



Short communication

Electrochemical properties of helical carbon nanomaterials formed on LiCoO₂ by chemical vapor deposition

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ABSTRACT

We fabricated LiCoO₂/carbon composites by forming helical carbon nanomaterials (HCNs) on the surface of LiCoO₂ particles by chemical vapor deposition (CVD). The aim was to inhibit the degradation of the conductive path between the cathode active materials and carbon by mitigating the expansion of the electrode through cycling. We estimated the electrochemical properties of the composites as cathodes of rechargeable lithium cells. Using scanning electron microscopy measurements, we observed HCNs formed firmly on the surface of LiCoO₂ particles. X-ray diffraction measurements indicated decomposition of LiCoO₂, which was the main reason for the inferiority of the electrochemical properties. We found that the electrochemical properties of cells with the HCNs were not as good as those of cells with acetylene black (AB). Successful use of these composites requires inhibition of cathode active material decomposition and improvement of HCN conductivity.

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1. Introduction

High-rate and long life lithium-ion batteries have long been expected to serve as automotive and next-generation industrial batteries. Several cathode active materials such as LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ or olivine-type lithium iron phosphate have been studied for use in such batteries to improve their capacity and rate capability [1–5].

In addition to improvements introduced by new type of active materials, cell performance must be stable during long-term operations. In Li-ion cells, Li⁺ ions are repeatedly intercalated and de-intercalated into active materials during charge–discharge cycles. This results in expansion and shrinking of the active materials, thereby degrading the conductive path between the active materials and carbon. Therefore, cathode active material/carbon composites have also been studied as a means of prolonging cell cycle life [6,7], because carbon formed on the cathode active material effectively inhibits degradation.

To produce Li-ion batteries for automotive and industrial use, the unit cell must be large. However, expansion and shrinking of active materials through cycling seriously deform a Li-ion cell. Thus we must inhibit this change in volume of the active materials through charging and discharging.

Some researchers have attempted to use chemical vapor deposition (CVD) to fabricate nanocarbon [8–11]. Nanocarbons produced by the CVD method are helical in shape and have been reported to be a semimetal with the possibility of serving as a superconductive material [12].

To investigate the validity of these possibilities, we used CVD to fabricate helical carbon nanomaterials (HCNs) on the surface of cathode active materials as a means of improving the rate capability and cycle life of the lithium-ion cells. The HCNs have high potential for use as conductive materials for the cathodes of lithium-ion cells. Their helical shape may act as protection against electrode expansion and shrinking through charge–discharge cycles, giving them the potential to produce safe and large Li-ion cells. This paper describes the electrochemical properties of the LiCoO₂/HCN composite material fabricated by CVD.

2. Experimental

2.1. Substrates

LiCoO₂ (Nippon Chemical Industrial Co., diameter: 10 μm) was used as the substrate on which carbon was formed by CVD. We also used FeCl₃-deposited LiCoO₂ as a substrate, which was prepared as follows:

Five grams of LiCoO₂ powder was added to 500 ml of 0.01 M FeCl₃ aqueous solution and stirred for a couple of hours. The mixture was then filtered and the powder collected on the filter was dried overnight at 110 °C.

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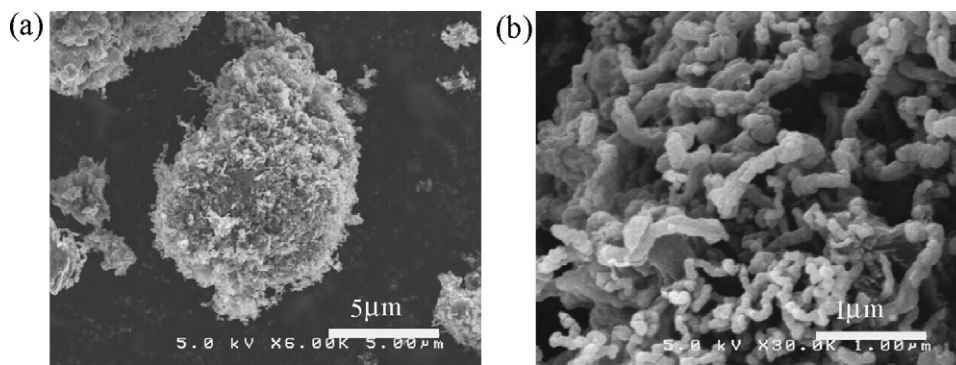


Fig. 1. SEM photos of LiCoO₂/HCN composites. (a) The composite prepared by CVD at 700 °C for 10 min under 60 ml min⁻¹ of C₂H₂ and 100 ml min⁻¹ of Ar. (b) The composite prepared by CVD at 650 °C for 20 min under 60 ml min⁻¹ of C₂H₂ and 150 ml min⁻¹ of Ar.

2.2. Composite fabrication by CVD

LiCoO₂/HCN composite material was fabricated by forming HCNs on the surface of LiCoO₂ particles in a quartz tube under 30–90 ml min⁻¹ of C₂H₂ gas as a carbon source and 100–300 ml min⁻¹ of Ar gas as a carrier at 350–700 °C for 1–30 min.

2.3. Electrochemical measurements

We estimated the electrochemical properties of the HCNs and compared them with those of acetylene black (AB, Denki Kagaku Kogyo Co.) using a lithium cell. HCNs were separated from the composite material and used as conductive carbon.

Cathode disks (area, 1.33 cm²) were fabricated by mixing 70 wt% of LiCoO₂, 25 wt% of HCNs or AB, and 5 wt% of PTFE powder. 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 discharged at constant current to 3.0 V at 21 °C with 10-min breaks in between.

3. Results and discussion

Fig. 1 shows SEM photos of a LiCoO₂/HCN composite. Mossy and helical carbon was formed on the surface of LiCoO₂ particles (Fig. 1(a)). The morphology of HCNs formed on the LiCoO₂ surface was carbon nanotwists (CNTws; Fig. 1(b)) [1]. Fig. 2 shows SEM

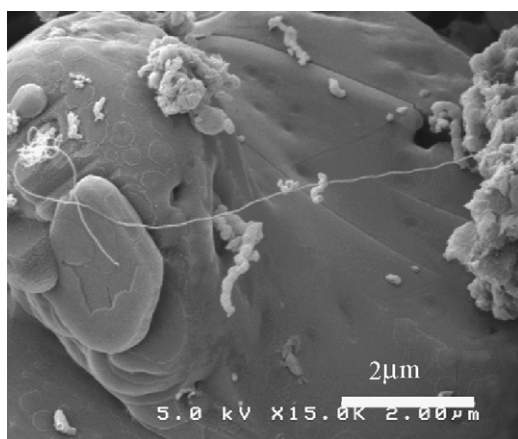


Fig. 2. SEM photo of HCNs formed on LiCoO₂ surface prepared by CVD at 700 °C for 10 min under 60 ml min⁻¹ of C₂H₂ and 100 ml min⁻¹ of Ar.

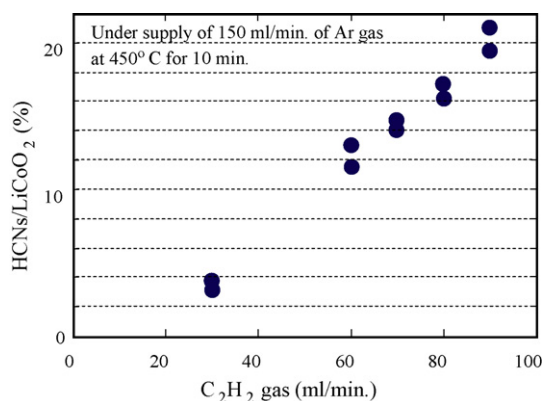


Fig. 3. Relationship between HCN amount and C₂H₂ supply at 450 °C for 10 min under 150 ml min⁻¹ of Ar gas.

photo of the LiCoO₂ particle where HCNs began to form at concave and convex regions of the surface. The photo suggests that HCNs formed firmly on the surface of the LiCoO₂ particles. They suggest that our LiCoO₂/HCN composites inhibit degradation of conductive path between cathode active materials and carbon, and that helical shape of the CNTws is able to mitigate change in cell volume that occur through expansion and shrinking of cathode active materials during charge–discharge cycling. This effect could prolong cell life.

We also estimated the dependence of C₂H₂ supply on HCN formation. Fig. 3 shows the relationship between C₂H₂ supply and HCN amount at constant Ar gas supply of 150 ml min⁻¹. It was found that the HCN amount increased linearly with an increase in the C₂H₂ supply. Fig. 4 also shows the relationship between C₂H₂ gas supply and HCN amount, in this time, under the condition of a con-

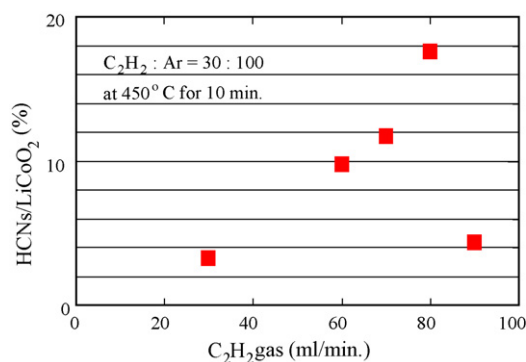


Fig. 4. Relationship between HCN amount and C₂H₂ supply at 450 °C for 10 min under a constant ratio of C₂H₂/Ar (30/100).

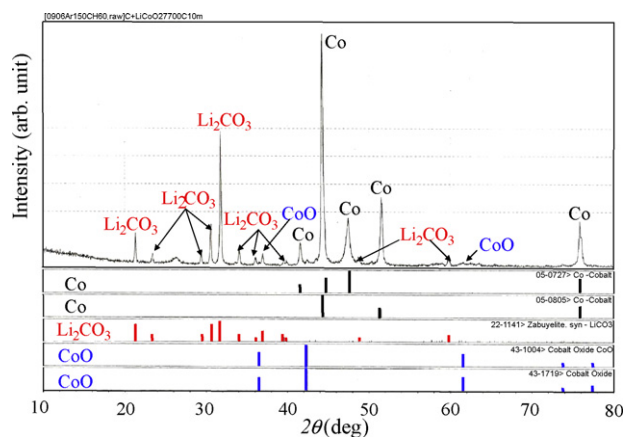


Fig. 5. XRD pattern of LiCoO₂/HCNs fabricated by CVD at 600 °C for 10 min under 60 ml min⁻¹ of C₂H₂ and 100 ml min⁻¹ of Ar.

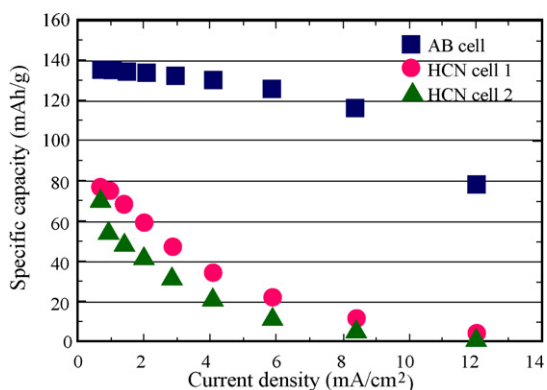


Fig. 6. Electrochemical properties of a lithium cell with HCNs compared with those of a cell with AB.

stant supply ratio of C₂H₂/Ar (30/100) for 10 min. The HCN amount increased as the C₂H₂ supply increased. The tendency, however, showed in the C₂H₂ supply of less than 80 ml min⁻¹. This suggests that an optimal range of raw material and carrier gas supply exists for HCN formation.

Furthermore, we used X-ray diffraction (XRD) measurements to estimate the stability of LiCoO₂ under our experimental conditions. Fig. 5 shows a typical XRD pattern of LiCoO₂/HCN composite material. The measurements showed that LiCoO₂ decomposed into CoO, Co, or Li₂CO₃ under our CVD conditions, which suggests that the LiCoO₂/HCN composite material obtained is not suitable for use as a cathode material.

We therefore collected HCNs separately from LiCoO₂/HCN composites to use them as conductive carbon for lithium cell cathodes and estimated performance of the cell to judge if HCNs show sufficient conductivity. We obtained the products containing decomposed and completely sintered LiCoO₂ when we fabricated the LiCoO₂/HCNs under 60 ml min⁻¹ of C₂H₂ and 150 ml min⁻¹ of Ar at 650 °C for 30 min, and we were able to separate HCNs from these samples.

Fig. 6 shows a comparison of the electrochemical properties of a lithium cell including HCNs with those of a cell including AB. For all measured currents, cells including HCNs showed specific capacities lower than those including AB. This suggests that the conductivity of HCNs obtained in this study is insufficient for use as the electrode conductive material of lithium cells. In future studies, we will focus on finding the optimum conditions for fabricating the LiCoO₂/HCN composites having highly conductive HCNs and less decomposed LiCoO₂.

We also confirmed the existence of three HCN morphologies other than CNTws. The three main morphologies found in the SEM photos were carbon nanocoils (CNCs; Fig. 7(a)), flowerlike HCNs (CNFls; Fig. 7(b)) and meshed HCNs (CNMs; Fig. 7(c)). In our study, CNTws were observed most frequently and CNFls were found when a large amount of HCNs was deposited on the surface. In contrast, CNC and CNM morphologies were rarely found. All morphologies were observed on the surface of FeCl₃-deposited LiCoO₂. On the

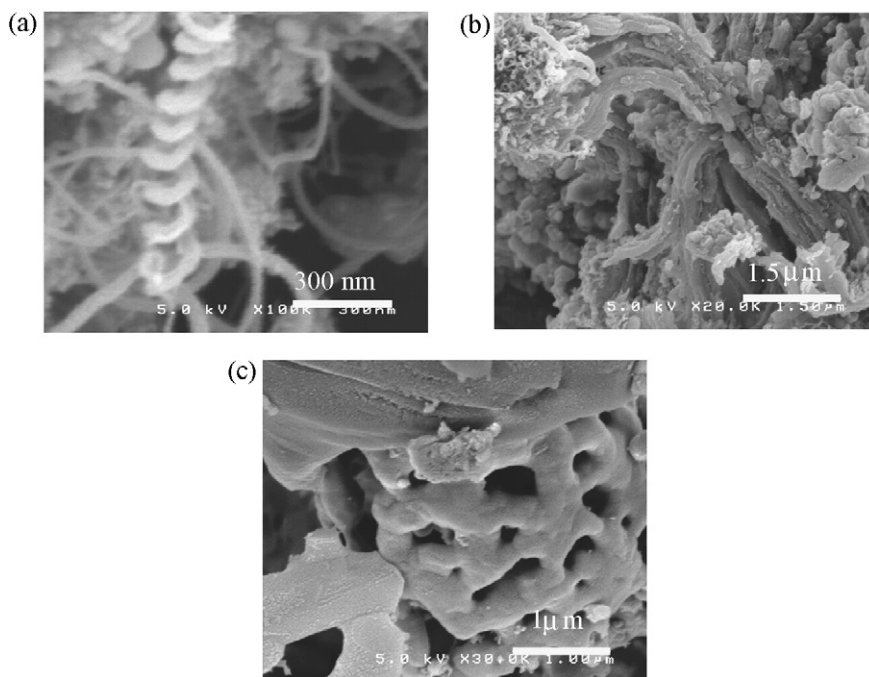


Fig. 7. SEM photos of HCNs fabricated by CVD. (a) Carbon nanocoils on the surface of LiCoO₂ with FeCl₃, prepared by CVD at 650 °C for 20 min under 60 ml min⁻¹ of C₂H₂ and 150 ml min⁻¹ of Ar. (b) Flowerlike HCNs on the surface of LiCoO₂ with FeCl₃, prepared by CVD at 650 °C for 20 min under 60 ml min⁻¹ of C₂H₂ and 150 ml min⁻¹ of Ar. (c) Meshed HCNs on the surface of LiCoO₂ with FeCl₃, prepared by CVD at 650 °C for 10 min under 30 ml min⁻¹ of C₂H₂ and 100 ml min⁻¹ of Ar.

other hand, CNTws and CNFls were mainly observed on the surface of LiCoO_2 . At the present stage, we expect that CNTws can absorb change in cell volume produced through charging and discharging. The morphological type may be effective for mitigating the effects of cell volume change, although further investigation will be necessary.

4. Conclusion

LiCoO_2 /helical nanocarbon (HCN) composite materials were fabricated by chemical vapor deposition (CVD) to improve the rate capability and cycle life of lithium-ion cells. The following results were obtained:

- (1) We fabricated LiCoO_2 /HCN composites that helical shape of HCNs was formed steadily on the surface of LiCoO_2 particles.
- (2) Under CVD conditions, the LiCoO_2 substrate decomposed into Co, CoO, and Li_2CO_3 .
- (3) For all measured currents, lithium cells with HCNs as the conductive material showed specific capacities lower than those with AB.

We successfully fabricated the LiCoO_2 /HCN composites by CVD, which could prolong cell life and allow fabrication of a safe and

large unit cell. We also found that we needed to inhibit LiCoO_2 decomposition and to improve conductivity of the HCNs.

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