Short communication

Improved electrochemical capacitive characteristics of the carbon nanotubes grown on the alumina templates with high pore density

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Abstract

Specific capacitances of the carbon nanotube (CNT) electrodes are significantly enhanced by using the nanoporous alumina templates with high pore density and uniform pore diameter. Well-ordered nanoporous alumina templates were fabricated by a two-step anodization method by applying a constant voltage of 25.0 V or 20.0 V in sulfuric acid solution. The cylindrical pore diameter and pore density of the templates prepared at the anodizing voltage of 25.0 V or 20.0 V were 53 ± 1 nm and 3.1×10^{10} cm^{-2} or 38 ± 2 nm and 3.8×10^{10} cm^{-2}, respectively. The CNTs with uniform diameters of 44 ± 2 nm in the 53 nm pores and of 32 ± 5 nm in the 38 nm pores, respectively, were grown on the porous alumina template. For the electrochemical double layer capacitors (EDLCs), the aluminum metal below the porous alumina layer was used as a current collector for the CNT electrode without any binding material. The EDLC characteristics were analyzed by measuring the capacitances from cyclic voltammograms and the charge–discharge curves. A maximum value of 175 F g^{-1} was achieved for the specific capacitances of the CNT electrodes prepared on the alumina templates with high pore density.
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1. Introduction

Electrochemical double layer capacitors (EDLCs) are of interest as high power devices since they have large capacitance, high power and long cycling life [1–8]. In EDLCs, charges are stored in the electric double-layer formed at the electrode/electrolyte interface, where a pure electrostatic attraction between electrolyte ions and the charged surface of an electrode takes place. High power rate of EDLCs results from the fast rate of charging/discharging the double layer at the interface. Therefore, electrodes of large surface areas are required for the EDLC applications. Various carbon materials (activated carbons, aerogels, xerogels, CNTs) have been extensively used as the electrode materials of EDLCs [1–3]. Carbon nanotubes can be used as a novel electrode material for EDLCs, because CNTs have a narrow distribution of size, highly accessible area,

low resistivity, and high stability. In order to increase the specific capacitances of the CNT electrodes, various attempts have been made in many research groups [3–9]. Enhancement of the specific capacitance for the CNT electrodes was generally realized by modifications such as an oxidation of CNTs to increase the surface functionality through chemical treatment [3–5] or plasma treatment [6], and the formation of CNT/conducting polymer composites [5,7]. The electrochemical capacitance of the CNTs with the diameter from 15 nm to 30 nm, was increased from 70 F g^{-1} to 120 F g^{-1} through an additional treatment of the CNTs by nitric acid [3]. The capacitance of CNTs was also able to enhance up to 130 F g^{-1} by oxygenated functionalization of the CNTs, and up to 170 F g^{-1} by coating the CNTs with conducting polypyrrole (PPy) [5]. The specific capacitance was also enhanced to 190 F g^{-1} by wall-coating the single-wall CNT with polyaniline [7], and increased from 39 F g^{-1} to 207 F g^{-1} by ammonia plasma treatments [6]. Utilizing both the inner- and outer-surfaces of the large diameter CNT arrays, high specific capacitances above 300 F g^{-1} were also achieved [8].

The channel-array materials of nanometer scale are applicable as a template structure for the CNT growth [6,8,9].

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On the Al surface, a surface oxide layer with a well-defined nanoporous structure can be formed. The oxide layer consists of close-packed cells in a local hexagonal arrangement with pores at their centers [10–13]. The usage of the nanoporous alumina templates was proposed as a novel method to increase the capacitances of the CNT electrode by preparing the CNTs with uniform diameters. The CNTs of homogeneous diameter of 50 ± 10 nm were grown on the porous alumina templates with pores of 90 nm diameter in the regular hexagonal cell and the pore density was ca. 1.0×10^{10} cm^{-2} [9]. The higher the electrode surface areas, the higher the capacitances. The BET surface area of the CNTs was 362 m^2 g^{-1}. Even though the surface area estimated by gas adsorption differs practically from the electroactive surface available for the charged species, the specific capacitance of the homogeneous CNT electrodes with 50 ± 10 nm diameter was 49 ± 3 F g^{-1}, which was larger than those of the CNTs with the comparable tube diameter from other groups. The specific capacitances of the CNT electrodes can be enhanced even more with the CNTs prepared on the template with higher pore density and smaller pore diameter. In this work, the CNT electrodes with the uniform and small tube diameter were prepared on the nanoporous alumina templates with high pore density at low anodic voltages and the specific capacitance of the CNT electrode was determined by electrochemical methods.

2. Experimental

The morphological shape of CNTs grown in the nanoholes is significantly affected by the size of catalytic Co particle or the nanohole structure, and characteristics of the CNTs can be controlled by those of the alumina/Al templates. Well ordered nanoporous alumina layer was prepared electrochemically by a two-step anodization method [8,10,11]. Anodization of an aluminum foil (99.99%, 100 μm thickness, Tokai) was performed in a thermostated sulfuric acid electrolyte solution with a two-electrode system: a 1 cm diameter Al disk anode and a Pt gauze cathode. The porous alumina hexagonal cell size and the pore diameter, and the density, and the length of the cylindrical nanopores were controlled by the anodizing conditions, such as the anodization voltage, the electrolytes, and the anodization time [9,12]. Thickness of the barrier layer and the hexagonal cell size depends on the applied anodic voltage, and the smaller cells can be formed only by decreasing the anodizing voltage. Surfaces of the aluminum disk-electrode were oxidized by applying constant voltage of 25.0 V or even lower voltage of 20.0 V in H$_2$SO$_4$. After the porous alumina layer formed during the first anodization process was etched away to leave the ordered hexagonal cell texture on the Al surface, well ordered porous alumina layer of ca. 2 μm thickness was able to grow by the second anodization process, which was the same condition as the first anodization step. After the second anodization, the alumina barrier layer at the bottom of the cylindrical alumina pore was uniformly etched by decreasing the anodization voltage stepwisely in a H$_3$PO$_4$ solution in order to expose the aluminum surface below the porous alumina layer. Details of the experimental procedure were reported in the previous work [9]. The

aluminum metal substrate below the porous alumina layer works directly as the current collector of the CNT electrodes for the EDLC application. Hence, no binding material is required for the CNTs and the metal substrate, which simplifies the fabrication process and removes the resistance between them.

The Co catalytic particles for the CNT growth were electrochemically deposited at the bottom of each cylindrical alumina pore by applying an ac voltage to the Al substrate in a Co^{2+} containing solution. The Co catalytic particles were uniformly embedded in the nanoholes [9]. The growth of CNTs was based on the chemical vapor deposition method. Densely packed CNTs on the alumina template were grown by catalytic pyrolysis in a gas mixture with 10 standard cubic centimeters per minute (sccm) of C$_2$H$_2$ and 100 sccm of H$_2$ at 600 °C for 30 min. CNTs were usually grown out of the nanoholes and covered the alumina template. The weight of CNTs on the disk (1 cm diameter) alumina template was ca. 1.0 mg.

The morphology of the nanoporous alumina template and the CNTs grown on the template was examined by a field emission scanning electron microscopy (FESEM, Hitach S-4700). The EDLC characteristics were analyzed electrochemically by measuring the capacitances from both the cyclic voltammograms (CVs) of the CNT electrode (1 cm diameter disk) and the charge–discharge curves of the cell made of two CNT electrodes. Before the electrochemical measurement, the CNT electrodes on the alumina/Al template were inserted in a mixture solution of sulfuric acid and hydrogen peroxide, and rinsed with distilled water, sequentially, in order to make the CNT electrode surfaces hydrophilic. Cyclic voltammetric measurements were made by a potentiostat/galvanostat (Zahner IM6) with a conventional three-electrode cell in 1.0 M H$_2$SO$_4$. A Ag/AgCl (saturated KCl) electrode and a Pt electrode were used as the reference and counter electrodes, respectively. The charge–discharge curves were measured by an automatic battery cycler (WonATech, WBCS 3000). The cells were constructed with two facing CNT electrodes and a polypropylene separator soaked in 1.0 M H$_2$SO$_4$ between two CNT electrodes.

3. Results and discussion

Geometry of the porous alumina is schematically represented as a close-packed array of columnar hexagonal cells, each containing a central pore normal to the aluminum substrate. The most characteristic feature of the nanoporous alumina has been emphasized with the extremely high aspect ratio (the length to diameter ratio) of the channels that are difficult to achieve with conventional lithographic techniques [11]. In this work, the alumina templates for the CNT growth were prepared applying low anodization voltage to the Al electrodes in order to obtain alumina layers of high pore densities. The hexagonal cell size depends linearly on the anodization voltage [12]. The SEM images of the CNTs grown on the templates and the porous alumina templates prepared by a two-step anodization process at the low anodization voltages of 25.0 V or 20.0 V are shown in Fig. 1. The cylindrical pore diameter and pore density of the templates prepared at the anodizing voltage of 25.0 V or at 20.0 V in the sulfuric acid were 53 ± 1 nm and 3.1×10^{10} cm^{-2} or 38 ± 2 nm and
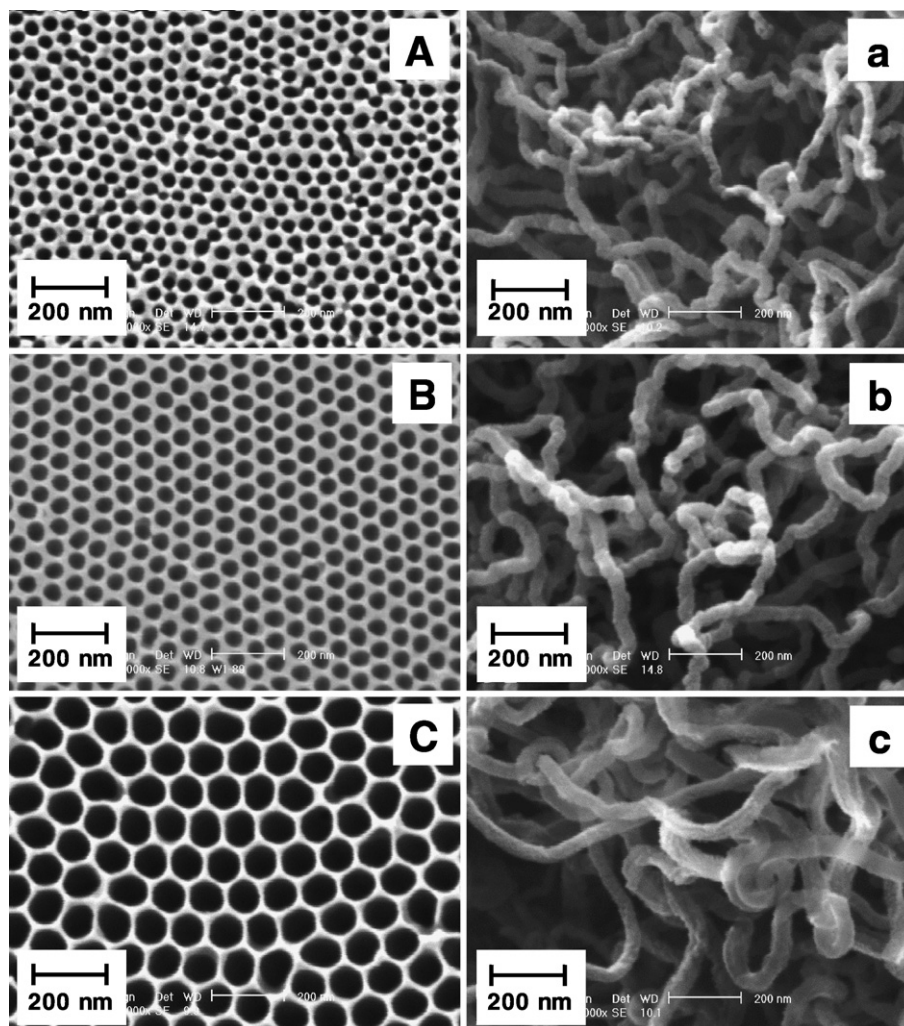
Fig. 1. The SEM images of the porous alumina templates (pore diameter: (A) 38 ± 2 nm, (B) 53 ± 1 nm, (C) 86 ± 5 nm) and the CNTs (tube diameter: (a) $\Phi = 32 \pm 5$ nm, (b) $\Phi = 44 \pm 2$ nm, (c) $\Phi = 50 \pm 10$ nm).

3.8×10^{10} cm^{-2}, respectively. Diameter of the CNTs grown on the porous alumina template is very uniform. The average diameters of the CNTs were 44 ± 2 nm and 32 ± 5 nm with the alumina template whose pore diameters were 53 ± 1 nm and 38 ± 2 nm, respectively. The SEM images of the template obtained at the anodization voltage of 40.0 V in an oxalic acid electrolyte and the corresponding CNTs are also shown in Fig. 1 for comparison. The CNTs with the average diameter of 50 ± 10 nm grown in the pores with 86 ± 5 nm diameter showed a specific capacitance of 49 F g^{-1} [9]. A large specific capacitance is expected with the CNTs of large surface area. It is also expected that CNTs of large surface area can be prepared with the CNTs of small tube diameter. Therefore, it is necessary to have an alumina layer of a rather small pore size to grow CNTs of small diameter. In this work, we were successful to obtain such alumina/Al templates by lowering anodization voltage and electrolyte conditions and the CNTs by using the templates as shown in Fig. 1.

The CVs obtained with the CNT electrodes on the templates in 1.0 M H$_2$SO$_4$ are shown in Fig. 2. Clearly shown are the capacitive charging/discharging currents in both anodic and cathodic scanning directions across the potential range of -0.2 V to 0.8 V

versus a Ag/AgCl reference electrode. A region of reversible pseudofaradaic reactions appears at ca. 0.5 V in the CVs on top of a typical rectangular shape of a capacitor. Electroactive functional surface groups of carbonyl and carboxyl group must be formed by the activation treatment in the mixture solution of H$_2$SO$_4$ and H$_2$O$_2$, before the CV measurement. The specific capacitance (C_{sp}) was calculated from the equation, $C_{sp} = i/(v \times m)$, where i is the current in the CVs, v the scan rate, and m is the mass of CNTs grown on the template. The current values at 0.3 V were taken for the calculation. The CNTs with uniform diameters of 44 ± 2 nm and 32 ± 5 nm give C_{sp} of 118 ± 5 F g^{-1} and 175 ± 5 F g^{-1}, respectively. The specific capacitance of the CNT electrode with the small tube diameter is larger.

The charge–discharge behavior of the CNT electrode was examined by chronopotentiometry. Typical result (E–t curve) in the potential range between 0.0 V and 1.0 V for the cell constructed with two facing CNT electrodes is shown in Fig. 3. The average specific capacitance of the CNT electrode can be calculated on the basis of the equation, $C_{sp} = 2i/[(dE/dt) \times A]$. The (d$E$/d$t$) indicates the slope of the linear charge–discharge
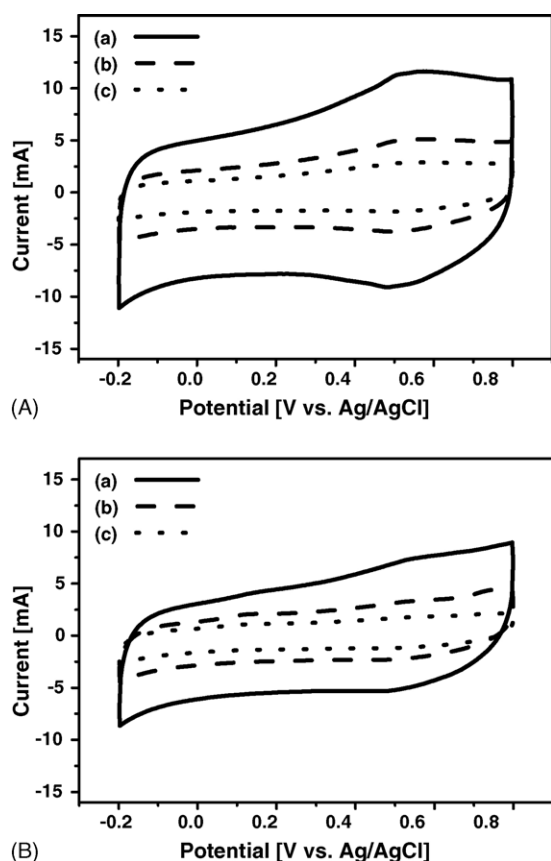
Fig. 2. Current–voltage curves of the CNT electrodes: (A) $\Phi = 32 \pm 5$ nm and (B) $\Phi = 44 \pm 2$ nm in 1.0 M H_2SO_4 with different scan rates: (a) 50 mV s^{-1}, (b) 20 mV s^{-1}, (c) 10 mV s^{-1}.
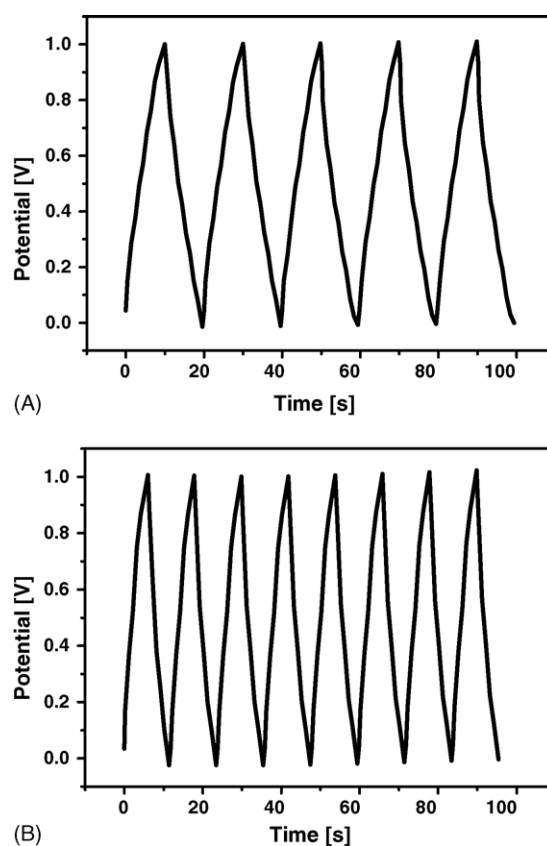

Fig. 3. Chronopotentiograms of the CNT electrodes measured in 1.0 M H_2SO_4 between 0.0 and 1.0 V at a constant current density: (A) the CNT electrode ($\Phi = 32 \pm 5$ nm, current density = 1.3 mA cm^{-2}) and (B) the CNT electrode ($\Phi = 44 \pm 2$ nm, current density = 1.5 mA cm^{-2}).

curve, i is the current, and A is the area of the electrode. The specific capacitances of the CNT electrode with uniform diameter of 44 ± 2 nm and 32 ± 5 nm were 116 ± 3 F g^{-1} and 171 ± 7 F g^{-1}, respectively. These values are close to those estimated from the CV curves. The specific capacitance of this work was listed with other works in Table 1. The specific capacitance of the CNT electrode we obtained by a high pore density alumina template is the largest and comparable with the other high values resulted by various modifications. It is known that the specific capacitance increases as the pore diameter decreases. The specific capacitances should have higher value when the nanotube materials have larger surface area. The homogeneous CNTs grown by using nanoporous alumina templates with the high pore density and uniform pore diameter show enhanced specific capacitance without any modifications.

4. Conclusions

The CNTs of uniform diameter grown on the porous alumina layer on the Al metal current collector are excellent and noble electrode materials for EDLC. The CNT diameters and the resultant specific capacitances were controlled by the pore diameter and density of the alumina layer. No binding materials for the CNTs and the current collector were added, which enhances the specific capacitances and also simplifies the fabrication processes of the EDLC electrodes. Specific capacitances of the electrodes with the CNT diameter of 44 ± 2 nm or 32 ± 5 nm were 118 ± 5 F g^{-1} and 175 ± 5 F g^{-1}, respectively. The largest specific capacitance of the CNT electrodes was able to obtaine by using the high pore density nanoporous alumina/Al template without any modifications. These values are much larger than those reported with the CNTs with the comparable diameters.

Table 1
Specific capacitances of CNT electrodes

C_{sp} (F g^{-1})	CNT diameter (nm)	Control	Reference
175	30–34	CNT diameter	This work
80	20–40	KOH activation	Refs. [4,5]
120	15–30	Nitric acid treatment	Ref. [3]
170	10–25	Modified by PPy	Ref. [5]
190	1.3	Coating polyaniline	Ref. [7]
207	20	Ammonia plasma treatment	Ref. [6]

References

[1] H. Shi, Electrochim. Acta 41 (1996) 1633.
[2] J.H. Jang, S. Han, T. Hyeon, S.M. Oh, J. Power Sources 123 (2003) 79.

[3] E. Frackowiak, F. Béguin, Carbon 39 (2001) 937.

[4] Q. Jiang, M.Z. Qu, G.M. Zhou, B.L. Zhang, Z.L. Yu, Mater. Lett. 57 (2002) 988.

[5] E. Frackowiak, F. Béguin, Carbon 40 (2002) 1775.

[6] B.J. Yoon, S.H. Jeong, K.H. Lee, H.S. Kim, C.G. Park, J.H. Han, Chem. Phys. Lett. 388 (2004) 170.

[7] Y. Zhou, B. He, W. Zhou, J. Huang, X. Li, B. Wu, H. Li, Electrochim. Acta 49 (2004) 257.

[8] Q.-L. Chen, K.-H. Xue, W. Shen, F.-F. Tao, S.-Y. Yin, W. Xu, Electrochim. Acta 49 (2004) 4157.

[9] M. Jung, H.G. Kim, J.K. Lee, O.S. Joo, S.-I. Mho, Electrochim. Acta 50 (2004) 857.

[10] H. Masuda, F. Hasegwa, S. Ono, J. Electrochem. Soc. 144 (1997) L127.

[11] H. Masuda, K. Fukuda, Science 268 (1995) 1466.

[12] A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, J. Appl. Phys. 84 (1998) 6023.

[13] F. Keller, M.S. Hunter, D.L. Robinson, J. Electrochem. Soc. 100 (1953) 411.