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Review article

Vapor-grown carbon fibers (VGCFs) Basic properties and their battery applications

M. Endo[a,*], Y.A. Kim[a], T. Hayashi[a], K. Nishimura[b], T. Matusita[a], K. Miyashita[a], M.S. Dresselhaus[c]

[a]*Faculty of Engineering, Shinshu University, 500 Wakasato, Nagano 380-8553, Japan*
[b]*Showa denko company, 13-9 Shiba Daimon1 Minato-Ku, Tokyo 105-8518, Japan*
[c]*Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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Abstract

Submicron vapor grown carbon fibers (VGCFs) obtained by a floating growth method were evaluated in terms of their microstructural development with heat treatment temperature (HTT), physical properties of a single fiber and of the bulk state, and additional effects, such as the filler in the electrode of a lead–acid battery and a Li-ion battery system. Its desirable properties, such as relatively high mechanical strength and electrical conductivity, both in the single fiber state and in the bulk state, including their very special network-like morphology, improved the performance of the electrodes in lead–acid batteries and Li-ion batteries, especially their cycle characteristics. © 2001 Published by Elsevier Science Ltd.

Keywords: A. Vapor grown carbon, Carbon fibers; B. Chemical vapor deposition; C. Raman spectroscopy; Transmission electron microscopy (TEM); D. Electrochemical properties

1. Introduction

Carbon materials have been used in battery systems, either as the electrode itself or as a support material for the active material, due to their unique combination of chemical, electrical, mechanical, and thermal properties. Among others, two major reasons for the application of carbon materials in battery systems are their high electrical conductivity and good corrosion resistance in many electrolytes.

Vapor-grown carbon fibers (VGCFs) have been grown by the decomposition of hydrocarbons, such as benzene and methane, using transition metal particles as a catalyst at a growth temperature of 1000–1300°C [1–9]. These fibers have been characterized in terms of the highly preferred orientation of their graphitic basal planes parallel to the fiber axis, with an annular ring texture in the cross section. This structure gives rise to excellent mechanical properties, very high electrical and thermal conductivity, and a high graphitizability of the fibers [4,5]. Therefore, many researchers have tried to reach the final target of ‘mass production’ of these fibers at low cost. Among the various processing methods, the most important one has been the development of the floating reactant method [6–8], which allows a three-dimensional dispersion of the hydrocarbon together with the catalytic particles derived from the pyrolysis of organometallic compounds, such as ferrocene, in a reaction chamber, resulting in a high yield and a rather uniform diameter of the resulting fibers. Therefore, the floating reactant method is thought to be a promising means for the mass production of carbon fibers at relatively low cost.

The fibers obtained by the floating reactant method have a narrow diameter distribution (from 0.1 to 0.2 μm), showing almost the same morphology as compared to that of normal VGCFs (10–20 μm), which consist of a central filament and an external deposit of pyrolytic carbon with the annular structure of a tree [4]. Furthermore, these fibers have a high possibility for application as a filler in composites and as an anode material in lithium ion

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*Corresponding author. Tel.: +81-262-264-101; fax: +81-262-237-754.

E-mail address: endo@endomoribu.shinshu-u.ac.jp (M. Endo).

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batteries, including additives to anode materials, due to their excellent conductivity and high surface to volume ratio.

In this study of submicron VGCFs obtained by a floating reactant method, the basic properties and microstructural development as a function of heat treatment temperature (HTT), the physical properties of a single fiber and of the bulk states were evaluated for the purpose of applying this material as the filler for the electrodes of lead–acid batteries and the Li-ion battery system.

2. Basic properties and structural development of s-VGCFs

Fig. 1 shows FE-SEM pictures of s-VGCFs at two different resolutions. As seen in Fig. 1a, s-VGCFs have a random orientation and sometimes aggregate into a few tens of fibers. The fibers have a semispherical tip and a homogeneous diameter, as do the thicker fibers (Fig. 1b). These kinds of morphology are very favorable when this fiber is applied as filler to improve electrical conductivity.

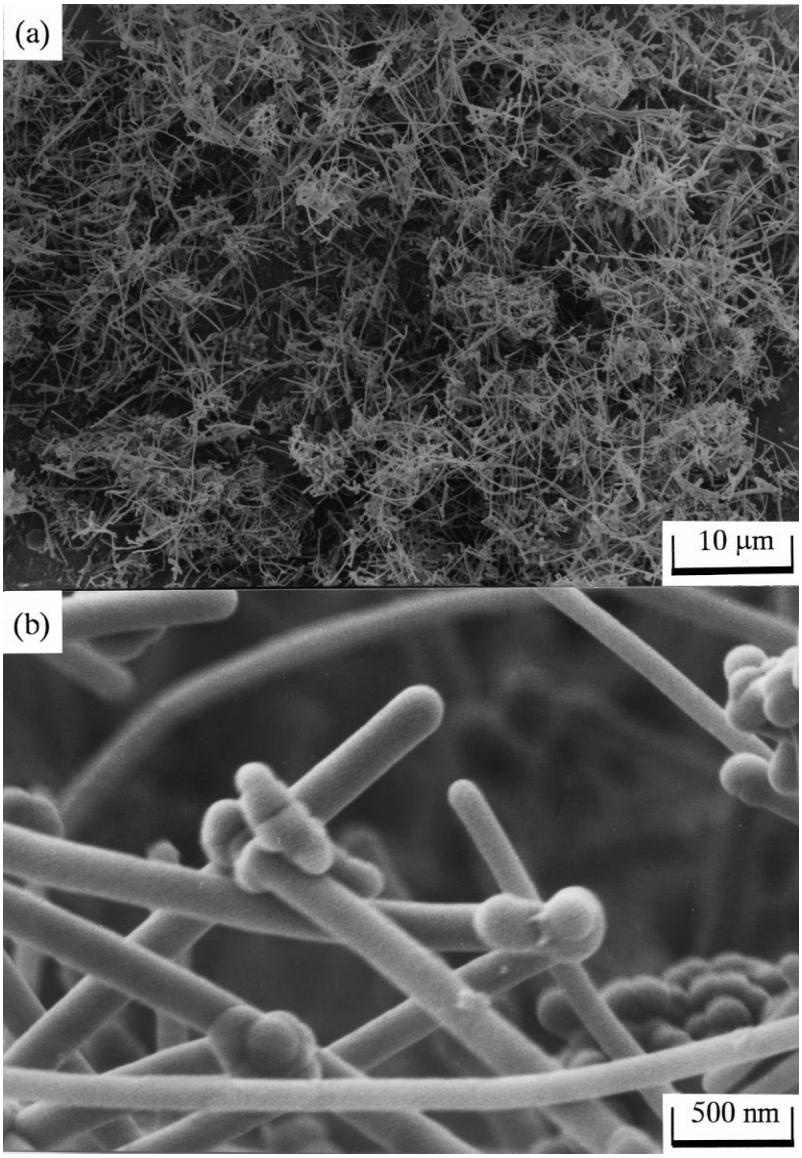

Fig. 1. Field-emission scanning electron microscope of submicron VGCFs at two different resolutions.

Table 1
Basic properties of submicron VGCFs

	Carbonized s-VGCFs[a]	Graphitized s-VGCFs[b]	Units	Method
Lattice constant (C_o)	6.900	6.775	Å	XRD
Diameter of fiber	0.2	0.2	μm	SEM
Length of fiber	10–20	10–20	μm	SEM
Volume density	0.02–0.07	0.02–0.07	g/cm^3	Tapping
Real density	1.9	2.1	g/cm^3	Pycnometer
Surface area (BET)	37	15	m^2/g	N_2 absorption
Ash content	1.5	0.03	%	SDK
pH	5	7	–	JIS-K6221
Starting temperature of oxidation	550	650	°C	TGA

[a] Carbonized s-VGCFs indicate the sample heat treated at 1200°C.
[b] Graphitized s-VGCFs indicate the sample heat treated at 2800°C.

The basic properties of carbonized and graphitized s-VGCFs are summarized in Table 1. The particular characteristics of interest are their high aspect ratio ($>10^2$) and extremely low volume density in the range 0.02–0.07 g/cm^3. These properties would be very favorable when using this material as the filler in an electrode. Furthermore, a very low content of ash, and a high oxidation resistance are also required. Fig. 2 shows: (a) the variation of the lattice constant (C_o) obtained by XRD, and (b) the relative intensities ($R = I_D/I_G$) from Raman spectroscopy of the D-band to the G-band as a function of HTT. It is expected that both values decrease continuously with increasing HTT because VGCFs are typical graphitizable carbons [3]. The strange phenomenon is that the interlayer distance C_o of s-VGCFs is much higher than those of normal VGCFs, whereas the R values of s-VGCFs show a similar value as compared to those of normal VGCFs. From these data, it is possible to say that the microstructures of both samples are almost similar at the near surface, based on the lower optical skin depth of the laser (about 400 nm) for s-VGCFs, and the lower bulk crystallinity of s-VGCFs in comparison to the corresponding behavior of normal VGCFs due to the small diameter of the s-VGCFs and taking into account the effect of curvature of the surface of the s-VGCFs.

The transmission electron micrograph of as-grown s-VGCFs (Fig. 3a) shows that the diameter of the hollow tube is a little smaller than the diameter of the catalytic particle. The hollow tube is remarkably straight and of constant diameter along the fiber length. The lattice image pattern taken from the near-surface of as-grown fiber (Fig. 3b) shows relatively disordered lamellae which induced broad diffraction spots, typical of turbostratic graphite. For the case of graphitized sample (Fig. 3c), deposited amorphous carbon with thickness of around 5 nm on the surface, called contaminated carbon, is formed during the industrial graphitization process. This amorphous carbon material could be helpful to increase the binding strength when used as the filler of CFRP. The (002) lattice fringe below the contaminated carbon is shown as stiff, regular flat layers. Especially, the sharp (00*l*) spots observed in the selected area electron diffraction pattern are indicative of the onset of AB interlayer correlation as 3D order is established. The process of graphitization involves the motion and rearrangement of carbon-layer planes. As the heat-treatment temperature increases, the surface layers tend to straighten out. This process indicates that atomic rearrangement of carbon atoms is taking place within the carbon fibers.

3. Electrical conductivity and mechanical strength of single s-VGCFs

One of the most important properties of carbon fibers is their electrical conductivity when used in electrodes, either as the electrode itself, or as a conductive support material for the electrochemically active materials. The longitudinal resistivity of the s-VGCFs was measured using a four-point method and the fiber diameter was observed by a scanning electron microscope. Carbonized s-VGCFs show an electrical resistivity of 1×10^{-3} Ω cm, whereas graphitized s-VGCFs show a value of 1×10^{-4} Ω cm. Based on data in Ref. [10], s-VGCFs have higher electrical conductivity than conventional carbon fibers, and lower values than normal VGCFs due to the lower crystallinity of s-VGCFs as shown in Fig. 1.

When this s-VGCF sample is used as the conductive filler in an electrode, mechanical properties, such as tensile strength, are a very important factor for affecting the performance of an electrode in a battery. The tensile strengths of graphitized s-VGCFs are measured by using a special apparatus consisting of a micromanipulator, a high-speed video camera and a scanning electron microscope etc., as shown in Fig. 4 [11]. Fig. 5 shows the relation

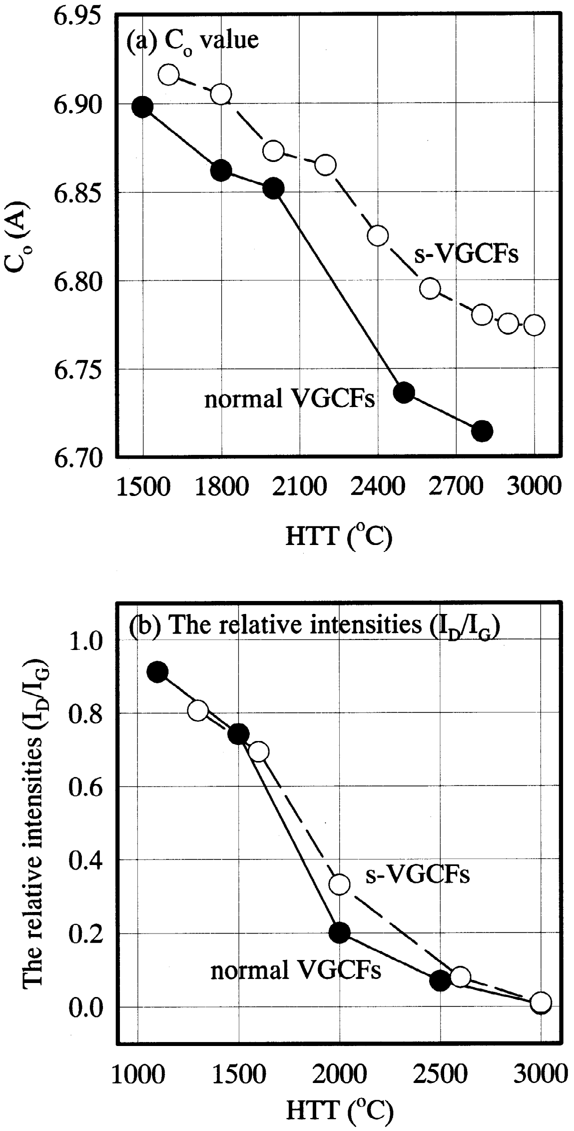

Fig. 2. The variation of (a) crystallite size (C_o) from XRD, (b) the relative intensities ($R = I_D/I_G$) from Raman spectroscopy for submicron VGCFs and normal VGCFs (diameter = 10 μm), as a function of heat treatment temperature.

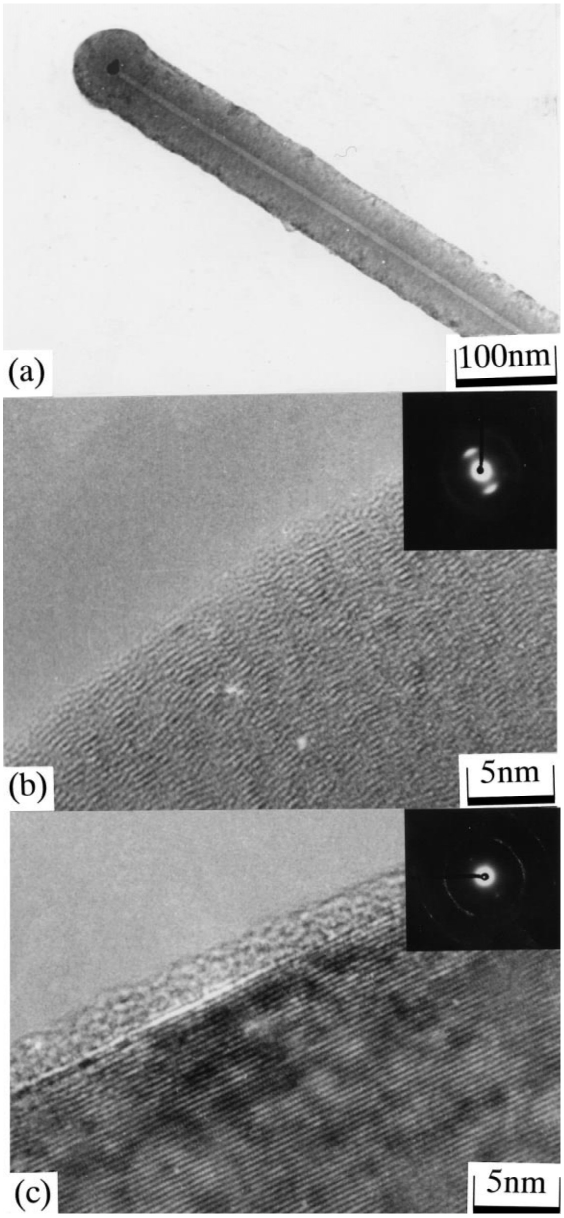

Fig. 3. Transmission electron micrographs of (a) as-grown submicron VGCFs at low magnification, (b) lattice image in the external of as-grown fiber and (c) lattice image in the external part of graphitized fiber.

between the fiber diameter and tensile strength for graphitized s-VGCFs, and these results are used for comparison to the corresponding results for conventional whiskers such as SiC and SiN, that have already been used as an anode filler [11]. The tensile strengths of all samples show a strong dependence on diameter, which is especially severe for the case of s-VGCFs. As a result, it is clear that graphitized s-VGCFs have tensile strengths comparable to those of conventional whiskers. On the other hand, the relationship between the tensile strength and tensile modulus for this s-VGCF sample are plotted in Fig. 6 to make a comparison to various carbon fibers [11,12]. Carbonized and graphitized s-VGCFs show relatively higher values of tensile strength and modulus as compared to those of general grade (isotropic pitch) carbon fibers. As a result of electrical conductivity and mechanical property measurements, it is clear that the s-VGCF samples used in this study are very promising as a filler for electrodes in batteries.

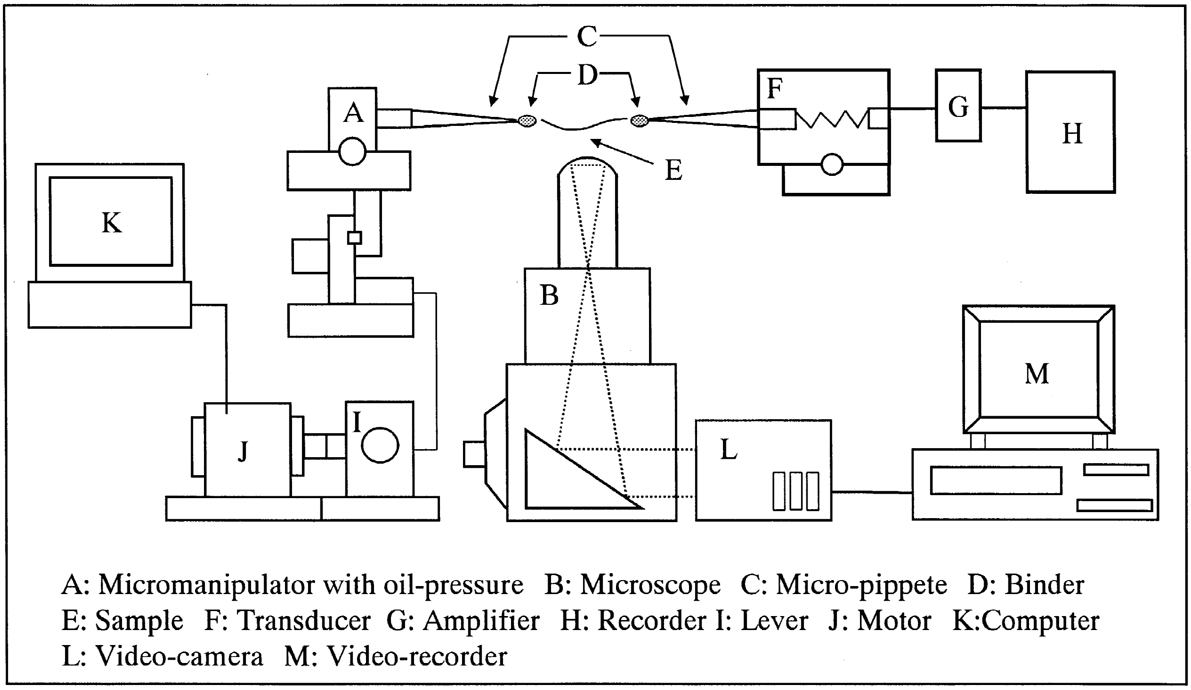

Fig. 4. Special apparatus attached with microscope to measure the mechanical properties of submicron VGCFs [11].

4. Volume resistivity and resiliency in the bulk state

Generally, the electrodes used in a battery system have to possess sufficiently high electrical conductivity and thermal conductance, enough mechanical strength to sustain volume changes during the charge and discharge processes, and during penetration of the electrolyte etc. to achieve the maximum performance of the battery. Therefore, if graphitized s-VGCFs are used as a filler to improve the properties of an electrode, not only do the basic properties of the fiber itself have to be evaluated, but also the packed state of the fibers, that is, in their bulky state, have to be characterized. In other words, the volume resistivity of the fibers in their bulky state has to be investigated, including the length and diameter of the fiber,

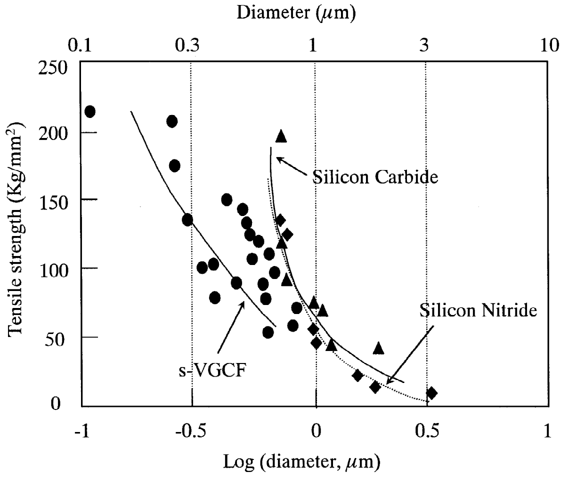

Fig. 5. Tensile strength of submicron VGCFs, SiN and SiC as a function of diameter [11].

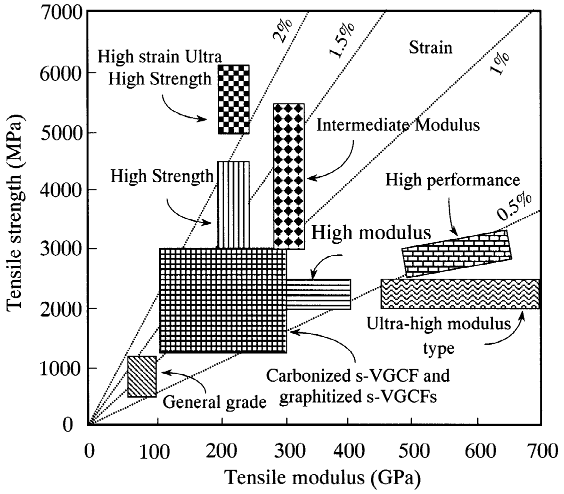

Fig. 6. Evaluation of tensile strength and tensile modulus for submicron VGCFs as compared with those of various carbon fibers [12].

its contact resistance, and the concentration of additives. A special apparatus to which was attached a testing cell was set up to evaluate the volume resistivity of the bulky samples, because it is not easy to test such samples by conventional methods under stable conditions due to their extremely low volume density in the range from 0.02 to 0.07 g/cm^3. That is, some portion of the sample is inserted into the testing cell, and pressure is applied to the cell from the upper part, and the volume resistivity vertical to the direction of the applied pressure is measured.

Fig. 7 shows the relation between the volume resistivity and HTT when the volume density is constant at 0.8 g/cm^3. The decrease in resistivity with increasing HTT is mainly attributed to the increased crystallinity with increasing HTT, such as decreased inter-layer spacing and increased crystallite size if we assume that the contact resistance is the same for all samples. The electrical resistance of a sample of packed carbon fibers is a sensitive function of the contact resistance between the fibers, as indicated by the decrease in volume resistivity as a function of volume density; that is, the value of applied pressure is strongly related to the decreased contact resistance, as shown in Fig. 8.

The s-VGCFs used in this study show unusual characteristics, such as small diameter and extremely small volume density, relatively good mechanical strength etc., and these properties make it difficult to obtain a high volume density of the fiber in a packed state by applying pressure. Conversely, when the applied pressure is released, the sample tends to be restored to its original state. This reversible response which we call 'resiliency' is very important for the performance of an electrode in a battery system, when this s-VGCF sample is used as the filler. The degree of resiliency is expected to depend on the diameter of the fiber, the aspect ratio, the mechanical strength and the morphology etc. As shown in Fig. 9a, a constant volume of a sample is inserted into the testing cell (V_0), and a constant pressure (P) is applied from above (V_1), and subsequently the applied pressure is released (V_2). The degree of resiliency ($R_V = (V_0 - V_1)/(V_0 - V_2)$) for our samples is compared with those of other conventional carbon fibers (Fig. 9b). Carbonized and graphitized s-VGCFs show much higher values as compared to those of conventional carbon fibers, mainly due to their special morphology such as intertwined entanglements. The higher value of the resiliency of graphitized s-VGCFs as compared to that of carbonized s-VGCFs is attributed to the higher mechanical strength caused by heat treatment.

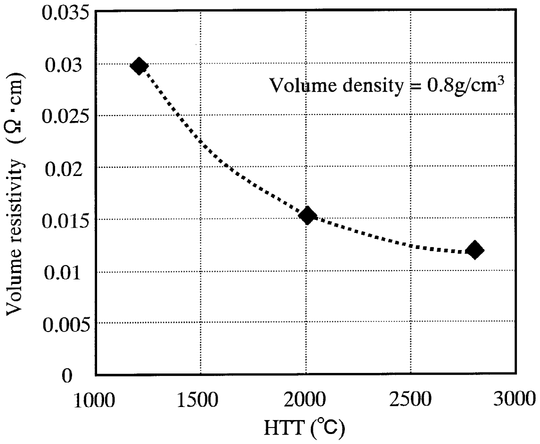

Fig. 7. The variation of volume resistivity for submicron VGCFs as a function of heat treatment temperature when the volume density is 0.8 g/cm^3.

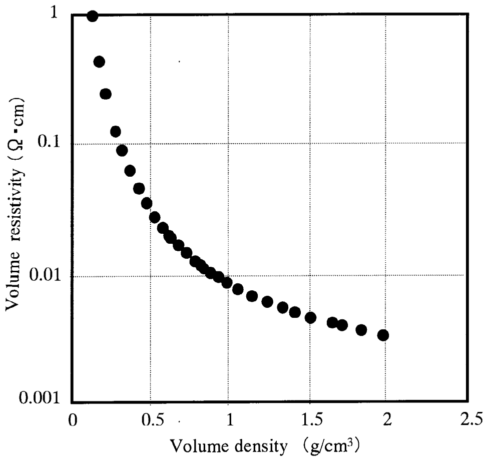

Fig. 8. The variation of volume resistivity for graphitized submicron VGCFs as a function of volume density.

It is expected that carbon materials used as the anode material in Li-ion battery systems undergo volume change during the charge and discharge processes, and these changes are especially severe for the case of soft carbons due to the intercalation and de-intercalation of lithium ions. This assumption indicates that degradation of the active anode materials would occur, resulting in increased contact resistance as the consecutive cycles proceed. Therefore, if s-VGCFs are used as a filler in the anode material of Li-ion batteries, it is expected that s-VGCFs would be able to absorb most of the stress caused by the volume change associated with battery cycling, and would also act as a physical binder for the active anode materials due to its superior resiliency property, resulting in improved battery cycle life.

5. Additives to the electrodes of lead–acid batteries [14]

In order to increase the conductivity of electrodes in lead–acid batteries, different weight percents of graphitized s-VGCFs are added to the active anode material (average diameter = 2–5 μm) of the positive electrode. As

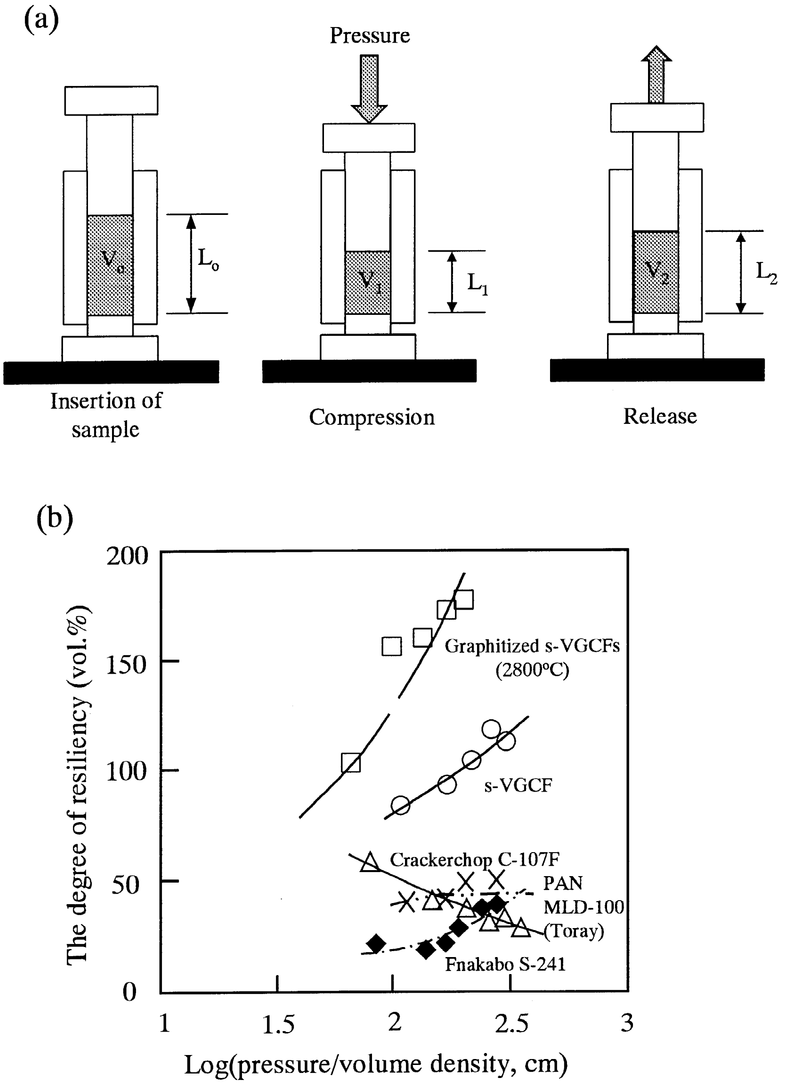

Fig. 9. (a) Schematic diagram of measuring the degree of resiliency ($R_v = (V_0 - V_2)/(V_0 - V_1) \times 100\%$). (b) Evaluation of the degree of resiliency (%) of submicron VGCFs as compared with those of conventional carbon materials.

shown in Fig. 10, the resistivity of the electrode is lowered for the case of 1.5% s-VGCFs addition. When this sample (0.5–1 wt.%) is incorporated in the negative electrode, the cycle characteristics are greatly improved as compared to that of an electrode without additive (Fig. 11). This is probably due to the ability of s-VGCFs to act as a physical binder, resulting in electrodes which undergo less mechanical disintegration and shedding of their active material than electrodes without graphitized s-VGCFs. Therefore, it is expected that the use of graphitized s-VGCFs as an electrode filler should show better cyclic behaviors for the electrodes in lead–acid batteries as compared to electrodes using conventional graphite powder, because the unusual morphology of s-VGCFs, such as the concentric orientation of their graphite crystallites along the fiber cross section, induces a high resistance to oxidation, and furthermore the network formation would induce an improved utilization of the active material in the electrode.

6. Anode performance and its additive effect in conventional anode materials of Li-ion batteries

Fig. 12 shows the charge–discharge curve of graphitized s-VGCFs during the first cycle. After contact is made, the potential decreases immediately to 0.8 V and the curve shows a shoulder at around 0.7 V only during the first discharging process, as is also observed in other carbon materials. The discharge capacity is 283 mAh/g, and the cycle efficiency is about 77%. As compared to data for

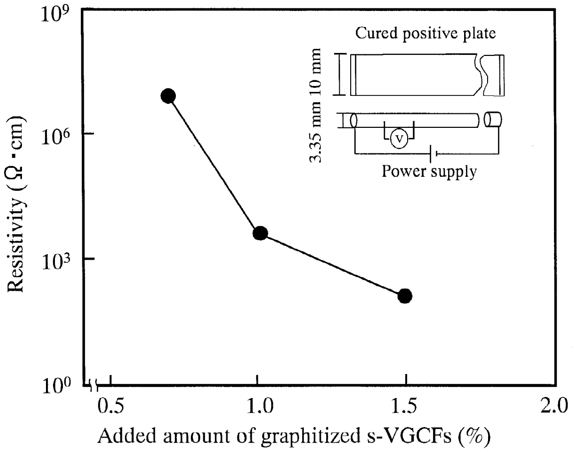

Fig. 10. Variation of the resistivity in the positive plate as a function of added weight percent of graphitized s-VGCFs (width of positive plate = 10 mm, thickness of positive plate = 3.35 mm) [14].

VGCFs with diameters of 2 μm [13], similarly graphitized s-VGCFs show a relatively higher capacity due to their high surface area which is caused by the smaller diameter of the s-VGCFs. Further experimental studies were done to determine the cycle characteristics of graphitized s-VGCFs when used as the anode materials. As shown in Fig. 13, fairly good cyclic efficiency was observed up to above 200 cycles, possibly because of its superior bulk properties, such as higher resiliency and lower volume resistivity.

As mentioned above, the s-VGCF sample used in this study shows acceptable properties as a filler for electrodes in Li-ion battery systems. Fig. 14 show the carbon anode sheet in a commercial cell, in which the carbon sheet was made up of synthetic graphite and s-VGCFs. The cyclic efficiency of a synthetic graphite (HTT = 2900°C) anode as a function of added weight percent of graphitized s-VGCFs is shown in Fig. 15 [15,16]. With increasing added weight percent of graphitized s-VGCFs, the cyclic efficiencies of the synthetic graphite anodes were increased continuously, and in particular when 10 wt.% of the s-VGCFs was added, the cyclic efficiency was maintained at almost 100% up to 50 cycles. At higher concentrations, the s-VGCF carbon fibers interconnect between graphite powder particles to form a continuous conductive network. The addition of graphitized s-VGCFs into anode materials improves the conductivity of the anode mixture, and also imparts other desirable properties that enhance the performance of Li-ion batteries, such as the ability to absorb and retain significant electrolyte and to provide resiliency and compressibility to the electrode structure. Furthermore, the relatively high capability of s-VGCFs for Li-ion intercalation when used

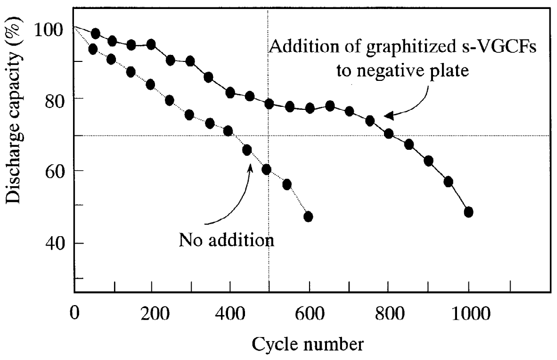

Fig. 11. Cycle characteristics of seal-type lead–acid battery (4 Ah) when graphitized s-VGCFs are used as the filler in the negative plate (discharge: 0.57 A to 1.70 V/cell, charge: 7.35 V (maximum 1.5 A)-6H) [14].

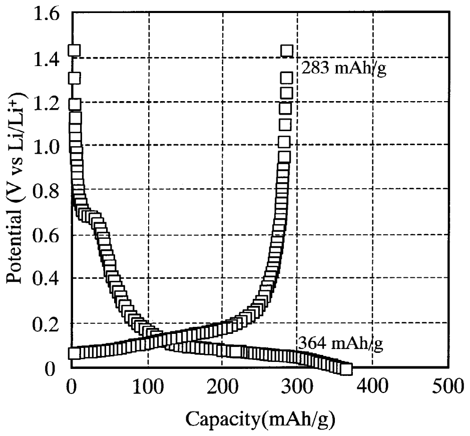

Fig. 12. Charge and discharge curves for graphitized s-VGCFs during the first cycle (lattice constant, $C_o = 6.775$ Å, coulombic efficiency = 77.7%).

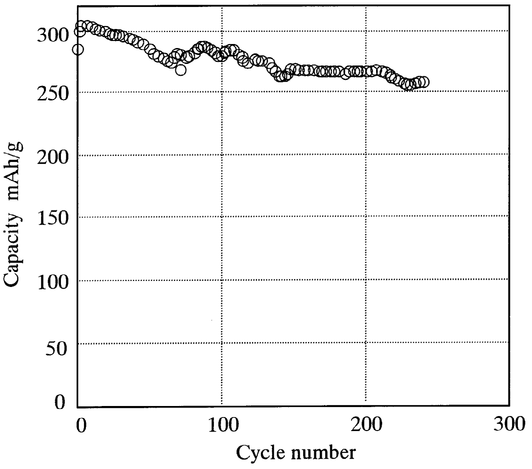

Fig. 13. The variation of discharge capacity when graphitized s-VGCFs are used as the anode material in the range 0 to 1.5 V with a current density of 0.2 mA/cm^2.

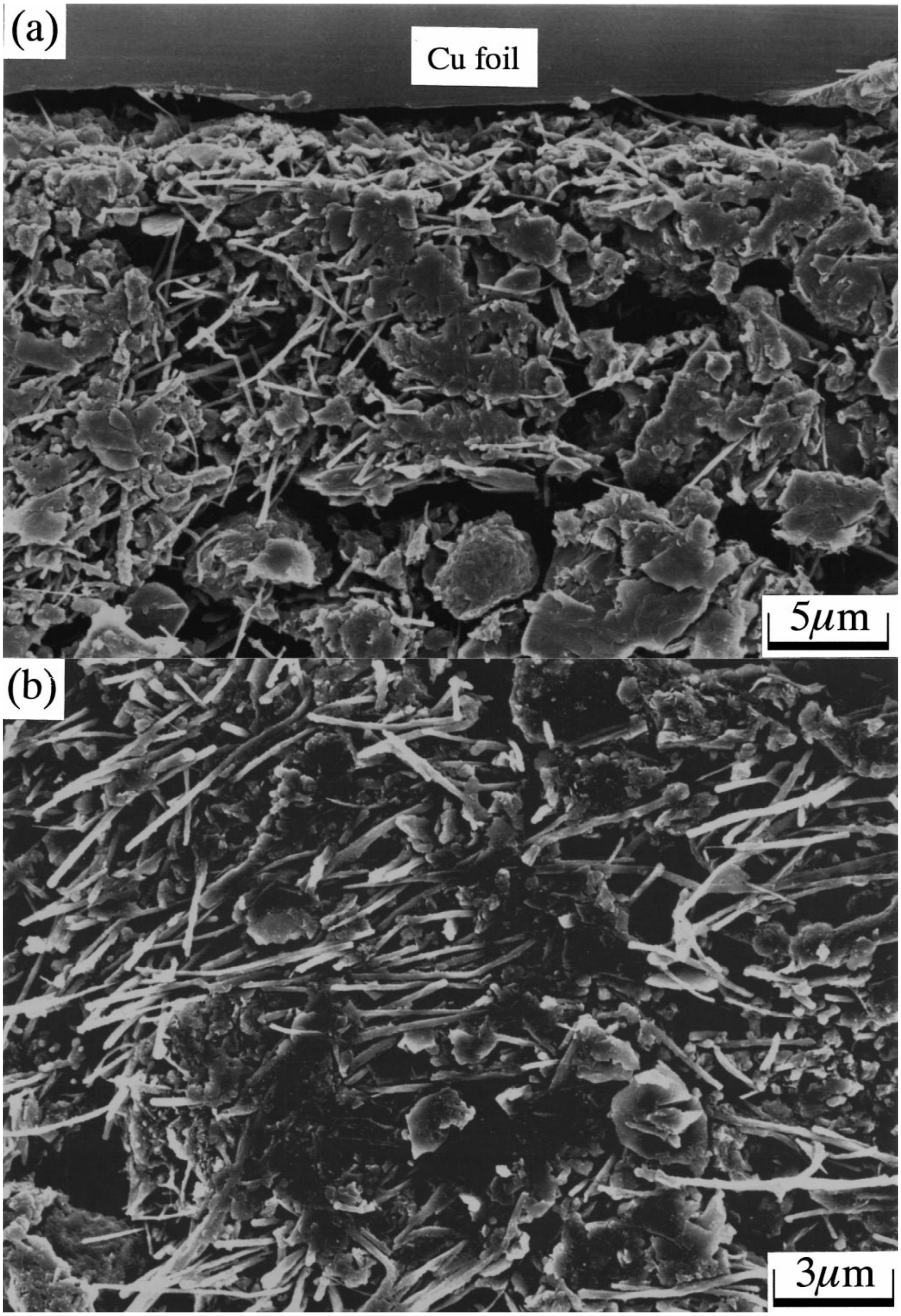

Fig. 14. SEM pictures of (a) the carbon anode sheet containing s-VGCFs in a commercial cell and (b) enlarged one.

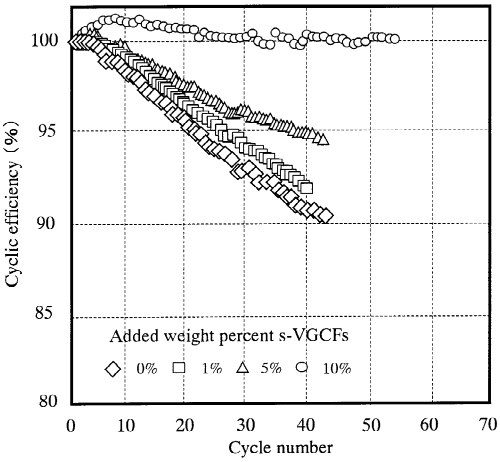

Fig. 15. Cyclic efficiency of synthetic graphite (HTT = 2900°C) as a function of added weight percent of graphitized s-VGCFs, in the range 0 to 1.5 V, with a current density of 0.2 mA/cm^2.

as an anode filler would also be beneficial for battery performance as compared to that of conventional whiskers.

7. Conclusions

For s-VGCFs obtained by a floating reactant method, the basic properties and microstructural development of these fibers with HTT, the physical properties of a single fiber and in the bulky state were evaluated for the purpose of applying this material as the filler in electrodes of lead–acid batteries and in the Li-ion battery system. Graphitized s-VGCFs showed desirable properties when used as a filler in electrodes, such as fairly high mechanical strength and electrical conductivity in a single fiber, a high degree of resiliency and a good volume conductivity in the bulky state. These desirable properties should yield improved performance in actual batteries.

We summarize the desirable characteristics of graphitized s-VGCFs for use as a filler, especially in the electrodes of Li-ion batteries as follows: (a) the small diameter of the fiber makes it possible to distribute the fibers homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte, (b) the improved electrical conductivity of the electrode is related to the high electrical conductivity of the fiber itself, and the network formation of the fibers with the graphite particles in the anode to form a fiber-mat. (c) As compared with that of conventional whiskers, the relatively high intercalation ability of s-VGCFs did not lower the capacity of anode materials itself upon cycling. (d) A high flexibility of the electrode is achieved due to the network formation of the s-VGCFs in a fiber-mat structure. (e) The high endurance of the electrode because s-VGCFs absorb the stress caused by intercalation of Li-ions. (f) Improved penetration of the electrolyte due to the homogeneous distribution of the fibers surrounding the anode material. (g) As compared with that of carbon black, the cyclic efficiency of the Li-ion battery was improved for a relatively long cycle time.

In the near future, the application of s-VGCFs as a filler material in various electrochemical systems is expected to become widespread due to the excellent properties of the s-VGCFs, especially, for applications where improved conductivity is needed.

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