



Short communication

Electrochemical properties of LiCoO₂/nanocarbon composites fabricated from organic liquids

Tomonobu Tsujikawa^{a,*}, Yusuke Uno^b, Toshiro Hirai^c^a NTT Facilities, Inc., 2-13-1 Kitaotsuka, Toshima-ku, Tokyo 170-0004, Japan^b Department of Mechanical Systems Engineering, Graduate School of Engineering, Toyama Prefectural University, Imizu-shi, Toyama-ken 939-0398, Japan^c Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu-shi, Toyama-ken 939-0398, Japan

ARTICLE INFO

Article history:

Received 1 October 2009

Received in revised form 7 December 2009

Accepted 17 December 2009

Available online 28 December 2009

Keywords:

Lithium-ion cell

Cathode active material

Nanocarbon

Organic liquids

ABSTRACT

We fabricated LiCoO₂/carbon composites by forming helical carbon nanomaterials (HCNs) from organic liquids as carbon sources on the surface of LiCoO₂ particles by chemical vapor deposition (CVD) and estimated their electrochemical properties as cathodes of rechargeable lithium cells. By scanning electron microscopy measurements, we observed HCNs called carbon nanotwists formed on the surface of LiCoO₂ particles. X-ray diffraction measurements suggested that acetic acid supplies LiCoO₂/HCNs with less decomposition of LiCoO₂ than C₂H₂ does. However, we found that the electrochemical properties of cells containing the composites were not as good as those of cells containing acetylene black (AB).

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

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

Some researchers have tried 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]. This suggests that it has high potential for use as a conductive material for the cathodes of lithium-ion cells.

To investigate the validity of these possibilities, we have studied cathode active material/carbon composites by fabricating helical carbon nanomaterials (HCNs) on the surface of the cathode active materials by CVD as a means of improving the rate capability and cycle life of the lithium-ion cells. We found serious decomposition of cathode active materials although the cathode active material/HCN composites were successfully fabricated [13]. This paper describes the LiCoO₂/HCN composites fabricated from organic liquids by CVD to diminish the decomposition of the LiCoO₂ and their electrochemical properties.

2. Experimental

2.1. Carbon sources

Five organic liquids, methanol, ethanol, ethylene glycol, formic acid, and acetic acid, were used as carbon sources.

2.2. Substrates

LiCoO₂ (Nippon Chemical Industrial Co., diameter: 10 μm) was used as the substrate on which carbon was formed by CVD.

2.3. Composite fabrication by CVD

The substrate, LiCoO₂ was in ceramic boat and set in a quartz tube at the position where was in an electric furnace. Organic liquid carbon source was also in ceramic boat and set in the quartz tube at the position where was at the entrance of the furnace. The LiCoO₂/HCN composites were fabricated by forming HCNs on the surface of LiCoO₂ particles in a quartz tube under 100 ml min⁻¹ of Ar as a carrier at 450 °C for 15–30 min. In this study, carbon sources could be supplied before reaching furnace temperature set and after finishing the set time. However, furnace temperature and time set are defined as reaction temperature and reaction time in this paper.

2.4. Electrochemical measurements

We estimated the electrochemical properties of the LiCoO₂/HCNs fabricated from acetic acid and compared them

* Corresponding author. Tel.: +81 3 5907 6332; fax: +81 3 5961 6424.
E-mail address: tomo@rd.ntt-f.co.jp (T. Tsujikawa).

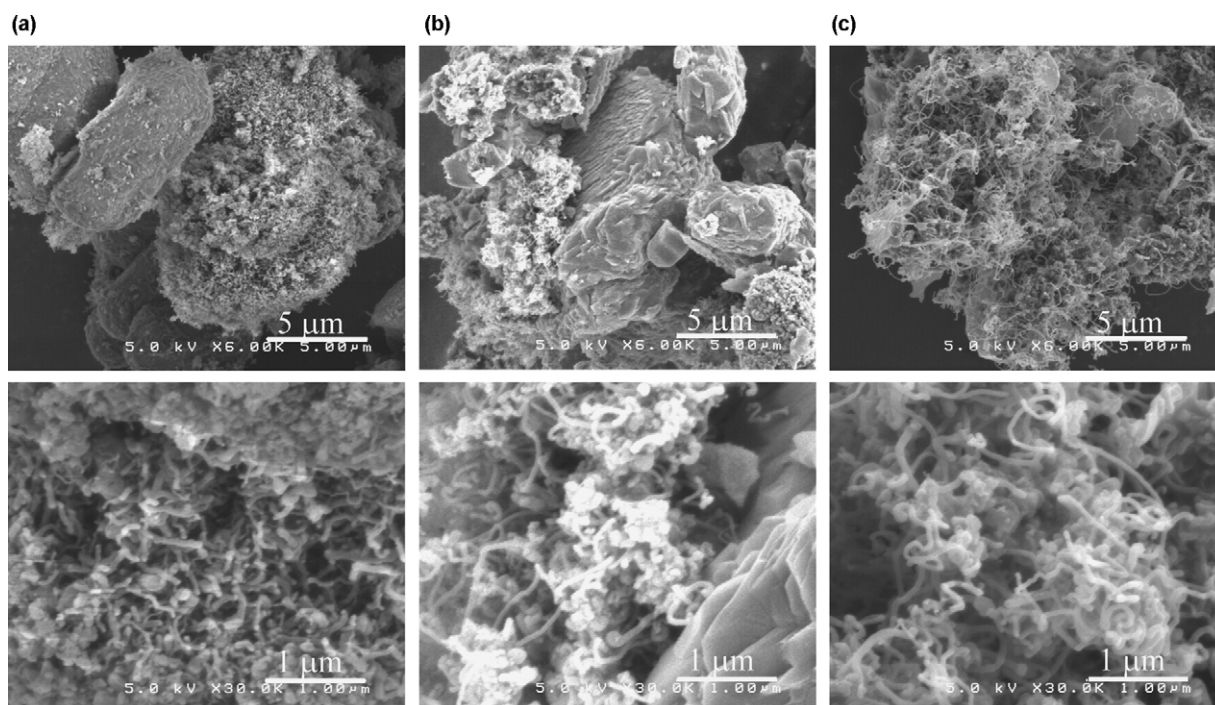


Fig. 1. SEM images of LiCoO₂/HCN composites prepared by CVD at 450 °C under 100 ml min⁻¹ of Ar. (a) Carbon source: methanol, reaction time: 30 min. (b) Carbon source: ethanol, reaction time: 15 min. (c) Carbon source: acetic acid, reaction time: 30 min

Table 1
Amount of HCNs formed on the surface of LiCoO₂.

Carbon sources (%)	C content (°C)	bp (°C)	Reaction temperature (h)	Reaction time (%)	HCNs/LiCoO ₂
Methanol	37.5	64.7	450	30	5.0
Ethanol	52.2	78.4	450	15	7.0
Acetic acid	40.0	118	450	30	14.4
Formic acid	26.1	100.75	450	30	3.2
Ethylene glycol	38.7	197.3	450	30	0.7

with those of the mixture of LiCoO₂ and acetylene black (AB, Denki Kagaku Kogyo Co.) using a lithium cell. Cathode disks (area, 1.33 cm²) were fabricated by mixing the composites, AB and PTFE powder or LiCoO₂, AB, and 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 (Tomiyaama 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 images of LiCoO₂/HCN composites fabricated from ethanol, ethanol and acetic acid. Morphology of HCNs formed on the surface of LiCoO₂ was irregularly helical nanocoils having diameter of around 10 nm and we did not observe obvious difference in the morphology depending carbon sources.

Table 1 shows the amount of HCNs formed on the surface of LiCoO₂ particles from five kinds of carbon sources together with their carbon content and boiling points. We indicate the amount of HCN formation as HCNs/LiCoO₂ in the table. Ethanol and acetic acid formed much amount of HCNs. On the other hand, formic acid and ethylene glycol formed less amount of HCNs. The carbon content and boiling point may affect the amount of HCN. Significant amounts of vaporized carbon sources were supplied to the LiCoO₂ substrate when they had a low boiling point, especially when lower

than 100 °C, such as in methanol and ethanol. Formic acid contains a small ratio of carbon and produced a smaller amount of HCNs.

Fig. 2 shows dependence of HCN amount formed on the LiCoO₂ from three kinds of carbon sources on reaction time. The HCN amount tended to increase with an increase in reaction time for all three carbon sources. We observed the dispersion of the HCN amount for acetic acid for 30 min, as shown in Fig. 2. This may be related to its high boiling point.

Furthermore, we estimated the stability of LiCoO₂ under our experimental conditions by X-ray diffraction (XRD) measurements.

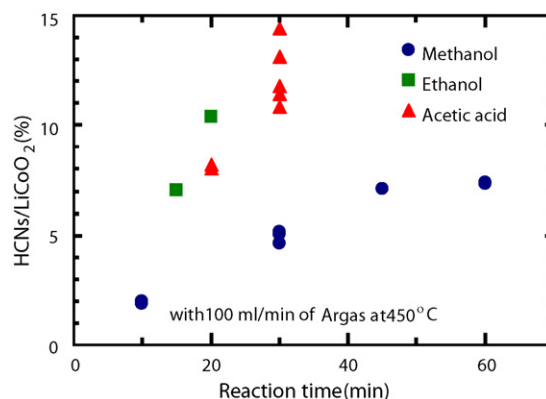


Fig. 2. Relationship between HCN amount and reaction time at 450 °C under 100 ml min⁻¹ of Ar.

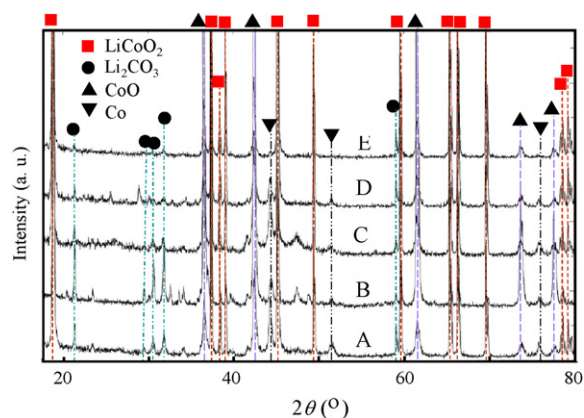


Fig. 3. XRD pattern of LiCoO₂/HCNs fabricated by CVD at 450 °C under 100 ml min⁻¹ of Ar. (A) Carbon source: methanol, reaction time: 30 min. (B) Carbon source: ethanol, reaction time: 15 min. (C) Carbon source: acetic acid, reaction time: 30 min. (D) Carbon source: formic acid, reaction time: 30 min. (E) Carbon source: ethylene glycol, reaction time: 30 min

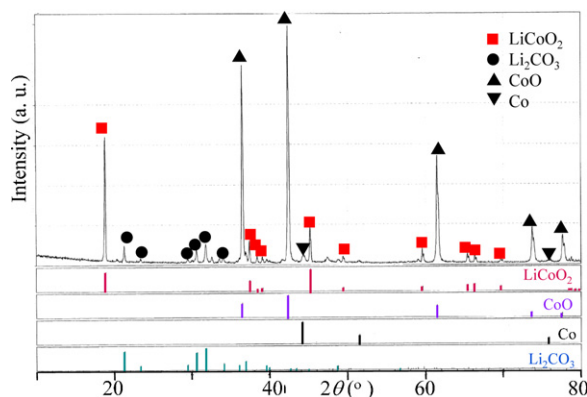


Fig. 4. XRD pattern of LiCoO₂/HCNs fabricated with ethanol by CVD at 450 °C for 15 min under 100 ml min⁻¹ of Ar.

Fig. 3 shows XRD pattern of LiCoO₂/HCN composites for five kinds of carbon sources. The measurements showed that LiCoO₂ decomposed into CoO, Co, or Li₂CO₃ for all five sources. Figs. 4 and 5 show XRD pattern of LiCoO₂/HCN composites fabricated from ethanol and acetic acid. In Fig. 4, peaks corresponding to CoO are stronger than those corresponding to LiCoO₂, which suggests that ethanol resulted in serious decomposition of LiCoO₂. On the other hand, in Fig. 5, peaks corresponding to CoO, Co, and Li₂CO₃ are weaker

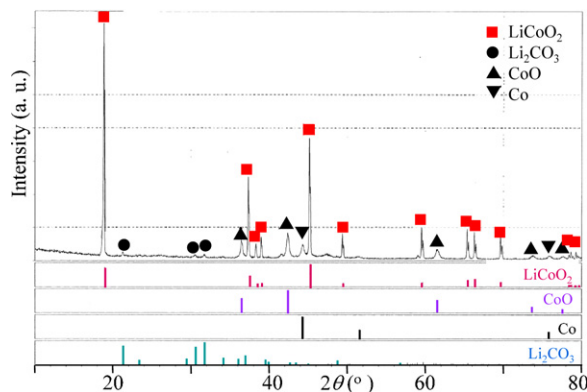


Fig. 5. XRD pattern of LiCoO₂/HCNs fabricated with acetic acid by CVD at 450 °C for 30 min under 100 ml min⁻¹ of Ar.

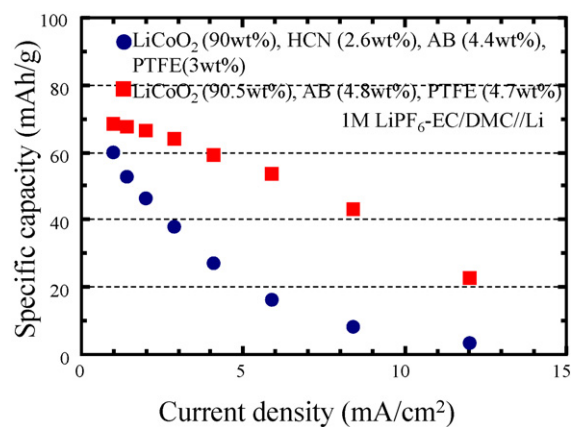


Fig. 6. Electrochemical properties of a lithium cell with LiCoO₂/HCNs compared with those of a cell with fresh LiCoO₂ and AB.

than those corresponding to LiCoO₂. This suggests that acetic acid provided HCNs with less decomposition of LiCoO₂.

We then used the LiCoO₂/HCNs prepared from acetic acid as cathode active material and conductive carbon for lithium cell cathodes. Unfortunately, the product did not contain HCNs enough to be cathode conductive and add acetylene black (AB) to cathode materials. Fig. 6 shows a comparison of the electrochemical properties of a lithium cell including LiCoO₂/HCNs and AB with those of a cell including fresh LiCoO₂ and AB. For all measured currents, cells including LiCoO₂/HCNs and AB showed specific capacities lower than those including fresh LiCoO₂ and AB. This suggests that LiCoO₂ decomposition degraded cell capacity and that the conductivity of HCNs obtained in this study is insufficient for use as the electrode conductive material of lithium cells. The low conductive HCNs on the LiCoO₂ surface inhibited the effective electron transfer even though the LiCoO₂/HCN cell contained more carbon than the fresh LiCoO₂ cell.

4. Conclusion

LiCoO₂/helical nanocarbon (HCN) composite materials were fabricated with five kinds of organic liquid by chemical vapor deposition (CVD) to improve the rate capability and cycle life of lithium-ion cells. The following results were obtained:

- (1) Morphology of HCNs formed on the surface of LiCoO₂ particles was irregularly helical nanocoils having diameter of around 10 nm. No obvious difference in the morphology was observed depending on carbon sources.
- (2) Decomposition of the LiCoO₂ substrate was observed in CVD process for all carbon sources. Acetic acid provided LiCoO₂/HCNs with least decomposition of LiCoO₂.
- (3) For all measured currents, lithium cells with LiCoO₂/HCN composites showed specific capacities lower than those with fresh LiCoO₂ and AB.

Acknowledgment

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

References

- [1] H. Huang, S.-C. Yin, L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170.
- [2] M. Tabuchi, Y. Nabeshima, K. Ado, T. Takeuchi, M. Shikano, H. Kageyama, K. Tatsumi, *Extended Abstract for the 47th Battery Symposium in Japan, Tokyo, 2D19, 2006*, pp. 362–363 (in Japanese).
- [3] T. Ohzuku, Y. Makimura, *Chem. Lett.* 30 (2001) 642.

- [4] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [5] K. Amine, H. Yasuda, M. Yamachi, *Electrochem. Solid-State Lett.* 3 (2000) 178.
- [6] A. Yamada, S.C. Chung, K. Hinokuma, *J. Electrochem. Soc.* 148 (2001) A224.
- [7] A.S. Andersson, J.O. Thomas, B. Kalsa, L. Haggstroem, *Electrochem. Solid-State Lett.* 3 (2000) 66.
- [8] R.T.K. Baker, J.J. Chludzinski Jr., *J. Catal.* 64 (1980) 464.
- [9] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov, J.B. Nagy, *Science* 265 (1994) 635.
- [10] M. Zhang, Y. Nakayama, L. Pan, *Jpn. J. Appl. Phys.* 39 (2000) L1242.
- [11] L. Pan, M. Zhang, Y. Nakayama, *Jpn. J. Appl. Phys.* 91 (2002) 10058.
- [12] K. Akagi, R. Tamura, M. Tsukada, *Phys. Rev. Lett.* 74 (1995) 2307.
- [13] Y. Uno, T. Tsujikawa, T. Hirai, *J. Power Sources* 195 (2010) 354–357.