Preparation of Carbon Nanofilaments Using Porous Anodic Alumina Templates and Polymer Precursors

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Introduction

Porous-type alumina films formed by anodizing of high purity aluminum in acid solutions, such as sulfuric acid, oxalic acid and phosphoric acid, have been received increased attention as template materials for preparation of various nano-structured materials. A range of materials, including metals, inorganic and organic materials, have been deposited within cylindrical pores of the anodic alumina with pore diameters of 10 to several 100 nm.

Using the porous alumina templates, nano-structured carbon materials have been also prepared. In most cases, gaseous hydrocarbons, such as acetylene, have been used as carbon precursors, and they were decomposed thermally within the pores of the anodic alumina to form multi-walled carbon nanotubes.

In the present study, carbon nanofilaments have been prepared simply by heating a mixture of porous anodic alumina templates and polymers, such as poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA), in an inert atmosphere. This process utilizes the facts that these polymers form low viscosity fluids during their carbonization processes.

Experimental

Porous anodic alumina templates were prepared by anodizing 99.99% pure aluminum sheets at 25 V in 0.3 mol dm-3 sulfuric acid and at 40 V in 0.3 mol dm-3 oxalic acid. They were post-treated in 5 wt% phosphoric acid for 2 h for pore widening. Commercial anodic alumina membrane filter (Whatman, Anodisc 25) and etched aluminum foils with numerous tunnel pits, provided by Japan Capacitor Industrial Co., Ltd. were also used as templates.

The mixture of the template and PVC or PVA was heated at 600ºC for 1 h in flowing high purity argon gas. During heating to this temperature at a rate of 400 K h^{-1}, temperature was kept at 300ºC for 30 min, at which the polymers formed low viscosity fluids. The alumina template was then removed from the heated mixture by dissolving in 10% NaOH solution and carbon precursors were obtained. Carbon nanofilaments were obtained by further heating the precursors at 1500ºC for 1 h. The products were characterized mainly using scanning electron microscopy and transmission electron microscopy. Further, anode characteristics of the carbon nanofilamants for lithium ion battery were evaluated.

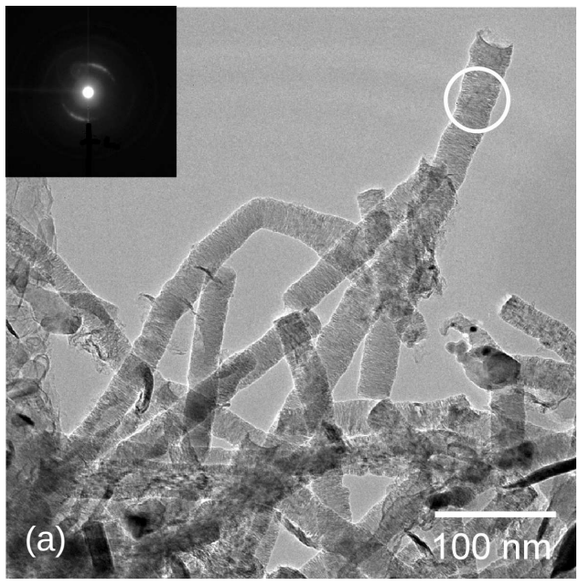
Results and Discussion

Fig. 1 shows transmission electron micrographs of carbon nanofilaments prepared from PVC and a template formed in sulfuric acid. Formation of fibrous carbon of approximately 50 nm in diameter is evident. Interestingly, from the high resolution image shown in Fig. 1(b), it is obvious that this template process results in the formation of carbon nanofilaments with graphene layers normal to the fiber axis. Similar carbon nanofilaments with a larger diameter have been prepared from mesophase pitch precursors [1]. We have also confirmed that carbon nanofilaments with this unique orientation could be formed using porous anodic alumina templates with pore diameters of 20 to 200 nm. The diameters of the carbon nanofilaments obtained agreed with the pore diameters of the templates used. From the PVA precursor, some of carbon nanofilaments formed appeared to be hollow, when templates with relatively larger pore diameters were used. Formation of hollow nanofilaments from this precursor is probably related to the viscosity of the fluid formed during carbonization process.

Carbon filaments with different orientation of graphene layers were formed when etched aluminum template was used. In this case, carbon materials with the graphene layers approximately parallel to the fiber axis. Thus, template materials influence strongly the orientation of fibrous carbons.

Reference

1. K. Jian, H.-S. Shin, A. Schwartzman, G.P. Crawford and R. H. Hurt, Adv. Mater., 15, 164 (2003).



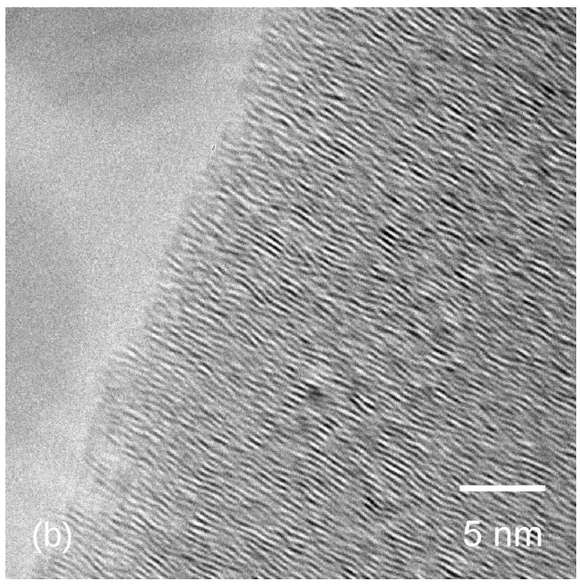


Fig. 1 (a) Transmission electron micrograph of carbon nanofilaments prepared from PVC and porous anodic alumina template formed in 0.3 mol dm^{-3} sulfuric acid electrolyte at 25 V. (b) High resolution image of (a).