Analysis of Electrochemical Reaction in Positive and Negative Electrodes during Capacity Recovery of Lithium Ion Battery Employing Recovery Electrodes

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ABSTRACT

Electrochemical reactions in positive and negative electrodes during recovery from capacity fades in lithium ion battery cells were evaluated for the purpose of revealing the recovery mechanisms. We fabricated laminated type cells with recovery electrodes, which sandwich the assemblies of negative electrodes, separators, and positive electrodes. The positive electrodes were replenished with Li^+ by applying current between the recovery and the positive electrodes. A discharge curve analysis revealed that Li^+ replenishment enabled the cells to recover from the capacity fade originating from capacity slippage between the positive and the negative electrodes. However, an issue is low recovery efficiency, which is defined as the ratio of recovery capacity of capacity slippage to the electric charge between the recovery and the positive electrodes. The cause of low recovery efficiency was elucidated by evaluating the positive and the negative electrodes after replenishment. It was found that the following mechanisms are involved in the replenishment of the positive electrodes: (a) Li^+ are intercalated into the positive electrodes as they are released from the recovery electrodes, which significantly contributes to recovery from capacity slippage; however, (b) some amount of Li^+ is released from the planes of the negative electrodes facing the positive electrodes as they are intercalated into the planes of the negative electrodes facing the recovery electrodes, which does not significantly contribute to recovery. Consequently, the recovery efficiencies were less than 50%. We conclude that, to increase recovery efficiency, process (b) should be suppressed.

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1. Introduction

Lithium ion batteries (LIBs) are used as power sources of various devices such as smartphones and electric vehicles because of their high energy density. Expansion of their range of application has increased demand for prolonging their lifetimes. However, the capacities of LIBs also decrease during use, just like with other batteries.

The reason for the capacity fades of LIBs are ascribed to those of positive and negative electrodes and the mutual “slippage” between the capacity of positive electrodes and that of negative electrodes.¹ The capacity fades of positive and negative electrodes are attributed to deactivation of active materials due to a decrease in the conducting paths of electrons and Li^+ . The decrease in electronic conducting paths is in turn ascribed to cracks in positive and negative active materials, detachment of conducting and active materials, etc. The decrease in conducting paths for Li^+ is ascribed to clogging of micropores in electrodes, depletion of an electrolyte, etc. Capacity slippage is attributed to not only the capacity fade of positive and negative electrodes but also deactivation of Li^+ . Deactivation of Li^+ is mainly due to immobilization through formation of solid electrolyte interfaces (SEIs) on negative electrodes.^{2,3}

A number of non-destructive methods have been proposed for analyzing the charge–discharge curves of LIBs, wherein the capacity fades are quantitatively evaluated according to certain factors.^{4–8} Boom et al. developed a differential voltage analysis method taking into account the relationship between discharge capacity Q and differential voltage dV/dQ .⁴ This method reconstructs a discharge

curve of a cell by superposing pre-measured discharge curves of a positive electrode and a negative electrode. This makes it possible to separate a discharge curve of a cell into discharge curves of a positive electrode and a negative electrode and obtain the capacities of both electrodes and the capacity slippage.

After considering the merits of the previous studies, we previously developed a mathematically advanced discharge curve analysis method.^{6–8} With this method, the usable masses of positive and negative active materials and capacity slippage can be quantitatively evaluated.

To increase the lifetimes of LIBs, material-based techniques have been reported for suppression of SEI growth.^{9–18} Yamada et al. reported that superconcentrated electrolytes exhibit high durability for reductive decomposition on negative electrodes because Li salts are preferentially decomposed and form suitable films in those electrolytes.^{9–13} Some groups have suppressed SEI growth by forming stable SEIs with additives.^{14–18} These techniques suppress the rate of capacity fades, but the capacities still monotonically decrease.

Another approach for increasing the lifetimes of LIBs is to decrease the capacity fade originating from capacity slippage by replenishing positive or negative electrodes with Li^+ from another Li reservoir.^{19–22} Wang et al. were the first to report the recovery phenomena by replenishing the positive electrodes with Li^+ as a paper. They opened the end cap of a degraded cylindrical cell and connected the opened cell to another electrochemical cell which contained a Li-conductive electrolyte and Li metal electrode. Li^+ could be supplied from the bottom of the cylindrical cell.¹⁹ Consequently, the cell recovered by more than 50 % of the capacity fade. In addition, Ye et al. investigated the structure of a cylindrical recovery cell to minimize the non-

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uniform distribution of the state of charge (SOC) in the recovered electrodes.^{20,21}

The methods for studying the recovery process in the previous papers mentioned above entail disassembly of the degraded cell, which is hardly applicable in practice. Therefore, Palanisamy et al. fabricated the CR-2032 coin-cell with Li metal as a reservoir electrode and proved that in situ replenishment is possible without disassembly of the cell.²² Similarly, in this research, we developed a laminated type cell with recovery electrodes, where the positive or the negative electrodes can be replenished without disassembly of the cell. As for the recovery electrode, Li metal is not suitable because it gradually becomes coated with passivation film formed by decomposition of the electrolytes. Instead, the materials we used for the recovery electrodes were the same as those of the positive electrodes. Such a recovery electrode is advantageous as it requires few changes to the manufacturing process.

In addition, the following recovery efficiency (η_r) is an important indicator related to the cell energy density and the cell cost.

$$\eta_r = \frac{Q_r}{Q_e} \times 100 \quad (1)$$

where Q_r means the recovery capacity of capacity slippage, and Q_e is the electric charge between the recovery electrodes and the positive or negative electrodes. A lower recovery efficiency means that the more recovery electrodes are needed to recover the same capacity. The previous paper¹⁹ reported that parasitic reactions on the battery casing material could affect recovery, but it did not elucidate the mechanism behind the low recovery efficiency. Thus, in this study, to obtain an optimum design for increased recovery efficiency, we investigated the mechanism of capacity recovery on the basis of the results of the discharge curve analysis and evaluation of the positive and the negative electrodes after recovery. Also, the effect of the recovery process on the discharging rate property was investigated.

To focus on the effect of the capacity recovery process on the lifetimes of LIBs, the capacity recovery was treated for the LIBs after the initial charge–discharge process, during which time there was little damage to the negative and the positive electrodes. Capacity slippage also occurs in the initial charge–discharge for activating LIBs. The capacity recovery discussed in this paper can be applied to LIBs in any degraded state.

2. Experimental

2.1 Preparation of materials

The positive and recovery electrodes were prepared with the same process. The positive and the recovery electrodes were made from a mixture consisting of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, acetylene black, and polyvinylidene fluoride, which respectively served as the active material, conductive material, and binder. A slurry was prepared by adding *n*-methyl-2-pyrrolidone to the mixture, which was then applied to 15- μm -thick aluminum foil. The density of the mixture was adjusted to 3.15 g cm^{-3} by using a hot roller press (load: 10 tons, roll temperature: 100°C).

The negative electrodes were made from a mixture consisting of graphite as the active material and styrene butadiene rubber and carboxymethyl cellulose as binders. A slurry was prepared by adding ultrapure water to the mixture, which was then applied to 10- μm -thick copper foil. The density of the mixture was adjusted to 1.55 g cm^{-3} by using the hot roller press.

The electrolyte was prepared by dissolving 1.0 mol L^{-1} of lithium hexafluorophosphate and $1.0\text{ wt\%}$ of vinylene carbonate in a mixed solvent of ethylene carbonate and ethyl methyl carbonate having a volume ratio of 1 : 2. The separator was composed of a three-layer structure of polypropylene/polyethylene/polypropylene, and its thickness was $30\text{ }\mu\text{m}$.

2.2 Charge–discharge conditions of positive and negative electrodes

Open circuit potential (OCP) curves of the positive and the negative electrodes were measured using half cells at 25°C . The working electrode of the half cell was a 15-mm ϕ section of the positive or the negative electrode, and the counter electrode was a 16-mm ϕ section of Li metal. 100 % SOC of the half cells was defined as the fully charged state of the positive or the negative electrode.

The half cells with the positive electrodes were charged at a constant current of 1 C to 4.3 V and held at that voltage until the current decreased to $1/20\text{ C}$. The rest after charge was 30 min. The following cycle was repeated until the cell voltage reached 2.7 V; the cells were discharged at a constant current of $1/5\text{ C}$ until the change in SOC reached 0.5 % and the circuit was kept open for 30 min.

The half cells with the negative electrodes were charged at a constant current of 1 C to 0.005 V and held at that cell voltage until the current decreased to $1/20\text{ C}$. The rest after charge was 30 min. The following cycle was repeated until the cell voltage reached 2.0 V; the cells were discharged at a constant current of $1/5\text{ C}$ until the change in SOC reached 0.5 % and the circuit was kept open for 30 min.

The OCP at each discharge capacity was the cell voltage just before discharge. The direct current resistance (DCR) at each discharge capacity was calculated from the cell voltage just before discharge, cell voltage 10 seconds after discharge, and the value of the discharge current.

2.3 Battery design

Figure 1 shows the stacked structure and an image of one of the laminated cells with recovery electrodes. Two sheets of positive electrodes wrapped with bag-shaped separators and three sheets of negative electrodes were interlaminated, and one sheet of recovery electrode wrapped with a bag-shaped separator was allocated to each side of the outside-most plane. The tab of the recovery electrodes was placed on the other side of the tabs of the positive and the negative electrodes to prevent the tabs from coming into contact with each other.

The area covered with the positive electrode mixture was 31.5 cm^2 per plane, and the area covered with the negative electrode mixture was 34.8 cm^2 per plane. The amount of electrolyte injected into the cells was 4 times more in volume than the theoretical vacancy volume of the electrode group. The design capacity of these cells was 0.290 Ah; therefore, 1 C rate was 0.290 A. The ratio of the capacity of the positive electrodes to that of the negative electrodes was 1.4 in these cells. 100 % SOC of the cells was defined as the fully charged state of the positive electrode.

2.4 Charge–discharge conditions of batteries

After injection of the electrolyte, the laminated cells were held at 25°C for 24 h to impregnate the electrodes with the electrolyte, and they were activated by the initial charge–discharge as follows: they were charged at a constant current of $1/20\text{ C}$ to 4.2 V and held at that voltage until the current decreased to $1/100\text{ C}$. After charging, they were discharged at a constant current of $1/20\text{ C}$ to 2.7 V. The rest after charge and discharge was 30 min.

Capacity slippage due to formation of SEIs on the negative electrodes also occurs during the initial charge–discharge. For a systematic analysis, capacity recovery was carried out after the initial charge–discharge because cells were only slightly damaged during the charge–discharge tests. The positive or the negative electrodes were replenished with Li^+ by applying current between them and the recovery electrodes. Current was continuously applied until Q_e reached a predetermined value. The current was set at a low rate, 0.002 A ($1/145\text{ C}$) for replenishment of the positive electrodes. Here, the concern was that capacity recovery could not be

Figure 1. Stacked structure and image of laminated cell with recovery electrodes.

completed at a high rate due to high electrochemical polarization as a result of the negative electrodes, which were steric hindrances between the recovery and the positive electrodes. On the other hand, the current was set at a relatively high rate, 0.145 A (1/2 C) for replenishment of the negative electrodes because the recovery electrodes faced the negative electrodes. Before capacity recovery, the cells were charged for replenishment of the positive electrodes and discharged for replenishment of the negative electrodes. This means capacity recovery was carried out after Li^+ were deintercalated from the electrodes that would receive Li^+ during the capacity recovery.

The discharge capacity evaluation and the galvanostatic intermittent titration (GITT) measurement were carried out before the charge–discharge cycle test and after a certain number of cycles.

In the discharge capacity evaluation, the laminated cells were charged at a constant current of 1/5 C to 4.2 V and held at that voltage until the current decreased to 1/100 C. After charging, the cells were discharged at various constant currents of 1/20, 1/5, 1/2 and 1 C to 2.7 V. The rest after charge and discharge was 30 min.

The GITT measurement was carried out in order to obtain open circuit voltage (OCV) curves and DCR curves. In the GITT measurement, the laminated cells were charged at a constant current of 1/5 C to 4.2 V and held at that voltage until the current decreased to 1/100 C. The rest after charge was 30 min. Then, the following cycle was repeated until the number of cycles reached 50 or the cell voltage reached 2.7 V; the cells were discharged at a constant current of 1 C until the discharge capacity reached 0.0058 Ah (= 2 % SOC), and the circuit was kept open for 30 min. The OCV at each discharge capacity was the cell voltage just before discharge. The DCR at each discharge capacity was calculated from the cell voltage just before discharge, cell voltage 10 seconds after discharge, and the value of the discharge current.

In the charge–discharge cycle test, the laminated cells were charged at a constant current of 1 C to 4.2 V and held at that voltage until the current decreased to 1/100 C. After charging, the cells were discharged at a constant current of 1 C to 3.0 V. The rest after charge and discharge was 30 min.

Charge–discharge cycle tests were carried out at 50 °C as acceleration tests; the other charge–discharge tests were conducted at 25 °C.

2.5 Half-cell measurement of electrodes obtained from laminated cells

The laminated cell after the capacity recovery treatment was dismantled in a glove box filled with Ar gas to obtain the positive, negative, and recovery electrodes. Prior to dismantling, the laminated cells were discharged at a constant current of 1 C to 2.7 V at 25 °C. After discharging, the aluminum laminate films were cut using ceramic scissors, and electrodes/separators assemblies

were pulled out. Negative electrodes were picked from the assemblies. To evaluate the electrochemical properties of the negative electrode on one plane of the electrode, the electrode on the opposite plane was removed. A negative electrode sample 15 mm in diameter was obtained by punching the electrode sheet. The sample was set in a half cell in which 16-mm ϕ Li metal was used as a counter electrode. The electrolyte and separator in the half cell were the same as those used in the laminated cell.

3. Results and Discussion

3.1 Mechanisms of capacity recovery

The capacity recovery by the replenishment of the positive electrodes with Li^+ was treated for the cells after the initial charge–discharge. Figure 2 indicates the discharge capacities of the cells after capacity recovery measured at 1/20 C. The horizontal axis shows Q_e . The measurement at 0 Ah of Q_e is for the case without capacity recovery.

The discharge capacities of the cells were increased by capacity recovery, but tended to reach a limit as Q_e increased. To clarify the reason, we analyzed the discharge curves.

Figure 3 shows the results of the discharge curve analysis before the charge–discharge cycle tests for the cell without capacity recovery. The horizontal axis shows the discharge capacity, where a negative value means a surplus charge capacity. The vertical axis shows the cell voltage and the positive and the negative electrodes potential vs. Li metal. The dots mean the measured cell OCV, and the solid lines are the OCP curves of the positive and the negative electrodes and the OCV curve of the cell as reconstructed by superposing the OCP curves of the positive and the negative electrodes. The details of the discharge curve analysis are described in previous papers.^{6–8}

Figure 2. Discharge capacities of cells after capacity recovery measured at 1/20 C. Horizontal axis shows electric charge between the recovery and the positive electrodes.

Figure 3. Results of discharge curve analysis before charge–discharge cycle tests for the cell without capacity recovery. Dots mean the measured cell OCV, and solid lines mean the OCP (vs. Li/Li⁺) curves of the positive and the negative electrodes and the OCV curve of cell reconstructed by superposing these OCP curves of the positive and the negative electrodes.

The discharge endpoint of the positive electrode curve was located at a higher discharge capacity than that of the negative electrode curve. This was caused by capacity slippage occurring during the initial charge–discharge. There was also around 0.08 Ah of surplus charge capacity in the negative electrodes even in the fully charged state. Hence, the cell capacity could be recovered by shifting the negative electrode curve toward the higher discharge capacity side. This corresponds to the positive electrodes being charged, or the negative electrodes being discharged, individually.

Figure 4 shows the results of the discharge curve analysis after capacity recovery, where the current for recovery (Q_r) was applied between the positive and the recovery electrodes. The values of Q_r were (a) 0, (b) 0.040, (c) 0.080, (d) 0.120, (e) 0.160, and (f) 0.200 Ah.

The discharge endpoints of the negative electrode curves gradually shifted to the higher discharge capacity side as Q_r increased. This indicates that capacity slippage can be mitigated by Li⁺ replenishment.

When recovery capacities are large, as shown in Figs. 4(e)–4(f), the discharge endpoints of the negative electrode curves are close to those of the positive electrode curves, and the discharge endpoints of

Figure 5. η_r at each Q_e . η_r is recovery efficiency, and Q_e is electric charge between recovery and positive electrodes.

the cells are restricted by the discharge endpoints of the positive electrodes. In such a case, the discharge capacity is not increased by further recovery from capacity slippage. This is the reason the discharge capacities of the cells tended to reach a limit.

Figure 5 illustrates η_r during capacity recovery discussed in the above. As described above, a recovery capacity of a cell and Q_r are not necessarily equal. The intrinsic phenomenon due to Li⁺ replenishment is recovery from capacity slippage; capacity recovery of a cell is a subsidiary phenomenon. Hence, the numerator of Formula (1) is Q_r .

Q_r was calculated from the shift of the discharge endpoints of the negative electrode curves due to capacity recovery. The capacity corresponding to 4.3 V on the positive electrode curve was set as the origin of the discharge endpoint of the negative electrode curve. This makes it possible to accurately evaluate the discharge endpoint of the negative electrode curve relative to the positive electrode curve even when the positive electrode potential in the fully charged state of the cell changes due to capacity recovery.

The values of η_r were under 50% for all Q_e and tended to decrease as Q_e increased.

To elucidate this behavior, the capacity recovery mechanisms were investigated. In particular, the amount of Li⁺ replenishing the positive electrodes was estimated from the change in OCV of the cells before and after capacity recovery. Figure 6 illustrates the estimated OCP of the positive electrodes and the estimated amount of Li⁺ replenishing the positive electrodes at each Q_e . The OCP of

Figure 4. Results of discharge curve analysis for cells after capacity recovery in which current was applied between positive and recovery electrodes. Q_r was (a) 0, (b) 0.040, (c) 0.080, (d) 0.120, (e) 0.160, and (f) 0.200 Ah.

Figure 6. Estimated OCP of positive electrodes and estimated amount of Li^+ replenishing positive electrodes at each Q_e , which is the electric charge between the recovery and the positive electrodes. The dashed line shows coordinates where Q_e and the amount of Li^+ replenishing the positive electrodes are equal.

the positive electrodes was estimated under the assumption that any change in cell OCV due to capacity recovery was completely derived from the change in OCP of positive electrodes because the results of the discharge curve analysis showed that the potential of the negative electrodes was invariant during capacity recovery. An amount of Li^+ replenishing the positive electrodes was calculated from the estimated change in OCP and the OCP curve of the positive electrode. The dashed line in this figure shows the coordinates where Q_e and the amount of Li^+ are equal.

The estimated OCP of the positive electrodes decreased as Q_e increased, and the estimated amount of Li^+ replenishing the positive electrodes roughly corresponded to Q_e . These results suggest that an amount of Li^+ corresponding to Q_e replenished the positive electrodes.

Figure 7 shows images of the negative electrodes after discharging the cells (a) without capacity recovery, (b) after capacity recovery for a Q_e of 0.200 Ah, and (c) after capacity recovery for a Q_e of 0.200 Ah and 20 charge–discharge cycles. The current for the recovery was applied between the positive and the recovery electrodes. As for the cell without capacity recovery (Fig. 7(a)), the color of the negative electrode planes facing the positive electrodes (inside planes) and those facing the recovery electrodes (outside planes) was black. This suggests the negative electrodes were in a discharged state. On the other hand, for the cell with capacity recovery (Fig. 7(b)), the inside planes of the negative electrodes were colored black, but the outside planes were colored gold. This suggests that the inside planes were in a discharged state, but the outside planes were in a highly charged state even though current was applied between the positive and the recovery electrodes. The reason why Li^+ were intercalated into the outside planes of the negative electrodes will be discussed later. After the 20th charge–discharge cycle, the gold regions in the outside planes of the negative electrodes changed to burnished dark brown and the color of the inside planes changed to ochre (Fig. 7(c)). This suggests that the amount of Li^+ in the outside planes of the negative electrodes decreased, and the amount of Li^+ in the inside planes increased during the charge–discharge cycles.

The amount of Li^+ in the outside planes of the negative electrodes was evaluated with half cells in which the planes were used as working electrodes. The working electrodes were 15-mm ϕ sections of the negative electrodes, and the counter electrodes were 16-mm ϕ sections of Li metal. The electrolyte and separators were the same as those used in the laminated cell. The half cells were oxidized at a constant current of 1/3 C to 1.0 V and held at that voltage until the current decreased to 1/30 C. The details of the half-cell measurement of the electrodes obtained from laminated cells are

Figure 7. Images of negative electrodes after discharging cells (a) without capacity recovery, (b) after capacity recovery for a Q_e of 0.200 Ah, and (c) after capacity recovery for a Q_e of 0.200 Ah and 20 charge–discharge cycles. Current was applied between the positive and the recovery electrodes during capacity recovery.

described in section 2.5. Figure 8 illustrates the discharge curves of the negative electrodes in the half cells. In particular, Fig. 8(a) shows the results for the negative electrode after capacity recovery for a Q_e of 0.200 Ah, and (b) shows the results for the negative electrode after capacity recovery for a Q_e of 0.200 Ah and 20 charge–discharge cycles. Note that current was applied between the positive and the recovery electrodes in these measurements.

In Fig. 8(a), the discharge capacity was 1.75 mAh cm⁻². The amount of Li^+ in one of the outside planes of the negative electrodes was estimated to correspond to 0.061 Ah by multiplying 1.75 mAh cm⁻² by the negative electrode area, 34.8 cm². Because the negative electrodes had two outside planes, the total amount of Li^+ corresponded to 0.122 Ah. This corresponds to 61 % of Q_e . The outside planes of the negative electrodes after capacity recovery were in a highly charged state corresponding to 85 % SOC of the laminated cell, since the total capacity of those planes, as determined by the design of the cell, was 0.144 Ah.

In Fig. 8(b), the discharge capacity was 1.56 mAh cm⁻². This means the planes were in a charged state corresponding to 75 % SOC, which was less than 85 % SOC just after capacity recovery. Hence, it was assumed that some of the Li^+ intercalated into the outside planes of the negative electrodes was released during cell discharge.

The above results reveal the following two points about the behavior of Li^+ during capacity recovery by replenishment of the positive electrodes with Li^+ :

(i) The positive electrodes were replenished with an amount of Li^+ corresponding to the total Q_e .

(ii) An amount of Li^+ corresponding to 61 % of Q_e was intercalated into the outside planes of the negative electrodes.

Figure 9 summarizes the two processes simultaneously occurring during the capacity recovery. Here, the cells are in a charged state before capacity recovery, and the inside planes of the negative electrodes have a large amount of Li^+ while the positive electrodes

Figure 8. Discharge curves of outside planes of negative electrodes unpacked from cells (a) after capacity recovery for a Q_e of 0.200 Ah and (b) after capacity recovery for a Q_e of 0.200 Ah and 20 charge–discharge cycles. Current was applied between the positive and the recovery electrodes during capacity recovery.

Figure 9. Schematic diagrams of capacity recovery process in which current is applied between positive and recovery electrodes; (a) Li^+ are intercalated into the positive electrodes as they are released from the recovery electrodes, and (b) transfer of electrons in the negative electrodes occurs while process (a) progresses.

have a small amount of Li^+ . In Fig. 9(a), Li^+ are intercalated into the positive electrodes as they are released from the recovery electrodes. Because this means individual discharge of the positive electrodes, the Li^+ intercalated into the positive electrodes directly contribute to recovery from capacity slippage. In the process shown in Fig. 9(b), however, Li^+ are released from the inside planes of the negative electrodes as they are intercalated into the outside planes of the negative electrodes by transfer of electrons in negative electrodes while process (a) progresses. Process (b) causes discharge of the inside planes of negative electrodes together with the discharge of the positive electrodes. The Li^+ intercalated into the outside planes of the negative electrodes are not easily released during the discharge between the positive and the negative electrodes. Thus, the Li^+ intercalated into the positive electrodes through process (b) contribute little to the recovery from capacity slippage, and this is the reason η_r was low.

Here, let us discuss the reason why Li^+ were released from the inside planes of the negative electrodes and intercalated into the outside planes. The probable causes are i) the SOC deviation

between the inside planes and the outside planes of the negative electrodes, and ii) the difference in Li^+ concentration between the inside electrolyte (between the negative and the positive electrodes) and outside electrolyte (between the negative and the recovery electrodes). When a cell is kept in a fully charged state, it is supposed that Li^+ deintercalation from the inside planes of the negative electrodes and Li^+ intercalation into the outside planes spontaneously proceeds because of the uneven distribution of Li^+ in the negative electrodes. In that case, the SOC converges towards uniform value in all of the negative electrodes. In this study, the cell was fabricated with two sheets of positive electrodes, three sheets of negative electrodes, and two sheets of recovery electrodes. In this configuration, the number of inside planes of the negative electrodes is four, and the number of outside planes of the negative electrodes is two. Because the four inside planes are at 100 % SOC, and the two outside planes are at 0 % SOC in the fully charged state, the SOC converges towards 67 % through a spontaneous process. The outside planes of the negative electrodes just after capacity recovery, when Q_e was 0.200 Ah between the positive and the recovery electrodes, corresponded to 85 % SOC, which was higher than 67 %. This indicates there is another factor related to the phenomenon that Li^+ are intercalated into the outside planes of the negative electrodes.

This other factor is assumed to be the gradient of Li^+ concentration in the electrolyte. In the case of capacity recovery, the Li^+ concentration increases in the electrolyte between the recovery and the negative electrodes while it decreases in the electrolyte between the positive and the negative electrodes, as shown in process (a). It is assumed that intercalation of Li^+ into the outside planes of the negative electrodes and the release of Li^+ from the inside planes of these electrodes occur to mitigate the concentration gradient. This phenomenon would progress as the concentration gradient increases, which is consistent with the experimental results shown in Fig. 5; i.e., η_r decreased as Q_e increased. Before capacity recovery, the SOC of the four inside planes of the negative electrodes was 100 %, while that of the two outside planes was 0 %. Because the SOC of the two outside planes of the negative electrodes was 85 % after capacity recovery, the SOC of the four inside planes is estimated to be 58 % as follows:

$$\frac{(100\% \times 4 + 0\% \times 2) - 85\% \times 2}{4} = 58\% \quad (2)$$

where 4 is the number of inside planes, and 2 is the number of outside planes.

For the cell just before capacity recovery, the negative electrodes corresponded to the stage structure at higher potential in 85 % SOC and the stage structure at lower potential in 58 % SOC (Fig. S1). This suggests that around 0.04 V of potential difference occurred during capacity recovery. On the basis of the variation in the

equilibrium potential and Li^+ concentration calculated in the supplementary note, the variation in the Li^+ concentration corresponding to the potential difference can arise through process (a). Therefore, suppression of the gradient of Li^+ concentration in electrolytes or suppression of the deviation of the amount of Li^+ in negative electrodes is necessary to suppress process (b) and increase η_r .

Process (b) prompts activation of the outside planes of the negative electrodes. This activation appeared as an increase in the usable masses of the negative active materials, which is shown as an expansion of the OCP curves of the negative electrodes in Fig. 4.

Q_r was 0.048 Ah during capacity recovery for a Q_e of 0.200 Ah. The amount of Li^+ in the outside planes of the negative electrodes was estimated to correspond to 0.122 Ah just after capacity recovery. Furthermore, the irreversible capacity of the outside planes of the negative electrodes was 0.023 Ah. The total amount of Li^+ corresponded to 0.193 Ah, which is approximately equal to Q_e . The difference of 0.007 Ah is assumed to be due to residual Li^+ in the regions of the negative electrodes not facing the positive electrodes that cannot be released.

Some of the Li^+ intercalated into the outside planes of the negative electrodes were released during the cell discharge, as described above. It was verified that the recovery proceeds by intercalating Li^+ into the outside planes of the negative electrodes. Figure 10 illustrates the discharge capacity measured at a constant current of 1/20 C at each charge–discharge cycle. Figure 10(a) shows the results for the cell with capacity recovery when Q_e was 0.200 Ah between the positive and the recovery electrodes. Figure 10(b) shows the results for the cell with capacity recovery when Q_e was 0.165 Ah between the negative and the recovery electrodes. Figure 10(c) shows the results for the cell without capacity recovery. The capacity recovery between the negative and the recovery electrodes was carried out at a high rate of 1/2 C. Since the current corresponded to 1 C in the area between the negative and the recovery electrodes, most of the Li^+ were assumed to be intercalated into the outside planes of the negative electrodes.

The discharge capacities of the cells with capacity recovery increased compared with that of the cell without capacity recovery and remained high after charge–discharge cycles. In particular, the discharge capacities increased until the 100th cycle in Fig. 10(b). This result strongly supports the assumption that some of the Li^+ intercalated into the outside planes of the negative electrodes was released during cell discharge and contributed to the recovery from capacity slippage.

Figure 10. Discharge capacity measured at a constant current of 1/20 C at each charge–discharge cycle; (a) cell with capacity recovery between the positive and the recovery electrodes, (b) cell with capacity recovery between the negative and the recovery electrodes, and (c) cell without capacity recovery.

However, it is considered to be difficult to completely extract Li^+ from the outside planes of the negative electrodes merely by repeating the charge–discharge cycle. We confirmed that the some amount of Li^+ existed in the outside planes after as many as 1000 charge–discharge cycles, as shown in Fig. S2. Hence, it is supposed that the increase in η_r requires suppression of Li^+ intercalation into the outside planes of the negative electrodes; this could be realized by suppression of the gradient of the Li^+ concentration in the electrolytes or suppression of the deviation of the amount of Li^+ in the negative electrodes.

3.2 Rate properties of cells with capacity recovery

Figure 11 illustrates the discharge capacities of the cells with capacity recovery between the positive and the recovery electrodes. The horizontal axis is the number of charge–discharge cycles. The measurement C-rates were (a) 1/20 C, (b) 1/5 C, (c) 1/2 C, and (d) 1 C. The Q_e values during capacity recovery were 0.040, 0.120, and 0.200 Ah. The plot at 0 Ah means the discharge capacity of the cell without capacity recovery.

The discharge capacities of the cells with capacity recovery measured at lower C-rates remained higher than those of the cell without capacity recovery. On the other hand, the decrease in the discharge capacities measured at higher C-rates tended to accelerate due to capacity recovery. To determine the reason for this result, we calculated the DCRs of these cells.

Figure 12 illustrates the DCR curves of the cells (a) just after capacity recovery and (b) after capacity recovery and the 1300th charge–discharge cycle. The horizontal axis shows the discharge capacity, where current was applied between the positive and the recovery electrodes.

The DCRs of the cells with capacity recovery were lower than that of the cell without capacity recovery in the vicinity of the discharge endpoint just after capacity recovery (Fig. 12(a)). Therefore, high capacity was obtained even at a higher C-rate. On the other hand, the DCRs of the cells with capacity recovery, when Q_e was more than 0.120 Ah, were higher than that of the cell without capacity recovery in the low SOC region of 0.150–0.200 Ah after the 1300th cycle (Fig. 12(b)). The increase in the DCRs of the cells with capacity recovery was gradual relative to that of the cell without capacity recovery in the vicinity of the discharge endpoint. Therefore, the discharge capacities of the cells with capacity recovery were lower at higher C-rates and higher at the lower C-rates than those of the cell without capacity recovery.

The difference between the DCR curves was due to the difference between the electrodes that restrict the discharge endpoints of the cells. Figure 13 illustrates the DCR curves of the positive and the negative electrodes. The vertical and horizontal axes are normalized by the areas of the electrodes and the mass of the active materials, respectively. This figure shows that the increase in resistance in the vicinity of the discharge endpoint is more gradual in the positive electrode than in the negative electrode.

Figure 14 shows the results of the discharge curve analysis for cells after capacity recovery and the 1300th charge–discharge cycle, where current was applied between the positive and the recovery electrodes. The discharge endpoints of the cells were restricted by those of the negative electrodes in the cell without capacity recovery (Fig. 14(a)) and in the cell with capacity recovery when Q_e was 0.040 Ah (Fig. 14(b)). However, the discharge endpoints of the cells were restricted by those of the positive electrodes in the cells with capacity recovery, when Q_e was 0.120 Ah (Fig. 14(c)) and 0.200 Ah (Fig. 14(d)).

This is the reason why the DCR curves of the cells with capacity recovery changed, similarly to the DCR curve of the positive electrode in the vicinity of the discharge endpoint. The reason why the discharge endpoints of the cells with capacity recovery, when Q_e was more than 0.120 Ah, were restricted by those of the positive

Figure 11. Discharge capacities of cells with capacity recovery between positive and recovery electrodes. Q_e was 0, 0.040, 0.120, and 0.200 Ah. Measurement C-rates were (a) 1/20 C, (b) 1/5 C, (c) 1/2 C, and (d) 1 C.

Figure 12. DCR curves of cells (a) just after capacity recovery and (b) after capacity recovery and the 1300th charge–discharge cycle. Current was applied between the positive and the recovery electrodes during capacity recovery, and Q_e was 0, 0.040, 0.120, and 0.200 Ah.

Figure 13. DCR curves of (a) positive electrode and (b) negative electrode. The vertical and horizontal axes are normalized by the areas of the electrodes and the mass of the active materials, respectively.

Figure 14. Results of the discharge curve analysis for cells after capacity recovery and the 1300th charge–discharge cycle. Q_c was (a) 0, (b) 0.040, (c) 0.120, and (d) 0.200 Ah. Current was applied between the positive and the recovery electrodes during capacity recovery.

electrodes was that the OCP curves of the positive electrodes of those cells became shorter than that of the cell without capacity recovery. The contraction of the OCP curves of the positive electrodes means a decrease in the capacities of the positive electrodes. The degradation of the positive electrodes was assumed to be accelerated by the use of the low potential region of the positive electrodes after capacity recovery.

We are currently investigating capacity recovery by suppressing the decrease in the capacities of the positive electrodes and improving lifetimes at higher rates.

4. Conclusions

The discharge capacities of lithium ion cells were recovered by using recovery electrodes and replenishing positive or negative electrodes with Li^+ . Discharge curve analysis revealed that capacity recovery was possible due to recovery from capacity slippage between the positive and the negative electrodes. The recovery efficiency, defined as the ratio of recovery capacity of capacity slippage to electric charge between the recovery and the positive electrodes, was less than 50 % and tended to decrease with increasing electric charge. This result was derived from the behavior of Li^+ during capacity recovery. Positive electrodes are replenished with Li^+ in the following two manners: (a) Li^+ are intercalated into positive electrodes as they are released from the recovery electrodes, contributing to recovery from capacity slippage; however, (b) some amount of Li^+ is released from the inside planes of negative electrodes as it is intercalated into the outside planes of the negative electrodes, which does not significantly contribute to recovery. Therefore, suppression of the Li^+ concentration gradient in the electrolytes or suppression of the deviation of the amount of Li^+ in the negative electrodes are necessary to suppress process (b) and increase recovery efficiency.

The decrease in the discharge capacity measured at higher C-rates tended to accelerate due to capacity recovery, while the discharge capacities of the cells with capacity recovery measured at

lower C-rates remained higher than those of the cell without capacity recovery. This finding was derived from the increase in DCRs in the low SOC region, and it was because the discharge endpoints of the cells became restricted by those of the positive electrodes following the decrease in the capacities of the positive electrodes.

For practical application of the capacity recovery, the current patterns and electric charges during capacity recovery should be optimized to increase recovery efficiency and improve lifetimes at higher discharging rates.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00138>.

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