Fabrication of LiCoO₂/Helical Nanocarbon Composites and Their Effect on Lithium Cell Performance

Toshiro Hirai\textsuperscript{a,c, *}, Toshihiro Yoshida\textsuperscript{a}, Yusuke Uno\textsuperscript{a,d}, and Tomonobu Tsukikawa\textsuperscript{b}

\textsuperscript{a} Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu-shi, Toyama-ken 939-0398, Japan

\textsuperscript{b} NTT Facilities, Inc., Toshima-ku, Tokyo 170-0004, Japan

\textsuperscript{c} Present address; SACI, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan

\textsuperscript{d} Present address; Chuo Branch, NTT Facilities, Inc., Minato-ku, Tokyo 108-0023, Japan

* Corresponding author

E-mail address: t-hirai@saci.kyoto-u.ac.jp

Fax: +81-75-383-3048

Phone: +81-75-383-3052
Abstract

We fabricate LiCoO$_2$/helical nanocarbon (HCN) composites by forming HCNs on LiCoO$_2$ on which iron oxides (Fe$_2$O$_3$ or Fe$_3$O$_4$) are dispersed (LiCoO$_2$(Fe$_2$O$_3$) or LiCoO$_2$(Fe$_3$O$_4$)) as catalysts for HCN formation, and estimate their electrochemical properties. Granular nanocarbons form on LiCoO$_2$(Fe$_2$O$_3$) and LiCoO$_2$(Fe$_3$O$_4$) at 350°C although HCNs of about 100 nm in diameter form on LiCoO$_2$(Fe$_2$O$_3$) at 450°C. Transmission electron microscopy and energy dispersive x-ray spectroscopy measurements show that HCNs consist of stacked graphene layers for LiCoO$_2$(Fe$_2$O$_3$)/HCN composites fabricated at 450°C. On the other hand, several-nm-thick tetragonal layer exists on the LiCoO$_2$ substrate and amorphous nanocarbons form on the tetragonal layer for LiCoO$_2$(Fe$_2$O$_3$)/HCN and LiCoO$_2$(Fe$_3$O$_4$)/HCN composites fabricated at 350°C. X-ray diffraction measurements suggest that Fe$_2$O$_3$ and Fe$_3$O$_4$ do not completely inhibit LiCoO$_2$ decomposition. Cathodes containing LiCoO$_2$(Fe$_2$O$_3$)/HCN or LiCoO$_2$(Fe$_3$O$_4$)/HCN fabricated at 350°C improve rate capability of lithium cells. However, this rate capability is not better than that of cathodes containing a mixture of LiCoO$_2$ and acetylene black.
**Introduction**

High-rate and long-life lithium-ion batteries have long been expected as automotive and next-generation industrial batteries. Cathode active material/carbon composites have been studied as means of prolonging cycle life of such batteries (1, 2) as well as cathode active materials have been studied to improve lithium-ion cell capacity and rate capability (3-7).

On the other hand, some researchers have fabricate nanocarbons using chemical vapor deposition (CVD) (8-11). Nanocarbons produced using CVD has a helical shape and are reported to be semimetals with the potential to be superconductive materials (12). This suggests that they have high potential for use as conductive materials for the cathodes of lithium-ion cells. We have fabricated LiCoO$_2$/helical nanocarbon (HCN) composites and evaluated their electrochemical properties (13). We successfully obtained composites from HCNs formed on a LiCoO$_2$ substrate. However, LiCoO$_2$ severely decomposed and a cell containing LiCoO$_2$/HCN composite exhibited a low specific capacity.

We used Fe$_2$O$_3$ and Fe$_3$O$_4$ as catalysts to fabricate LiCoO$_2$/HCNs effectively without LiCoO$_2$ decomposition at lower temperature to show better performance as cathode active material. We prepared a LiCoO$_2$ substrate on which iron oxides (Fe$_2$O$_3$ or Fe$_3$O$_4$) were dispersed (LiCoO$_2$(Fe$_2$O$_3$) or LiCoO$_2$(Fe$_3$O$_4$)) as catalysts for HCN formation. We then formed HCNs on LiCoO$_2$(Fe$_2$O$_3$) or LiCoO$_2$(Fe$_3$O$_4$) at 450°C or lower and estimated effect of the composites on lithium cell performance.
Experimental

We used LiCoO₂ (Nippon Chemical Industrial Co., Diameter: 10µm) as a substrate and Fe₂O₃ and Fe₃O₄ (Wako Pure Chemical Industries, Ltd.) as catalysts for helical nanocarbon (HCN) formation using chemical vapor deposition (CVD).

We prepared slurries by dispersing 10 g of LiCoO₂ and 0.5 g of Fe₂O₃ or Fe₃O₄ into 50 ml of distilled water to uniformly and effectively disperse Fe₂O₃ or Fe₃O₄ on the surface of LiCoO₂ particles and stirred a solution containing the mixture in a beaker overnight on a hot plate at about 80°C to evaporate water. The mixture was then dried overnight in a vacuum at 80°C.

We fabricated the composites by forming HCNs on the surface of LiCoO₂/Fe₂O₃ or LiCoO₂/Fe₃O₄ powder mounted on a ceramic boat using CVD in a quartz tube and supplied 60 ml min⁻¹ of C₂H₂ gas as a carbon source and 50 ml min⁻¹ of Ar as a carrier at 450°C or 350°C for 10 min.

We estimated the electrochemical properties of the composites using a lithium cell. We fabricated cathode disks (area, 1.33 cm²) by mixing the obtained composites, acetylene black (AB, Denki Kagaku Kogyo Co.) and PTFE powder with a ratio of 70 wt% of LiCoO₂, 25 wt% of AB and HCNs formed using CVD, and 5 wt% of PTFE, and rolling the mixture into a flat sheet. We fabricated CR2032 coin-type cells for evaluating electrochemical properties. Each coin-type cell consisted of a cathode, a lithium anode (Honjo Chemical Co.: area, 1.13 cm²) and a 1 M LiPF₆-ethylene carbonate/dimethyl carbonate (volume ratio: 1/1) electrolyte (Tomiyama Pure
Chemicals Co.). Test cells were charged at 0.75 mA cm\(^{-2}\) to 4.3 V and then discharged at constant current to 3.0 V at 21°C after a 10-min rest.

**Results and Discussion**

Figure 1 shows a scanning electron microscope (SEM) image of the LiCoO\(_2\)/HCN composite. HCNs are formed on the LiCoO\(_2\) surface. However, the HCNs are not distributed uniformly and the bare LiCoO\(_2\) surface can be seen. HCNs have a helical shape with a diameter of 200 nm or smaller. We generally observed HCNs with an irregular helical shape. We have not found an optimum fabrication condition of HCNs with a regular helical shape.

Figure 2 shows transmission electron microscope (TEM) photos of the composites fabricated from HCNs formed on LiCoO\(_2\) substrate without iron oxides at 450°C. HCNs contain many crystalline boundaries of graphene layers and serious turbulence was also observed, indicated with the circle in Fig. 2, which may result in an irregular helical shape of HCNs. We measured contents of the composites by energy dispersive x-ray spectroscopy (EDS). Figure 3 shows areas for EDS measurements as squares. The results are listed in Table 1. Carbon mainly existed in dark areas 1, 2, 3, and 4 around the white area. On the other hand, white area 5 contained more than 60% Co, which is larger than the Co percentage of LiCoO\(_2\). This suggests that area 5 contained Co and CoO formed from decomposed LiCoO\(_2\).

Furthermore, we used X-ray diffraction (XRD) to estimate the stability of LiCoO\(_2\) under our experimental conditions. Figure 4 shows XRD patterns of LiCoO\(_2\)/HCN composites fabricated at
450°C. The XRD contains peaks of Li$_2$CO$_3$, Co, and CoO and no peaks of LiCoO$_2$, which shows that LiCoO$_2$ decomposed without iron oxides. The results coincide with those of EDS measurements.

We then fabricated a composite from HCNs formed on LiCoO$_2$ substrate with Fe$_2$O$_3$ or Fe$_3$O$_4$ and estimate its effect on inhibition of LiCoO$_2$ decomposition. Figure 5 shows SEM photo of the composite fabricated with Fe$_2$O$_3$ at 450°C. HCNs were successfully formed on LiCoO$_2$ particles and there was no significant difference in the HCN formation from the composites fabricated without iron oxides. We obtained the same results for the composite fabricated with Fe$_3$O$_4$. On the other hand, we observed nanocarbons were not helical shaped for the composites fabricated at 350°C (Fig. 6). “Immature” and particulate HCNs formed on the substrate at 350°C.

Figure 7 shows TEM photos of the composite fabricated with Fe$_2$O$_3$ at 350°C. Figure 7(a) shows TEM image of the area where there was Fe$_2$O$_3$, and Fig. 7(b) shows TEM image of the area where there was no Fe$_2$O$_3$.

By fabricating at 350°C, amorphous nanocarbons (C in Fig. 7), formed on the LiCoO$_2$ substrate (A in Fig. 7), and there was no significant difference in shape due to the existence of Fe$_2$O$_3$. We also observed a tetragonal thin layer (B in Fig. 7) on the substrate A. Figure 8 shows TEM photos of the composite fabricated with Fe$_3$O$_4$ at 350°C. We observed the same condition for the composite fabricated with Fe$_3$O$_4$ at 350°C shown in both of Fig. 8 (a) and (b) as that for the composite fabricated with Fe$_2$O$_3$ at 350°C.
We observed a tetragonal layer on as-received LiCoO$_2$ particles. We therefore do not conclude that this layer formed using CVD. Kobayashi et al. reported a layer on Li(NiCo)$_2$O$_2$ (14), which corresponds to what we observed.

Figure 9 shows XRD patterns of LiCoO$_2$/nanocarbon composites prepared with and without Fe$_2$O$_3$; LiCoO$_2$(Fe$_2$O$_3$)/HCN (350$^\circ$C), LiCoO$_2$(Fe$_2$O$_3$)/HCN (450$^\circ$C), and LiCoO$_2$/HCN (450$^\circ$C). The XRD patterns indicate that LiCoO$_2$ retained its original structure in part but it also suggests that addition of Fe$_2$O$_3$ did not prevent LiCoO$_2$ from decomposing.

We also measured XRD for LiCoO$_2$(Fe$_3$O$_4$)/HCN composite fabricated at 350$^\circ$C and confirmed addition of Fe$_3$O$_4$ inhibited LiCoO$_2$ decomposition through HCN fabrication.

We evaluated LiCoO$_2$ decomposition in relation to the addition of Fe$_2$O$_3$ and HCN fabrication temperature. Table 2 shows intensity ratios of main peaks of Li$_2$CO$_3$ (peak B in Fig. 9), CoO (peak C in Fig. 9), and Co (peak D in Fig. 9) based on LiCoO$_2$ peak (peak A in Fig. 9). XRD peak intensity ratios indicate that LiCoO$_2$ decomposition was significantly inhibited by coating with Fe$_2$O$_3$ and that HCN fabrication temperature decreased.

We estimated the electrochemical properties of LiCoO$_2$/nanocarbon composites using a lithium cell. Figure 10 shows rate capability of lithium cells containing LiCoO$_2$(Fe$_2$O$_3$)/HCN composites, LiCoO$_2$(Fe$_2$O$_3$)/HCN (350$^\circ$C) and LiCoO$_2$(Fe$_2$O$_3$)/HCN (450$^\circ$C), compared with that of a lithium cell containing as-received LiCoO$_2$. The cell containing LiCoO$_2$(Fe$_2$O$_3$)/HCN (350$^\circ$C) showed better rate capability than cell containing LiCoO$_2$(Fe$_2$O$_3$)/HCN (450$^\circ$C). However, the rate
capability of our composites is currently inferior to that of as-received LiCoO$_2$. We also estimated
the rate capability of a lithium cell containing LiCoO$_2$(Fe$_3$O$_4$)/HCN composite (350$^\circ$C). The results
are shown in Fig. 11. The LiCoO$_2$(Fe$_3$O$_4$)/HCN (350$^\circ$C) cell showed the same rate capability as the
LiCoO$_2$(Fe$_2$O$_3$)/HCN (350$^\circ$C) cell. By using iron oxide catalysts and fabricating the composites at
lower temperature, LiCoO$_2$ decomposed less and the composites showed better cell performance
than that of composites fabricated without the catalysts at higher temperature. The challenge is to
fabricate composites with more crystallized HCN for better rate capability of lithium cells than that
of the cathode mixed with LiCoO$_2$ and AB.
Conclusion

We fabricated LiCoO$_2$/helical nanocarbon (HCN) composites by forming HCNs on LiCoO$_2$ on which iron oxides (Fe$_2$O$_3$ or Fe$_3$O$_4$) were dispersed (LiCoO$_2$(Fe$_2$O$_3$) or LiCoO$_2$(Fe$_3$O$_4$)) as catalysts for HCN formation, and estimated their electrochemical properties.

Cathode active material/nanocarbon composites were fabricated by forming HCNs on LiCoO$_2$ coated with iron oxides (Fe$_2$O$_3$ or Fe$_3$O$_4$) to inhibit LiCoO$_2$ degradation. The following results were obtained:

(1) Granular nanocarbons were generated on LiCoO$_2$ with Fe$_2$O$_3$ and LiCoO$_2$ with Fe$_3$O$_4$ at 350°C although HCNs with about 100 nm diameter were generated on LiCoO$_2$ with Fe$_2$O$_3$ at 450°C.

(2) TEM measurements showed that HCNs consisted of stacked graphene layers for LiCoO$_2$/HCN fabricated at 450°C. On the other hand, several-nm-thick tetragonal layer existed on the LiCoO$_2$ and amorphous nanocarbons formed on the tetragonal layer for LiCoO$_2$(Fe$_2$O$_3$)/HCN and LiCoO$_2$(Fe$_3$O$_4$)/HCN composites fabricated at 350°C.

(3) XRD measurements suggested that Fe$_2$O$_3$ and Fe$_3$O$_4$ did not completely inhibit LiCoO$_2$ decomposition.

(4) Cathodes containing LiCoO$_2$(Fe$_2$O$_3$)/HCN or LiCoO$_2$(Fe$_3$O$_4$)/HCN composites fabricated at 350°C improved rate capability, but this capability is not as good as that of cathodes containing a mixture of LiCoO$_2$ and AB.
Acknowledgments

The authors thank Nippon Chemical Industrial, Co. Ltd. for providing cathode active materials.
References


Table 1 Results of EDS measurements

<table>
<thead>
<tr>
<th>Area</th>
<th>C</th>
<th>O</th>
<th>Co</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.52</td>
<td>0.41</td>
<td>0.06</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>99.04</td>
<td>0.74</td>
<td>0.22</td>
<td>100.00</td>
</tr>
<tr>
<td>3</td>
<td>89.96</td>
<td>5.94</td>
<td>4.10</td>
<td>100.00</td>
</tr>
<tr>
<td>4</td>
<td>99.64</td>
<td>0.28</td>
<td>0.09</td>
<td>100.00</td>
</tr>
<tr>
<td>5</td>
<td>25.92</td>
<td>11.27</td>
<td>62.80</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Table 2 XRD peak intensity ratio for LiCoO$_2$/nanocarbon composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>A/B</th>
<th>A/C</th>
<th>A/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$(Fe$_2$O$_3$)/HCN (350°C)</td>
<td>10.37</td>
<td>335.8</td>
<td>386.7</td>
</tr>
<tr>
<td>LiCoO$_2$(Fe$_2$O$_3$)/HCN (450°C)</td>
<td>11.86</td>
<td>4.123</td>
<td>17.34</td>
</tr>
<tr>
<td>LiCoO$_2$/HCN (450°C)</td>
<td>1.984</td>
<td>1.051</td>
<td>0.0313</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 SEM image of LiCoO$_2$/HCN composites fabricated at 450°C for 10 min

Fig. 2 TEM image of LiCoO$_2$/HCN composite fabricated at 450°C for 10 min

Fig. 3 TEM image of LiCoO$_2$/HCN composite fabricated at 450°C for 10 min, and areas for EDS measurements

Fig. 4 XRD patterns of LiCoO$_2$/HCN (450°C)

Fig. 5 SEM photo of LiCoO$_2$(Fe$_2$O$_3$)/HCN fabricated at 450°C

Fig. 6 SEM photo of LiCoO$_2$(Fe$_2$O$_3$)/nanocarbon fabricated at 350°C

Fig. 7 TEM images of LiCoO$_2$(Fe$_2$O$_3$)/nanocarbon composites fabricated at 350°C for 10 min.
   A: LiCoO$_2$ substrate, B: tetragonal layer, C: nanocarbon fabricated using CVD, and D: deposited Ti layer for TEM measurements

Fig. 8 TEM images of LiCoO$_2$(Fe$_3$O$_4$)/nanocarbon composites fabricated at 350°C for 10 min.
   A: LiCoO$_2$ substrate, B: tetragonal layer, C: nanocarbon fabricated by CVD, and D: deposited Ti layer for TEM measurements

Fig. 9 XRD patterns of LiCoO$_2$/nanocarbon composites fabricated with and without Fe$_2$O$_3$

Fig. 10 Rate capability of lithium cells containing LiCoO$_2$(Fe$_2$O$_3$)/HCN composite and cell containing as-received LiCoO$_2$

Fig. 11 Rate capability of lithium cells containing LiCoO$_2$(Fe$_2$O$_3$)/HCN and LiCoO$_2$(Fe$_3$O$_4$)/HCN composites fabricated at 350°C
Fig. 1
Substrate

5 nm

Graphen

Fig. 2
Fig. 3
Graphite (002)
Fig. 5
Fig. 7

(a) (b)
Fig. 9

Graphite (002)

LiCoO$_2$(Fe$_2$O$_3$)/HCN (350$^\circ$C)

LiCoO$_2$(Fe$_2$O$_3$)/HCN (450$^\circ$C)

LiCoO$_2$/HCN (450$^\circ$C)
Fig. 10

[Graph showing the relationship between current density (mA cm\(^{-2}\)) and specific capacity (mAh g\(^{-1}\)) for different samples: LiCoO\(_2\) (Fe\(_2\)O\(_3\))/HCN (350\(^\circ\)C), LiCoO\(_2\) (Fe\(_2\)O\(_3\))/HCN (450\(^\circ\)C), and LiCoO\(_2\).]
Fig. 11

[Graph showing the specific capacity (mAh g\(^{-1}\)) vs. current density (mA cm\(^{-2}\)) for two different materials: LiCoO\(_2\)(Fe\(_3\)O\(_4\))/HCN(350\(^{\circ}\)C) and LiCoO\(_2\)(Fe\(_2\)O\(_3\))/HCN(350\(^{\circ}\)C).]