Relationship between Electrochemical Pre-Treatment and Cycle Performance of a Li-Rich Solid-Solution Layered $\text{Li}_{1-a}[\text{Ni}_{0.18}\text{Li}_{0.20+a}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ Cathode for Li-Ion Secondary Batteries

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ABSTRACT

In our previous paper (*J. Power Sources*, **183**, 344 (2008)), we proposed the application of a pre-cycling treatment to a Li-rich solid-solution layered cathode ($x\text{Li}_2\text{MnO}_3 \cdot y\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \cdot z\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ where $(x + y + z = 1)$) before the charge/discharge cycling process to obtain enhanced capacities stable above 250 mAh g^{-1} . The aim of the present work is to reduce the duration of this pre-cycling process. The cycling performance dependence of $\text{Li}_{1-a}[\text{Ni}_{0.18}\text{Li}_{0.20+a}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ on the pre-cycling processing parameters, such as the number of cycles, voltage limits, and current density was explored. The processing conditions were then optimized, which ultimately reduced the pre-cycling treatment time from one week to 6.5 h.

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Keywords : Li-rich Solid-Solution Layered Cathode, Lithium-Ion Battery, Electrochemical Pre-Treatment

1. Introduction

Lithium-ion batteries (LIBs) are the state-of-the-art power source for portable appliances, such as notebook computers, cellular phones, and digital cameras, and are a prime energy storage candidate for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs) because of their high energy density, high power density, superior cyclability and safety. HEVs and EVs equipped with LIBs are already common in many countries. Because of the successful popularity of HEVs, PHEVs, and EVs with LIBs, there has been great demand for the development of high performance anode and cathode materials for LIBs, which combine high energy storage capabilities with cyclic durability and low material cost.¹ The development of a higher capacity cathode material in particular is a matter of great urgency for the automobile industry because the attainable capacity of current commercially available cathode materials for Li-ion batteries, such as LiCoO_2 and LiMn_2O_4 , is much lower than that of the anode materials and limits the expansion of LIB usage.² A great deal of attention has recently been focused on the Li-rich solid-solution layered cathode material $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M} = \text{Co}, \text{Ni}$, etc.), which exhibits a discharge capacity of more than 200 mAh g^{-1} when operated above 4.6 V.³ The structural compatibility between Li_2MnO_3 , which is electrochemically inactive and has a large theoretical capacity, and LiMO_2 , which is electrochemically active but has lower stable capacity, allows for the structural integration of these components at the atomic level. As a result, the electrochemically inactive Li_2MnO_3 can participate in the charge/discharge process after activation with release of some oxygen from the lattice during the charging process;⁴ the capacity of LiMO_2 can be improved by the Li_2MnO_3 component that stabilizes the layered LiMO_2 structure when more than 50% of the Li^+ ions are deintercalated. To the best of our knowledge, Numata and coworkers were the first to report on the application of a solid-solution layered

material composed of Li_2MnO_3 and LiMO_2 as cathode and its improved stability in 1997.⁵ Dahn et al. reported in 2002 that solid-solution layered cathode materials could deliver a discharge capacity of $200\text{--}240 \text{ mAh g}^{-1}$ between 2.0 and 4.8 V.^{6,7} Following the publication of these studies, many researchers investigated the preparation conditions,^{8,9} structure,^{10,11} and electrochemical behavior^{12–14} of solid-solution cathode materials, such as $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot (1-x)\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$,^{8,10,11} $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot (1-x)\text{LiCrO}_2$,^{10,13} and $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot (1-x)\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$.^{12,14} The preparation conditions and structural details of these materials have been clarified in many papers; however, the poor cycle durability of these cathode materials remained unresolved and unexplored. Although both surface modification^{15,16} and fluorine substitution^{17,18} have been examined as methods to improve cyclic durability, these approaches do not appear to offer a complete solution. We originally proposed an electrochemical pre-cycling treatment of a Li-rich solid-solution layered cathode to improve cyclic durability. $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$, which can also be written as $(3/5)\text{Li}_2\text{MnO}_3 \cdot (1/5)\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \cdot (1/5)\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, exhibited a stable reversible capacity of approximately 250 mAh g^{-1} after our pre-cycling treatment with a fixed discharge cutoff voltage of 2.0 V and a charge cutoff voltage that increased incrementally by 0.1 V every two cycles from 4.5 to 4.7 V.¹⁹ It was found that gradually increasing the quantity of Li^+ ions extracted from and inserted into the cathode layers during the charge/discharge process by controlling the charge voltage limit above 4.5 V led to an increased cyclic durability. Transmission electron microscopy (TEM) studies elucidated the difference between the crystal periodicity of the two materials either with or without the pre-cycling treatment after the charge/discharge cycles. These studies revealed that the deterioration begins at an initial charge/discharge potential of 4.5 V, above which micro-cracks in the crystal surface, distortions in the crystal periodicity, and further non-crystallizations were observed.²⁰ However, the cathode material crystals treated with the pre-cycling treatment

neither cracked nor suffered from any distortions even after 50 charge/discharge cycles.²⁰ These observations emphasize the importance of the pre-cycling treatment involving a stepwise increase in the charge voltage limit to improve cyclic durability. Additionally, several of our recent studies have reported on the local structure of an as-prepared Li-rich solid-solution layered cathode material,²¹ and the structural²² and valence state (of Ni, Co, and Mn in the cathode)²³ changes that occurred during its first charge/discharge cycle. The elucidation of the mechanism responsible for this improvement from the electrochemical pre-treatment, with regards to changes in the crystal structure and the valence states of the metals in the cathode during charge/discharge cycling, is still in progress.

In this study, the performance of the cathode material was investigated in detail by varying the charge/discharge voltage limits, cycle numbers, and current densities during the pre-cycling treatment to reduce the duration of the pre-cycling process. We expect that our pre-cycling treatment will be recognized as a practical means to reduce the pre-treatment time of commercially available Li-ion batteries. In our investigation, we use $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ as the Li-rich solid-solution layered cathode. This composition was selected for two primary reasons. The first reason was its reversible capacity that is larger than that of the $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ used in our previous studies. The second reason for this material choice was its decreased cobalt content, which is both toxic and expensive. The cathode materials used in both the current and previous studies exhibited the same cyclic stability following the pre-cycling treatment, which required approximately one week to complete.

2. Experimental

2.1 Preparation and characterization of the cathode material

The active cathode material $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ was prepared via the spray-drying and post-annealing processes. $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ (Wako, Japan), $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ (Wako, Japan), $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$ (Wako, Japan), and $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ (Wako, Japan) were used as precursors, with a stoichiometric amount of each dissolved in 2 M aqueous citric solution to maintain an atomic ratio in the synthesized cathode of Ni:Co:Mn = 0.18:0.03:0.58. A 7% molar excess of lithium was provided to compensate for any possible losses. The total concentration of metal ions in the solution was adjusted to 2 M, and the resulting solution was pumped into a spray-dry instrument (B-290, Büchi) to form the cathode material precursor. The obtained precursor was pre-heated at 450°C for 6 h in air, thoroughly ground, and then pressed into pellets. These pellets were then sintered at 900°C for 12 h in air and then quenched with liquid N_2 . The cathode material was thoroughly ground again before being mixed with a conductive binder. Powder X-ray diffraction (XRD) measurements for structural characterization were completed using the beam line of the synchrotron radiation facility SPring-8. The Li:Ni:Co:Mn elemental ratio for the synthesized cathode material was determined via inductively coupled plasma spectroscopy using a SPS1500VR (SEIKO) spectrometer. The average size of the as-prepared particles was measured using a field-emission scanning electron microscope (FE-SEM, S-4000, Hitachi).

2.2 Cell preparation and electrochemical tests

Electrochemical tests were performed using a CR2032 coin-type cell. The cathode was fabricated from 20 mg of $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ active material and 12 mg of a conductive binder (Teflonized acetylene black, TAB-2), which were kneaded together until a homogenous mixture was formed. This product was then shaped into a disc and pressed into a pellet, which contained a 200 mm² stainless steel mesh as the current collector, under a

pressure of 300 kg cm⁻². The resulting product was dried at 130°C for 5 h in a vacuum drying oven. The test cell was composed of the cathode pellet and a lithium metal anode separated by a porous polypropylene film (Celgard 3401). The electrolyte used in the tests was a 1 M LiPF_6 -ethylene carbonate (EC)/dimethylcarbonate (DMC) solution (1:2 by vol., Ube Chemicals, Japan). The charge/discharge cycling was performed using a multichannel battery tester (model BTS2004, Nagano Corp., Japan), with all the tests performed at room temperature. The constant-current (CC) mode was used for both the pre-treatment process and the cycle tests. The charge/discharge cycle tests that followed the pre-treatment process were performed at a charge/discharge current density of 0.2 mA cm⁻² with a cutoff voltage of 2.0–4.8 V. During the pre-cycling treatment process, the charge/discharge conditions, such as current density and cutoff voltage, were examined in terms of their capacity and cyclic durability. The charge/discharge capacities observed during the pre-cycling process are hereafter included with the results of the charge/discharge cycle tests in results and the discussion section.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ cathode material, which was used in this study, and $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ cathode materials, which was used in our previous works. The peaks can be indexed as the layered rocksalt type symmetry ($R\bar{3}m$). No impurity phase was found, and the peak shift due to the difference in the composition of the two samples was observed. The broad peaks detected in the range of 22–25° show that these materials have the super lattice structure, in which Li^+ ions order themselves in the transition metal layer. The Li:Ni:Co:Mn elemental ratio for the synthesized cathode material was determined to be 1.2:0.18:0.03:0.58 using an ICP spectrometer. In this paper, the cathode material was written as $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ because the amount of Li^+ ions in the transition layer can not be determined by the X-ray diffraction patterns shown in Fig. 1. The average size of the as-prepared particles was approximately 300 nm, as observed with SEM.

Figure 2 illustrates the differences in the cycle performance of the as-prepared sample vs. the samples treated via electrochemical pre-cycling. In the case of the as-prepared samples (non-treated samples), the cell was cycled at 0.2 mA cm⁻² between 2.0 and 4.8 V. Conversely, during the pre-cycling process, the cell was treated with a stepwise pre-cycling until the 6th cycle; that is, for two cycles between 2.0 and 4.5 V, between 2.0 and 4.6 V, and 2.0 and 4.7 V with 0.2 mA cm⁻² (total six cycles, which we will later refer to as “conventional pre-cycling”), followed by cycle testing between 2.0 and 4.8 V. As shown in the figure, the capacity of the untreated sample cell faded rapidly between the 1st and 20th cycles before reaching a stable reversible capacity of 200 mAh g⁻¹ (Fig. 2(a)). Although the pre-treated cell showed minor capacity fading during the early stages, a stable and reversible capacity of approximately 275 mAh g⁻¹ was retained after several cycles (Fig. 2(b)). These results strongly suggest that the stepwise pre-cycling treatment by increasing the charge voltage limit effectively improved the capacity stability. The as-prepared $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ sample used in this study exhibited behavior similar to $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$, which was tested in our previous study, with respect to the effectiveness of the pre-cycling treatment.²⁰ In addition, the reversible capacity of $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ after the pre-cycling treatment was 20–25 mAh g⁻¹ greater than that observed for $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$.

As mentioned earlier, a sample cycled between 2.0 and 4.8 V without the pre-cycling treatment showed micro-cracks on the crystal surface, distortion of the crystal periodicity, and further decrystallization after charge/discharge cycling. These results

Figure 1. Comparison of the synchrotron X-ray diffraction profiles of $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$, using magnified presentations of (i) 104 as typical peak.

Figure 2. Cycle performance of the untreated (a) (▲, △) and treated $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ electrodes. The charge voltage limit was increased stepwise by 0.1 V every two cycles from 4.5 to 4.7 V and the discharge voltage limit was fixed at 2.0 V with a current density of 0.2 mA cm^{-2} during the pre-cycling process (b) (●, ○). A charge/discharge cycle between 4.8 and 2.0 V with a current density of 0.05 mA cm^{-2} was used during the pre-cycling process (c) (■, □). Charge capacity: ▲, ●, ■, discharge capacity: △, ○, □.

suggest that the rapid deintercalation/intercalation of Li^+ ions from/into the cathode decomposes the crystal structure. Therefore, it is believed that significantly lower charging rates influence the cycle durability. After significantly low current density of 0.05 mA cm^{-2} was employed for the pre-treatment with the voltage limits of 2.0 and 4.8 V, the charge/discharge cycle test was initiated at 0.2 mA cm^{-2} with identical cutoff voltage limits. The charge/discharge pre-cycling with 0.05 mA cm^{-2} required five to six days. However, even for the cell treated at 0.05 mA cm^{-2} , a significant capacity fading was observed during the early stages (Fig. 2(c)); the discharge capacity reached approximately 200 mAh g^{-1} after 10 cycles. It was therefore determined that a lower current density during the pre-cycling treatment was not a key parameter in suppressing the capacity fading during the early charge/discharge cycles.

We next examined the influence of the individual pre-cycling voltage steps on the cyclic durability by excluding a single or

multiple steps during the pre-cycling treatment. We considered six patterns for the pre-cycling treatment: 1) 2 cycles at 4.5 V, 2) 2 cycles at 4.6 V, 3) 2 cycles at 4.7 V, 4) 2 cycles at 4.5 V and 2 cycles at 4.6 V, 5) 2 cycles at 4.5 V and 2 cycles at 4.7 V, and 6) 2 cycles at 4.6 V and 2 cycles at 4.7 V. Figure 3 shows the results of the charge/discharge cyclic durability tests for the cells receiving pre-cycling treatment according to these six patterns. Upon the 7th cycle, all of the cells pre-treated according to the six patterns possessed lower capacities than the cell treated with all of the voltage charge limits (4.5, 4.6, and 4.7 V). It cannot be determined from a comparison of the results in Fig. 3 which specific step had the largest contribution to the improved cycling performance of the pre-treated cell. The removal of some of the pre-cycling voltage steps suggests that the amount of Li^+ deintercalation and intercalation increases in the subsequent step. Increased Li^+ deintercalation during pre-cycling might negatively influence the cycle performance, and the pre-cycling process seems to require a strict stepwise increase of Li^+ deintercalation via the repeated Li^+ deintercalation and intercalation process from and into the cathode material. The two cycles for each step were also required to obtain stable capacities after 30 cycles. Therefore, this cycle pattern (two cycles for each step of the three upper voltage limits) is essential to the pre-cycling treatment in order to obtain stable capacity during the charge/discharge cycle tests.

A simple approach to reduce the pre-cycling treatment time is to set the discharge voltage limits to values greater than 2.0 V. If the discharge limit is higher, the amount of Li^+ ions returned to the cathode diminishes, thus reducing the time required for discharge. Figure 4 shows the dependence of the cycle performance for the pre-cycled cathode samples on the discharge limit using values from 3.5 to 4.3 V. As clearly demonstrated in the figure, increasing the discharge limit enhances the cycle deterioration. The results obtained at a discharge limit of 3.5 V are comparable to those obtained at a discharge limit of 2.0 V, as shown in Fig. 2(b), which might indicate that the amount of Li^+ ions discharged at 3.5 V were sufficient to either retain the initial crystal structure or transform it into one displaying an improved stable capacity.

Increasing the current density of the pre-cycling process is also a proven means of reducing the pre-cycling time. One limitation of this approach, however, is the low electronic and Li^+ ion conductivities intrinsic to the family of Li-rich solid-solution layered cathode materials.²⁴ These poor transportation abilities could be derived from the existence of transition metal ions in the Li^+ layers and/or Li^+ in the transition metal layers. Initially, the current density limits that can be used during conventional pre-cycling to obtain

Figure 3. Cycle dependence of the discharge capacity for $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ pre-treated with different charge voltage limits. The voltage limit patterns used during the pre-treatment were as follows: (a): (1) 2 cycles between 2.0–4.5 V ($\circ$), (2) 2 cycles between 2.0–4.6 V ($\blacktriangle$), (3) 2 cycles between 2.0–4.7 V ($\blacklozenge$), (b): (4) 2 cycles between both 2.0–4.5 V and 2.0–4.6 V ($\bullet$), (5) 2 cycles between both 2.0–4.5 V and 2.0–4.7 V ($\triangle$), (6) 2 cycles between both 2.0–4.6 V and 2.0–4.7 V ($\diamond$). A current density of 0.2 mA cm^{-2} was used during the pre-treatment process.

Figure 4. Cycle dependence of the discharge capacity for $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ pre-treated with different discharge voltage limits. The discharge voltage limits used during the pre-treatment were 3.5 ($\bullet$), 3.7 ($\triangle$), 3.9 ($\blacktriangle$), 4.1 ($\square$), and 4.3 V ($\blacksquare$). The charge voltage limit was increased stepwise by 0.1 V every two cycles from 4.5 to 4.7 V with a current density of 0.2 mA cm^{-2} .

Figure 5. Cycle dependence of the discharge capacity for $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ pre-treated with different current densities. During the pre-treatment process, the charge voltage was increased stepwise by 0.1 V every two cycles from 4.5 to 4.7 V, and the discharge voltage was fixed at 2.0 V. Current densities of 0.4 ($\bullet$), 0.8 ($\triangle$), 1.2 ($\blacktriangle$), 1.6 ($\square$), and 3.2 ($\blacksquare$) mA cm^{-2} were used during the pre-cycling process. Cycling tests after the 7th cycle were performed at 0.2 mA cm^{-2} .

stable capacities were explored. Figure 5 shows the cycle performance of cells pre-treated by cycling at $0.4\text{--}3.2 \text{ mA cm}^{-2}$. The results observed for the range of $0.4\text{--}1.2 \text{ mA cm}^{-2}$ displayed stable capacities greater than 270 mAh g^{-1} , and current densities of $0.2\text{--}1.2 \text{ mA cm}^{-2}$ can be applied during conventional pre-cycling. However, the results obtained at 1.6 and 3.2 mA cm^{-2} clearly displayed gradual cycle deterioration. The influence of the voltage loss caused by high current densities can be observed in the voltage curves observed at 1.6 mA cm^{-2} (Fig. 6). In the case of (a), which involved upper voltage limits of 4.5, 4.6, and 4.7 V, a plateau region can only be observed around 4.65 V during the 5th cycle. The capacity of this plateau region is insufficient to release oxygen from the cathode material and transform the crystal structure, compared with the capacity observed in the plateau region with the conventional pre-treatment and current density of 0.2 mA cm^{-2} . Therefore, during the 7th cycle (1st cycle of the charge/discharge cycle tests) at 0.2 mA cm^{-2} , a wide plateau region still appears at approximately 4.5 V to complete the change in the crystal structure. The charge/discharge capacities faded to 240 mAh g^{-1} after 20 cycles. The difference between 4.7 and 4.5 V, where the plateau regions appeared at high and conventional current densities, proves that the voltage loss distorted the charge/discharge curves toward higher voltages. In the next case, to compensate for the voltage loss, the starting value of the upper voltage limits was increased by +0.1 V; that is, charge voltage limits of 4.6, 4.7, and 4.8 V were used at 1.6 mA cm^{-2} . The resultant pre-cycling charging curves displayed a wide plateau region at approximately 4.7 V (Fig. 6(b)). These samples exhibited capacities and cycle stabilities similar to those observed at $0.2\text{--}1.2 \text{ mA cm}^{-2}$ with charge limits of 4.5, 4.6, and 4.7 V and discharge limits of 2.0 V. The highest current density that can be used during the pre-cycling process was discovered to be 3.2 mA cm^{-2} . This current density required a stepwise increase in the upper voltage limits of 4.7, 4.8, and 4.9 V. Stable cycling performance was not observed when current densities greater than 3.2 mA cm^{-2} were used during the pre-cycling process because the electrolyte solution could oxidize at charge voltage limits greater than 4.9 V. Other interpretations of the current density limit might be related to the relaxation time required to change the crystal structure before exhibiting stable capacity. The shortest pre-cycling time was 6.5 h when using a current density of 3.2 mA cm^{-2} (1.2 C-rate) with stepwise charge voltage limits of 4.7, 4.8, and 4.9 V.

Figure 6. Charge/discharge curves for $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ pre-treated at 1.6 mA cm^{-2} . During the pre-treatment process, the charge voltage was increased stepwise by 0.1 V every two cycles from either 4.5 to 4.7 V (a) or 4.6 to 4.8 V (b), and the discharge voltage was fixed at 2.0 V.

4. Conclusions

The relationship between the processing conditions of the pre-treatment and cycle performance of $\text{Li}_{1-\alpha}[\text{Ni}_{0.18}\text{Li}_{0.20+\alpha}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ was examined. The processing conditions of the pre-treatment were then optimized to reduce the pre-treatment time. During the pre-cycling process, repeated charge/discharge cycles with a stepwise increase in the amount of deintercalated Li^+ ions was a definite requirement for better cyclic durability. Each step required two charge/discharge cycles at the same charge cutoff voltage limit. It was then determined that the charge voltage limit should then be increased by 0.1 V to gradually deintercalate the Li^+ ions from the cathode. An increase of more than 0.1 V clearly reduced the cyclic durability because of the sudden increase in the amount of deintercalated Li^+ ions. It is necessary to employ a set of six charge/discharge cycles to incrementally deintercalate and intercalate the Li^+ ions, the cycle pattern is both fundamental and essential to the pre-cycling treatment. The voltage limits and current

density are controllable parameters of the pre-cycling process that must be adjusted to control the deintercalation and intercalation of the Li^+ ions. The large differences in the amount of Li^+ ions that moved between the pre-cycling voltage steps and the charge/discharge within each step led to cycle deterioration. The fact that pre-cycling was completed in 6.5 h indicates that the crystal structure change occurred on the same time scale. The structural changes and the valence state changes of the Ni, Co, and Mn in the cathode material that occurred during the charge/discharge cycles under various pre-cycling conditions need to be analyzed in detail to clarify why the cycle performance is improved following pre-cycling. The results of such an investigation will be reported in our future papers.

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