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Activation of a Li-rich Solid-Solution Layered Li[$Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}$]$O_2$ Cathode and Retention of High Capacities via an Electrochemical Pretreatment with a Low Discharge Voltage Limit

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The magnitude and cycle stability of the charge–discharge capacities of a Li-rich solid-solution layered cathode material, Li[$Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}$]$O_2$, were examined over large voltage windows of 1.2–4.4 V (vs. Li/Li^+). Discharging to below 1.5 V activated the cathode material and enabled it to reach larger charge–discharge capacities of over 300 mA h g^{-1}. Moreover, to retain a high capacity of over 300 mA h g^{-1}, our original electrochemical precycling treatment (stepwise control of the discharge voltage limit) was applied, resulting in improved stability of the charge–discharge capacity of over 300 mA h g^{-1} for at least 35 cycles.

In recent years, Li-rich solid-solution layered cathode materials comprising layered $LiMO_2$ (M: transition metals) and Li_2MnO_3 have attracted much interest because some of them exhibit high capacities of approximately 250 mA h g^{-1}(for example, in the voltage region between 2.0 and 4.8 V).[1,2] The electrochemically inactive Li_2MnO_3 can participate in the charge–discharge process after activation above 4.6 V with oxygen release from the lattice during the charging process,[3] and the capacity of $LiMO_2$ can also be improved because the Li_2MnO_3 component acts to stabilize the layered structure of $LiMO_2$ when more than 50% of the Li^+ ions are deintercalated. In contrast, Johnson et al. have investigated the electrochemical behaviors of $x LiMO_2 \cdot (1-x) Li_2M'O_3$ (in which M = Mn, Ni; M′ = Mn, Ti) Li-rich solid-solution cathode materials when they were cycled at the charge voltage limit and discharge voltage limit of 4.5 and 1.0 V, respectively, and have demonstrated that a capacity above 250 mA h g^{-1} can be obtained, even at a charge voltage of less than 4.5 V.[4,5] However, they did not succeed in obtaining high and stable capacities in charge–discharge cycle tests. For example, their Li[$Ni_{0.46}Li_{0.02}Ti_{0.05}Mn_{0.46}$]$O_2$ cathode exhibited a decrease in discharge capacity from approximately 260 mA h g^{-1} at the first cycle to 222 mA h g^{-1} at the 20th cycle.[4] In this study, we developed a method to maintain the higher capacities of Li[$Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}$]$O_2$ ((3/5)$Li_2MnO_3 \cdot$(1/5)Li[$Ni_{0.5}Mn_{0.5}$]$O_2 \cdot$(1/5)Li[$Ni_{1/3}Co_{1/3}Mn_{1/3}$]O_2) by applying our original electrochemical precycling treatment;[6] in our treatment, the charge voltage limit was fixed at 4.4 V, and the discharge voltage limit was decreased stepwise by 0.1 V every two cycles (shown in the inset of Figure 1).

Li[$Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}$]$O_2$ was prepared via the spray-drying and postannealing processes. $CH_3COOLi \cdot 2H_2O$ (Wako, Japan), $(CH_3COO)_2Ni \cdot 4H_2O$ (Wako, Japan), $(CH_3COO)_2Co \cdot 4H_2O$ (Wako, Japan), and $(CH_3COO)_2Mn \cdot 4H_2O$ (Wako, Japan) were used as the starting materials.[7] Electrochemical tests were performed with a CR2032 coin-type cell. The test cell consisted of a cathode and a lithium metal anode separated by a porous polypropylene film (Celgard 3401). The electrolyte used in the tests was a mixture of 1 M $LiPF_6$–ethylene carbonate/dimethyl carbonate (1:2 by vol, Ube Chemicals, Japan). All tests were performed at room temperature. A constant-current (CC) mode of 20 mA g^{-1} was applied to both the pretreatment process and the cycle tests. The charge–discharge cycle tests following the precycling process were performed with voltage limits of 1.2 and 4.4 V. A sample for XANES (X-ray absorption near-edge structure) measurements was prepared by mixing the powder sample with a boron nitride (BN) powder to form disks. The XANES experiments were performed on Beam Line 14B02 of SPring-8. The XANES scans that covered the Ni, Co, and Mn K-edges were taken in transmission mode.[8]

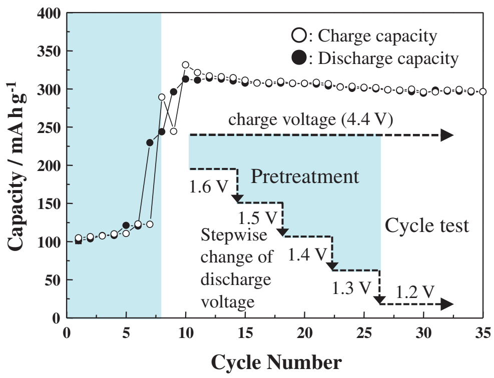

Figure 1. Cycle performance of electrochemically treated Li[$Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}$]$O_2$ electrodes. In the pretreatment process, the discharge voltage was lowered stepwise by 0.1 V every two cycles from 1.6 to 1.2 V, and the charge voltage was fixed at 4.4 V.

Figures 1 and 2 show the cycle performance and the voltage curves, respectively, with a charge voltage limit of 4.4 V and a stepwise-lowered discharge voltage limit from 1.6 to 1.2 V. In the pretreatment process, a capacity of 100–250 mA h g^{-1} was observed. After the pretreatment, the charge–discharge capacities did not vary from 300 mA h g^{-1} until 35 cycles had occurred (Figure 1). When the cell was discharged at the 8th cycle, a plateau at 100 mA h g^{-1} appeared at approximately 1.3 V, and immediately after the appearance of the plateau, a new capacity was created in the voltage region between 2.0 and 3.5 V (Figure 2). This behavior suggests that instead of polarization over 4.5 V, discharging to 1.2 V also activates a Li-rich solid-solution layered cathode material. The discharge process demonstrated a capacity of approximately 194 mA h g^{-1} between 2.0 and

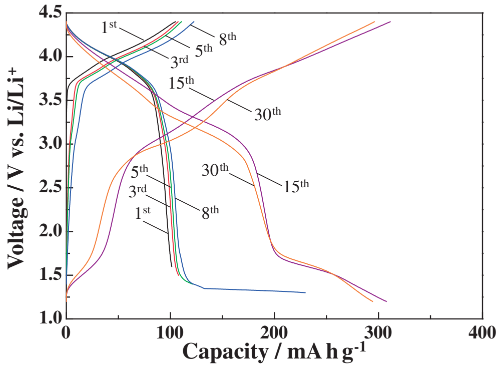

Figure 2. Charge and discharge curves of $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ with pretreatment. In the pretreatment process, the discharge voltage was lowered stepwise by 0.1 V every two cycles from 1.6 to 1.2 V, and the charge voltage was fixed at 4.4 V.

4.4 V and of approximately 300 $mA\,h\,g^{-1}$ between 1.2 and 4.4 V. The discharge capacity of 194 $mA\,h\,g^{-1}$ observed between 2.0 and 4.4 V is comparable to that observed after activation with O_2 release when charged over 4.5 V.[9] It can be surmised that the increase in a reversible capacity between 1.2 and 4.4 V after pretreatment arises from a Mn^{3+}/Mn^{4+} redox reaction and redox reactions of other elements in the cathode material. Johnson et al. have argued that the plateaus at approximately 1.3 V in the discharge process correspond to the $LiMO_2$ to Li_2MO_2 transition, which is kinetically hindered because of the rearrangement of Li^+ ions in the crystal structure and the extrusion of transition metals from the crystal structures.[4] The stability of the charge–discharge cycles may be improved by conditioning the crystal structure to withstand a large transformation and its back-transformation. The plateau observed at approximately 1.3 V might correspond to phase reconstruction with Li^+ ion insertion into the cathode. A stepwise traverse of the plateau in the precycling process allows for Li^+ ions to be gradually inserted into and removed from the cathode material. The number of Li^+ ions moved in the precycling increases as the discharge voltage limit is lowered. Phase reconstruction was conditioned by repeating the process steps.

Figure 3 shows the XANES spectra for the Mn and Co K-edges of $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ as-prepared and discharged and those of the reference Mn and Co compounds. The Mn K-edge and Co K-edge absorption energies for as-prepared $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ were similar to those for $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. The valence states of Mn and Co are 4+ and 3+, respectively. After being fully discharged to 1.0 V, the valence states of Mn and Co were changed to 3.0+ to 3.5+ and 2.0+ to 3.0+, respectively. Although not shown here, the valence state of Ni remained at 2+. It is thought that Mn and Co were reduced during the discharge process so that Li^+ ions were intercalated to the empty octahedral sites in close-packed oxygen arrays and that excess Li^+ ions could be inserted into the tetragonal sites by changing the cathode crystal structure. Activation of $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ might accompany the reconstruction with insertion of excess Li^+ ions.

In this study, a new activation process for the Li-rich solid-solution layered cathode material $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ was developed, producing results of approximately 300 $mA\,h\,g^{-1}$ in the charge–discharge cycles between 1.2 and 4.4 V. Discharging to below 1.5 V activates $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$. The discharge curves show a characteristic voltage plateau at approximately 1.3 V, where reconstruction of the crystal structure by insertion of excess Li^+ ions into the cathode material may occur. Repeated charge–discharge cycling steps are a definite requirement for high and stable capacity beyond 35 cycles. The structural changes that occur in the cathode materials when discharging to below 1.5 V should be analyzed.

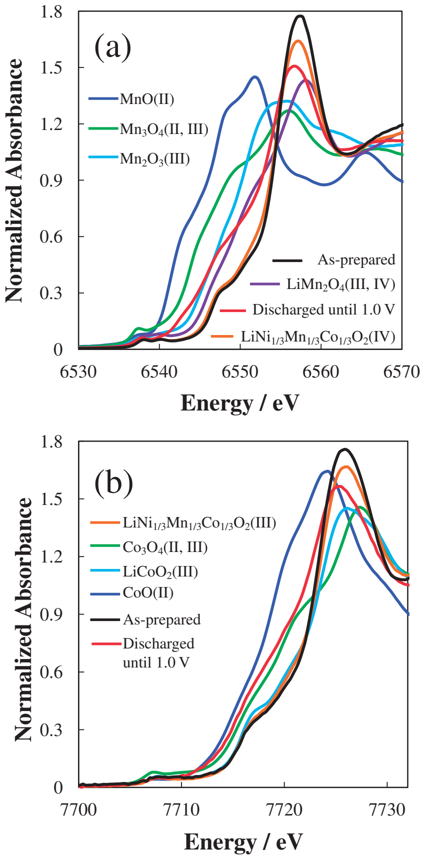

Figure 3. Comparison between normalized XANES spectra of the Mn K-edge (a) and the Co K-edge (b) of $Li[Ni_{0.18}Li_{0.20}Co_{0.03}Mn_{0.58}]O_2$ as-prepared and discharged until 1.0 V and those of the reference Mn and Co compounds.

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