— Headline —

Impact of Excess Li on the Structural and Electrochemical Properties of $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ Materials for Lithium-Ion Batteries

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$\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ materials have been investigated as promising positive electrode materials for lithium-ion secondary batteries, in which cobalt ions are simultaneously substituted with nickel and manganese ions while preserving the $\alpha\text{-NaFeO}_2$ structure. The materials can be regarded as solid solutions of LiNiO_2 , LiCoO_2 , and LiMnO_2 , in which the transition metals are trivalent in all three materials, whereas the transition metals found in $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ materials are Ni^{2+} , Co^{3+} , and Mn^{4+} . The electrochemical lithium deintercalation-intercalation processes of these materials are mainly accompanied by the $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$ redox reactions, whereas Mn^{4+} ions do not participate in the electrochemical redox reaction. Recently, Li^+ substitution for transition metals in $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$, so called overlithiation, has been introduced to improve their structural integrity and electrochemical performances.

In this paper, we introduce the overlithiation effects on the structural and electrochemical properties of the $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials having different x - and z -values in the ranges from $x = 0.00$ to $x = 0.17$ and $z = 0.00$ to $z = 0.50$.

Key Words : $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$, Positive Electrode Materials, Lithium Intercalation, Overlithiation, Charge/Discharge Curves

1 Introduction

Lithium-ion secondary batteries (LIBs) have become important power sources for portable electronics and electric vehicles because of their high energy densities. An LIB is mainly composed of a positive electrode, a nonaqueous electrolyte, and a negative electrode. Among them, the positive electrode material largely contributes to factors such as toxicity, cost, thermal safety, energy density, and power density, all of which affect the performance of the battery. Among various positive electrode materials, LiCoO_2 is most widely used due to its ease of synthesis, an acceptable specific capacity, and high C rate performance. However, the relatively high cost of cobalt and concerns about toxicity and thermal safety of LiCoO_2 have led to the development of other alternate materials.

Recently, $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ materials have been investigated as promising positive electrode materials for LIBs in which cobalt ions are simultaneously substituted with nickel and manganese ions while preserving the $\alpha\text{-NaFeO}_2$ structure.¹⁻⁶⁾ The materials can be regarded as solid solutions of LiNiO_2 , LiCoO_2 , and LiMnO_2 , in which the transition metals are trivalent in all three materials. The transition metals found in $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ materials are Ni^{2+} , Co^{3+} , and Mn^{4+} . The electrochemical lithium deintercalation-intercalation processes of these materials are mainly accompanied by the $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$ redox reactions, whereas Mn^{4+} ions do not participate in the electrochemical redox reaction.

It is commonly believed that the double substitution of

Ni and Mn for Co benefits material economy. However, the C rate performance of $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ tends to degrade with decreasing Co content. Sun *et al.*⁶⁾ have reported that the rate performance of $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ material rapidly falls with decreasing Co content, especially when the z -value is lower than 0.3 even though the electric conductivities of the materials are independent of the Co content. On the other hand, the Li^+ ion diffusion coefficient of $\text{Li}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)\text{O}_2$ decreases with decreasing Co content.⁷⁾ One of the reasons for the degradation of the rate performance of $\text{LiNi}_z\text{Co}_{1-2z}\text{Mn}_z\text{O}_2$ with decreasing Co content (increasing Ni and/or Mn content) is the structural disordering, the so-called cation mixing; Ni^{2+} can readily exchange its structural site for Li^+ due to the similar ionic radii of Ni^{2+} ($r = 0.69 \text{ \AA}$ ⁸⁾) and Li^+ ($0.74 \text{ \AA}$ ⁸⁾) in these materials. For example, about 11 and 6% cation mixing has been reported in $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ ⁹⁻¹¹⁾ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ⁵⁾ respectively. Whittingham has mentioned that the degree of the cation mixing in the $\text{LiNi}_y\text{Co}_{1-y-z}\text{Mn}_z\text{O}_2$ materials tends to increase as the ratio of Co/Ni decreases.¹²⁾

Recently, Li^+ substitution for transition metals in $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$, so-called overlithiation, was introduced to improve their structural integrity and electrochemical performances.^{11,13-18)} The overlithiation procedure was used to stabilize the structures of positive electrode materials. For example, (i) Li^+ substitution for Mn in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ increases the relative Mn^{4+} ion concentration in the spinel structure, which suppresses manganese dissolution into the electrolytes¹⁹⁻²¹⁾; and (ii) the charge

curves of $\text{Li}_{1+x}\text{CoO}_2$ ($x > 0$) do not present monoclinic distortion upon deintercalation, which is observed in lithium-stoichiometric LiCoO_2 .²² In this review, we introduce the overlithiation effects on the structural and electrochemical properties of the $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials ($0.00 \leq x \leq 0.17$ and $0.00 \leq z \leq 0.50$).

2 Co-Free $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$ Materials with Li Excess Composition

Recently, Co-free $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ has become attractive as a positive electrode material for LIBs due to its lower cost, greater stability at high voltage, and better thermal stability than LiCoO_2 .^{3,9,23-28} $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ has a layered structure, similar to LiCoO_2 , with complex cation orderings.⁹ On the basis of theoretical calculations and spectroscopic studies, it is now widely accepted that the Ni and Mn ions have oxidation states of +2 and +4, respectively. Ohzuku and Makimura³ have reported that $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ electrodes deliver a reversible capacity of 150 mAh g^{-1} (2.5–4.3 V; 0.1 mA cm^{-2}) and show a milder thermal runaway than that of LiCoO_2 at the fully charged state. Although the material shows a high reversible capacity at a very low rate, the high rate performance of the material does not meet commercial needs due to structural ordering (cation mixing). Kang *et al.*⁹ have reported that the rate performance of $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ having a low cation mixing of 4.3% is superior to that of the material having a cation mixing of 10.9%. This result implies that the structural ordering of this material should be reduced to enhance its electrochemical properties.

In order to improve the structural integrity, overlithiation is introduced into the material. Figure 1 shows neutron diffraction patterns and Rietveld refinement results of the overlithiated $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$ prepared by an

Fig. 1 Neutron diffraction patterns of (a) $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and (b) $\text{Li}_{1.06}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{O}_2$.

emulsion drying method.¹⁰ The refinement results show good agreement between the observed and calculated patterns based on the $\alpha\text{-NaFeO}_2$ structure. The cation mixing was found to be 7.3% for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and 2.6% for $\text{Li}_{1.06}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{O}_2$, and the excess lithium is located in the transition metal layer. Recently, Kang *et al.*¹⁶ have also reported that the cation mixing decreases from 10.4 to 2.4% when x in $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$ increases from 0 to 0.15.

If excess lithium is substituted for the transition metals in $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and there is no oxygen deficiency, the oxidation of the transition metals would account for charge compensation. In this case, $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$ could be rewritten as $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{Li}_x]\text{O}_2$ in $\alpha\text{-NaFeO}_2$ structure notation. Figure 2 shows the Ni and Mn *K*-edge X-ray absorption near edge spectroscopy (XANES) spectra of $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ to compare the oxidation states of the absorber atoms in both materials. The Ni *K*-edge spectra of the materials are compared with those of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and layered LiNiO_2 , where the average oxidation states of Ni are +2 and +3, respectively. The spectrum of the Ni *K*-edge for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ is close to that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, suggesting that the oxidation state of Ni in $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ is close to +2. However, the spectrum for $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ is shifted slightly toward a higher energy position relative to that for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$. This result implies that the oxidation state of Ni in $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ is greater than that in $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$, but lower than that in LiNiO_2 . For Mn *K*-edge spectra, the synthesized materials are compared with the

Fig. 2 (a) Ni *K*-edge and (b) Mn *K*-edge XANES spectra for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$.

orthorhombic LiMnO_2 and the rock-salt-type Li_2MnO_3 , where the oxidation states of Mn are +3 and +4, respectively. The Mn *K*-edge spectra of both materials are practically identical to that of Li_2MnO_3 , indicating that the Mn ion is tetravalent in both materials.

The oxidation of transition metals would result in changes in the lattice parameters. Figure 3 shows variations in the lattice parameters of the $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{Li}_x]\text{O}_2$ ($x = 0-0.06$). With an increase in the Li content in the transition metal layer, the *a*- and *c*-axis constants and unit-cell volume decrease monotonically without changes in the *c/a* ratios. As observed by XANES spectra in Fig. 2, the oxidation state of Ni for $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ is slightly higher relative to that for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$, which indicates that a larger amount of Ni^{3+} is contained in $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ compared to $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$. When the ionic radii of Ni^{2+} (0.69 Å⁸) and Ni^{3+} (0.56 Å⁸) are taken into account, it is reasonable to think that the formation of the smaller Ni^{3+} and the suppression of cation mixing by excess Li incorporation into the oxide matrix led to the linear decrease in the lattice parameters. Such a linear variation in the lattice parameter is usually observed in a solid solution by following Vegard's law, suggesting that excess lithium is readily substituted for the Ni and Mn.

The changes in the structural integrity and oxidation states of the transition metals by the overlithiation affect the electrochemical properties of the materials. Figure 4 shows the continuous charge and discharge curves of $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$. For $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$, the capacity fades gradually as the cycle progresses. In addition, the operation voltage drops gradually during cycling. On the other hand, $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ retains its initial capacity well during 50 cyclings, and the capacity retention is approximately 95%. The $\text{Li}/\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ cell also shows much less of a decrease in the operation voltage upon cycling. Kang *et al.*¹⁶⁾ have reported that the C rate capability is improved significantly with an increase in the lithium excess. The improved rate capability and cyclability of

the overlithiated materials could be attributed to the reduced Ni content in the lithium layer and the improved Li^+ ion diffusivity. The thermal stability of the charged electrode in the electrolyte is enhanced slightly by the overlithiation.¹¹⁾

3 $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ Materials with Li Excess Composition

$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is an attractive material for LIBs due to its higher reversible capacity and small Co content, and it has been intensively investigated by many researchers and battery developers. On the basis of computational and experimental studies, it is now accepted that $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ has Ni^{2+} , Co^{3+} , and Mn^{4+} ions and the intercalation and deintercalation processes of Li^+ ions are accompanied by redox reactions of $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$, whereas Mn^{4+} does not participate in the process.^{4,5,29,30)} The use of overlithiated $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ materials has also been studied to improve the electrochemical performance.^{13,31-34)} Figure 5 shows the X-ray diffraction (XRD) patterns and changes in the lattice parameters of the $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ materials synthesized by a spray-drying method. The main intense diffraction peaks could be indexed on the basis of a hexagonal structure, and the hexagonal lattice parameters of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ gradually decrease with increasing *x* as does $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$. X-ray photoelectron spectroscopy (XPS) and XANES studies revealed that one of the reasons for the decrease in the lattice parameters of the material with increasing *x* is the oxidation of Ni^{2+} ions to Ni^{3+} ions for charge compensation.^{32,34)} Figure 6 shows the charge-discharge curves of $\text{Li}/\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cells. All the cells show a similar cycling curve, but the discharge capacity of the cells increases with an increase in the value of *x* when the cells are cycled between 4.5 and 2.8 V versus Li/Li^+ , whereas the reversible capacity of $\text{Li}/\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cells gradually decreases when the cells are cycled between

Fig. 3 Variations in lattice parameters and *c/a* ratios of $\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{Li}_x]\text{O}_2$.

Fig. 4 Continuous charge and discharge curves of (a) $\text{Li}/\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and (b) $\text{Li}/\text{Li}[(\text{Ni}_{1/2}\text{Mn}_{1/2})_{0.94}\text{Li}_{0.06}]\text{O}_2$ cells. The applied current density across the positive electrode is 20 mA g^{-1} at 25 °C.

Fig. 5 (a) XRD patterns of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x = 0.00\text{--}0.17$) materials calcined at 950°C for 24 hours in air and (b) changes in their hexagonal lattice parameters.

Fig. 6 Continuous charge and discharge curves of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x = 0.00\text{--}0.17$) materials cycled between 4.5 and 2.8 V versus Li/Li^+ with a current density of 30 mA g^{-1} in 1.0 mol dm^{-3} $\text{LiPF}_6/\text{ethylene carbonate (EC)-diethylene carbonate (DEC)}$ (1 : 2 in volume) at 25°C .

4.3 and 3.0 V.¹³) The overlithiated materials, however, show better capacity retention than the lithium stoichiometric one. Furthermore, the C rate performance of the $\text{Li}/\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cell was improved with increasing x -value. Figure 7 shows the C rate performance of $\text{Li}/\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cells. The rate capability is significantly improved with increasing amounts of excess lithium. This improvement in the cell performance could be attributed to increasing structural ordering and electronic conductivity.^{17,18)}

On the basis of results from first-principle calculations,²⁹⁾ $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ shows smaller changes in the lattice parameters than LiCoO_2 and LiNiO_2 during lithium extraction. Structural studies³⁵⁾ reveal that $\text{Li}_{1-y}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ maintains the initial O3 phase (trigonal, $R\bar{3}m$; ABCABC oxygen stacking sequence perpendicular to c_{hex} axis) up to 0.70–0.75 mol of Li^+ extraction, and an additional Li^+ extraction results in the appearance of the O1 phase (trigonal, $P\bar{3}m1$; ABAB oxygen stacking sequence). The structural modification of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ is due to the overlithiation. The overlithiated materials retain the pristine structure and show smaller volume change than the lithium stoichiometric one. Figure 8 shows *ex-situ* XRD patterns of the $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x = 0\text{--}0.17$) materials at the fully charged and discharged states in comparison with the pristine materials. The lithium stoichiometric material shows a significant (003) peak broadening and a new peak relating to the O1 phase emerges around 19.32° in 2θ ($d = \text{ca. } 4.59\text{ \AA}$) at the first fully charged state, the new peak disappears at the first fully discharged state, whereas the overlithiated materials show no new peak during the first cycle. At the fifth charged state, the new peak is intensified for the lithium stoichiometric material. A similar peak is observed at the fifth charge for the overlithiated material with $x = 0.11$, whereas the overlithiated material with $x = 0.17$ shows no new peak. Figure 9 shows the changes in the lattice parameters of the materials during the first electrochemical lithium extraction. The overlithiated materials show smaller changes in lattice parameters and unit-cell volume than

Fig. 7 C rates versus discharge capacities of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x = 0.00\text{--}0.17$) materials.

Fig. 8 *Ex-situ* XRD patterns of the pristine, the first charged and discharged, and fifth charged states for $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ materials with $x =$ (a) 0.00, (b) 0.11, and (c) 0.17. The materials were cycled using the CC-CV (constant current - constant voltage) mode at about the 1/100 C rate until the capacity reached the theoretical value of 1. Al in the XRD patterns indicates an aluminum foil current collector, which was used as an internal standard for calibration. The new peaks are marked by the asterisk.

Fig. 9 The variations in the hexagonal lattice parameters (a_{hex} and c_{hex}) and unit-cell volume for $\text{Li}_{1+x-y}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x = 0.00, 0.11$, and 0.17) during the initial charge. The y -values in $\text{Li}_{1+x-y}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ material were estimated based on the charge capacities, and the possible error in the y value is in the range of -0.02 to $+0.02$.

those of the stoichiometric one. In addition, the volume change decreases with increasing x -value.

4 $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ Materials with Different z -values

Recently, other overlithiated $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials have also been reported. Tran *et al.*¹⁵⁾ have reported that $\text{Li}_{1+x}(\text{Ni}_{0.425}\text{Co}_{0.15}\text{Mn}_{0.425})_{1-x}\text{O}_2$ ($x = 0.00-0.12$) materials having an $R\bar{3}m$ structure show a decrease in the Ni occupancy in the Li layer with increasing x -value. Redox titrations and XPS spectra of the transition metals show the oxidation of Ni^{2+} ions into Ni^{3+} ions with increasing overlithiation of the materials; the manganese and cobalt ions are at the tetravalent and trivalent states, respectively. This material also shows a decrease in the Ni occupancy in the Li layer with increasing overlithiation as confirmed by the magnetic measurements and structural refinement results.¹⁵⁾ The electronic conductivities of these materials increase with overlithiation, which is attributed to a hopping between Ni^{2+} and Ni^{3+} ions.¹⁵⁾ However, they found that the thermal stability of the charged electrode in the electrolyte is degraded by the overlithiation,¹⁵⁾ which is in contrast to the result with $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$.¹¹⁾

$\text{Li}_{1+x}(\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.4})_{1-x}\text{O}_2$ materials also show improved electrochemical properties with overlithiation.³⁶⁾ Figure 10 shows the capacity retention characteristics of

Fig. 10 Capacity versus cycle number for $\text{Li}/\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})_{1-x}\text{O}_2$ ($x = 0$ and 0.06) cells cycled in the voltage windows of (a) 4.3–2.8, (b) 4.5–2.8, and (c) 4.7–2.0 V versus Li/Li^+ . The open and closed symbols represent charge and discharge capacities, respectively.

$\text{Li}_{1+x}(\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.4})_{1-x}\text{O}_2$ ($x = 0.00$ and 0.06) materials under different operating voltage windows. The overlithiated material shows better cycling behavior than the stoichiometric one in all the operating voltage windows, and a conspicuous overlithiation effect on the cycling behavior is observed when the materials are cycled at a higher voltage. Shizuka *et al.*¹⁷⁾ have reported that the C rate performances of $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials ($x = 0.00$ – 0.20 and $z = 0.33$ – 0.475) deteriorate with decreasing Co amount but improve with increasing overlithiation, relating to both the cation mixing and the electrical conductivity associated with composition variations.

Recently, we have investigated the effects of overlithiation on the cell performances of the $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials with different Co/(Ni + Mn) ratios. Figure 11 shows the continuous charge-discharge curves of $\text{Li}/\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials ($x = 0.00$ – 0.17 and $z = 0.10$ – 0.40) cells. The capacity retention ability of the material with a Co/(Ni + Mn) ratio < 1 ($z = 0.30$ and 0.40) is found to be improved by overlithiation, whereas it deteriorates when the Co/(Ni+Mn) ratio is > 1 ($z = 0.10$ and 0.20).

Fig. 11 Continuous charge and discharge curves of $\text{Li}/\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ cells with (a) $z = 0.1$ and $x = 0.00$, (b) $z = 0.1$ and $x = 0.05$, (c) $z = 0.2$ and $x = 0.00$, (d) $z = 0.2$ and $x = 0.07$, (e) $z = 0.3$ and $x = 0.00$, (f) $z = 0.3$ and $x = 0.07$, (g) $z = 0.4$ and $x = 0.00$, and (h) $z = 0.4$ and $x = 0.05$ cycled between 4.5 and 2.8 V versus Li/Li^+ with a current density of 30 mA g^{-1} in 1.0 mol dm^{-3} LiPF_6 /ethylene carbonate (EC)-dimethyl carbonate (DMC) (3 : 7 in volume) at 25°C .

5 Conclusion

The overlithiation of $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ causes (i) the oxidation of Ni ions for charge compensation, (ii) decreasing Ni amount in the Li layer, and (iii) increasing electronic conductivity caused by the electronic hopping between Ni^{2+} and Ni^{3+} ions. It seems that overlithiation of $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials improves the structural integrity and electrochemical properties but the effects are more pronounced in materials with higher Ni and Mn content. On the basis of the literature available, it is suggested that overlithiation of $\text{Li}_{1+x}(\text{Ni}_z\text{Co}_{1-2z}\text{Mn}_z)_{1-x}\text{O}_2$ materials ($0.3 \leq z \leq 0.5$) would be an effective way to improve their electrochemical performance. These materials can be adopted as new positive electrode materials for LIBs for high power consumption electronics or electric vehicles after adjusting the excess lithium amount to obtain the best battery performances.

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