Examining the Long-Term Cyclabilities of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ Using a Full-Cell Configuration Including LTO-Counter Electrodes with Extra Capacity

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**Examining the Long-Term Cyclabilities of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$
Using a Full-Cell Configuration Including LTO-Counter Electrodes with Extra Capacity**

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Abstract

In this study, a novel cell configuration was developed for evaluating the cyclabilities of lithium insertion materials. In this cell, the $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO) counter electrode has excess capacity on both the charge and discharge sides (EQ-LTO). The EQ-LTO/ $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ (LiNiMO) cell shows superior cyclability when compared to other cell configurations, such as Li/LiNiMO and LTO/LiNiMO cells. In Li/LiNiMO cells, drastic capacity fading is observed within 100 cycles. While LTO/LiNiMO cells are suited for long-term use, capacity fading occurs mainly due to the different charge states of LTO and LiNiMO rather than the deterioration of LiNiMO. Herein, long-term (more than 6 months) cycling tests are performed for $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO) in an EQ-LTO cell to assess whether this cell configuration is suitable for evaluating long term cyclabilities; LAMO in this cell shows higher capacity retention than that in an LTO cell. The capacity fading as a function of cycle number is found to be very small for LAMO ($10 \text{ ppm cycle}^{-1}$). From these results, we concluded that the EQ-cell configuration provides accurate capacity fading values for lithium insertion materials.

Keywords: lithium-ion battery, lithium insertion material, cyclability, cell configuration

1. Introduction

Lithium-ion batteries (LIBs) are used as power sources in electronic devices for both stationary and portable applications because of their high energy densities. The performance of LIBs primarily depends upon the electrochemical properties of the lithium insertion materials used as the positive and negative electrodes [1-5]. There are various evaluation criteria for electrode materials, ranging from their basic electrochemical properties such as operating voltage and reversible capacity, to electrode performance parameters such as input/output-power characteristics, rate capability, and cyclability. These parameters are measured using electrochemical techniques: operating voltages and reversible capacities are obtained using constant current charge-discharge tests, input/output-power characteristics using electrochemical impedance spectroscopy, and cyclability using long-term cycling tests.

To measure these characteristics appropriately, it is important to consider the cell configuration used: half-cell vs. full-cell configurations, and two-electrode vs. three-electrode configurations [6]. In general, the three-electrode configuration (an electrochemical cell with a reference electrode) is most suitable for electrochemical measurements, because it provides electrochemical information for a single electrode (the working electrode) [7,8]. Indeed, there have been many reports on the application of three-electrode cells to battery electrode materials [9-13]. However, there is a crucial problem with the three-electrode configuration in that it is difficult to locate the reference electrode appropriately in the cell.

In contrast, two-electrode cells consisting of positive and negative electrodes are widely applied when examining electrode materials, because of their simple design and ease of

fabrication. The two-electrode configuration can be split into two categories: the half-cell configuration that uses a Li metal electrode, and the full-cell configuration that uses a negative electrode of graphite [14,15], silicon [16,17], $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO) [18-20], or other alternatives. The half-cell configuration using a Li metal electrode as the negative electrode (where it acts as both a counter and an auxiliary electrode) is suitable for characterizing electrode materials because of the surplus capacity and constant electrode potential of the Li metal electrode. Therefore, the half-cell configuration can be used satisfactorily when operating conditions include a low current or when the resistance of the working electrode is much larger than that of the Li metal electrode. The full-cell configuration can be used for performance evaluation in a more similar environment to that of an actual battery, where the positive and negative electrodes may affect each other. However, it is difficult to investigate the characteristics of a single electrode without introducing a reliable reference electrode.

In recent years, long-life LIBs have attracted attention for automobile and stationary applications. Because the lifetime of LIBs depends on the cyclability of the materials used as positive and negative electrodes, determination of the accurate cyclabilities of electrode materials allows for the development of Li-ion batteries with long lifetimes. Although various cell configurations have been used to evaluate the cycling performance of electrode materials, each cell configuration has limitations. At present, a cell configuration suitable for evaluating cycling characteristics has not been established. To this end, long-term cycling tests were conducted in this study using $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ (LiNiMO) [21-24] as a model electrode in various cell configurations in order to clarify which cell configuration is the most suitable for evaluating electrode cyclability. In addition to clarifying problems encountered when accurately

measuring cyclability in half-cell (Li/LiNiMO) and full-cell (LTO/LiNiMO) configurations, we propose a new cell configuration for long-term testing, the EQ-LTO/LiNiMO cell, in which the counter LTO electrode has extra capacity when both charging and discharging (EQ-LTO). In order to demonstrate the usefulness of this new cell configuration, we evaluated the long-term cyclability of a known long-life material, the $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO) electrode [25,26], using an EQ-LTO/LAMO cell.

2. Experimental

2.1 Electrode preparation and cell fabrication

Lithium titanium oxide (LTO, $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) [19,26], lithium aluminum manganese oxide (LAMO, $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$) [25,26], and lithium nickel manganese oxide (LiNiMO, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$) [21-23] were used as electrode materials. Prior to cell performance measurements, the structural and electrochemical properties of LTO, LAMO, and LiNiMO were confirmed by X-ray diffraction (XRD) and electrochemical methods. The LTO, LAMO, and LiNiMO used in this study exhibited reversible capacities of more than 90% of their theoretical capacities, with small polarizations and no noticeable capacity fading during cycling. The active material and a conductive binder (acetylene black) were mixed in an agate pot with a binder (polyvinylidene fluoride (PVdF) dissolved in N-methyl-2-pyrrolidone (NMP)). The mixture was stirred for 10 min to form a slurry. The composition of each electrode was set to 88 wt% active material, 6 wt% acetylene black, and 6 wt% PVdF. Aluminum foil was used as the current collector, and the obtained slurry was applied to obtain electrodes with a certain thickness. The applied slurry was dried in vacuo at 80 °C for about 1 h, followed by further

vacuum-drying overnight at 150 °C. After drying, 2 cm² electrodes were punched out of the foils. Two sheets of Celgard 2500 were used as separators. The electrolyte employed herein was 1 M LiPF₆ in a 3:7 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Kishida Chemical Co., Ltd., Japan). Electrochemical cells were prepared and fabricated as described in a previous paper [26], and were electrochemically tested using a battery cycler (Battery Laboratory System, Keisokuki Center Co., Ltd., Japan). Other experimental conditions are described in the Results and Discussion section.

3. Results and Discussion

3. 1 Half-cell configuration with a lithium metal electrode

Figure 1a shows the results of a cyclability test for a LiNiMO electrode examined in a half-cell (Li/LiNiMO) configuration. The cell showed a voltage plateau at 4.7 V, with a reversible capacity of at least 125 mAh/g. The charge-discharge curves of the cell consisted of two potential plateaus, which is a clear sign that the reactions of LiNiMO proceeded in a two-phase manner. From these curves, one can estimate electrode potential and polarization as a function of capacity. Therefore, the half-cell configuration is suitable for characterizing the reversible capacity, electrode potential, and polarization of an electrode material. When the LiNiMO electrode was cycled in the half-cell configuration, the capacity of the cell faded as cycle number increased, with only 64% of capacity being retained after 80 cycles. This degree of capacity fading was significantly faster than that expected from previous reports of LTO/LiNiMO cells [22]; however, such rapid capacity fading is almost always observed for

half-cells using lithium metal electrodes when performing long-term cycle tests with over 100 cycles. This suggests that the capacity fading of the cell was mainly due to deterioration of the lithium metal electrode [27,28], rather than deterioration of the LiNiMO electrode.

To assess whether deterioration of the Li metal electrode caused capacity fading, the Li metal electrode was replaced with a new electrode of the same type after the cycling test. Replacing the Li metal electrode led to a dramatic recovery of cell capacity to 128 mAh g^{-1} (Fig. 1b and 1c). This result indicates that the capacity fading shown in Fig. 1a was caused by the deterioration of the Li metal electrode during cycling. However, replacing the Li metal would be expected to improve the capacity fading rate, which was not observed, as the capacity loss after replacing the Li metal was similar to that observed at the end of the previous round of cycling. Since only the Li metal side of the separator was replaced, this was probably due to deterioration of the separator on the LiNiMO side. Thus, the rapid degradation of the Li metal electrode was probably due to influence of oxidation products generated at the LiNiMO electrode. Electrolyte decomposition cannot be avoided for LiNiMO electrodes because of their high electrode potential (4.7 V). A similar phenomenon has been observed in previous studies [29-31], in which side reaction products affected the counter electrodes in cells with graphite or LTO negative electrodes. This indicates that in the Li/LiNiMO cell, side products generated at the LiNiMO electrode caused rapid degradation of the Li metal electrode. Thus, cyclability tests using Li half-cells are limited only to tens of cycles due to deterioration of the Li metal electrode, making this setup unsuitable for evaluating the long-term cyclability of an electrode.

3. 2 Full-cell configuration with LTO electrode

Lithium-ion full-cells utilize different lithium insertion materials to avoid the problems

described for half-cells, resulting in excellent cyclability. There are several possible negative electrode materials that can be used to examine the properties of positive electrode materials in full cells, including graphite, silicon, and LTO. Such electrode materials have several requirements, such as a flat electrode potential, low polarization, and excellent cyclability. Of the possible negative electrodes, the zero-strain insertion material LTO fulfills these requirements; however, full-cell setups with LTO electrodes have another potential problem in that cell capacity fades during cycling even when no deterioration of the lithium insertion material occurs. According to both experimental and computational analysis [32-34], this capacity fading occurs due to an imbalance between the states of charge (SOCs) of the positive and negative electrodes, which occurs due to the difference between the current efficiencies of the lithium insertion reactions at each electrode due to the presence of different side reactions. Figure 2a shows a schematic illustration of capacity fading in an LTO/LiNiMO cell during cycling, which is caused by the different SOC of the electrodes. LiNiMO has two types of crystal structures: the first contains ordered Ni^{2+} and Mn^{4+} cations (space group of $P4_332$), and the second has a random distribution of cations (space group of $Fd-3m$) [35,36]. LiNiMO containing non-stoichiometric amounts of oxygen takes the second form, and shows a voltage step at 4 V. By using the voltage step as an indicator, it is possible to visualize how the SOC of both electrodes shift during cycling for an LTO/LiNiMO cell. To depict the imbalance between the SOC clearly, LiNiMO with a voltage step of 4 V was used for the illustration in Figure 2a. In this case, cell capacity decreases after cycling despite there being no degradation of either electrode. Next, an LTO/LiNiMO cell was fabricated by combining electrodes that had not been pre-cycled. Cyclability testing of this full LTO/LiNiMO cell (Fig. 2b) resulted in similar behavior to the illustrated example (Fig. 2a), with capacity at 2.5 V decreasing with

cycle number. From these results, capacity loss can occur in a full cell even with electrodes showing excellent cyclabilities, as a loss in reversible capacity does not correspond to a deterioration of the electrode of interest.

3. 3 Full-cell configuration using an LTO electrode with extra capacity (EQ-LTO cell)

In order to evaluate the long-term cyclability of lithium insertion electrodes, it was necessary to develop a new cell configuration instead of using the conventional half- and full-cell setups. Figure 3 shows a novel cell configuration for evaluating the long-term cyclabilities of lithium insertion electrodes, which consists of a two-electrode cell with a counter electrode that possesses an expanded capacity window. In this cell, there is no chance of capacity fading except via deterioration of the positive electrode, because the LTO electrode has extra capacity for both charging and discharging, preventing capacity fading due to imbalanced SOC.

Lithium-ion cells with extra LTO capacity (EQ-LTO cells) were fabricated as follows. First, LTO-negative and LiNiMO-positive electrodes were prepared, with the area-specific capacity of the LTO electrode being twice that of the LiNiMO electrode (2.75 and 5.10 mAh cm⁻² for LiNiMO and LTO, respectively). These positive and negative electrodes were then combined with Li metal and cycled in advance to check their electrochemical properties. The LiNiMO-positive electrode was then fully discharged to its reduced state, while the LTO-negative electrode was partially reduced (to 1.0 mAh cm⁻² in this case). Finally, the two electrodes were combined in a new cell. The difference between the EQ-LTO/LiNiMO cell and the normal LTO/LiNiMO full cell is that the LTO negative electrode is partially reduced to have extra

capacity on both the charging and discharging sides. As illustrated in Fig. 3, the cell capacity is limited by the LiNiMO-positive electrode during both charging and discharging, meaning that the capacity of the cell is equal to the capacity of the LiNiMO-positive electrode. Consequently, this cell configuration allows the long-term cyclabilities of LiNiMO-positive electrodes to be measured without any other causes of capacity fading interfering with the results.

Figure 4 shows the results of long-term cycling tests for cells containing LiNiMO and LTO with (Fig. 4a) and without (Fig. 4b) extra capacity. When charge and discharge curves were merged into a single curve, no increase in polarization was observed. After charging, operating voltage sharply increased to a charge-end voltage of 3.6 V (5.15 V versus Li). No significant capacity fading was observed, except over the initial 20 cycles. This capacity fading during the initial cycles was probably caused by slow transportation of Li ions in the microporous membrane used as a separator [37]. Capacity fading after 100 cycles was 4.2 mAh g^{-1} (5.1% of the initial capacity). In LiNiMO-positive electrodes, such stable cycling is characteristic of highly crystallized materials with large particle sizes ($> 1 \text{ }\mu\text{m}$) [22,23]. The cyclability of the EQ-LTO/LiNiMO cell (Fig. 4a) was superior to that of the cell utilizing LTO without extra capacity (Fig. 4b), indicating that the capacity fading measured when using the EQ-LTO cell only involved the deterioration of the LiNiMO electrode.

3. 4 Long-term cyclability testing of LAMO in an EQ-LTO cell

Long-term cyclability tests were performed using an EQ-LTO cell to assess whether it was

suitable for examining cyclability for periods of over one year. LAMO was used as the positive electrode instead of LiNiMO because of its superior cyclability, which is due to its operating voltage being approximately 1 V lower. In our previous study [25], the cyclability of LAMO was examined in lithium cells with lithium metal electrodes, or in lithium-ion cells with LTO electrodes. Although the cells showed excellent cyclability, the capacity retention of the cell did not correspond to that of LAMO because of capacity fading, which was caused by the deterioration of the Li metal electrode in the lithium cell and the imbalanced SOC in the lithium-ion cell.

Long-term cyclability studies of LAMO were performed at 25 and 40 °C as described for the LiNiMO electrode above, and the results are shown in Figure 5. When a cell using a microporous membrane as a separator is cycled at a high current density, the capacity decreases due to slow Li-ion transportation during cycling [37]. On the other hand, when a nonwoven cloth is used, such capacity fading does not occur even at high current densities [37]. Therefore, nonwoven cloth was used as a separator in both cells. Cycle tests were carried out at a high current density of 0.75 mA cm⁻², and the area-specific capacities of the LAMO electrodes in both cells were approximately 1.5 mAh cm⁻², meaning each cycle took approximately 4 h. During the cycle test at 25 °C, the operating voltage of LAMO rose sharply to a charge-end voltage of 3.5 V, corresponding to a LAMO electrode potential of 5.05 V vs. Li. The capacity increased at the beginning of the cycles for the EQ-LTO/LAMO cells, probably due to the increasing of the number of reaction sites inside the electrode resulting from the impregnation of the electrolyte into the electrode during cycling, as the charge-discharge curves normalized by the SOC remained virtually the same. The maximum capacity of LAMO at 25 °C was 105

mAh g⁻¹ indicating almost 100% utilization of the LAMO electrode even at moderate current densities. After 2323 cycles (8860 h, approximately 1 year), capacity loss was negligible, at 2.3% of the maximum discharge capacity. The capacity retention of LAMO was significantly higher when examined in the EQ-LTO cell than when measured in a conventional LTO/LAMO cell, at 99.0% for the former and 98.3% for the latter [25]. This was because of the lack of capacity fading from SOC mismatches in the EQ-Cell. In other words, the deviation of SOC is the main reason for capacity fading in conventional LTO/LAMO cells.

When the LAMO electrode was cycled at 40 °C for 1711 cycles (7300 h, approximately 10 months), the cycling behavior was similar to that observed at 25 °C except for a slight increase in capacity fading. The initial discharge capacity was also slightly higher than at 25 °C, i.e., 109.4 mAh g⁻¹. Coulombic efficiency was almost constant at 99.9% in the first 4000 h, indicating that side reactions on the LAMO electrode resulting from electrolyte decomposition or manganese dissolution were limited even at 40 °C, despite higher temperatures accelerating such reactions [38]. The sharp rise and fall in operating voltage at the ends of the charging and discharging cycles remained during cycling at 40 °C, and while capacity fading was higher at 40 °C than at 25 °C, it was still only 8.6 mAh g⁻¹.

Figure 5c shows that the discharge capacities of the LAMO electrodes decreased linearly, indicating the capacities of the electrodes faded at a constant rate. The capacity fading at 40 °C showed a good fit with a linear approximation rather than a square-root approximation. The data at 25 °C could be approximated by either method because of the limited capacity fading. In this paper, we used the linear approximation, which expected shorter lifetimes than the square-root approximation. The capacity retention of LAMO was estimated by calculating the

rate of capacity loss per cycle dQ/dn from a linear approximation of the discharge capacity as a function of cycle number, using the following equation:

$$dQ/dn = \frac{1-Q_p/Q_q}{p-q} \quad (p < q)$$

where p and q are cycle numbers, and Q_p and Q_q are discharge capacities at cycle numbers p and q , respectively. The units “ppm cycle⁻¹” were more suitable than “% cycle⁻¹” for dQ/dn because the dQ/dn of LAMO was quite small, e.g., 0.001% cycle⁻¹ for LAMO at 25 °C. Thus, the capacity fading rate of LAMO was calculated to be 10 and 46 ppm cycle⁻¹ at 25 and 40 °C, respectively. These values indicate that high temperature operation reduced the cycle life of the LAMO electrode by 1/5. The capacity retention of LAMO electrodes (%) can be estimated from the value of dQ/dn using the following equation:

$$Q(n) = \{1 - (dQ/dn) \times n\} \times 100 \text{ [%] after } n\text{th cycle}$$

Based on the above equation, the lifetimes of the LAMO electrodes as defined by 80% capacity retention are 20000 and 4350 cycles at 25 and 40 °C, respectively. In other words, LAMO electrodes can be used for more than 3600 cycles, or for 10 years of service based on one cycle per day. This result indicates that if electrode materials have excellent cyclability (e.g., LTO and LAMO), the main cause of capacity fading in LIBs containing such materials is an imbalance between the SOC of the electrodes [26], rather than deterioration of the electrode materials.

Conclusion

In this work, the cyclabilities of LiNiMO electrodes were studied using electrochemical cells with three different configurations: a half-cell with a Li metal electrode, a full-cell with an LTO

electrode, and a full-cell with an LTO electrode having extra capacities at both the charging and discharging sides. The first two cells were not suitable for evaluating the cyclability of these electrode materials because the capacity fading of the cells did not reflect the degradation of the LiNiMO electrodes alone. In the Li/LiNiMO half-cell, the Li metal electrode deteriorated, limiting cyclability tests to only 100 cycles. In the LTO/LiNiMO full-cell, long-term cycling was possible, but additional capacity loss was caused by the imbalanced states of charges of the LTO and LiNiMO electrodes. Such additional sources of capacity fading other than material deterioration hinder the accurate evaluation of the cyclability of LiNiMO. The novel full-cell configuration, in which a LiNiMO electrode was combined with an LTO electrode having extra capacity (EQ-LTO), allowed the accurate measurement of the cyclability of LiNiMO electrodes. Using the full-cell configuration with EQ-LTO, the cyclability of a LAMO electrode at a low current density was evaluated over a period of one year. The capacity fading rate (loss of capacity per cycle) of the LAMO electrode was only 0.001% cycle⁻¹ (10 ppm cycle⁻¹) at 25 °C, indicating that the EQ-cell configuration is suitable for evaluating the long-term cyclabilities of lithium insertion materials. Such accurate evaluations of the cyclabilities of lithium insertion materials are important for the design of lithium-ion batteries with longer lives.

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Figure 1. Cyclability tests for a Li/LiNiMO cell (a) over initial 80 cycles and (b) after replacing the Li-metal electrode. (c) Normalized discharge capacity during cyclability tests. Discharge capacity decreased over the first 80 cycles, after which it recovered due to replacement of the Li-metal electrode. The charge-discharge curves are shown every 10 cycles for (a) and every 2 cycles for (b).

Figure 2. (a) Capacity fading mechanism in an LTO/LiNiMO cell derived from a deviation between the SOC of LTO and LiNiMO electrodes. (b) Cyclability test of an LTO/LiNiMO cell. LiNiMO has voltage step at 4 V that shows the deviation between the SOC of the electrodes during cycling.

Figure 3. Illustration of a cell containing an LTO electrode with extra capacity in both the charging and discharging regions (red arrows). The cell consisted of a fresh-LiNiMO electrode and a partially reduced LTO electrode.

Figure 4. Charge-discharge curves of (a) EQ-LTO/LiNiMO and (b) LTO/LiNiMO cells at a rate of 0.5 mA cm⁻² at 25 °C. (c) Capacities of LiNiMO cells with counter electrodes of EQ-LTO (red), LTO (blue), and Li metal (black) as a function of cycle number.

Fig. 5 Prolonged cycling tests of LAMO electrodes examined in EQ-LTO cells at (a) 25 and (b) 40 °C. (c) Capacities plotted against cycle number.