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High rate performance of highly dispersed C_{60} on activated carbon capacitor

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Abstract

Fullerene-activated carbon composite electrodes were prepared and their charge/discharge characteristics were studied for use in a high power electric double-layer capacitor. The capacitance of the C_{60}-loaded activated carbon fiber (ACF) electrodes became greater than that of the unloaded ACF at charge/discharge current densities above 50 mA/cm^2. In order to obtain a highly dispersed C_{60}-loaded electrode, an ultrasonic treatment was performed. The size of the C_{60} agglomerate decreased from 1–2 to 0.1 μm or less, and the capacitance of the C_{60}-loaded ACF electrodes increased with an increase in the ultrasonic treatment time. A higher capacitance of 172 F/g was obtained at 50 mA/cm^2 on a 1 wt% C_{60}-loaded electrode with ultrasonic treatment, and the C_{60}-loaded ACF electrode also showed a higher cycle performance.

Keywords: Supercapacitor; Fullerene; C_{60}; Activated carbon electrode

1. Introduction

Electric double-layer capacitors have recently become of major interest as energy storage systems for a hybrid electric vehicle (HEV) because of their higher power density than those of dielectric capacitors, and have a longer cycle life than batteries [1,2]. Many studies have been done to improve the performance of the electric double-layer capacitor [3–5]. Activated carbon fibers (ACFs) are popular materials for the electrode of the electric double-layer capacitor because of their high specific surface area and high conductivity [6–8]. The surface condition of ACFs is sensitive to the capacitance [9–11], and many attempts to modify the surface condition of the activated carbon have been extensively examined [12–15]. Recently, fullerenes have attracted a great deal of interest as new carbon materials. In particular, carbon nanotubes have been investigated in anticipation of their high specific surface area and high adsorption property. Many studies and novel results have been recently reported [16–20]. We selected C_{60}, the representative material of the fullerene, as a novel carbon material for use in a supercapacitor.

Fullerene, C_{60}, has delocalized π-electrons due to its unique molecular structure. Two reduction waves corresponding to C_{60}^{-} and C_{60}^{2-} have been reported using cyclic voltammetry [21,22]. Moreover, considering the threefold degenerate LUMOs [23,24], C_{60} is expected to accept six electrons. In fact, 6 one-electron reduction waves have been observed during the cyclic voltammetry of C_{60} in a DMF–toluene mixture at low temperature [25]. In this study, focus was made on an electric double-layer capacitor consisting of C_{60}-loaded ACF electrodes. We prepared highly dispersed C_{60}-ACF electrode and evaluated its capacitance properties.

2. Experimental

An activated carbon fiber cloth was used and powdered. Its specific surface area was 1500 m^2/g (Toyobo, KF-1500M). The powdered ACF was then mixed with carbon black (Denka, AB-03) and PTFE binder (Daikin, F-104). The weight ratio was 8:1:1. The C_{60} powder (MTR Ltd., 99.9%)

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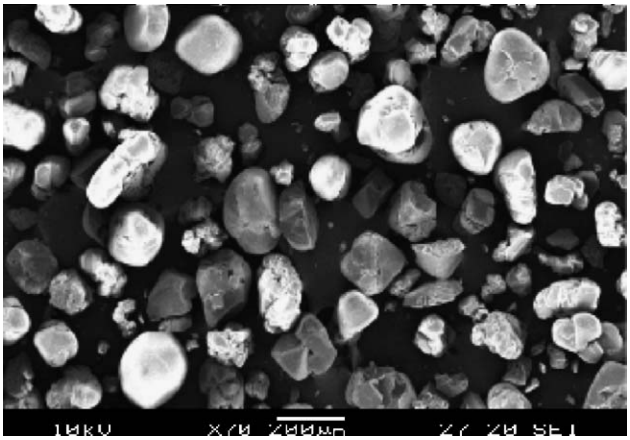

Fig. 1. SEM image of as-received C_{60} powder.

was added and kneaded with ethanol. The as-received C_{60} powder consisted of agglomerated particles having a diameter of approximately 200 μm as shown in Fig. 1. The C_{60} content was 1–30% in comparison with the weight of the powdered ACF. The mixture was then dried and pressed at 10 MPa to form a pellet with a diameter of 16 mm and a thickness of 0.6 mm, and then the pellet was annealed in a vacuum at 330 °C for 5 h. The cluster structure of C_{60} is stable to heat treatment [26–28], and the desorption of C_{60} was not confirmed.

For the electrochemical measurement, two pieces of the pellet-formed electrodes separated by the separator, which were immersed in an electrolyte solution under a vacuum of 10 Pa, were inserted into a two-electrode coin-type shaped cell. As the electrolyte solution, 0.5 mol/L H_2SO_4 was used for all the measurements. A glass filter was used as the separator. The galvanostatic charge/discharge measurements were carried out at room temperature using a battery test system (HIOKI, EDLC evaluation system). The investigated voltage range was 0–1 V at a constant current density of 2.5–100 mA/cm^2.

The capacitance of the cell was calculated from the time period, Δt, which corresponds to a voltage change, ΔV, using the following equation [29,30]:

$$C = I\frac{\Delta t}{\Delta V} \quad (1)$$

where C is the capacitance, I the constant output current, Δt the discharge time and ΔV is the potential change. Δt was recorded from 0.6 to 0.5 V under constant current discharge conditions. The specific capacitance was then calculated by dividing the capacitance by the weight of the electrode.

The morphology of the C_{60}-loaded ACF surface was observed by scanning electron microscopy (JEOL, JSM-5600). The pore structure of the C_{60}-loaded ACF was studied by the N_2 adsorption process (BEL Japan, Bellsorp 18plus). The specific surface areas of the C_{60}-loaded ACF samples were determined by the Brunauer, Emmett and Teller (BET) method, and the micropore size distribution was calculated by the MP method.

3. Results and discussion

Fig. 2 shows the relationship between the discharge current density and the capacitance of the C_{60}-ACF electrodes. At the low charge/discharge constant current density of 2.5 mA/cm^2, the capacitance of the C_{60}-ACF electrodes was lower than that of an untreated ACF electrode. However, the capacitance of C_{60}-ACF electrodes became greater than that of the untreated ACF at a higher charge/discharge current density. The specific capacitances of the C_{60}-loaded ACF electrodes at 50 mA/cm^2 were 109 and 123 F/g for the C_{60} contents of 1 and 10 wt%, respectively. Fig. 3 shows the discharge curves at the constant charge/discharge current density of 50 mA/cm^2. The discharge time for the 10 wt% C_{60}-loaded electrode (c) increased 61% in comparison with the untreated electrode (a). The load characteristic for the C_{60}-ACF composite electrode was improved when compared

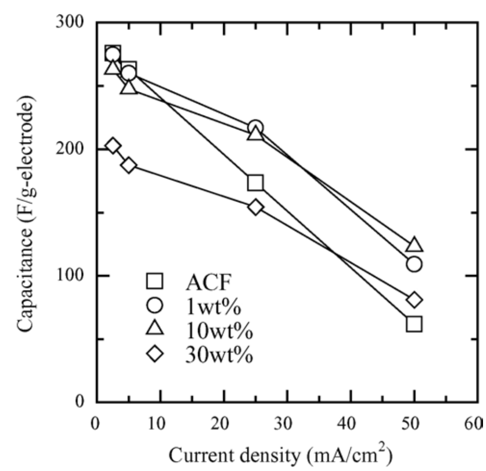

Fig. 2. Relationship between discharge current density and capacitance of C_{60}-activated carbon composite electrodes.

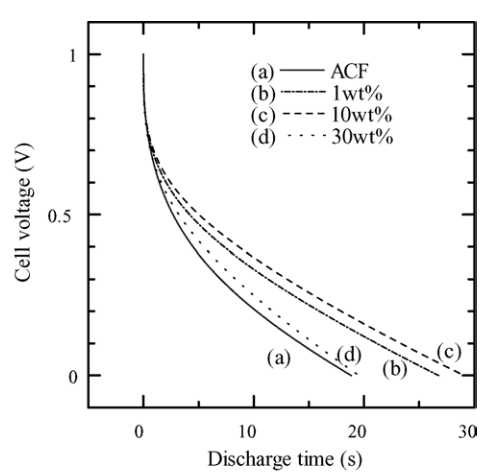

Fig. 3. Discharge curves of C_{60}-loaded ACF electrodes at 50 mA/cm^2.