Toluene-insoluble fraction of fullerene-soot as the electrode of a double-layer capacitor

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Abstract

Several electrochemical properties of the heat-treated toluene-insoluble fraction separated from fullerene-soot (Fs-TI) were investigated to find their application as an advanced electrical double-layer capacitor (EDLC) electrode material using an organic solvent electrolyte. The heat-treated Fs-TI at 900 °C (Fs-TI-900) showed as high as $58\,F\,g^{-1}$ of capacitance, which is ascribed to its high capacitance per unit surface area as well as its reasonable surface area. In addition, the capacitor cell with Fs-TI-900 electrodes exhibited a better rate stability than that with conventional active carbon fiber electrodes due to its high electronic conductivity. The material heat-treated at 2400 °C (Fs-TI-2400) showed much smaller capacitance than Fs-TI-900 due to its smaller surface area. A unique rate dependence of capacitance was observed when the ion size of electrolyte was varied.
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Keywords: Electrical double-layer capacitor; Fullerene-soot; Organic solvent electrolyte

1. Introduction

The electrical double-layer capacitor (EDLC) has been recognized as an important device, not only as a substitute for the dielectric capacitor but as a next-generation rechargeable power source, because of its large (farad order) capacitance [1]. The required characteristics for an EDLC electrode material are large surface area, appropriate pore size distribution at the range of several nanometers, high electric conductivity, and ease of fabrication [2,3]. Many efforts have been done to find or produce an activated carbon with adequate properties [3–6]. However, in many cases a highly porous structure and a good conductivity in carbon material are in a trade-off relationship because in general porous carbons are produced from carbons with lower electronic conductivity than graphitic carbons, such as resin-based and biomaterial-based activated carbons.

Previously, the author prepared such unique carbonaceous materials by heat-treatment of the residual fraction of fullerene-containing soot produced by the arc discharge method [7]. The residue of fullerene-containing soot basically provided two kinds of carbons by the heat-treatment at different temperature region. For example, the carbonaceous material prepared by the heat-treatment of this residue at 900 °C shows ca. $1000\,m^2\,g^{-1}$ of surface area and the order of $10\,S\,cm^{-1}$ of conductivity. The carbonaceous material obtained by the further heat-treatment at 2400 °C exhibits a higher conductivity and uniform pore size distribution around 2 nm, while the surface area was markedly reduced. The authors expected that these unique properties of the heat-treated fullerene-soot residue should be adequate for an advanced EDLC electrode.

In the present study, we evaluated the electrochemical properties of this material in terms of its potential for use as an EDLC electrode material.

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2. Experimental

The preparation of fullerene-containing soot and the isolation of toluene-insoluble fraction (Fs-TI) from the fullerene-containing soot were carried out as reported elsewhere [7,8]. The Fs-TI was dried, and then molded into disk form to serve heat-treatments at 900 °C in a tube furnace under argon flow. Some of these materials were further heat-treated at 2400 °C in a graphite furnace. Fs-TI heat-treated at 900 and 2400 °C was ascribed as Fs-TI-900 and Fs-TI-2400 later in this text, respectively. The disks after the heat-treatment were ground with 5 w/o Teflon binder, and shaped into a 10 mm pellets (thickness; ca. 0.1 mm).

Two of these pellets and 1 M tetraethylammonium tetrafluoroborate (TEABF$_4$)/propylene carbonate (PC) or 1 M tetrabutylammonium tetrafluoroborate (TBABF$_4$)/PC electrolyte (both electrolytes were provided by Tomiyama Pure Chemical Co., Japan) were assembled into a stain-less steel coin-type cell with 20 mm of diameter under a glove box filled with dry argon. The charge–discharge tests for these coin-type cells were performed by the constant-current method under the following conditions, the current density of 0.5 or 2.0 mA cm^{-2} and the cut-off voltage of 0.5 and 2.5 V with a charge–discharge cycler (Hokuto Denko Co., Japan). In all cases the rest time between the charge and discharge was fixed at 30 min. The electrochemical properties of commercially available activated carbon fiber derived from phenoic resin (Ph-ACF; surface area = 909 m^2 g^{-1}, provided by Nippon Kynol Co., Japan) were tested as a comparison.

3. Results

3.1. The properties of heat-treated Fs-TI

The heat-treated Fs-TIs at 900 and 2400 °C exhibited both large surface area (498 m^2 g^{-1} for Fs-TI-900 and
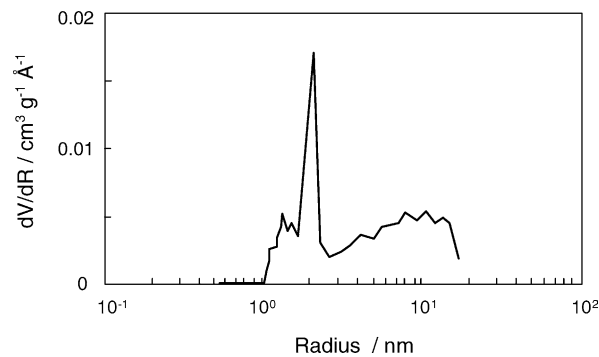

Fig. 1. The pore size distribution of Fs-TI-2400.

183 m^2 g^{-1} for Fs-TI-2400) and electronic conductivity as high as 10^2 S cm^{-1} [7]. Since there was no activation process, heat-treated Fs-TIs contained very few hetero atoms (below 0.5 wt.% by elemental analyses). Heat-treatment at 2400 °C reduced surface area but provided uniform pores (ca. 2 nm in diameter), as shown in Fig. 1, the pore size distribution of Fs-TI-2400 from BET surface area measurement [7]. The Fs-TI disk suffered no macroscopic shrinkage during the heat-treatment.

Fig. 2 shows TEM images of Fs-TI-900 (a) and Fs-TI-2400 (b). Fs-TI-900 had an amorphous structure with small randomly located hexagonal planes, shown as black lines in TEM photos. In contrast, Fs-TI-2400 had spherical microdomains of 5–10 nm whose walls were turbostratically stacked. The scanning probe microscope showed that these nanospheres maintained their shape during heat-treatment, and the stacking inside the wall became ordered [9].

3.2. The charge–discharge properties of the heat-treated Fs-TI

Fig. 3 shows the discharge profiles of coin cells with Fs-TI heat-treated at 900 and 2400 °C under constant-currents
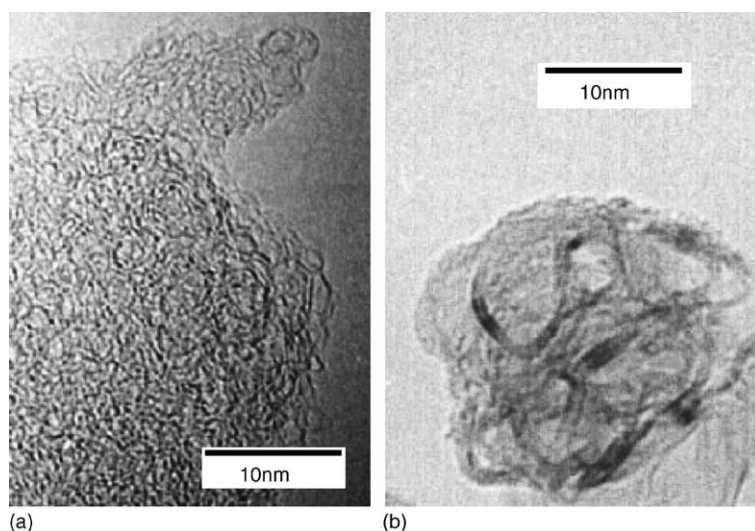

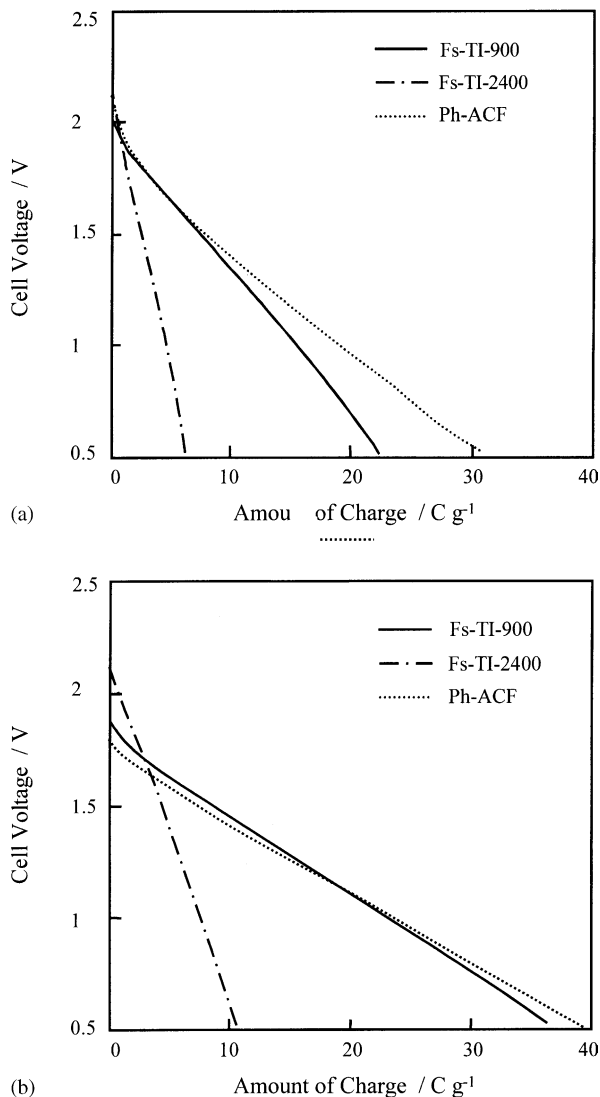Fig. 2. TEM bright field images of (a) Fs-TI-900 and (b) Fs-TI-2400.

(a)

(b)

Fig. 3. The constant-current discharge profiles of EDLC cells consisted of various carbons electrodes. Electrolyte: 1 M TEABF$_4$/PC: (a) at 0.5 mA cm^{-2} and (b) at 2.0 mA cm^{-2}.

of 0.5 mA cm^{-2} (a) and 2.0 mA cm^{-2} (b), respectively. The profiles of Ph-ACF are also included as comparison. In all cases straight discharge profiles were obtained, while the initial voltage decreased to around 2 V due to the internal re-

sistance of test-cells. The capacitances of unit electrodes per their weight and per their surface area estimated from Fig. 3 are summarized in Table 1. The calculation of cell capacitance was based on the following equation by assuming the discharge profiles were perfectly linear;

$$Q = C_{\text{cell}} V_{\text{init}} \tag{1}$$

Here Q is the charge, C_{cell} the cell capacitance and V_{init} the initial voltage. The capacitance of the single electrode (C_1) is related to C_{cell} by the following equation;

$$\frac{4}{C_1} = \frac{1}{C_{\text{cell}}} \tag{2}$$

Fs-TI-900 showed a capacitance per weight of 58 F g^{-1}, comparable to that with Ph-ACF. The highest capacity per unit surface area (118 mF m^{-2}) was noted at the current density of 0.5 mA cm^{-2}. Fs-TI-2400 exhibited rather small capacitance per weight, however, its capacitance per surface area (83 mF m^{-2}) was comparable with that of Ph-ACF. Even when the current density was increased to 2.0 mA cm^{-2}, both Fs-TI-900 and Fs-TI-2400 maintained their capacitances, whereas the capacitance of Ph-ACF decreased sharply from 85 to 64 F g^{-1}. In terms of the capacitance per volume, Fs-TI-900 has higher capacitance than Ph-ACF at this rate. The high electronic conductivity of Fs-TI-900 and Fs-TI-2400 may aid the high capacitance under such a large current.

The open-circuit voltage of capacitor cells using Fs-TI-900 and Ph-ACF electrodes after the 2 h constant-voltage charge process are plotted versus time in Fig. 4(a). The Fs-TI-900 electrodes retained its open circuit voltage. Concerning the microscopic situation of such a self-discharge process of a double-layer capacitor, Ricketts and Ton-That proposed the following relationship of the amount in initial several minutes of cell voltage decrease (V) with time (t) from the assumption of a plane electrode surface, and the dominating factor of the self-discharge process diffusion of ions and ohmic leakage [10];

$$V = V_0 - mt^{1/2}, \quad \text{where } m = \frac{c_{R_0} D^{1/2}}{C_c \pi^{1/2}} \tag{3}$$

Here V_0 is the initial voltage, c_{R_0} the initial surface concentration of the ion excess region with the thickness of $2h$, D the diffusion coefficient of ions (assuming that the value for both

Table 1
Capacitances of cells with various porous carbon electrodes

	Current density (mA cm^{-2})	Capacitance		SSA[a] (m^2 g^{-1})	Capacitance per surface area (mF m^{-2})
		(F g^{-1})	(F cm^{-3})		
Fs-TI-900	0.5	58	110	491	118
	2.0	56	106		114
Fs-TI-2400	0.5	15	24	183	83
	2.0	13	21		71
Ph-ACF	0.5	80	128	909	88
	2.0	64	103		70

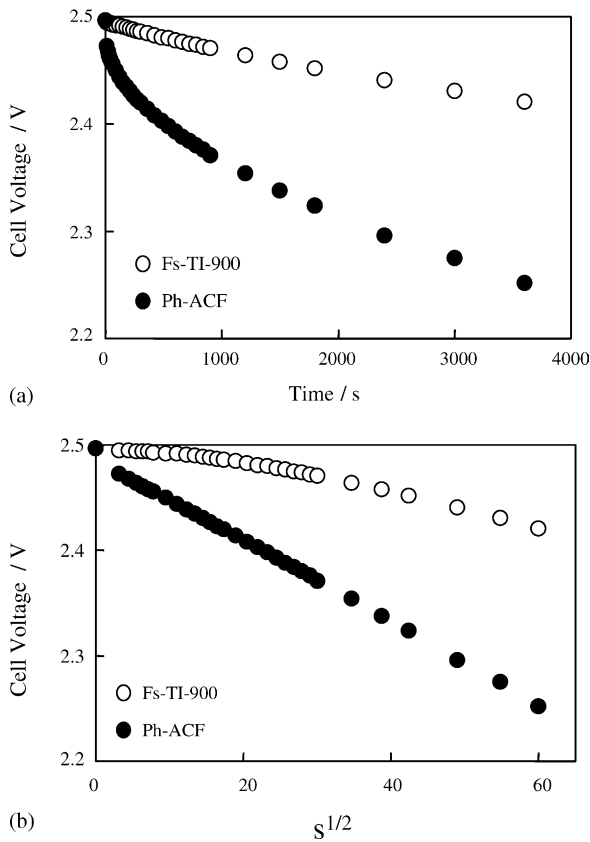[a] Specific surface area.

(a)

(b)

Fig. 4. (a) The time-course plots of open-circuit voltage of EDLC cells after the 2 h constant-voltage charge and (b) the $t^{1/2}$ – expressions for the relationships shown in (a).
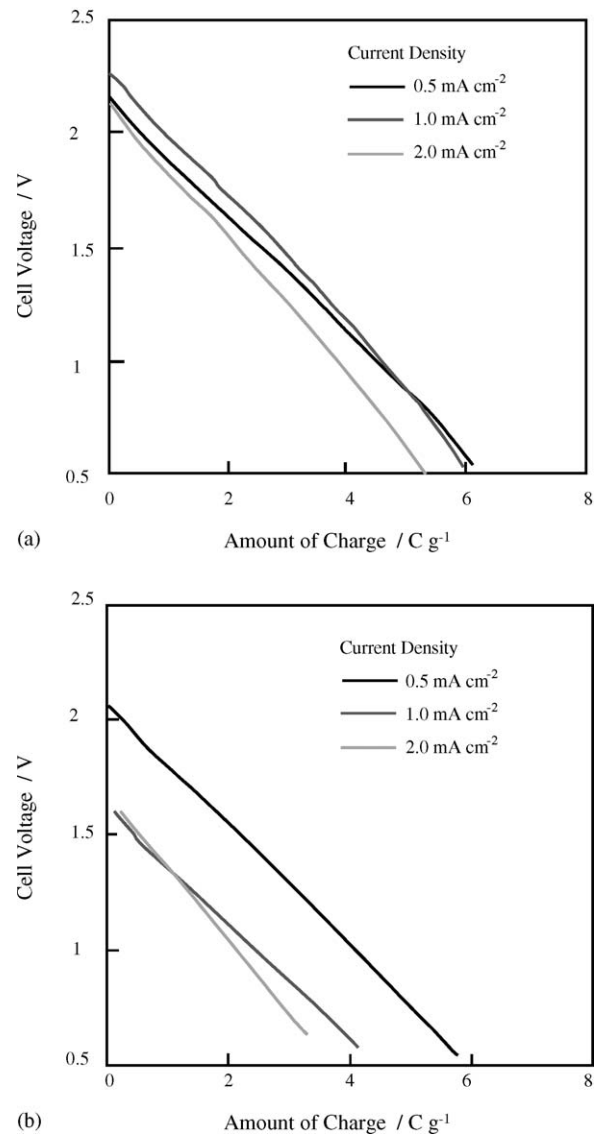

(a)

(b)

Fig. 5. The constant-current discharge profiles of EDLC cells consisted of Fs-TI-2400 electrodes under various discharge currents. Electrolyte: (a) 1 M TEABF$_4$/PC and (b) 1 M TBABF$_4$/PC.

cation and anion are similar), q the charge carried to the electrode surface by each ion, and C_c the capacitance of the cell. Generally the value of m ranges from 3 to 7 mV s$^{-1/2}$ when the electrolyte is TEABF$_4$/PC. The relationships of V with $t^{1/2}$ are plotted in Fig. 4(b). The self-discharge behavior of the capacitor cell with Ph-ACF electrodes showed the correspondence clearly to the Eq. (3) with the m value of 3.6 mV s$^{-1/2}$. In contrast, Fs-TI-900 electrodes did not show the correspondence to the Eq. (3). The difference in these two materials may be due to the small value of h^2/D. Such tendency may originate from the unique, probably more accessible, pore structure of Fs-TI-900 or the electric field distribution of the double-layer between Fs-TI-900 and electrolyte, since Fs-TI, formed by the condensation of carbon cluster in He atmosphere, has very small amount of surface functional groups where ions may have a special interaction with electrode.

3.3. Pore size effect of Fs-TI-2400 electrode to discharge behavior

Fig. 5 shows the discharge profiles of Fs-TI-2400 electrode with 1 M TEABF$_4$/PC (a) or 1 M TBABF$_4$/PC (b) electrolytes under various current densities. TBA cation has an ion size of 0.412 nm (using a spherical assumption) and is slightly larger than TEA (ion size of 0.335 nm) [11]. When the electrolyte was 1 M TEABF$_4$/PC, the discharge curves are similar regardless of the current density. In contrast, a remarkable voltage drop was observed at the larger current density than 1.0 mA cm^{-2}, when the electrolyte was 1 M TBABF$_4$/PC. The capacitance of the cell, assigned by the slope of the curve, seems rather unchanged, because the ion size of TBA cation was small enough to form double-layer in the pore of Fs-TI-2400, which has the almost uniform pore size of 2 nm. The initial voltage drop may be caused by the resistance of ion diffusion into pore. In this result, it is indicated that the diffusion accessibility of ion into pore provides larger influence on the capacitor performance than expected.

4. Discussion

From the results shown above, Fs-TI-900 has advantages for an electrode material of double-layer capacitor, such as a high capacitance per surface area, capacitance retention for the high rate discharge, and self-discharge inhibition. It is important to recognize the relationship of such unique electrochemical properties of this material with its structural factors.

In the heat-treated Fs-TI, the double-layer was developed efficiently on the effective surface of electrode. Such a large capacitance per surface area of Fs-TI-900 may be derived from its amorphous structure. Fs-TI-900 has a highly amorphous structure when observed both on X-ray diffraction and TEM. Therefore, this material may expose a larger amount of edge on its surface than Ph-ACF. In aqueous electrolyte, the edge of graphitic structure is known to have a larger value of double-layer capacitance per surface area (50–$100\,\mathrm{mF\,m^{-2}}$) [12] than the basal plane ($3\,\mathrm{mF\,m^{-2}}$) [13]. An edge structure on carbon surface may provide a higher capacitance also in non-aqueous electrolyte. The origin of a large capacitance on an edge structure may be its great surface roughness. Indeed, it is still questionable whether the BET surface area of an edge structure rigorously corresponds to its electrochemically effective surface area. In addition, a partial intercalation of ions into layer may be possible to occur. Carlin et al. reported that several organic cations and anions are intercalated into graphite [14]. In the case of Fs-TI, the space between graphene sheets is larger than graphite, therefore, even a quaternary ammonium cation is able to be inserted there.

The high performance at high rate is thought to come mainly from the high conductivity of Fs-TI-900, and also of Fs-TI-2400. The conductivity of these materials is markedly high compared with conventional porous carbons. In addition, the accessibility of the ions to the pore at high rate may also be improved in Fs-TI-900 or Fs-TI-2400 compared with conventional porous carbons. Heat-treated materials of Fs-TI have open pores, originated from inter-particle spaces of nanospheres. Such open pores are thought to enable to assure the better accessibility of ions. The incorrespondence of the self-discharge behavior of Fs-TI-900 electrode to Eq. (3) suggests that the mode of ion diffusion may be unique on the surface of this electrode.

In general, the pore size distribution of a porous carbon is rather broad and not uniform. Thus the electrochemical behavior of such a porous carbon electrode is not able to be determined clearly. In contrast, by the use of Fs-TI-2400, having rather uniform pore size distribution, the electrochemical behavior of ions on the pore can be observed clearly.

5. Conclusion

The heat-treatment product of the residue of fullerene-soot at $900\,^\circ\mathrm{C}$ (Fs-TI-900) exhibited a comparable relative capacitance ($58\,\mathrm{F\,g^{-1}}$) with a conventional active carbon fiber (Ph-ACF) when it was used as electrodes of electrical double-layer capacitor. The capacitor cell with Fs-TI-900 electrodes retained its capacitance under a large current density charge–discharge process, due to the high electronic conductivity of Fs-TI-900. The self-discharge behavior of the capacitor cell implied that the ion diffusion process at the surface of porous electrode was less affected to the electrical output in case of Fs-TI-900 electrode than in case of Ph-ACF electrode. The residue of fullerene-soot at $2400\,^\circ\mathrm{C}$ (Fs-TI-2400) has a uniform pore size distribution around $2\,\mathrm{nm}$, therefore the influence of pore size to the charge–discharge behavior of capacitor was observed by using this material as electrodes together with various organic solvent electrolytes. When tetrabutylammonium tetrafluoroborate salt was used as an electrolyte salt, the voltage drop due to the ion diffusion resistance into electrode pores was observed under a large current charge–discharge condition.

Acknowledgement

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