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Short communication

Fabrication of $LiCoO_2$/helical nanocarbon composites and their effect on lithium cell performance

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ABSTRACT

We fabricate $LiCoO_2$/helical nanocarbon (HCN) composites by forming HCNs on $LiCoO_2$ on which iron oxides (Fe_2O_3 or Fe_3O_4) are dispersed ($LiCoO_2(Fe_2O_3)$ or $LiCoO_2(Fe_3O_4)$) as catalysts for HCN formation, and estimate their electrochemical properties. Granular nanocarbons form on $LiCoO_2(Fe_2O_3)$ and $LiCoO_2(Fe_3O_4)$ at 350 °C although HCNs of about 100 nm in diameter form on $LiCoO_2(Fe_2O_3)$ at 450 °C. Transmission electron microscopy and energy dispersive X-ray spectroscopy measurements show that HCNs consist of stacked graphene layers for $LiCoO_2(Fe_2O_3)$/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 $LiCoO_2(Fe_2O_3)$/HCN and $LiCoO_2(Fe_3O_4)$/HCN composites fabricated at 350 °C. X-ray diffraction measurements suggest that Fe_2O_3 and Fe_3O_4 do not completely inhibit $LiCoO_2$ decomposition. Cathodes containing $LiCoO_2(Fe_2O_3)$/HCN or $LiCoO_2(Fe_3O_4)$/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.

1. 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 fabricated nanocarbons using chemical vapor deposition (CVD) [8–11]. Nanocarbons produced using CVD have 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_2O_3 and Fe_3O_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_2O_3 or Fe_3O_4) were dispersed ($LiCoO_2(Fe_2O_3)$ or $LiCoO_2(Fe_3O_4)$) as catalysts for HCN formation. We then formed HCNs on $LiCoO_2(Fe_2O_3)$ or $LiCoO_2(Fe_3O_4)$ at 450 °C or lower and estimated effect of the composites on lithium cell performance.

2. Experimental

We used $LiCoO_2$ (Nippon Chemical Industrial Co., diameter: 10 μm) as a substrate and Fe_2O_3 and Fe_3O_4 (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 $LiCoO_2$ and 0.5 g of Fe_2O_3 or Fe_3O_4 into 50 ml of distilled water to uniformly and effectively disperse Fe_2O_3 or Fe_3O_4 on the surface of $LiCoO_2$ particles and stirred the 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 vacuum at 80 °C.

We fabricated the composites by forming HCNs on the surface of $LiCoO_2/Fe_2O_3$ or $LiCoO_2/Fe_3O_4$ powder mounted on a ceramic boat using CVD in a quartz tube and supplied 60 ml min^{-1} of C_2H_2 gas as a carbon source and 50 ml min^{-1} of Ar as a carrier at 450 °C or 350 °C for 10 min.

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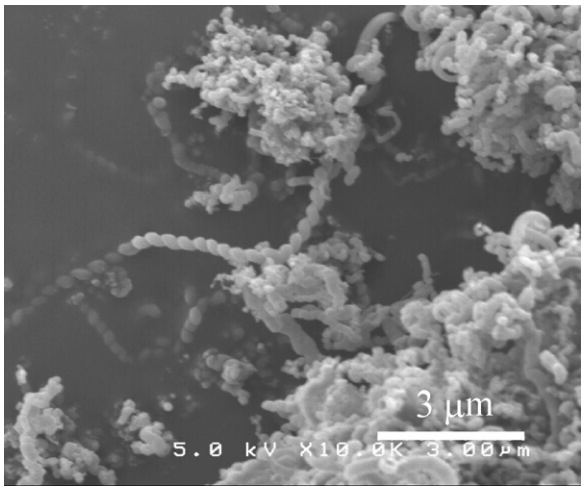

Fig. 1. SEM image of $LiCoO_2$/HCN composites fabricated at 450 °C for 10 min.

We estimated the electrochemical properties of the composites using a lithium cell. We fabricated cathode disks (area, 1.33 cm^2) by mixing the obtained composites, acetylene black (AB, Denki Kagaku Kogyo Co.) and PTFE powder with a ratio of 70 wt% of $LiCoO_2$, 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 cm^2) and a 1 M $LiPF_6$–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.

3. Results and discussion

Fig. 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.

Fig. 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). Fig. 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 $LiCoO_2$.

Table 1
Results of EDS measurements.

Area	Amount of atoms (%)			
	C	O	Co	Total
1	99.52	0.41	0.06	100.00
2	99.04	0.74	0.22	100.00
3	89.96	5.94	4.10	100.00
4	99.64	0.28	0.09	100.00
5	25.92	11.27	62.80	100.00

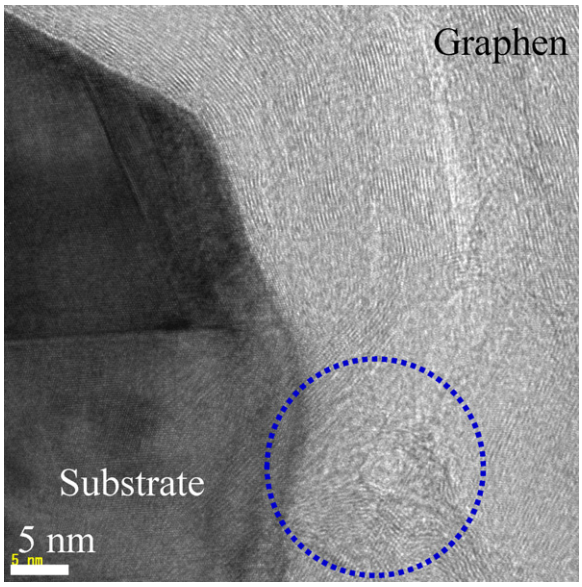

Fig. 2. TEM image of $LiCoO_2$/HCN composite fabricated at 450 °C for 10 min.

Furthermore, we used X-ray diffraction (XRD) to estimate the stability of $LiCoO_2$ under our experimental conditions. Fig. 4 shows XRD patterns of $LiCoO_2$/HCN composites fabricated at 450 °C. The XRD contains peaks of Li_2CO_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_2O_3 or Fe_3O_4 and estimate its effect on inhibition of $LiCoO_2$ decomposition. Fig. 5 shows SEM photos of the composite fabricated with Fe_2O_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_3O_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.

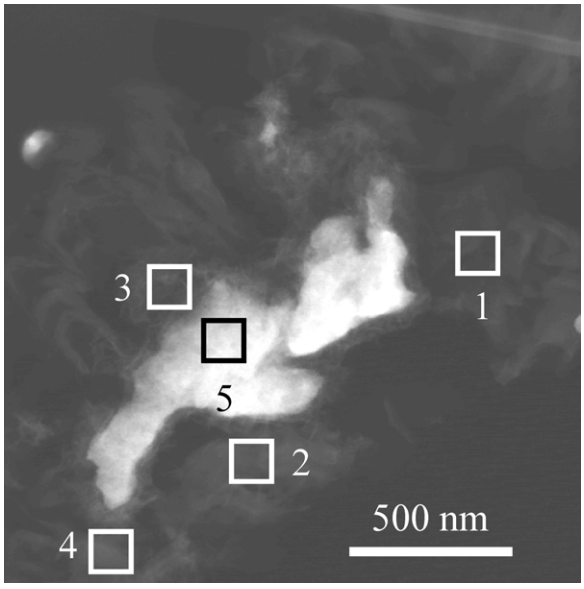

Fig. 3. TEM image of $LiCoO_2$/HCN composite fabricated at 450 °C for 10 min, and areas for EDS measurements.