Storage Characteristics of LiNi$_{0.8}$Co$_{0.1+x}$Mn$_{0.1-x}$O$_2$

(x = 0, 0.03, and 0.06) Cathode Materials for Lithium Batteries

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High Ni-content cathode (with a Ni amount in LiNi$_{0.8}$Co$_{0.1+x}$Mn$_{0.1-x}$O$_2$ equal or larger than 0.8)\(^{1,8}\) materials for lithium batteries are among the most actively studied cathodes. However, these cathodes have large amounts of residual Li$_2$CO$_3$ and LiOH impurities compared to low Ni-content cathodes (for instance, LiNi$_{0.8}$Co$_{0.12}$Mn$_{0.08}$O$_2$ (Ref. 9-14)) on the particle surfaces upon exposure to air. This is due to the slow and spontaneous reduction of Ni$^{3+}$ to Ni$^{2+}$ that occurs to materials during storage.\(^{15-21}\) Corrosion of the Ni-based cathodes with LiCoO$_2$, although this leads to a change in the oxidation state of the Ni and Mn ions after 4.3 V charging upon storage at 90°C were measured using X-ray absorption near-edge spectra, and Ni$^{4+}$ was found to reduce to Ni$^{3+}$ while the oxidation state of the predominant Mn$^{3+}$ did not change. However, residual Mn$^{3+}$ ions in the cathodes dissolved into the electrolytes. Moreover, the cathodes stored at 90°C for 7 days were transformed into a spinel phase (Fe$_3$O$_4$), regardless of the Co content. In an effort to resolve this dissolution problem, Al$_2$O$_3$ and Co$_3$(PO$_4$)$_2$ nanoparticles were coated onto the cathode (LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$) with the highest amounts of metal at 90°C. The results showed that the Co$_3$(PO$_4$)$_2$-coated cathode exhibited a greatly decreased metal dissolution and decreased its irreversible capacity by 5% compared with a bare and Al$_2$O$_3$-coated cathode.


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Experimental

Coprecipitated Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$OH$_2$ powder consisting of ultrafine spherical grains was prepared by dissolving metal nitrates in water and adjusting the pH to approximately 11 using NaOH and NH$_4$OH at 50°C. The details of these experimental procedures are described elsewhere.\(^3,4\) Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$(OH)$_2$ powder and LiOH·H$_2$O with a molar ratio of 1:1.03 were mixed thoroughly and fired at 480 and 800°C for 4 and 15 h, respectively. After sieving, powders with an average particle size of <15 μm were used for further Al$_2$O$_3$ and Co$_3$(PO$_4$)$_2$ coatings and analyses; detailed coating methods were described elsewhere.\(^24,25\) A weight portion of the coating material in the cathode was approximately 3 wt %. The Li content of the as-fired sample was 1.0, as confirmed by an inductively coupled plasma-mass spectroscopy (ICP-MS) analysis. In order to determine the moisture content (OH) in the sample, a Karl-Fisher moisture titrator was used at 250°C (prior to measuring, the sample was vacuum-dried at 150°C for 2 h to remove the H$_2$O molecules that had adsorbed on the sample).

The electrochemical properties were tested in a coin-type 2016R cell with lithium metal as an anode, and the cathode consisted of the following active material: Super P carbon black: poly(vinylidene fluoride) binder with a weight ratio of 94:3:3. The electrolyte for the coin-type half-cells (2016 type) was 1 M LiPF$_6$ with ethylene carbonate/diethylene carbonate/ethyl methyl carbonate (30:30:40 vol %) (Cheil Industries, Korea). The capacity and capacity retention were measured between 3 and 4.3 V at a rate of 0.2 C (1 C = 180 mA/g). To measure metal contents and X-ray diffraction (XRD) patterns of the charged samples stored in the electrolytes, the coin-type half cells containing the cathodes were charged to 4.3 V, followed by immediate removal of the electrodes for the cells. The removed electrodes were immersed in the electrolyte at the tightly sealed vials and stored at 90°C. XRD patterns were obtained using a Cu Kα X-source on a Rigaku instrument operated at 11 kW. Auger electron spectroscopy was utilized with a VG Scientific MAS00 scanning Auger microscope fitted with a 10 keV argon ion gun. The X-ray photoelectron spectra were recorded with a Physical Electronics Quantum 2000 ESCA spectrometer with a Mg Kα anode (1253.6 eV) as the X-ray source operated at 24.1 W in a vacuum of <10$^{-9}$ Torr. The binding energy was corrected to the C 1s peak at 284.5 eV.

Ni, Co, and Mn K-edge X-ray absorption spectra were recorded on a BL7C1 beam line from a Pohang light source with a ring current of 130–185 mA at 2.5 GeV. A Si(111) double-crystal monochromator was employed to monochromatize the X-ray photon energy. The data were collected in transmission or fluorescence modes with N$_2$ gas-filled ionization chambers as detectors. Higher-order harmonic contamination was eliminated by detuning to reduce the incident X-ray intensity by ~30%.

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Results and Discussion

Figure 1 shows XRD patterns of the LiNi_{0.8}Co_{0.1+}Mn_{0.1−}O_{2} (x = 0, 0.03, and 0.06) cathode powders along with LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} coated with Al_{2}O_{3} and Co_{3}(PO_{4})_{2} nanoparticles. These can all be indexed based on the R3\bar{m} space group and are consistent with the layered structure of α-NaFeO_{2}. The amount of Ni in the Li sites was estimated by a Rietveld analysis of the XRD patterns in Fig. 2. The lattice constants c and calculated from the Rietveld analysis are shown Table I, and both the a and c lattice constants increase with an increase in the Co content. This is caused by the slightly larger ionic radius of Co^{3+} (0.545 Å) compared to that of Mn^{4+} (0.53 Å). As the Co content increases, Co^{3+} replaces Mn^{4+} ions in the 3b sites, resulting in an increase in the lattice constants. Co_{3}(PO_{4})_{2} and Al_{2}O_{3} coatings do not influence the lattice constants, nor do the Ni amounts in the Li sites. In addition, as the Co content increases, the amounts of the Ni^{2+} content in the 3a sites decreases. Figures 3a and b shows scanning electron microscopy (SEM) images for x = 0 and 0.06, respectively; both images show round-shaped particles aggregated with ultrafine particles of ~0.5 μm. This is the typical morphology for powders prepared using the coprecipitation method. Figure 4 shows transmission electron microscopy (TEM) images of bare LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} and Co_{3}(PO_{4})_{2} and Al_{2}O_{3}-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}; the coating layer cannot be observed for the Co_{3}(PO_{4})_{2}-coated cathode, indicating that the formation of the Li-CoPO_{4} phase is the result of a reaction between Li sources (LiOH and Li_{2}CO_{3} or Li in the bulk) and Co_{3}(PO_{4})_{2}, in an analogy to the case of the LiCoO_{2} and LiNi_{0.8}Co_{0.16}Al_{0.04}O_{2}. Moreover, we cannot eliminate the possible formation of the solid solution phase between LiCoPO_{4} and the bulk. As described in the Introduction, the cathode surface has abundant stable Ni^{2+} ions; therefore, they may also be involved in the reaction with the Co_{3}(PO_{4})_{2} at 700°C. However, the Al_{2}O_{3}-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} clearly shows the Al_{2}O_{3} coating layer with a thickness of ~20 nm, and its coating layer has many voids and did not formulate good coverage of the cathode.

Figure 5 exhibits the voltage profiles of the LiNi_{0.8}Co_{0.1+}Mn_{0.1−}O_{2} (x = 0, 0.03, and 0.06) cathodes between 3 and 4.3 V at a rate of 0.2 C (= 36 mAh/g). The capacity with x = 0 shows the highest discharge capacity of 192 mAh/g but slightly decreases to 186 and 184 mAh/g for x = 0.03 and 0.06, respectively. The irreversible capacity ratio of the cathodes with x = 0, 0.03, and 0.06 decreases to 13, 12, and 8%, respectively, which is in accordance with the decreasing Ni^{2+} content in Li sites. The reversible capacity of the Co_{3}(PO_{4})_{2}-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} is identical.

Table I. Rietveld analysis results of the LiNi_{0.8}Co_{0.1+}Mn_{0.1−}O_{2} (x = 0, 0.03, and 0.06).

<table>
<thead>
<tr>
<th>Composition</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>Rp</th>
<th>Rwp</th>
<th>RB (%)</th>
<th>Ni in Li sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>2.8746(2)</td>
<td>14.209(1)</td>
<td>4.943</td>
<td>13.4</td>
<td>12.5</td>
<td>2.9</td>
<td>0.04</td>
</tr>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} after Al_{2}O_{3} coating</td>
<td>2.8743(2)</td>
<td>14.208(1)</td>
<td>4.943</td>
<td>13.1</td>
<td>12.4</td>
<td>2.9</td>
<td>0.04</td>
</tr>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} after Co_{3}(PO_{4})_{2} coating</td>
<td>2.8744(2)</td>
<td>14.210(1)</td>
<td>4.944</td>
<td>13.2</td>
<td>12.2</td>
<td>2.7</td>
<td>0.04</td>
</tr>
</tbody>
</table>
to that of the corresponding bare cathode, but its irreversible capacity decreases by 5% compared with the bare cathode. However, the Al$_2$O$_3$-coated sample shows a reversible capacity of 170 mAh/g; this may be due to the thick Al$_2$O$_3$ coating layer that impedes Li diffusion into the bulk particles. A weight portion of used Al$_2$O$_3$ coating material in this study was approximately 3 wt%, which was a higher coating concentration than in previously reported coated cathodes, which used 1 wt% coating concentration. This leads to a decrease in capacity of the Al$_2$O$_3$-coated cathode. When the coating concentration is lower than 2 wt%, the Al$_2$O$_3$ coating has been proven to improve the cycle life performance of the cells and consists of many Al$_2$O$_3$ nanoparticles with higher surface area and thus improves the electrolyte/electrode contact areas.

Table II shows the moisture (OH in LiOH) and carbon (C in Li$_2$CO$_3$) contents in the cathodes after 1 and 7 days of exposure in air with a relative humidity of 40% (samples were taken from the top in the stored sample vials). Their values after 1 day of storage are similar to each other. With exposure to air for 7 days, the water and carbon contents strongly depend on the Co content. As the Co content increases, the moisture and carbon content decrease. LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ shows 4540 and 3590 ppm for moisture and carbon, respectively, while LiNi$_{0.8}$Co$_{0.16}$Mn$_{0.04}$O$_2$ shows 1700 and 1650 ppm for moisture and carbon, respectively. When the CO$_2$ in air reacts with H$_2$O, H$_2$CO$_3$ is formed and the pH of the water decreases to 5.5. Hence, when slightly acidic CO$_3^{2-}$ ions dissolve in H$_2$O on the cathode surface, they attack the particle surface, and, therefore Li$^+$ ions can be easily leached from the bulk, forming LiOH and Li$_2$CO$_3$. Lithium loss from the cathode is accompanied by the loss of the oxygen, leading to the reduction of Ni$^{3+}$ to Ni$^{2+}$ according to the reaction Ni$_2$CO$_3$ → NiO + 1/2O$_2$.

It was reported that the spontaneous reduction of Ni$^{3+}$ to stable Ni$^{2+}$ and the evolution of oxygen species from the surface also contributed to the formation of LiOH and Li$_2$CO$_3$ in Ni-rich cathode materials. We believe that Ni$^{2+}$ ions are uniformly distributed throughout the fresh particles, but with increasing the exposure time in air, the particle surface gets to react with moisture at first, and therefore it is reasonable to think that Ni$^{2+}$ is more abundant at the particle surface than inward from the particles. A similar result was reported by Liu et al.; they proposed that more Ni$^{2+}$ appeared on the surface based upon X-ray photoelectron spectroscopy (XPS) analysis, although direct evidence for the distribution of the Ni$^{2+}$ ions in the particle was not provided. Decreased LiOH and Li$_2$CO$_3$ contents with increasing the Co content in the cathode is related to an increase in the structural stability against moisture attack.
The Co₃(PO₄)₂-coated cathode shows a threefold decrease in the moisture and carbon values compared with a corresponding bare sample, although the amount of Ni⁺³ in the Li sites is identical compared with the corresponding bare cathode. For the evidence of the Ni²⁺ and Co²⁺ in the surface of the coated LiNi₀.₈Co₀.₁Mn₀.₁O₂ sample. XPS analysis of the coated sample was conducted as shown in Fig. 6. Although the spectrum of the main Ni⁺³ peak is superimposed with that of Ni⁺², which occurs centered at ~856 and 855 eV, respectively, the peak position of Ni⁺² can be discerned by the small shoulder peak in the main Ni⁺³ peak. The coated sample shows that the weak shoulder peak at ~855 eV can be assigned to the Ni⁺² peak, as compared with the NiO spectrum. In the case of the Co 2Pₓ, XPS spectrum of the coated sample, its spectrum is broader than that of the reference LiCoPO₄, which has only Co⁺² ions. This result implies the coexistence of Co⁺³ and Co⁺² ions in the coated sample. These results propose that Ni⁺² ion may be incorporated with the LiCoPO₄ phase, and thus become partially substituted into the Co⁺² sites.

For the Al₂O₃-coated cathode, although the moisture and carbon values after 7 days of storage are higher than those of the Co₃(PO₄)₂-coated samples, the coating reduces the reaction with air. Al₂O₃-coated LiNi₀.₈Co₀.₁Mn₀.₁O₂ demonstrates the reduced amounts of LiOH and Li₂CO₃, compared with the uncoated counterpart, but the Al₂O₃ coating is not effective, as compared with uncoated LiNi₀.₈Co₀.₁₄Mn₀.₀₆O₂. As can be seen in Fig. 4c, the Al₂O₃ coating layer is not uniform, and there are many voids between the coating layer and the bulk, suggesting that the coating layer cannot effectively block the reaction with the air. Due to this, greatly accelerated side reactions with the electrolyte can be expected when the Al₂O₃-coated cathode is immersed with the electrolyte and kept at elevated temperatures, metal dissolution can be accelerated. Moisture on the particle surface tuned into Li₂CO₃ and LiOH as discussed above; therefore, LiOH is a major contributor to making HF. Hence, the coated sample, although the cathode surface appears to be covered impurities, the original morphology is distinguishable. Given that one of the covered phases is expected to be Li₂CO₃, the thickness of the Li₂CO₃ impurity layer was estimated using an Auger analysis of carbon, as shown in Fig. 8. The carbon thickness of the bare sample is estimated to ~200 nm, but the thickness of the Al₂O₃- and Co₃(PO₄)₂-coated cathodes decreased to ~100 and ~30 nm, respectively. This indicates that the coating layers are effective in reducing the reaction with air. In Al₂O₃-coated and bare cathodes, we did not detect the transition metals into the depth of ~100 and 200 nm from the particle surfaces. However, in the case of the Co₃(PO₄)₂-coated cathode, Co, P, and Ni atoms were detected at the particle surfaces (8 out of 10 spots), but at some spots, carbon was only detected down to the depth of ~10 nm from the surface, indicating that some portions of the cathode were not covered by the LiCoPO₄ coating layer.

The Li₂CO₃ and LiOH impurities significantly affect the discharge capacity of the samples, as these impurities act as an “insulator layer” for Li ions, while the bare sample showed no capacity after 7 days of storage. The Al₂O₃ and Co₃(PO₄)₂ coatings exhibit discharge capacities of 155 and 182 mAh/g, respectively, which correspond to 95 and 91% capacity retention, respectively.

When the electrodes are prepared using the air-exposed samples, LiOH as a surface impurity can directly create H₂O, which leads to the formation of HF by a reaction with LiPF₆ and H₂O in the electrolyte according to the reactions LiOH + HF → H₂O + LiF, H₂O + LiPF₆ → LiF + HF + POF₃. When the electrodes are kept at elevated temperatures, metal dissolution can be accelerated. Moisture on the particle surface tuned into Li₂CO₃ and LiOH as discussed above; therefore, LiOH is a major contributor to making HF. Hence,
metal ions in the cathodes can be dissolved into the electrolytes, resulting in structural rearrangements on the surface. Table III shows the amounts of metal ion (Ni, Co, and Mn) dissolution measured after 1 and 7 days of storage in the electrolyte obtained from 4.3 V charged electrodes prepared from fresh cathodes at 90 ℃ for 7 days (cathodes were charged to 4.3 V). Units are ppm.

<table>
<thead>
<tr>
<th>X</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>57</td>
<td>21</td>
<td>3</td>
</tr>
<tr>
<td>7 days</td>
<td>370</td>
<td>280</td>
<td>8</td>
</tr>
<tr>
<td>0.03</td>
<td>48</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>7 days</td>
<td>380</td>
<td>220</td>
<td>82</td>
</tr>
<tr>
<td>0.06</td>
<td>45</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>7 days</td>
<td>360</td>
<td>150</td>
<td>2</td>
</tr>
<tr>
<td>Co3PO4 coating</td>
<td>95</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>7 days</td>
<td>45</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Al2O3 coating</td>
<td>220</td>
<td>180</td>
<td>2</td>
</tr>
</tbody>
</table>

The authors on the LiNi0.5Co0.15Mn0.35O2 cathode with Mn4+ only did not show Mn dissolution,25 but the present study shows some evidence of the presence of mixed Mn3+/Mn4+ in the cathodes. In addition, with x = 0.06, a decreased Mn dissolution is shown compared with x = 0, which shows only 150 ppm. This is due to the decreased amounts of Mn3+ ions in the sample. In the case of Co3PO4-coated LiNi0.5Co0.15Mn0.35O2, the dissolved amounts of Ni and Mn ions were significantly reduced by the Li2CoPO4 layer. In particular, the amount of dissolved Ni3+ ions after a Co3PO4 coating decreased by 1/4 compared with the corresponding bare cathode. Because the highly oxidant Ni4+ ions are not stable as an independent ion, it may present as a form of the Ni3+ or Ni2+ as a result of the loss of oxygen from the lattice during storage after charging. It is found that the Al2O3 coating layer is not effective for protection against Ni and Mn ion dissolution, showing higher amounts of metal dissolution than the Co3PO4 coating. In the storage test at 90 ℃, the amounts of the dissolved metals appear to be reduced, compared with the uncoated counterpart, but the Al2O3 coating is less effective than the uncoated LiNi0.5Co0.15Mn0.35O2 for protecting metal dissolution.

Figure 9 shows XRD patterns of the cathodes with LiNi0.5Co0.15Mn0.35O2 with x = 0 and 0.06 before charging and after 4.3 V charging, and after 1 and 7 days storage at 4.3 V, along with Co3PO4- and Al2O3-coated LiNi0.5Co0.15Mn0.35O2 cathodes under the same conditions.

Figure 9. XRD patterns of the cathodes with LiNi0.5Co0.15Mn0.35O2 with x = 0 and 0.06 before charging and after 4.3 V charging, and after 1 and 7 days storage at 4.3 V, along with Co3PO4- and Al2O3-coated LiNi0.5Co0.15Mn0.35O2 cathodes under the same conditions.
odes. In addition, unidentified peaks were also observed, and it is believed that these peaks may be from the reactions between the electrolytes and cathodes. However, when the Co content was \( x = 0.06 \), although a major spinel phase was observed, the peak intensities of the unidentified phase decreased. A similar trend was observed in the Al2O3-coated cathode, but such unidentified peaks were reduced significantly compared to the bare cathodes. In the case of the Co3(PO4)2 coating, due to the formation of the Li\(x\)CoPO4 solid solution phase near the surface of the bulk, no formation of the spinel phase was observed; instead, peak broadening of the cathode was observed. The TEM image of the Co3(PO4)2-coated LiNi0.8Co0.1Mn0.1O2 cathode after storage shows the existence of the LiCoPO4 coating layer with a lattice fringe of (111) plane corresponding to a \( d \) spacing value of 3.44 Å (Fig. 10).

In consequence, the increased Co content or an Al2O3 coating decreases the side reactions with the electrolytes. Despite this, the Co3(PO4)2 coating can solve both the occurrence of the side reactions and the formation of the spinel phase at the same time. The coating can act as a kinetic barrier of the coating layer, which may slow the side reactions at 90°C, but it could not stop the reactions. However, note that the storage test of the charged electrode was performed at the most severe condition.

To examine the oxidation state of Ni, Co, and Mn for the samples after storage at 90°C for 7 days after 4.3 V charging, the Ni, Co, and Mn K-edge XANES spectra of the cathodes with \( x = 0 \) and 0.06 were measured using reference samples with oxidation states of +2, +3, and +4, respectively (Fig. 11). When the cathode was charged to 4.3 V, the edge position of the Ni K-edge XANES spectra shifted to a higher energy value. This positive shift shows the increase of the average oxidation state of the Ni ion from \( 2^+ / 3^+ \) to approximately 4+. The decrease of peak B at 4.3 V implies that the delithiation gives rise to a transition of the hole state (\( L \)) from oxygen to the Ni atom. Upon delithiation, the \( 3d^L \) state of the LMCT (ligand to metal charge transfer) process is replaced by the \( 3d^L \) state of predominantly the Ni\(^{4+} \) ion as another hole state, which implies that the hole state is relatively localized at the Ni atomic site under the local structurally distorted environment. The abrupt disappearance of peak B is another hint regarding the local structural distortion by the formation of the Ni\(^{4+} \) ion. The spectrum measured after 90°C storage shows a negative shift compared to that of the sample charged at 4.3 V with an oxidation state of Ni\(^{3+} \). This provides evidence for Ni\(^{3+} \) dissolution and a reduction to Ni\(^{3+} \) during storage at 90°C.

However, in the case of the Co K-edge XANES spectra, the edge position and spectra shapes of the cathodes show the same oxidation state of \( 3+ \) before and after charging. The same states are shown again after charging to 4.3 V and after storage at 90°C. A slight difference in the shape of the spectra implies that there may be a modest difference in metal-metal long-range patterns between the samples and the references. For the Mn K-edge spectra (Fig. 11), the pre-edge and edge peaks indicate that the Mn oxidation state after 4.3 V charging is predominantly 4+. As the peaks A1 and A2 correspond to the electronic transition to unoccupied \( t_2g \) and \( e_g \) energy levels, respectively, the Mn\(^{4+} \) is relatively rich when \( x = 0.1 \). Even after storage at 90°C for 7 days, the overall spectra shapes show the predominant existence of Mn\(^{4+} \), but small amounts of Mn\(^{3+} \) ions exist in the cathode nonetheless. However, after storage at 90°C for
7 days, note that a decreased A2 intensity can be observed, suggesting the possible dissolution of Mn\(^{3+}\) to Mn\(^{2+}\) and Mn\(^{4+}\) by the disproportion reaction, despite the fact that the overall edge peaks show the dominant Mn\(^{4+}\) state. Note that with the Co\(_3\)(PO\(_4\))\(_2\)-coated sample after charging and storage at 90°C for 7 days, the peak shape is quite similar to that of the charged sample, indicating that Mn\(^{3+}\) was not dissolved into the electrolytes.

**Conclusion**

In order to improve upon the structural instability of Ni-rich LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) cathode materials during storage in air and in electrolyte at 90°C, the Co content in the LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) cathode was varied between 0 and 0.06. Among the compositions, the cathode with x = 0.06 showed the smallest formation of LiOH and Li\(_2\)CO\(_3\) in air and the lowest amount of Ni and Mn ion dissolution at 90°C in the electrolytes used in the study. However, typical structural degradation with storage at 90°C could not be avoided. In order to mitigate this problem, Co\(_3\)(PO\(_4\))\(_2\) coating was introduced, and no phase transformation into the spinel phase as well as a greatly decreased metal dissolution rates resulted.

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