Available online at www.sciencedirect.com

SCIENCE DIRECT®

Electrochemistry Communications 7 (2005) 10–13

electrochemistry communications

www.elsevier.com/locate/elecom

# Low-temperature synthesis of graphitized nanofibers for reversible lithium-ion insertion/extraction

Takayuki Doi [a], Akihito Fukuda [a], Yasutoshi Iriyama [a], Takeshi Abe [a,*], Zempachi Ogumi [a], Kiyoharu Nakagawa [b], Toshihiro Ando [b]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*
[b] *National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

Received 14 October 2004; accepted 25 October 2004
Available online 11 November 2004

## Abstract

Graphitized carbon nanofibers are prepared from 2-propanol at 673 K by spray pyrolysis in which dc high voltage is applied to the spray nozzle. A mixture of helical and straight carbon nanofibers is observed, and their diameters are ca. 100–300 nm. The resultant carbon nanofibers show large capacity of around 340 mAh $g^{-1}$ and high reversibility with little hysteresis after the 2nd cycle in insertion/extraction reactions of lithium-ion, while a large irreversible capacity of 400 mAh $g^{-1}$ is observed at potentials below 0.9 V in the 1st cycle.

*Keywords:* Nanofibres; Carbon lithium ion insertion; Low temperature synthesis; Lithium ion batteries

## 1. Introduction

Lithium-ion batteries are now used in a wide variety of portable electronic devices due to their high energy densities. However, there is still a need to improve lithium-ion batteries for use in hybrid electric vehicles (HEV) [1,2]. Rapid charge and discharge reactions are required when lithium-ion batteries are used for high power application. Thus, lithium-ion transfer must be very rapid in such batteries. Lithium-ion transfer in batteries consists of five different steps; lithium-ion diffusion through the active electrode materials at each electrode, lithium-ion transport through an electrolyte, and lithium-ion transfer across the interfaces between the electrolyte and active electrode materials. Of these steps, the diffusion of lithium-ion through active electrode materials is well known to be slow, and therefore fine particles of battery active materials (ca. 10–20 nm) are used to reduce the diffusion path in commercial lithium-ion batteries [3,4]. In lithium-ion batteries intended for high power use, a further decrease in the particle sizes of active materials will be needed.

Carbonaceous materials have been used as negative electrodes for lithium-ion batteries. Highly crystallized graphite has generally been used for commercial applications because of its acceptably high capacity and very flat potential, which is identical to that of lithium metal in charge/discharge processes [1]. Various other carbonaceous materials have been investigated to improve the performance of lithium-ion batteries [5–7]. The use of nano-size particles of carbonaceous materials makes it possible to shorten the diffusion paths of lithium-ion within them, resulting in the apparent fast diffusion of lithium-ion. Nano-size particles, which possess a large specific surface area, present a relatively large number of lithium-ion insertion sites on their surface. Therefore,

---

[*] Corresponding author. Tel.: +81 75 383 2483; fax: +81 75 383 2488.
*E-mail address:* abe@elech.kuic.kyoto-u.ac.jp (T. Abe).

1388-2481/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2004.10.009

charge-transfer resistances at the interface between the electrolyte and active electrode materials are expected to be small. Based on the above considerations, nano-size carbonaceous materials are advantageous for use as negative electrode materials in lithium-ion batteries intended for high power use [8].

Since the discovery of carbon nanotubes, various kinds of nano-size carbon, such as single- and multi-walled carbon nanotubes, nanofibers, and nanocoils, have been intensively studied as negative electrode materials in lithium-ion batteries [8–10]. Several types of nano-size carbon have been reported to exhibit higher reversible capacity than graphitic carbon (~372 mAh $g^{-1}$). Despite this attractive feature, two issues remain to be solved before any practical application: the large irreversible capacity during the 1st cycle, and the large divergence of about 1 V (vs. $Li/Li^+$) between the insertion and extraction potentials, which is commonly referred as hysteresis [9,10]. The former is mainly due to electrolyte decomposition, which forms a protective surface film on the electrode. Hence, the irreversible capacity should increase with an increase in electrode surface area. The latter is also observed with some graphitizing or non-graphitizable carbon electrodes, and can be explained by the existence of hydrogen in the carbon and/or interstitial carbon atoms between the graphitic planes [5,10]. On the other hand, a graphite electrode exhibits little hysteresis, and therefore highly graphitized nano-size carbon is suitable for use as a negative electrode material in lithium-ion batteries.

Highly graphitized nano-size carbon, such as carbon nanotubes, nanofibers, and nanocoils, can be synthesized by chemical vapor deposition (CVD) [11]. This method offers great advantages over other synthesis methods, i.e., it is possible to control the direction of the growth of nano-size carbon on a substrate, various starting materials can be used, and mass production is possible. CVD uses hydrocarbon gases of benzene, carbon monooxide, methane, ethylene, and acetylene as carbon sources and catalysts comprised of transition metal, transition metal oxide, metallocene, etc. [11]. The gases are catalytically decomposed to form nano-size carbon at temperatures usually exceeding 823 K. Liquid solutions can also be used as a carbon source. Vivekchand et al. [12] synthesized multi-walled carbon nanotubes from a solution of toluene containing ferrocene at temperatures between 1073 and 1273 K. Maruyama et al. [13] reported single-walled carbon nanotubes prepared at 823 K using ethanol as a carbon source with a catalyst of Fe/Co on zeolite. The combustion of alcohol is known to yield less soot than that of hydrocarbon, and hence the use of alcohol is favorable for the formation of graphitizable nano-size carbon. However, the formation of highly graphitized carbon generally requires higher reaction temperatures; carbon nanofibers synthesized at temperature as low as 673 K have been reported to be amorphous [14].

In this paper, we describe the preparation of graphitized carbon nanofibers at 673 K by the spray pyrolysis method in which dc high voltage was applied to the spray nozzle. The electrochemical properties of the carbon nanofibers were studied in lithium-ion insertion/extraction reactions by chronopotentiometry.

## 2. Experimental

A starting solution of 2-propanol containing $10^{-4}$ mol $dm^{-3}$ nickel acetylacetonate ($Ni(acac)_2$) or ferrocene was used. The solution was sprayed at a flow rate of 1.0 sccm together with 500 sccm of argon in a quartz glass tube. Dc voltage of +15 kV was applied to the spray nozzle. The sprayed mist was subsequently pyrolyzed in the tube, and the temperature was kept at 673 K with a furnace. Carbonaceous materials were deposited on Fe substrates heated at 673 K for 1.5 h. After deposition, the substrates were cooled slowly at 2 K $min^{-1}$. The deposits were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Their morphology and microstructure were investigated by transmission electron microscopy (TEM). Electrochemical properties were studied by charge–discharge measurements at a constant current rate of 15.5 mA $g^{-1}$ using a three-electrode cell. The working electrode was prepared by coating a mixture of the resultant materials and polyvinylidene fluoride (PVDF) on copper foil. A liquid electrolyte of 1 mol $dm^{-3}$ $LiClO_4$ dissolved in EC + DEC (1:1 by volume) was used. Lithium metal was used for both counter and reference electrodes. Unless otherwise stated, the potential is given vs. $Li/Li^+$. All experiments were conducted under an argon atmosphere with a dew point below −60 °C.

## 3. Results and discussion

Fig. 1(a) shows typical TEM images of as-deposited carbonaceous materials using a starting solution of $10^{-4}$ mol $dm^{-3}$ $Ni(acac)_2$ dissolved in 2-propanol. A mixture of helical and straight carbon nanofibers is observed, and their diameters are ca. 100–300 nm. In Fig. 1(b), a layered structure of graphene sheets is clearly observed at the surface of the carbon nanofibers, and the layers stack parallel to the fiber axis in the same way. Their external walls are covered with a very small amount of amorphous carbon. Almost identical features are observed for carbon nanofibers prepared from 2-propanol containing ferrocene.

Fig. 2 shows an XRD pattern of as-deposited carbon nanofibers obtained from a solution of $Ni(acac)_2$ in 2-propanol. A very strong peak at 26.24° in $2\theta$ is assigned to the (0 0 2) diffraction line and the peaks at 43.3°, 53.8° and 78.1° are indexed as (1 0), (0 0 4) and (1 1) reflections,