M$_3$(PO$_4$)$_2$-Nanoparticle-Coated LiCoO$_2$ vs LiCo$_{0.96}$M$_{0.04}$O$_2$ (M = Mg and Zn) on Electrochemical and Storage Characteristics

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The electrochemical cycling and storage characteristics of LiCo$_{0.96}$M$_{0.04}$O$_2$ and M$_3$(PO$_4$)$_2$ nanoparticle-coated LiCoO$_2$ cathode materials (M = Zn and Mg) were compared at room temperature and 90°C between 3 and 4.5 V. The doped cathodes showed degraded electrochemical performance at room temperature compared to the uncoated cathode. The first discharge capacities of the uncoated and the doped cathodes were 186 and 175 mAh/g, respectively. The doped cathodes showed 30 mAh/g after 30 cycles, while the uncoated cathode showed 100 mAh/g after 50 cycles at a 1 C rate. Mg$_3$(PO$_4$)$_2$ and Zn$_3$(PO$_4$)$_2$-coated LiCoO$_2$ showed discharge capacities of 179 and 187 mAh/g, respectively, and had significantly improved capacity retention, showing 133 and 153 mAh/g, respectively, after 50 cycles. After storage at 90°C, in the electrolytes using 4.5 V charged electrodes, the doped cathodes showed both greatly decreased side reactions with the electrolytes and formation of Co$_3$O$_4$ and CoO phases from Li and Co dissolution. However, the coated cathodes did not show either structural transformation into the Co$_3$O$_4$ and CoO phases or side reactions with the electrolytes.

At present, LiCoO$_2$ powders are the most widely used cathode material in Li-ion batteries for mobile electronics, which alter the charge cutoff voltage from 4.2 V (vs graphite) to 4.4 V (vs lithium metal) to 4.4 V (vs graphite) (−4.5 V vs lithium metal). By increasing the cutoff voltage, the energy density of the cell can be increased by ~15%. However, due to side reactions with the electrolytes on the particle surface and continuous structural destruction from the dissolution of Li and Co ions, the capacity of LiCoO$_2$ rapidly fades. Previous studies have focused on improvements of electrochemical performances at room temperature using doped LiCo$_{0.96}$M$_{0.04}$O$_2$ (M = Al, Zn, Ti, and Mg) coatings.$^{1,2}$,4-14 Here, coatings may be an attractive method for improving such problems as it applies only to final LiCoO$_2$ materials. For doped cathodes, depending on the dopant (M) in LiCo$_{0.96}$M$_{0.04}$O$_2$ and the value of x, the specific capacity varies. In addition, uniform substitution of dopants into the Co 3b sites in the LiCoO$_2$ are difficult to achieve in mass-production processes that use solid-state reactions.

Only a small number of storage studies at elevated temperatures (e.g., 90°C) have been reported $^{15,17}$ thus far. MPO$_4$ coatings (M = metal) have been reported to be effective in improving not only thermal stability but also electrochemical properties, depending on the M factor.$^{15}$ In a FePO$_4$ coating, Fe ions were observed to be dissolved into the electrolytes during 90°C storage. For an AlPO$_4$ coating, despite improving the structural stability at 90°C, it has been observed that the capacity decreases at a 1 C rate as the electrode density increases.$^{15}$ Recently, the authors investigated a CO$_3$(PO$_4$)$_2$ coating on LiCoO$_2$ and LiNi$_{0.8}$(Co$_{0.2}$Al$_{0.0}$)O$_2$ cathodes, which resulted in better rate capabilities compared to an AlPO$_4$ coating at higher C rates.$^{16,17}$ However, it is difficult to obtain a systematic comparison of coated and doped cathodes in terms of cycling and structural stability at 90°C with a reported value.

In this study, a comparison of Mg$_3$(PO$_4$)$_2$ and Zn$_3$(PO$_4$)$_2$ coatings on LiCoO$_2$ vs doped LiCo$_{0.96}$M$_{0.04}$O$_2$ (M = Mg and Zn) cathodes is made regarding the electrochemical properties at room temperature and the structural stability when in storage at 90°C after charging at 4.5 V in electrolytes.

**Experimental**

LiCoO$_2$ was prepared by stoichiometric mixing of Co$_3$O$_4$ (99.99%, average particle size 3 μm) and Li$_2$CO$_3$ and firing at 1000°C for 3 h. LiCo$_{0.95}$M$_{0.05}$O$_2$ (M = Zn and Mg) was prepared by stoichiometric mixing of Mg(OH)$_2$ or ZnO with Co$_3$O$_4$ by dry milling at 300 rpm for 48 h. The mixture was then thoroughly mixed with Li$_2$CO$_3$ by dry milling at 200 rpm, followed by firing at 600°C for 5 h. The cooled powders were mixed and fixed at 1000°C for 3 h. The average particle size of 10 μm uncoated and doped LiCoO$_2$ were used for the electrochemical tests (Brunauer–Emmett–Teller surface area of the samples was 0.5 m$^2$/g). For scientific accuracy, same uncoated LiCoO$_2$ was used for coatings. Inductively coupled plasma-mass spectroscopy (ICP-MS) results of lithium stoichiometry (x) in the uncoated Li$_3$Co$_2$O$_2$ showed 1.01. To prepare the coating solution, 3 g of Mg or Zn nitrates and 1.14 g of (NH$_4$)$_2$HPO$_4$ were dissolved in 30 g of distilled water, and M$_3$(PO$_4$)$_2$ particles that were pink in color instantly precipitated in the solution, which was stirred for 20 min at pH ~4. This coating concentration was a 3 wt% coating concentration (the weight of cathode was fixed at 100 g). For instance, a 1.5 wt% coating concentration was a coating concentration that used 1.5 g of zinc nitrate and 0.57 g of (NH$_4$)$_2$HPO$_4$ per 100 g of cathode powders. The coated cathodes were annealed at 800°C for 5 h in air. For the storage test at 90°C, the charged cathodes at 4.5 V were disassembled from coin-type half cells in a glove box and were immersed in electrolyte and tightly sealed in vials. The vials were kept at 90°C for 1 day and cooled to room temperature.

The field-emission transmission electron microscope (FE-TEM) (JEOL 2100F operating at 200 kV) samples were prepared by evaporation of the dispersed particles in acetone or hexane on carbon-coated copper grids. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max2000 with a Cu target tube. ICP-MS (ICPS-1000IV, Shimadzu) was used to determine the metal contents. The electrochemical properties were tested in a coin-type 2016R cell with lithium metal as the anode. The cathode consisted of 94 wt% active material, 3 wt% Super P carbon black, and 3 wt% polyvinylidene fluoride binder. The electrolyte for the coin-type half-cells (2016 type) was 1 M LiPF$_6$ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (30:30:40 vol %) (Cheil Ind. Korea). The capacity and capacity retention were measured to be between 3 and 4.5 V at a rate of 0.1, 0.2, 0.5, and 1C (1C = 180 mA/g). Specific capacities of the cathodes were calculated using only the active material. The HF level in the electrolyte solution was determined by gas chromatography.

**Results and Discussion**

Figure 1 shows XRD patterns of the coated LiCoO$_2$ and doped LiCo$_{0.95}$M$_{0.05}$O$_2$ (M = Mg and Zn) powders. Characteristic lines of α-Fe$_2$O$_3$ structure can be observed. Single-phase oxide was ob-
tained, for which Miller indexes (hkl) are indexed for a hexagonal setting. For the LiCoO2:Mg0.05O2 powders, the lattice constants a and c values increase while those of the coated cathodes are identical to those of uncoated sample, as shown in Table I. The increase in lattice constants in the doped cathodes may be due to the larger size of Mg2+ and Zn2+ compared with that of the Co3+ ions (rMg2+ = 0.72 Å, rCo3+ = 0.545 Å, rZn2+ = 0.74 Å). Figure 2 shows TEM images of the LiCoO2:Mg0.05O2 (M = Zn and Mg) and the coated samples. The doped samples show typical lattice fringes of the (003) plane corresponding to 4.68 Å. In the case of the Zn3(PO4)2-coated sample, its low-magnification image (Fig. 2c) does not show any coating layer, but its high-resolution image (2d) shows an amorphous coating layer with a thickness of ~5 nm. It was found that, depending on the metal (M) in M3(PO4)2, the crystallinity and coating thickness varied. For instance, for the Co3(PO4)2-coated sample, the Co3(PO4)2 coating layer became olivine LiCoPO4 as a result of a reaction with Li in LiCoO2 during the annealing process. For the AlPO4 coating, the coating layer was amorphous and its thickness was ~15 to 20 nm. For the Mg3(PO4)2-coated sample, nanoparticles ~50 nm were coated on the LiCoO2 (Fig. 2e), and the amorphous coating layer that consisted of many pores and rough surfaces with a coating thickness of ~5 nm was also observed (Fig. 2f). In contrast to Co3(PO4)2 coating that exhibited the disappearance of the coating layer due to its complete reaction with the bulk surface, Mg3(PO4)2-coated LiCoO2 cathodes (M = Zn and Mg) showed the clearly distinguishable coating layer on the cathode surface, consisting of amorphous phase. Thus, it is believed that Mg3(PO4)2 nanoparticles had a partial reaction of bulk LiCoO2 during an annealing process at 800°C.

Figure 3 shows the charge and discharge curves of the uncoated and doped cathodes for each first cycle at 0.1, 0.2, 0.5, and 1C rates (1C = 180 mA/g) and after 30 or 50 cycles in coin-type half cells. For an uncoated cathode, the first charge and discharge capacities are 190 and 186 mAh/g, respectively. However, for the Mg-doped cathode, the first charge capacity is similar to that of uncoated cathode at 188 mAh/g, but its discharge capacity decreases to 174 mAh/g. The Zn-doped cathode shows charge and discharge capacities of 188 and 175 mAh/g, respectively. A decrease in the discharge capacities of the doped cathodes is associated with a decrease in the concentration of active Co3+ ions and M2+ ions substituted into Co sites, leading to the creation of an equal number of Co4+ ions for the charge balance. Both LiCoO2,Zn0.05O2 and LiCoO2,Mg0.05O2 exhibit a capacity retention rate of 57% after only 30 cycles, compared with the first discharge capacity at 1C. This retention value is inferior to that of the uncoated cathode with capacity retention of 63% after 50 cycles.

The Mg3(PO4)2 and Zn3(PO4)2-coated samples (3 wt % coating concentration) show first discharge capacities of 178 and 187 mAh/g, respectively, as shown in Fig. 4. Differential voltage profiles for the uncoated 3, and 1.5 wt % Mg3(PO4)2-coated cathodes were added in Fig. 5. The presence of the plateaus between 4 and 4.2 V, indicative of order/disorder phase transition, depends on the coating concentration, and only the 3 wt % coated sample shows the plateau. Our previous study on the AlPO4 coating concentration effect on LiCoO2 also showed a similar result. At this time, we do not know the detailed mechanism for such a phenomenon but doubt it is related to Li stoichiometry difference near the cathode surface. ICP-MS results of lithium stoichiometry (x) in the uncoated LiCoO2 showed 1.01. Pereira et al. reported that order-disorder reactions disappeared when the Li stoichiometry (x) was x = 1.05 in Li2CoO2. Accordingly, higher Mg3(PO4)2 coating concentration may induce the increased difference in Li concentration at the surface and inward, leading to more developed plateaus.

The capacity retention of the Mg3(PO4)2 and Zn3(PO4)2-coated

![Figure 1. XRD patterns of the LiCoO2:Mg0.05O2, (M = Zn and Mg) and Mg3(PO4)2 and Zn3(PO4)2 nanoparticle-coated LiCoO2 powders.](https://example.com/f1.png)

![Figure 2. TEM images of the (a) LiCoO2,Zn0.05O2 and (b) LiCoO2,Mg0.05O2 cathode particles (c and d) Zn3(PO4)2 nanoparticle-coated LiCoO2 particle [(d) is a magnified image of (c)] and (e and f) Mg3(PO4)2 nanoparticle-coated LiCoO2 particle [(f) is a magnified image of (e)].](https://example.com/f2.png)

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å) ± 0.001 Å</th>
<th>c (Å) ± 0.001 Å</th>
<th>c/a</th>
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<td>14.034</td>
<td>4.984</td>
</tr>
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<td>2.819</td>
<td>14.059</td>
<td>4.987</td>
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<tr>
<td>LiCoO2,Mg0.05O2</td>
<td>2.819</td>
<td>14.060</td>
<td>4.988</td>
</tr>
<tr>
<td>Zn3(PO4)2 coating</td>
<td>2.816</td>
<td>14.034</td>
<td>4.984</td>
</tr>
<tr>
<td>Mg3(PO4)2 coating</td>
<td>2.816</td>
<td>14.035</td>
<td>4.984</td>
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</table>
samples (3 wt % coating) was 84 and 90%, respectively, after 50 cycles. The decreased capacity retention with the Mg3(PO4)2 coating relative to Zn3(PO4)2 coating occurred because the nonuniform coating layer with coated nanoparticles <50 nm in size impedes Li-ion diffusivity into the bulk particle. A similar result was observed in the SrHPO4 and CePO4-coated LiNi0.9Co0.1O2 cathodes.

When the coating concentration of the Zn3(PO4)2 coating decreases to 1.5 wt %, the first discharge capacity is slightly larger than that of the Mg3(PO4)2 coating, at 187 mAh/g. However, the capacity retention at 1C rate cycling decreases to 140 mAh/g, which is comparable with that of Mg3(PO4)2-coated LiCoO2. Table II summarizes the capacities of the uncoated, coated, and doped cathodes at different rates and after 30 and 50 cycles of the samples. Overall, the coated samples demonstrate enhanced capacity retention at 1C rate cycling. It is believed that Mg3(PO4)2 nanoparticles exist as an amorphous solid solution on the particle surface with a partial reaction of bulk LiCoO2 during an annealing process at 800°C, which may enhance both Li-ion and electronic conductivities.

Based upon the above results, a more uniform coating is beneficial for both Li ion diffusivity and electronic conductivity. It is well...
known that large internal strains and subsequent mechanical degradation of the cathode materials originate from the dissolution of Li⁺ and M⁴⁺ ions, and that the formation of by-products between reaction-dissolved ions and electrolytes at the interface enhances the structural degradation of the cathodes. This effect becomes evident during storage at elevated temperatures. A previous TEM result showed that an uncoated cathode charged at 4.5 V showed a structural transformation into the spinel phase at the particle surface, while that of the LiCo₀.₉₆Zn₀.₀₄O₂ electrode after storage at 90°C for 1 day after charging to 4.5 V vs lithium metal.

Table II. Comparison of the first discharge capacities of LiCo₀.₉₆Mg₀.₀₄O₂ (M = Zn and Mg) and Mg₃(PO₄)₂ and Zn₃(PO₄)₂ nanoparticles-coated LiCoO₂ during storage at 90°C after 1 day after charging to 4.5 V vs lithium metal.

<table>
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<tr>
<th>Material</th>
<th>0.1C</th>
<th>0.2C</th>
<th>0.5C</th>
<th>1C</th>
<th>1C, 30 cycles</th>
<th>1C, 50 cycles</th>
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<tbody>
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<td>LiCoO₂</td>
<td>186</td>
<td>183</td>
<td>174</td>
<td>163</td>
<td>125</td>
<td>100</td>
</tr>
<tr>
<td>LiCo₀.₉₆Zn₀.₀₄O₂</td>
<td>175</td>
<td>164</td>
<td>151</td>
<td>139</td>
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<td>79</td>
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<tr>
<td>Mg₃(PO₄)₂ coating</td>
<td>179</td>
<td>174</td>
<td>166</td>
<td>159</td>
<td>143</td>
<td>133</td>
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<td>Zn₃(PO₄)₂ coating (1.5 wt %)</td>
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<td>178</td>
<td>162</td>
<td>156</td>
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<td>131</td>
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<td>Zn₃(PO₄)₂ coating (3 wt %)</td>
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<td>182</td>
<td>176</td>
<td>171</td>
<td>159</td>
<td>153</td>
</tr>
</tbody>
</table>

Table III. Amounts of the dissolved Co ions into the electrolytes and HF contents in LiCo₀.₉₆Mg₀.₀₄O₂ (M = Zn and Mg) and Mg₃(PO₄)₂ and Zn₃(PO₄)₂ nanoparticles-coated LiCoO₂ during storage at 90°C after 1 day after charging to 4.5 V vs lithium metal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Co before storage (ppm)</th>
<th>Co after storage (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
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<td>200</td>
</tr>
<tr>
<td>LiCo₀.₉₆Zn₀.₀₄O₂</td>
<td>270</td>
<td>190</td>
</tr>
<tr>
<td>LiCo₀.₉₆Mg₀.₀₄O₂</td>
<td>900</td>
<td>210</td>
</tr>
<tr>
<td>Zn₃(PO₄)₂ coating (3 wt %)</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>Mg₃(PO₄)₂ coating</td>
<td>90</td>
<td>100</td>
</tr>
</tbody>
</table>

Fisher moisture titrator. Hence, it is important to blacken the Co⁴⁺ dissolution initially. In addition, the dissolved Li⁺ ions are solvated and combine with Co⁴⁺-oxidized solvent molecules to form lithium-containing organic products. As shown in Table III, the Co content in the uncoated sample after storage was 3500 ppm (before storage its amount was negligible). The HF content of the uncoated sample after storage increases to 800 ppm, compared to 200 ppm before storage. In consequence, the charged uncoated cathode undergoes severe structural instability at 90°C. The low-magnification TEM images of the uncoated cathode after storage at 90°C in Fig. 7a show the presence of rough surfaces and different contrasts near the surfaces, which indicates the presence of a highly defected phase. Essentially, the high-resolution image in Fig. 7b shows the formation of the amorphous phase that resulted from the severe dissolution of Li and Co at 90°C.

XRD patterns of the doped cathodes are, however, quite different from those of the uncoated cathode after storage at 90°C (Fig. 8). XRD patterns of the charged LiCo₀.₉₆Mg₀.₀₄O₂ electrode stored at 90°C show that the peak intensities of unknown phases are significantly decreased, although Co₃O₄ and CoO peaks continue to be present. For LiCo₀.₉₆Zn₀.₀₄O₂, unknown peaks including CoO and Co₃O₄ phases are not observed, except for a slightly increased peak-broadening effect, compared to that of the charged cathode.

This result indicates that Zn or Mg doping into the LiCoO₂ causes an improvement in structural stability and reduces surface reactivity with the electrolyte, although Zn doping leads to a better result. This result is further supported by the amount of dissolved Co content in the electrolyte at 90°C. The Co contents of the Mg- and Zn-doped cathodes after storage were 900 and 270 ppm, respectively. Similarly, the HF content decreased in the doped cathodes; they were measured at 300 and 350 ppm, respectively, as shown in Table III. This result agrees with the XRD patterns of the doped cathodes kept at 90°C, as shown in Fig. 6. The TEM image (Fig. 9) of the LiCo₀.₉₆Zn₀.₀₄O₂ electrode shows the formation of the Co₃O₄ phase at the particle surface, while that of the LiCo₀.₉₆Zn₀.₀₄O₂ electrode shows a pristine layered phase.

Figure 6. XRD patterns of an uncoated LiCoO₂ electrode after a 4.5 V charge and after storage at 90°C for 1 h. After charging the cell, the electrode was separated from the cell and kept in the electrolyte in a vial.

Figure 7. TEM images of uncoated electrodes after storage at 90°C for 1 day at 4.5 V.
Mg₃PO₄ coating was separated from the cell and kept in the electrolyte in a vial.

As shown in Fig. 8, XRD patterns of the LiCo₀.₉₆M₀.₀₄O₂ (M = Zn and Mg) and Mg₃(PO₄)₂, and Zn₃(PO₄)₂ nanoparticle-coated LiCoO₂ electrodes after a 4.5 V charge and storage at 90°C for 1 h. After charging the cell, the electrode was separated from the cell and kept in the electrolyte in a vial.

In terms of electrochemical cycling and storage characteristics at 90°C, coated samples showed much-improved results relative to doped cathodes. In contrast to the doped cathodes, the coated samples were effective in retarding direct reactions between the electrolyte and the cathode surface that consisted of highly oxidized Co⁴⁺ ions. Overall, Zn₃(PO₄)₂-coated cathodes showed a first discharge capacity of 187 mAh/g and excellent capacity retention at 1C rate after 50 cycles, as shown by a 154 mAh/g measurement. This result indicates that the amorphous-like coating layer was effective for improving electrochemical activity and that it decreased side reactions with the electrolytes at 90°C as well.

Conclusions

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