O$_2$. 
Fig. 3. 9  Particle morphology observed by SEM for LiCo$_{1/2}$Ni$_{1/2}$O$_2$ prepared by heating a reaction mixture of LiNO$_3$, CoCO$_3$, and NiCO$_3$ at 650°C for 5 h in O$_2$ and then at (a) 750, (b) 800, (c) 825, (d) 850, (e) 900, and (f) 1000°C for 12 h in O$_2$.

Fig. 3. 10  Particle morphology observed by SEM for LiCo$_{1/4}$Ni$_{3/4}$O$_2$ prepared by heating a reaction mixture of LiNO$_3$, CoCO$_3$, and NiCO$_3$ at 650°C for 5 h in O$_2$ and then at (a) 750, (b) 800, (c) 850, and (d) 900°C for 12 h in O$_2$. 
3. 3. 4 Detailed examinations of LiCo$_x$Ni$_{1-x}$O$_2$ with $x$ ranging from 0 to 1

Table 3. 5 summarizes the structural and electrochemical properties of LiCo$_x$Ni$_{1-x}$O$_2$ for totally 13 samples for $x$ ranging from 0 to 1, prepared at approximately optimum temperature. All the samples are examined in lithium cells at room temperature. The rechargeable capacity is determined in voltage ranging from 2.6 to 4.2 V. As seen in Table 3. 5, some of these samples show the rechargeable capacity of over 175 mAh g$^{-1}$ for $x$ ranging from 0 to 1/4 in LiCo$_x$Ni$_{1-x}$O$_2$. Of these, the rechargeable capacity of more than 200 mAh g$^{-1}$ is observed in a limiting composition of $x$ ranging from 0.05 to 0.1, which is quite attractive in considering high energy density lithium-ion batteries as will be discussed in a latter section.

<table>
<thead>
<tr>
<th>x</th>
<th>Optimum temp. ºC</th>
<th>Lattice parameters Å</th>
<th>1st charge capacity mAh g$^{-1}$</th>
<th>1st irreversible capacity mAh g$^{-1}$</th>
<th>5th discharge capacity mAh g$^{-1}$</th>
<th>polarization at 50 mAh g$^{-1}$ mV</th>
<th>polarization at 100 mAh g$^{-1}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000</td>
<td>a = 2.816, c = 14.058</td>
<td>141</td>
<td>2</td>
<td>142</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>0.95</td>
<td>900</td>
<td>a = 2.818, c = 14.059</td>
<td>144</td>
<td>9</td>
<td>134</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>0.9</td>
<td>900</td>
<td>a = 2.820, c = 14.065</td>
<td>144</td>
<td>7</td>
<td>134</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>0.75</td>
<td>875</td>
<td>a = 2.827, c = 14.088</td>
<td>147</td>
<td>3</td>
<td>142</td>
<td>41</td>
<td>20</td>
</tr>
<tr>
<td>0.67</td>
<td>850</td>
<td>a = 2.833, c = 14.102</td>
<td>149</td>
<td>5</td>
<td>143</td>
<td>42</td>
<td>27</td>
</tr>
<tr>
<td>0.5</td>
<td>825</td>
<td>a = 2.843, c = 14.113</td>
<td>161</td>
<td>3</td>
<td>153</td>
<td>37</td>
<td>31</td>
</tr>
<tr>
<td>0.33</td>
<td>800</td>
<td>a = 2.855, c = 14.147</td>
<td>180</td>
<td>7</td>
<td>173</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>0.25</td>
<td>800</td>
<td>a = 2.860, c = 14.150</td>
<td>194</td>
<td>13</td>
<td>178</td>
<td>43</td>
<td>31</td>
</tr>
<tr>
<td>0.2</td>
<td>750</td>
<td>a = 2.864, c = 14.160</td>
<td>198</td>
<td>19</td>
<td>181</td>
<td>30</td>
<td>21</td>
</tr>
<tr>
<td>0.15</td>
<td>750</td>
<td>a = 2.868, c = 14.170</td>
<td>206</td>
<td>30</td>
<td>184</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>0.1</td>
<td>750</td>
<td>a = 2.872, c = 14.181</td>
<td>221</td>
<td>20</td>
<td>208</td>
<td>26</td>
<td>21</td>
</tr>
<tr>
<td>0.05</td>
<td>750</td>
<td>a = 2.875, c = 14.186</td>
<td>230</td>
<td>19</td>
<td>211</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>0</td>
<td>750</td>
<td>a = 2.878, c = 14.198</td>
<td>217</td>
<td>40</td>
<td>176</td>
<td>47</td>
<td>43</td>
</tr>
</tbody>
</table>
Figure 3. 11 shows the hexagonal lattice parameters as a function of x in LiCo_{x}Ni_{1-x}O_{2}. The hexagonal lattice parameters, a_h and c_h, linearly increase as x in LiCo_{x}Ni_{1-x}O_{2} decreases from x = 1 for LiCoO_{2} to x = 0 for LiNiO_{2}, indicating that LiCo_{x}Ni_{1-x}O_{2} is a solid solution of LiCoO_{2} and LiNiO_{2} in an entire range, as has already been described [8] and widely accepted in academic community associated with lithium-ion batteries. Figure 3. 12 shows the particle morphology observed by SEM for a series of samples listed in Table 3. 5. The primary particles become smaller in their sizes from LiCoO_{2} to LiNiO_{2}. This is because the optimum temperature shifts toward lower temperature from 1000°C for LiCoO_{2} to 750 °C for LiNiO_{2}. Primary particle sizes for LiCo_{x}Ni_{1-x}O_{2} prepared at 750°C with x = 0 to 0.05 are less than 1 µm without any crystal habit while those for LiCoO_{2} prepared at 1000°C are larger than 5 µm with smooth (0001) facets, strongly depend on heating temperature and chemistry of materials.

![Graph showing hexagonal lattice parameters](image)

**Fig. 3. 11** The hexagonal lattice parameters as a function of x in LiCo_{x}Ni_{1-x}O_{2} prepared at the optimum temperatures.
3. 3. 5 Rechargeable capacity of more than 200 mAh g\(^{-1}\) under upper-voltage constraint of 4.2 V

As has been described in the previous section, LiCo\(_{0.05}\)Ni\(_{0.95}\)O\(_2\) and LiCo\(_{0.1}\)Ni\(_{0.9}\)O\(_2\) prepared at optimum temperature of 750ºC show the rechargeable capacity of above 200 mAh g\(^{-1}\) in non-aqueous lithium cells, examined in voltage ranging from 2.6 to 4.2 V. The potential profile is similar to those for a series of samples as has already shown in Fig. 3. 6.
Figure 3. 13 illustrates the first charge capacity together with the irreversible capacity as a function of \( x \) in LiCo\(_x\)Ni\(_{1-x}\)O\(_2\) prepared at optimum temperature. The first charge capacity increases from 140 to 220 mAh g\(^{-1}\) as \( x \) decreases from 1 to 0.05. Similarly, the irreversible capacity increases from a negligibly small value to 20 mAh g\(^{-1}\) or more as the composition continuously changes from LiCoO\(_2\) to LiNiO\(_2\). The irreversible capacity described above is calculated from the first charge and discharge capacity. Although an origin of the irreversible capacity is not known and still debatable subject, it is evident that the irreversible capacity depends on the nickel content in the samples. The irreversible capacity is less than 10 mAh g\(^{-1}\) for a LiCoO\(_2\)-rich region in Fig. 3. 13 while it is \textit{ca.} 20 mAh g\(^{-1}\) or more in a LiNiO\(_2\)-rich region. Of these, LiNiO\(_2\) shows the largest irreversible capacity of \textit{ca.} 40 mAh g\(^{-1}\) among a series of LiCo\(_x\)Ni\(_{1-x}\)O\(_2\).

Minimizing the irreversible capacity is important in applying lithium insertion materials to lithium-ion batteries. However, the most important character is the rechargeable
capacity and the second is polarization. In order to evaluate these characters for a series of LiCo$_x$Ni$_{1-x}$O$_2$, the rechargeable capacity together with polarization as a function of $x$ in LiCo$_x$Ni$_{1-x}$O$_2$ is shown in Fig. 3.14. Polarization in mV is obtained in the same manner as described in section 3.3.2. As clearly seen in Fig. 3.14, the rechargeable capacity is showing a tendency to increase from 140 mAh g$^{-1}$ for LiCoO$_2$ to 210 mAh g$^{-1}$ for LiCo$_{0.05}$Ni$_{0.95}$O$_2$. In other words, the rechargeable capacity of LiCo$_{0.05}$Ni$_{0.95}$O$_2$ or LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is 1.5 times larger than that of LiCoO$_2$. The polarization for LiCo$_{0.05}$Ni$_{0.95}$O$_2$ or LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is almost the same as that for LiCoO$_2$. Lithium nickel oxide of LiNiO$_2$ appears to be less active than LiCo$_{0.05}$Ni$_{0.95}$O$_2$ or LiCo$_{0.1}$Ni$_{0.9}$O$_2$. This is because the battery-active LiNiO$_2$ is still difficult to prepare in a highly crystallized form, as have been discussed by several authors [1, 4, 5]. From these results, LiCo$_{0.05-0.10}$Ni$_{0.90-0.95}$O$_2$ is selected as a possible alternative to LiCoO$_2$ for high energy density lithium-ion batteries.

![Graph](image)

Fig. 3.14 Summary on (a) dischargeable capacity and (b) polarization observed for the Li / LiCo$_x$Ni$_{1-x}$O$_2$ cells operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. The samples are prepared at the optimum temperatures. The polarization is determined at 50 mAh g$^{-1}$ (closed triangles) and 100 mAh g$^{-1}$ (open triangles) of charge capacity at the 5th cycle.
3.3.6 Electrochemical behavior of LiCo_{0.1}Ni_{0.9}O_{2} in non-aqueous lithium cells

In the previous section, the possibility of high-capacity lithium insertion materials is described. As seen in Figs. 3.4 and 3.6, the potential profile for a series of LiCo_{x}Ni_{1-x}O_{2} does not show any dramatic change. In order to examine what is the difference among LiCo_{0.2}Ni_{0.8}O_{2}, LiCo_{0.1}Ni_{0.9}O_{2}, and LiNiO_{2} in terms of the solid state redox reactions, the differential chronopotentiograms are calculated from the charge and discharge curves and shown in Fig. 3.15. The solid-state redox reaction of LiNiO_{2} consists of four redox couples characterized by 3.65, 3.78, 3.99, and 4.20 V of the mid potential between anodic and cathodic peaks, as seen in Fig. 3.15(c). Because Li / LiNiO_{2} cells cannot be cycled well in voltage ranging from 2.6 to 4.3 V, they are cycled in voltage ranging from 2.6 to 4.2 V, so that the well-defined redox peaks do not show up at 4.20 V. The Li / LiCo_{0.1}Ni_{1.9}O_{2} and Li/LiCo_{0.2}Ni_{0.8}O_{2} cells are cycled well in voltage ranging from 2.6 to 4.3 V. Consequently, the redox peaks at about 4.2 V are clearly observed as seen in Fig. 3.15(a). As seen in Fig. 3.15(b), the redox couple at 3.99 V does not change when it compares with that for LiNiO_{2} while the redox couples at 4.16 and 3.53 V seemingly move toward cathodic direction by ca. 50 and 100 mV, respectively, when an amount of 10 atomic percent cobalt is dissolved in LiNiO_{2}, i.e., LiCo_{0.1}Ni_{0.9}O_{2}. The redox couple at 3.78 V for LiNiO_{2} changes its shape to a broad peak or ill-defined redox peaks characterized by 3.65 and 3.73 V for LiCo_{0.1}Ni_{0.9}O_{2}. For LiCo_{0.2}Ni_{0.8}O_{2}, all the peaks are rounded or broad compared to those for LiCo_{0.1}Ni_{0.9}O_{2}. From these observations, it is evident that the rechargeable capacity of more than 200 mAh g^{-1} is derived from the participation of the redox reaction characterized by 4.16 V in Fig. 3.15(b).

In order to examine whether or not the material of LiCo_{0.1}Ni_{0.9}O_{2} is stably cycled in a non-aqueous lithium cell in voltage ranging from 2.6 to 4.2 V, a Li / LiCo_{0.1}Ni_{0.9}O_{2} cell is fabricated and its cycle-ability is examined. Figure 3.16 shows the charge and discharge curves of a Li/ LiCo_{0.1}Ni_{0.9}O_{2} cell examined at a rate of 0.17 mA cm^{-2}. On charge the constant current of 0.17 mA cm^{-2} is applied to the cell until the terminal voltage reaches 4.2 V and then the constant voltage of 4.2 V is imposed to the cell for 12 h. After charging, the cell is discharged at the constant current of 0.17 mA cm^{-2} to 2.6 V, which is repeated 30 times. As clearly seen in Fig. 3.16, LiCo_{0.1}Ni_{0.9}O_{2} shows more than 200 mAh g^{-1} of rechargeable capacity and it stably cycles for 30 cycles.
Fig. 3. 15  Differential chronopotentiograms calculated from the second cycle of charge and discharge curves of (a) LiCo$_{0.2}$Ni$_{0.8}$O$_2$, (b) LiCo$_{0.1}$Ni$_{0.9}$O$_2$, and (c) LiNiO$_2$ in non-aqueous lithium cells. The Li / LiNiO$_2$ cell is examine in voltage ranging from 2.6 to 4.2 V while other cells are examined in voltage ranging from 2.6 to 4.3 V at a rate of 0.17 mA cm$^{-2}$.

Fig. 3. 16  Charge and discharge curves of a Li / LiCo$_{0.1}$Ni$_{0.9}$O$_2$ cell. The cell is charged to 4.2 V at a rate of 0.17 mA cm$^{-2}$ then kept at that voltage for 12 h, so called a CCCV-charging mode. After charging, the cell is discharged at 0.17 mA cm$^{-2}$ to 2.6 V. Discharge capacities as a function of cycle number are also shown in the inset.
Figure 3. 17 shows the charge and discharge curve of a Li / LiCo$_{0.1}$Ni$_{0.9}$O$_2$ cell together with that of a Li / LiCoO$_2$ cell. Both are operated at 0.17 mA cm$^{-2}$ in voltage ranging from 2.6 to 4.2 V at room temperature. Although the operating voltage of a Li / LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is slightly lower than that of a Li / LiCoO$_2$ cell, the rechargeable capacity of LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is 1.5 times larger than that of LiCoO$_2$. Table 3. 6 summarizes the energy density calculated for LiCoO$_2$ and LiCo$_{0.1}$Ni$_{0.9}$O$_2$. The XRD density of LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is smaller than that of LiCoO$_2$. The average voltage is also lower than that of LiCoO$_2$. However, the gravimetric and volumetric energy densities of LiCo$_{0.1}$Ni$_{0.9}$O$_2$ are calculated to exceed that of LiCoO$_2$ because of rechargeable capacity as described above. Consequently, the energy density of a lithium-ion battery consisting of LiCo$_{0.1}$Ni$_{0.9}$O$_2$ and graphite should be larger than that of LiCoO$_2$ and graphite.

![Charge and discharge curves of (a) Li / LiCo$_{0.1}$Ni$_{0.9}$O$_2$ cell and (b) Li / LiCoO$_2$ cell. The cells are operated at a rate of 0.17 mA cm$^{-2}$ in voltage of 2.6 to 4.2 V. The 2nd to 5th cycles are shown in figures.](image)
Table 3.6  Comparison between LiCoO$_2$ and LiCo$_{0.1}$Ni$_{0.9}$O

<table>
<thead>
<tr>
<th></th>
<th>LiCoO$_2$</th>
<th>LiCo$<em>{0.1}$Ni$</em>{0.9}$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD Density g cm$^{-3}$</td>
<td>5.06</td>
<td>4.80</td>
</tr>
<tr>
<td>Average voltage V</td>
<td>3.93</td>
<td>3.80</td>
</tr>
<tr>
<td>Rechargeable capacity mAh g$^{-1}$</td>
<td>142</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>mAh cm$^{-3}$</td>
<td>720</td>
</tr>
<tr>
<td>Energy density for Li cell Wh kg$^{-1}$</td>
<td>560</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td>Wh dm$^{-3}$</td>
<td>2830</td>
</tr>
</tbody>
</table>

3.4 Summary

In this chapter, the solid solution of LiCoO$_2$ and LiNiO$_2$ has been re-examined and the optimum temperature to prepare the battery-active LiCo$_x$Ni$_{1-x}$O$_2$ has been determined. Among a series of LiCo$_x$Ni$_{1-x}$O$_2$, LiCo$_{0.05-0.10}$Ni$_{0.90-0.95}$O$_2$ shows the highest rechargeable capacity of more than 200 mAh g$^{-1}$ in voltage ranging from 2.6 to 4.2 V against a lithium metal electrode. Cycle-ability of LiCo$_{0.1}$Ni$_{0.9}$O$_2$ is good in a preliminary test in non-aqueous lithium cell. Because the rechargeable capacity is 1.5 times larger than that of LiCoO$_2$ currently used in lithium-ion batteries, it is concluded that LiCo$_{0.05-0.10}$Ni$_{0.90-0.95}$O$_2$ is possible alternative to LiCoO$_2$.

Reference

Chapter 4
High Energy Density Lithium-Ion Batteries Consisting of Lithium Nickel Oxide and Graphite: Performance of the 18650-Cylindrical Batteries

4.1 Introduction

In previous chapters, the possibility of high-capacity positive-electrode materials has been described. Of these, lithium nickel oxides containing a small amount of cobalt are attractive because it is easy to replace lithium cobalt oxide of LiCoO₂ currently used as a positive-electrode material to new lithium nickel oxides. The current lithium-ion batteries consisting of LiCoO₂ and graphite, specifically graphitized carbon in contrast to non-graphitized carbon, operate in voltage ranging of 2.5 to 4.2 V. The upper voltage limit of 4.2 V is a key to operate safely with acceptable cycle performance for current lithium-ion batteries at present. An introduction of new positive-electrode materials, such as high-capacity lithium insertion materials described in Chapter 2, will take long time to examine and adjust several conditions in fabricating lithium-ion batteries and their battery management systems.

Lithium nickel oxides have already known to potentially have higher capacity than LiCoO₂ under the upper voltage limit of 4.2 V [1-12]. However, the formation of nickel dioxide and resulting decomposition leading to thermal runaway under abused conditions impedes the reality of lithium-ion batteries consisting of lithium nickel oxide and graphite in addition to the difficulty of the preparation of battery-active lithium nickel oxide, specifically LiNiO₂, for a long time. Basic research of a series of trials on the formation of solid solution of LiNiO₂ and α-LiAlO₂ clearly tells that thermal stability of the oxidation products of lithium nickel oxides remarkably increases when aluminum is added into LiNiO₂ [13, 14], resulting in safe operation under both normal and abused conditions, while the rechargeable capacity decreases [13-16]. Therefore, the high-capacity positive-electrode materials described in Chapter 3 are slightly modified in their
composition [10, 11, 17, 18] and examined in prototype or practical 18650-cylindrical lithium-ion batteries, and a discussion is given as to whether or not the new batteries exceed a critical limit of 500 Wh dm\(^{-3}\) for conventional lithium-ion batteries consisting of LiCoO\(_2\) and graphite.

4. 2 Experimental

4. 2. 1 18650-cylindrical battery

In order to fabricate lithium-ion batteries, the positive-electrode material of high-capacity lithium nickel oxide in Chapter 3 is slightly modified to be LiNi\(_{0.82}\)Co\(_{0.15}\)Al\(_{0.03}\)O\(_2\), abbreviated as NCA hereafter. The NCA-positive electrodes were prepared by blending NCA, acetylene black (AB), and polyvinylidene fluoride (PVdF) in the weight ratio of 100:1:1, respectively, in N-methyl-2-pyrrolidone (NMP), coating on both sides of aluminum foil 15 \(\mu\)m thick with a coater, and pressing it to obtain an even thickness of the desired value. The graphitized carbon-negative electrodes were prepared by the same method except its composition, i.e., graphitized carbon and binder in the weight ratio of 100:1. The electrodes were heated at about 100°C to remove NMP. The positive and negative electrodes were dried at 100°C for 12 h under vacuum before use. Polyethylene microporous membrane 20 \(\mu\)m thick was used as a separator. The electrolyte used is 1.2 M LiPF\(_6\) ethylene carbonate (EC) / ethyl-methyl carbonate (EMC) / dimethyl carbonate (DMC) (15/20/65 by volume) solution.

To assemble the 18650-cylindrical batteries (18 mm in diameter and 65.0 mm in height), the NCA-positive and graphitized carbon-negative electrodes were wound together with separators to make an element and then sealed in an 18650-cylindrical can with the electrolyte. The weight of NCA-positive electrode mix is 15.4 g and that of graphitized carbon-negative electrode mix is 9.6 g in the battery. The thickness of the positive and negative electrodes is 127 and 151 \(\mu\)m, respectively, including 15 \(\mu\)m of aluminum foil. The geometrical electrode areas are calculated to be 754 and 806 cm\(^2\) for the positive and negative electrodes, respectively, so that the active electrode area is 754 cm\(^2\) in this case.
The weight of NCA loaded on the electrode is 20.4 mg cm\(^{-2}\) and that of graphitized carbon is 11.9 mg cm\(^{-2}\). The fresh batteries are first charged at 1000 mA up to 4.1 V and discharged at 1000 mA to 2.5 V, which is repeated twice. The fully charged batteries are stored or aged for a week at room temperature before the examinations of batteries.

4. 2. 2 Electrochemical examinations

The 18650-cylindrical batteries are examined in temperature ranging from \(-30\) to \(45^\circ\)C in a temperature-controlled electric oven (Nagano Scientific Co. Ltd., Japan). The charge and discharge of the batteries are performed by using automatic battery cyclers (Type K5V10A, Nittetsu Elex Co. Ltd., Japan). Because a contact resistance between battery terminals and the connecting wires from a cycler is usually a problem, nickel tabs were welded to the positive and negative terminals by a resistance method. The batteries are normally charged at a constant current until the terminal voltage reaches 4.2 V and then kept at that voltage until current reduces to a given current, typically 50 mA, so-called the constant-current and constant-voltage charging mode, abbreviated as a CCCV-charging mode. After a 20-min rest, the charged batteries are discharge at a constant current to 2.5 V. The procedure of charging and discharging is repeated for desired times planned.

Impedance measurements are performed by using the frequency-response analyzer (Solartron 1250) connected to a potentiostat (Solartron SI1287). The frequency is scanned stepwise in a frequency range between 0.01 and 63500 Hz with 5 steps per decade. To monitor the impedance of the battery during cycle life tests, the impedance of a battery is measured after a 20-min rest of the fully charged battery by a 1-kHz impedance meter. Other sets of experimental conditions are given in the results and discussion section.

4. 3 Results and Discussion

4. 3. 1 Determination of nominal capacity
The nominal capacity of a battery is determined in an arbitrary way by a battery producer. However, the nominal capacity is the capacity the battery producer certifies for battery users, so that the discharge capacity observed by the users is normally more than the nominal capacity listed in the certification.

Figure 4.1 shows the charge and discharge curves of the 18650 batteries examined in voltage ranging from 2.5 to 4.2 V at a rate of 550 mA at 25°C. Five cells are examined in the same condition and shown in Fig. 4.1. Four charge and discharge curves merge in a single charge and discharge curve, indicative of high reproducibility. The rechargeable capacity observed is 2750 mAh and the applied current is 550 mA. It takes 5 hours for discharging the battery. In other words, the nominal capacity of 2750 mAh is determined by the five-hour rate of discharge. The value is determined by the continuous constant-current charge and discharge, so that the capacity more than the nominal capacity is obtained when a CCCV-charging mode is applied to the 18650 batteries. Because the nominal capacity of the 18650 batteries is known, the current of 550 mA corresponds to 0.2C-rate, in which C is the nominal capacity. The C-rate notation is usually used in a battery field.

![Charge and discharge curves of 18650-cylindrical cells continuously operated at a rate of 550 mA in voltage ranging from 2.5 to 4.2 V at 25°C. Five cells are examined for 2 cycles and all the data are shown in this figure. Rechargeable capacity is observed to be 2750 mAh.](image)
4. 3. 2 Impedance of 18650-cylindrical battery

Figure 4. 2 shows a record on the cell history for the impedance measurements of the 18650 battery consisting of NCA and graphitized carbon electrodes. The cell is charged at 500 mA to a target state of charge (SOC) at 25°C and open-circuited for 5 h. After a 5-h rest, the open-circuit potential is recorded and then the impedance is measured in frequency ranging from 0.01 to 63500 Hz. In measuring impedance at SOC = 0, a signal of the sinusoidal voltage with peak amplitude of 10 mV is imposed to the open-circuit potential. For other SOC, a signal of the sinusoidal current with peak amplitude of 500 mA is imposed to the battery in order not to disturb the SOC during the impedance measurements. As seen in Fig. 4. 2, the open-circuit potential follows just below the charging curve at 500 mA, indicating that the impedance measurements are correctly performed.

![Graph showing the relationship between state of charge and voltage](image)

Fig. 4. 2  Record on the cell history to measure impedance as a function of state of charge (SOC). The cell is successively charged at 500 mA to a desired SOC and open-circuited for 5 h, and then the impedance is measured. The nominal capacity is 2750 mAh.
Figure 4. 3 shows the Bode plots of impedance spectra observed for the 18650 battery. In the SOC range between 25 to 100%, the absolute values of complex impedance are from 30 to 50 mΩ in frequency between 0.01 and 500 Hz, in which phase angles are close to 0°, indicating that the battery behaves like a pure resistor. As seen in Fig. 4. 3, the phase angles are positive in frequencies larger than 1 kHz. The inductance observed for the 18650 battery is derived from a spirally wound electrode configuration, which behaves like a coil. The electrochemical system including the lithium insertion electrodes does not contain any inductance except by accident.

At SOC = 0, 5, or 10%, the absolute values of complex impedance increases as the frequency decreases concurrently with the deviation from 0° in phase angles. An exact origin of the increase in the absolute values of complex impedance in low frequency region at SOC < 10% is not known at present, but it is clear that the 18650 battery shows low impedance of 40 ± 10 mΩ in SOC ranging from 10 to 100%, suggesting that the battery is capable of high power input and output as will be shown in latter section.

Fig. 4. 3 The Bode plots of impedance measured at 25°C for an 18650-battery at 0, 5, 10, 25, 50, 75, 90, 95, and 100% SOC. The nominal capacity is 2750 mAh.
4.3.3 Preliminary examinations on a charging mode

In order to examine charging modes appropriate for the 18650 batteries consisting of NCA and graphitized carbon, the batteries having the nominal capacity of 2750 mAh are charged in different ways.

![Charging curve of 18650-cylindrical cell consisting of graphitized carbon and LiNi$_{0.82}$Co$_{0.15}$Al$_{0.03}$O$_2$: (a) terminal voltage, (b) state of charge (SOC), and (c) charging current as a function of time. The cell is charged at a rate of 825 mA to 4.20 V at 25°C and then kept at that voltage until current reduces to 50 mA, so-called constant-current and constant-voltage (CCCV) charging mode. Because the nominal capacity is determined to be 2750 mAh, a current of 825 mA corresponds to 0.3C rate.](image)

Figure 4.4 shows the current in A, terminal voltage in V, and the state of charge (SOC) of the battery in % as a function of time in h during a typical CCCV-charging mode. The SOC of battery is defined by the ratio of the capacity stored in a battery to the nominal capacity, i.e., 2750 mAh in this case. As seen in Fig. 4.4, when the constant current of 825 mA is applied to the fully discharged battery with SOC = 0, the terminal voltage raises from 3.3 to 4.2 V and concurrently the SOC increases linearly as a function of time, which is a constant-current charging mode. When the terminal voltage reaches the upper voltage limit of 4.2
V, the constant current of 825 mA is switched off and the constant voltage of 4.2 V is imposed to the battery, which is a constant-voltage charging mode. At 4.2 V, the current decays from 825 mA to lower current with storing more electricity, evidenced by an increase in SOC in Fig. 4. When there is no current limit, the battery is always charged at 4.2 V, so that the current limit or charging preset time is determined to terminate battery charging. In Fig. 4.4, a current of 50 mA is the end of a charging period. As clearly seen in Fig. 4.4, about 95% of the capacity is stored in the constant-current region and remaining 5% is in the constant-voltage region. Such a charging mode in Fig. 4.4 is described as the constant-current charge at 825 mA (0.3C) to 4.2 V and the constant-voltage charge of 4.2 V until the current reduces to 50 mA, abbreviated as CCCV (825 mA(0.3C)-4.2 V, 50 mA).

![Charge and discharge curves of 18650-cylindrical cells consisting of graphitized carbon and LiNi_{0.82}Co_{0.15}Al_{0.03}O_{2} operated in voltage ranging from 2.5 to 4.2 V: (a) discharge curve at 550 mA (0.2C) together with charging curves at (b) 1650 (0.6C), (c) 825 (0.3C), and (d) 412 mA (0.15C) at 25°C. The cell is charged to 4.2 V at constant current and then clumped at that voltage until current decreases to 50 mA. The nominal capacity is 2750 mAh.](image_url)
Figure 4.5 shows the effect of charging current upon the charge curves and consequently the capacity stored in a constant-current charging mode. The discharging current is fixed to be 550 mA (0.2C). As clearly seen in Fig. 4.5, charge curves shift upward when the current increases from 412 mA (0.15C) to 1650 mA (0.6C) because of polarization due mainly to the internal resistance. Therefore, high current charge results in smaller charge capacity in a constant-current charge mode, because the terminal voltage early reaches 4.2 V. This is better illustrated in Fig. 4.6. When the charging current of 550 mA (0.2C) is applied to the battery, about 95% of the nominal capacity is stored in a constant-current mode. However, when 5500 mA (2C) is applied, about 80% is stored in a battery. High-current charge corresponds to “quick charge”. In other words, quick charge within 30 minute is possible for the 18650 batteries under consideration.

Fig. 4.6 The state of charge (SOC) as a function of C-rate on charge for the 18650-cylindrical cells having a nominal capacity of 2750 mAh. The cells are charged at constant current to 4.2 V at 25°C. Because the constant-current charge cannot be fully stored the electricity in the cells, the CCCV-charging mode is usually applied.
Figure 4.7 shows the effect of temperature upon the potential profiles on charge for the 18650 batteries. All the batteries are discharge to 2.5 V at a rate of 550 mA (0.2C) at 25°C while the temperatures on charge are 0, 10, 25, and 45°C. In order to equilibrate the cell temperature for charging, a 3-h rest at a desired temperature is allowed after discharge. In examining the cells at 0°C, the charging current is reduced to 412 mA (0.15C) substituting for 825 mA (0.3C). As clearly seen in Fig. 4.5, the 18650 batteries consisting of NCA and graphitized carbon work well in a normal condition for five hours or more in an ambient temperature ranging from 0 to 45°C by using a CCCV-charging mode.

Fig. 4. 7 The effect of temperature upon the potential profiles on charge for the 18650-cylindrical cells. All the cells are discharge to 2.5 V at a rate of 550 mA (0.2C) at 25°C while the temperatures on charge are (a) 0, (b) 10, (c) 25, and (d) 45°C. The cells are charged at 825 mA (0.3C) to 4.2 V and then clamped until the current decreases to 50 mA (0.02C) except the current at 0°C. In examining the cells at 0°C, they are charged at 412 mA (0.15C).
4. 3. 4 An effect of temperature upon battery performance

Lithium-ion batteries are used in several environments from the tropical zone to cold districts, such as the Arctic or Antarctic regions, at the top of Himalayas, etc., in addition to a mild or soft climate zone. Ambient temperature ranges from −30 to +45°C, so that the batteries have to be examined at temperatures ranging from −30 to +45°C. Because the freezing point of water is 0°C, it is very hard to operate the batteries at a below-zero temperature for both aqueous and non-aqueous batteries.

Figure 4. 8 shows the discharge curves of the 18650 batteries examined at −30°C at a rate of 550 mA (0.2C) or 825 mA (0.3C). The batteries are charged at 25°C in a CCCV-charging mode (825 mA-4.2 V, 50 mA), so that every battery is fully charged. At −30°C the batteries deliver electricity of ca. 1200 mAh out of 2750-mAh nominal capacity. As seen in Fig. 4. 8, the batteries operate even at −30°C, but it is not in good shape. This is due to an electrolyte solution used in the 18650 batteries. The electrolyte looks like a sherbet whose conductivity is extremely low, about a tenth compare to that at 25°C, as seen in Table 4. 1. In general, the conductivity of an electrolyte decreases as temperature falls. Below a freezing point an electrolyte is not a solution anymore, resulting in an insulating solid. Figure 4. 9 shows the results on the 18650 batteries examined at −20°C.

Table 4. 1 Conductivity of the electrolyte used in the 18650-cylindrical cells in temperature ranging from −30 to +25°C.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Conductivity in mS cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−30°C</td>
</tr>
<tr>
<td>1.2M LiPF₆ EC/EMC/DMC (15/20/65)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Although the discharge curves are not in good shape, the discharge characteristics
are quite better than that at $-30^\circ$C in Fig. 4.8. High-rate discharge at 5500 mA (2C), 4125 mA (1.5C), or 1750 mA (1.0C) is possible at $-20^\circ$C while the discharge capacity is about half of the nominal capacity. On discharge at high current, the terminal voltage once drops and recovers, as seen in Fig. 4.9 (a), (b) and (c), which is a strange behavior. However, it can be explained in terms of power dissipation generating heat inside a battery due to polarization. After charging the battery, the open-circuit potential is above 4.1 V. When a current of 4125 mA is imposed to the battery, the potential suddenly drops below 3 V. The potential drop of ca. 1 V is polarization, which consumes ca. 4 W of power generating heat inside the battery. Heating at a rate of 4 J s$^{-1}$ induces a rise in temperature inside the battery although the ambient temperature is $-20^\circ$C. Such a behavior is also seen when the battery is examined at $-10^\circ$C in Figs. 4.10 or at 0$^\circ$C in Fig. 4.11, especially at high current.

Fig. 4.8 Discharge curves of the 18650-cylindrical cells examined at (a) 550 mA (0.2C) and (b) 825 mA (0.3C) at $-30^\circ$C. The cells are charged at 825 mA (0.3C) to 4.2 V and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25$^\circ$C.
Fig. 4.9 Discharge curves of the 18650-cylindrical cells examined at (a) 5500 mA (2.0C), (b) 4125 mA (1.5C), (c) 2750 mA (1.0C), (d) 1375 mA (0.5C), and (e) 550 mA (0.2C) at −20°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C.

Fig. 4.10 Discharge curves of the 18650-cylindrical cells examined at (a) 5500 mA (2.0C), (b) 4125 mA (1.5C), (c) 2750 mA (1.0C), (d) 1375 mA (0.5C), and (e) 550 mA (0.2C) at −10°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C.
Fig. 4.11 Discharge curves of the 18650-cylindrical cells examined at (a) 5500 mA (2.0C), (b) 4125 mA (1.5C), (c) 2750 mA (1.0C), (d) 1375 mA (0.5C), and (e) 550 mA (0.2C) at 0°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C.

When the batteries are warmed up from −20 to 0°C via. −10°C, the operating voltage is improved and the discharge capacity is getting better. At 0°C the discharge performance illustrated in the E in V vs. Q in mAh plots looks quite better compared to those examined at temperature below the freezing point. At 25°C the nominal capacity of 2750 mAh is delivered at current ranging from 550 (0.2C) to 5500 mA (2C), as shown in Fig. 4.12. No further improvement can be expected. When the battery is examined at 40°C, the performance is almost the same as that examined at 25°C, as shown in Fig. 4.13. Because the discharge curves are good in shape, the direct-current internal resistance is estimated from the terminal voltage at half of the discharge capacity against the current to be 44.2 mΩ at 25°C and 42.5 mΩ at 40°C.
Fig. 4.12 Discharge curves of the 18650-cylindrical cells examined at (a) 5500 mA (2.0C), (b) 4125 mA (1.5C), (c) 2750 mA (1.0C), (d) 1375 mA (0.5C), and (e) 550 mA (0.2C) at 25°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. After a 25-minute rest, each examination is carried out.

Fig. 4.13 Discharge curves of the 18650-cylindrical cells examined at (a) 5500 mA (2.0C), (b) 4125 mA (1.5C), (c) 2750 mA (1.0C), (d) 1375 mA (0.5C), and (e) 550 mA (0.2C) at 40°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C.
Figure 4.14 shows the effect of temperature upon the discharge capacities of the 18650-cylindrical batteries examined at a discharge current of 550 mA (0.2C). The batteries are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. As clearly seen in Fig. 4.14, the discharge capacity depends on ambient temperature. About 80% of the nominal capacity can be used even at −20°C for the 18650 batteries consisting of NCA and graphitized carbon. The batteries still work at −30°C, but are inferior to those at −20°C or above as seen in Fig. 4.14.

Fig. 4.14  The effect of temperature upon the discharge capacities of the 18650-cylindrical cells examined at 550 mA (0.2C). The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. After charge at 25°C, the cells are open-circuited for 20 min. In changing the temperature, the cells are allowed a 3-h rest at a desired temperature in order to reach temperature equilibrium.

Figure 4.15 shows the effect of temperature on the discharge performance when the fully-charged batteries are discharged at 550 mA (0.2C). Figure 4.16 shows the same effect of temperature for the batteries examined at 2750 mA (1C).
The difference between them is the discharge current. One is examined at 550 mA and the other is 2750 mA, which is five times larger current. No noticeable difference can be seen at 25°C. The operating voltage at 2750 mA is slightly lower than that at 550 mA when the batteries are examined at 25°C. The discharge performance observed at 2750 mA at 0 or −10°C is better than that expected from data at 550 mA because of heat generation inside the batteries. Ohmic drop or more generally polarization is usually undesirable in considering advanced lithium-ion batteries. However, it shows a beneficial effect on low-temperature battery performance. Figure 4.17 summarizes the performance of the 18650 batteries in temperature ranging from −20 to +50°C. As have been described above, the batteries can store and deliver electricity in an environment of our living conditions.

![Discharge performance of the 18650-cylindrical cells examined at the 0.2C rate of discharge.](image)

The cells are discharged to 2.5 V at 550 mA (0.2C) at (a) −10, (b) 0, and (c) +25°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. The nominal capacity determined at 25°C at the 5-hour rate of discharge is 2750 mA.
Fig. 4.16 Discharge performance of the 18650-cylindrical cells examined at the 1.0C rate of discharge. The cells are discharged to 2.5 V at 2759 mA (1.0C) at (a) −10, (b) 0, and (c) +25°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. The nominal capacity determined at 25°C at the 5-hour rate of discharge is 2750 mAh.

Fig. 4.17 Performance of the 18650-cylindrical cells examined at 550 mA (0.2C) at (a) −20, (b) 0, (c) +25, and (d) +50°C. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. The nominal capacity determined at 25°C at the 5-hour rate of discharge is 2750 mAh.
4.3.5 High-rate capability tests at 25°C

In the previous section, heat generation inside a battery is described with respect to a beneficial effect. The heat generation is usually observed in charging or discharging a battery at high current. Figure 4.18 shows the discharge curves of a fully-charged battery examined at a rate of 2750 (1.0C) mA or 5500 mA (2.0C). In examining the high rate performance, temperature on the surface of the battery is monitored and shown in Fig. 4.18. The ambient temperature is controlled to be 25°C. When the battery is discharged at 2750 mA or 1C rate, the battery temperature slightly increases at the beginning of discharge and follows almost a straight line until the discharge voltage falls sharply. At the end of discharge, the temperature sharply raises because of increase in polarization as can be seen in Fig. 4.18. When 5500 mA (2.0C) is applied to the battery, an increase in battery surface temperature is remarkable from 25 to 40°C. General observation is the same as that at 2750 mA or 1C rate. The final temperature of 40°C is detectable as “hot”, but it is still under control, as seen in Fig. 4.13.

Fig. 4.18 High-rate discharge performance of the 18650-cylindrical cells examined at (a) 2750 (1.0C) and (b) 5500 mA (2.0C) at 25°C with monitoring the surface temperature of the cell. The cells are charged to 4.2 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C) at 25°C. The nominal capacity determined at 25°C at the 5-hour rate of discharge is 2750 mAh.
As clearly seen in Fig. 4. 18, the 18650 batteries safely operate at high rate discharge.

4. 3. 6 Ah- and Wh-efficiencies at 25°C

Efficiency is a common measure to evaluate a system. The function of a secondary battery is to store “electricity” and then to deliver “electricity”. The amount of electricity is measured in terms of ampere-hour (Ah) capacity in a battery field, which follows a Faraday’s law. The electrical energy in Wh stored in and delivered from a battery is also measureable, leading to a concept of Wh-efficiency or energy efficiency in addition to conventional Ah-efficiency.

![Chart showing Ah and Wh efficiencies](chart.png)

Fig. 4. 19  Performance of the 18650-cylindrical cells having a nominal capacity of 2750 mAh in terms of (a) ampere-hour (Ah) and (b) watt-hour (Wh) efficiency ($\eta$) as a function of the C-rate of discharge.

Figure 4. 19 shows the Wh-efficiency together with the Ah-efficiency for the 18650-batteries measured at 25°C. The Ah-efficiency is more than 97% even
when a battery is discharged at a 2C rate, i.e., 5500 mA, at which the Wh-efficiency is more than 87%, as clearly seen in Fig. 4. 19. The loss of energy is consumed to generate heat, as has discussed in previous sections, and the loss of Ah-efficiency is due mainly to a mass transport problem. The Ah-efficiency approach 100% when the applied current is reduced from 2 to 0.2C rate. Thus the 18650 batteries are well characterized in terms of Ah- and Wh-efficiency.

4. 3. 7 1000-cycle tests at 25°C

Lithium-ion batteries are usually used in mobile phones and lap-top computers at temperature in our living conditions. From a standpoint of users, long lasting batteries are better than short service life. Although a permanent battery, never dies, is ideal, such a battery is not available at present. Therefore, a charge-discharge mode in which a battery is lasting more is examined and the information from the results are programmed in a battery management system to control a battery.

Figure 4. 20 shows the effect of charging current upon the cycle life of the 18650 batteries under consideration. The discharge current is fixed to be 2750 mA (1C) and temperature is controlled to be 25°C. In examining the cycle life, the impedance of the battery is monitored by using a 1-kHz impedance meter. As clearly seen in Fig. 4. 20, the charging current heavily affects the cycle life. High-rate or quick charging makes a battery life short. When a current of 550-825 mA is used on charge, a capacity more than 70% of nominal capacity retains even after 1000 cycles. A current of 550-825 mA corresponds to a rate of 0.2-0.3 C, meaning that it takes about 3-5 h for charging. In other words, overnight charging is preferable to the extension of cycle life and quick charging takes year off the battery life.

Figure 4. 21 shows the effect of discharge current upon the cycle life at 25°C. All batteries are charged to 4.2V at 1375 mA (0.5C) and clamped at that voltage until current decrease to 50 mA (0.02C). As seen in Fig. 4. 21, the discharge current does not affect so much the cycle life when the current is below 1375 mA (0.5C), which is different from that for charging in Fig. 4. 20.
The effect of charging current upon the cycle life of the 18650-cylindrical cells having a nominal capacity of 2750 mAh at 25°C. The cells are charged to 4.2 V at (a) 2750 (1.0C), (b) 1925 (0.7C), (c) 1375 (0.5C), (d) 825 (0.3), or (e) 550 (0.2) mA and then clamped at that voltage until the current decreases to 50 mA (0.02C). After a 20-minute rest, the cells are discharged to 2.5 V at 2750 mA (1.0C) and charged after a 20-minute rest. Cell impedance is also monitored by using a 1-kHz impedance meter and shown in this figure.

The above arguments are at 25°C. However, the lithium-ion batteries tend to use inside an electronic devise generating heat, so that additional information on a temperature effect is needed to supply the lithium-ion batteries to such users. The results on the effect of charging current upon the cycle life at 45°C are shown in Fig. 4.22. The experimental conditions are the same as those in Fig. 4.20 except temperature. General observation is the same as that in Fig. 4.20, i.e., overnight charging is preferable to the extension of cycle life.

As have been described above, the 18650 batteries consisting of NCA and graphite show the cycle life, typically 500 cycles, required from users for mobile phones and lap-top computers, i.e., information and communication technology use.
The effect of discharge current upon the cycle life of the 18650-cylindrical cells having a nominal capacity of 2750 mAh at 25°C. The cells are charged to 4.2 V at 1375 mA (0.5C) and clamped at that voltage until current decrease to 50 mA (0.02C). After a 20-minute rest, the cells are discharged to 2.5 V at (a) 2750 (1.0C), (b) 1375 (0.5C), or (c) 550 mA (0.2C) and charged after a 20-minute rest. Cell impedance is also monitored by using a 1-kHz impedance meter and shown in this figure.
Fig. 4.22 The effect of charging current upon the cycle life of the 18650-cylindrical cells having a nominal capacity of 2750 mAh. The cells are charged at 45°C to 4.2 V at (a) 2750 (1.0C), (b) 1925 (0.7C), (c) 1375 (0.5C), (d) 825 (0.3), or (e) 550 (0.2) mA and then clamped at that voltage until the current decreases to 50 mA (0.02C). After a 20-minute rest, the cells are discharged at 45°C to 2.5 V at 2750 mA (1.0C) and charged again after a 20-minute rest. Cell impedance is also monitored by using a 1-kHz impedance meter and shown in this figure.

4.3.8 Extended cycle tests to 4000 cycles

A target for the cycle life of lithium-ion batteries is to attain 3600 cycles for a 10-year service in the second stage of the research and development on lithium-ion batteries. Although the 18650 batteries described herein are not designed for such a long-cycle use, the extended cycle tests to 4000 cycles are carried out in order to examine whether or not the lithium-ion batteries consisting of NCA and graphite survive for such a long cycle of charge and discharge.

Fig. 4.23 Extended cycle tests of the 18650-cylindrical cells having a nominal capacity of 2750 mAh, examined at (a) 25 and (b) 45°C. The cells are charged to 4.1 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C). After a 20-minute rest, the cells are discharged to 2.5 V at 2750 mA (1.0C) and charged again after a 20-minute rest.
Figure 4. 23 shows the results on the extended cycle tests of the 18650-cylindrical batteries having a nominal capacity of 2750 mAh examined at 25 and 45°C. The batteries are charged to 4.1 V at 825 mA (0.3C) and then clamped at that voltage until the current decreases to 50 mA (0.02C). The batteries are discharged to 2.5 V at 2750 mA (1.0C) and charged again after a 20-minute rest. As seen in Fig. 4. 23, the rechargeable capacity retains ca. 60% compared with the initial capacity when it operates at 25°C. However, the capacity fades when it operates at 45°C, i.e., below 40% after 3600 cycles. A desirable value of the capacity retention would be more than 70% after 4000 cycles. No loss of rechargeable capacity is ideal, but aiming at 100% capacity retention is out of touch in reality. Therefore, the realistic value of 70% is tentatively determined. Figure 4. 23 clearly shows that the batteries have a function of storing and delivering electricity in spite of capacity fading, so that an optimum condition on a charge and discharge mode is examined in order to extend the cycle life.

Fig. 4. 24 Discharge capacity of 18650-batteries at 45°C as a function of cycle number. Charging and discharging conditions were (a) 0.3 C charging to 4.1 V and 1.0 C discharging to 2.5 V, (b) 0.2 C charging to 4.1 V and 1.0 C discharging to 2.5 V, (c) 0.15 C charging to 4.1 V and 1.0 C discharging to 2.5 V, (d) 0.3 C charging to 4.0 V and 1.0 C discharging to 2.5 V, (e) 0.3 C charging to 3.9 V and 1.0 C discharging to 2.5 V, and (f) 0.3 C charging to 4.0 V and 1.0 C discharging to 3.55 V.
The charging current varies from 410 (0.15C) to 825 mA (0.3C) while the discharging current is fixed to be 2750 mA (1C). The charge-end voltage also varies from 3.9 to 4.1 V, and the discharge-end voltage varies from 2.5 to 3.55 V. As clearly seen in Fig. 4.24, the charging current does not affect so much the capacity retention when the batteries are examined in voltage between 2.5 and 4.1 V. When the batteries are examined in voltage ranging from 2.5 to 3.9 V, the capacity retention fairly improve, i.e., more than 60% capacity retention after 4000 cycles at 45°C. When the batteries are charged at a rate of 825 mA (0.3C) to 4.0 V and discharged at 2750 mA (1C) to 3.55 V, the rechargeable capacity retains more than 70% after 4000 cycles. Therefore, the 18650 batteries can be operated for both high-rate and long-life applications by using an appropriate battery management system.

4.4 Summary

As have been described above, the 18650 lithium-ion batteries consisting of lithium nickel oxide and graphite show the nominal capacity of 2750 mAh, which is 3.5 times larger capacity than that of 750 mAh for a staring lithium-ion battery consisting of LiCoO$_2$ and non-graphitized carbon in 1991. The volumetric energy density of 580 Wh dm$^{-3}$ is about 3 times superior to that for a lithium-ion battery consisting of LiCoO$_2$ and graphitized carbon in 1991-1994 or 2 times larger than that for current nickel metal hydride batteries. An increase in volumetric energy density is mainly due to the improvement of an engineering aspect in addition to a material innovation and an introduction of the battery management systems. As has been discussed in General Introduction, the energy density of lithium-ion batteries consisting of LiCoO$_2$ and graphitized carbon has already approached a critical limit, somewhere around 500 Wh dm$^{-3}$. The 18650 batteries clearly exceed the critical limit and there is still research space to extend the capacity and energy density, which make it possible to realize an 8-hour running lap-top computer and an 8-hour driving electric car. Some of them have already been in a market. Thus, the high energy density lithium-ion batteries consisting of lithium nickel oxide, specifically LiNi$_{0.82}$Co$_{0.15}$Al$_{0.03}$O$_2$, and graphitized carbon have been achieved.
References

Concluding Remarks

The researches described herein have been done during the academic years of 2009-2011 after a 20-year break in the scientific research on lithium nickel oxide in 1990-1992 under the direction of Professor Tsutomu Ohzuku. Throughout the research some fundamentals on the solid state electrochemistry of insertion materials for advanced lithium ion batteries have been intended to establish in both electrochemical science and battery technology. Among possible lithium insertion materials, lithium nickel oxides, specifically LiNiO₂, have been selected and investigated in 1990-1992, which is now used in high energy density lithium-ion batteries. At that time, LiNiO₂ was used to be said “That is a visionary material, not practical, because nobody succeeded to make battery-active LiNiO₂”. Since then, a gap between theory and practice associated with lithium insertion materials for advanced lithium-ion batteries has been filled in a research division in Panasonic Corp. Ltd., because the author has discussed with many engineers about battery technology combined with materials science associated with lithium insertion materials, and then the author has partly succeeded in connecting basic research results to the developments on practical high energy density lithium-ion batteries as have been summarized.

In Chapter 1, the precision dilatometer originally designed and fabricated has been described and a new concept of area-specific deformation is given. In general, a lithium insertion electrode is characterized by area-specific capacity in mAh cm⁻² and area-specific impedance in Ω cm⁻², which have been used in designing lithium-ion batteries. In addition to these parametric factors, area-specific deformation in μm/(mAh cm⁻²) gives unique character associated with lithium insertion electrodes. By applying the concept, an electrode deformation in lithium-ion batteries can be properly estimated from basic results in a single electrode level in advance of the fabrication of prototype lithium-ion batteries. The basic concept together with a dilatometer technique accelerates the research and development on high-energy density lithium-ion batteries as have been described in Chapter 4. In other words, in designing the batteries consisting of lithium insertion electrodes, if the ASD as a function of the state of charge (SOC) of the electrode in % combined with the
area-specific capacity in mAh cm\(^{-2}\) for both positive and negative electrodes is known, the deformation of the electrodes during a cell operation is calculated and consequently a mechanical cell failure is properly predicted in advance of making a prototype battery.

In Chapter 2, high-capacity lithium nickel manganese dioxides have been described. The material potentially has the rechargeable capacity of 350 mAh g\(^{-1}\), which clearly exceeds a critical limit of 300 mAh g\(^{-1}\) with respect to the previous concept of lithium insertion materials based on a topotactic reaction of LiMeO\(_2\) ↔ Li\(^+\) + e\(^-\) + □MeO\(_2\). Although the irreversible reaction observed at first charge of a cell to 5 V against a lithium metal electrode is still a debatable subject, all of experimental results can be explained in terms of lithium insertion materials. Full understanding of solid-state chemistry and electrochemistry underlying such a high rechargeable capacity more than 300 mAh g\(^{-1}\) is difficult at present, but it will open a new window toward an innovative concept on lithium insertion materials for advanced lithium-ion batteries. The material will be used in next-generation high-energy lithium-ion batteries.

In Chapter 3, a high-capacity positive-electrode material under the upper voltage constraint of 4.2 V is described. The material is found in a series of trials on the solid solution of LiNiO\(_2\) and LiCoO\(_2\). The preparation conditions have been optimized for LiCo\(_x\)Ni\(_{1-x}\)O\(_2\) where x = 0, 1/4, 1/2, 3/4, and 1. None of them shows the rechargeable capacity more than 200 mAh g\(^{-1}\) when the materials are examined in lithium cells operated in voltage ranging from 2.5 to 4.2 V. However, when 5 – 10 atomic percent of cobalt is added to lithium nickel oxide, the rechargeable capacity exceeds 200 mAh g\(^{-1}\). The reaction mechanism is also examined and shown that the small addition of cobalt affects the solid state redox reaction of trivalent and tetravalent nickel ions in a solid matrix, i.e., 50 mV negative shift, resulting in the rechargeable capacity more than 200 mAh g\(^{-1}\) in the upper voltage constraint of 4.2 V.

In Chapter 4, the performance of 18650-cylindrical lithium-ion batteries (18 mm in diameter and 65.0 mm in height) consisting of lithium nickel oxide and graphite have been described. The positive-electrode material is the lithium nickel oxide described in Chapter 3 after small modification in its composition. The batteries have effectively been designed using the basic concept on lithium insertion electrodes in Chapter 1. The nominal capacity determined at the five-hours rate of discharge is 2750 mAh and the volumetric energy density is 580 Wh dm\(^{-3}\), which exceeds a critical
limit of 500 Wh dm\(^{-3}\) for the lithium-ion batteries consisting of LiCoO\(_2\) and graphite as has been discussed in General Introduction. Rate capability, the effect of temperature upon battery performance, and cycle life are shown. According to the results on cycle life tests of 18650-cylindrical batteries examined in voltage ranging from 2.5 to 4.1 V, the batteries are still alive even after 4000 cycles, indicative of long-life high-energy lithium-ion batteries. Lithium-ion batteries described herein may extend their use from 12-h use laptop computers to the 8-h or 500-km driving electric vehicles together with the 8-h electric storage systems.

As have been briefly summarized above, the author has succeeded to fill the gap between theory and practice associated with lithium insertion materials for advanced lithium-ion batteries. The present author hopes that researches on materials science and engineering associated with lithium insertion materials for advanced lithium-ion batteries will grow though the studies outlined herein in the future.


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