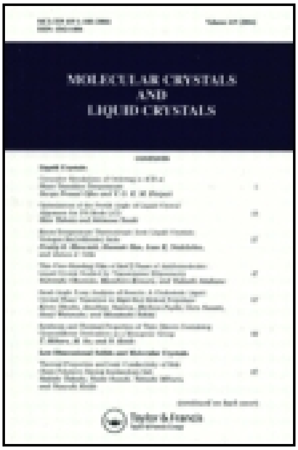

Molecular Crystals and Liquid Crystals

A Characteristic of Alkaline Activated Mesophase Based Carbon for Electrochemical Capacitor

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A CHARACTERISTIC OF ALKALINE ACTIVATED MESOPHASE BASED CARBON FOR ELECTROCHEMICAL CAPACITOR

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Activated graphitizing carbons, mesophase carbons prepared by alkaline activation for electrochemical Capacitors (Electric double-layer capacitors; EDLCs) with organic liquid electrolytes showed larger specific capacitance per unit volume (F/cm^3) than those of conventional activated carbon materials. The physical characteristic is lower specific surface area, compared with a conventional activated carbon. It has been supposed that the electric double-layer interfaces of alkaline activated mesophase carbon which have high density per unit volume were dominated by the edge plane of hexagonal lattice, compared with those of conventional activated carbon material.

Keywords: mesophase pitch; electric double-layer capacitor; alkaline activation

INTRODUCTION

Electrochemical capacitor using organic liquid electrolytes has been widely used as energy storage devices of memory back up system. Electric charge caused by the shift of potentials is stored at the interface between a polarizable electrode and an electrolyte, and performance of capacitors is determined by capacitance of activated carbon electrodes and operating voltage. EDLCs have the advantage of high power density, over 1,000 w/L, excellent cycle-life, and wide temperature operating ranges, compared with secondary batteries. However, in the view of energy storage, their performance is low energy density, for example commercially available capacitors so-called supercapacitors having 3 wh/L [1]. Therefore, their application has been limited to low-energy devices.

For enlargement of application area, we have widely researched for larger capacitance per unit volume than those of conventional activated carbon materials. As the result, in 1995, we discovered a fact that activated carbon prepared by alkaline activation of PVC (polyvinylchloride)-based carbon (carbonized PVC) showed an excellent capacitance as electric double layer capacitors [2]. In 1996, as it was confirmed that activated carbons prepared by alkaline activation of mesophase pitch-based carbon had an excellent capacitance, we suggested the concept of "alkaline activated graphitizing carbon" [3]. The performance of these capacitor cells is over 30 F/cm^3 for total volume of naked carbon electrodes, compared with conventional capacitor cells having 13 $\sim$ 20 F/cm^3.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

For the preparation of graphitizing carbon characterized by a high degree of orientation, we almost used PVC resin or mesophase pitch with low metal impurities.

2.2. Carbonization and Alkaline Activation Procedure

The preparation of alkaline activated graphitizing carbon consists of carbonization and alkaline activation in a nitrogen-gas flow. To obtain suitable pore distributions for EDLCs, alkaline activated graphitizing carbon must be prepared by controlling some parameters of carbonization temperatures, ratios of KOH/C, activation time, and activation temperatures. In this work, PVC resin and mesophase pitch was carbonized at temperatures between 500°C and 800°C. Mesophase carbon was heated with KOH below 400°C for absorption and dehydration, followed by, heated at temperatures between 700°C and 900°C for activation, after cooling down, washed using hot water or diluted aqueous HCl solution for the removal of potassium compounds.

2.3. Electrodes Preparation

PTFE-bonded sheet-type electrodes were prepared by mixing activated carbon, carbon black and PTFE binder, then was kneaded and rolled. Separator was sandwiched with a pair of the electrodes to form electrodes assembly (capacitor unit). The capacitor unit was dried under vacuum, impregnated with an electrolyte under low vacuum in glove boxes. The electrolyte composed of Quaternary ammonium tetrafluoroborate salts and propylene carbonate was used in this study. All the experiments were conducted at room temperature.

2.4. Measurement of Performance

All capacitance results were obtained by two-electrode system without reference electrode (Fig. 1). It should be notice the differential capacitance on EDLC calculation. Three-electrode system has a capacitance around 4 times higher than that of two-electrode system, because the capacitance obtained by dividing the sum of the weight of both electrodes and by calculating a factor of series circuit.

2.5. Characterization of Activated Carbon

Measurements of specific surface area was carried out by BET method (N_2 at 77 K) using an automatic adsorption system. Activated carbons were observed by Transmission Electron Microscope (Philips CM200).

2.6. The Behavior of Thickness of Electrodes Assembly

Electrodes assembly which was loaded under the pressure of 100 kPa (1kgf/cm^2) was expanded/returned in charge/discharging process. That is, a thickness of electrodes depends on operating voltage. The unique behavior was recorded as the increase of electrodes thickness by laser displacement meter (KEYENCE LC-2400) (Fig. 1).

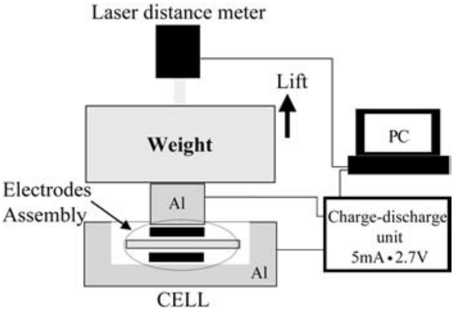

FIGURE 1 Schematic view of a capacitor unit and recording method of thickness changing (See Color Plate VIII).

3. RESULTS AND DISCUSSION

Table 1 compared physical properties of alkaline activated carbon with that of conventional activated carbon in this study. The physical characteristic of the alkaline activated graphitizing carbon has low BET surface area of 70–1000 m^2/g compared with commercially available activated carbon, of 1000–3500 m^2/g. It is apparently different from those of commercially available activated carbon which prepared by water vapor activation of phenol resin-based, isotropic pitch-based, cellulose-based carbon, and by alkaline activation of coal-based carbon. Relationships between specific capacitance per weight (F/g) or capacitance per volume (F/cm^3) and specific surface area (m^2/g) of activated carbons were shown in Figure 2 or Figure 3.

For conventional activated carbon material, specific capacitance per weight increases with increasing the specific surface area. However, the capacitance of mesophase based activated carbons is greatly divided from the line obtained from conventional activated carbons. Although mesophase based activated carbon has specific surface area as low as around 1000 m^2/g, it shows high capacitance corresponding the conventional activated carbon material with around 2500 m^2/g.

For using as commercial energy source, the high capacitance per volume (F/cm^3) is the most important factor. Activated mesophase carbons show twice larger specific capacitance per unit volume (F/cm^3) than those of conventional activated carbon materials (Fig. 3). The maximum value of the capacitance per volume was taken around 2000 m^2/g in conventional activated carbon, and then it decreases again (4). To meet the convenience for the comparison among the novel and the conventional method, capacitance convert into specific capacitance per unit area ($\mu F/cm^2$) (Fig. 4). The result from novel method shows 2–3 times larger capacitance than those of conventional activated carbon materials.

Figure 5 shows charge/discharge curves and the changes of thickness of electrodes assembly. The rate of increase in the thickness of mesophase based activated carbon electrodes reach the value of 140% compared with

TABLE 1 Summary of Physical Properties of Alkaline Activated and Conventional Activated Carbon

Activated carbon	BET value m^2/g	Specific capacitance F/g	Specific capacitance F/cm^3
Conventional activated carbon	1000–3500	25–45	15–22
Alkaline activated graphitizing carbon	70–1000	30–45	25–35

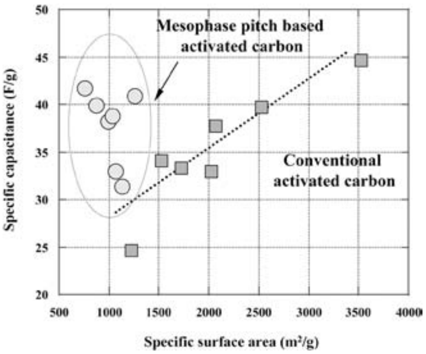

FIGURE 2 A relationship between specific capacitance per weight (F/g) and specific surface area (m^2/g) of activated carbons (See Color Plate IX).

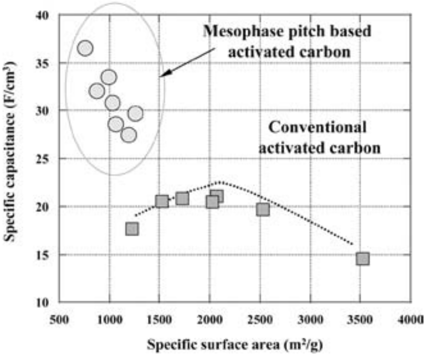

FIGURE 3 A relationship between capacitance per volume (F/cm^3) and specific surface area (m^2/g) of activated carbons (See Color Plate X).

those of conventional activated carbon (only 102%). The change of thickness of electrode assembly apparently depend on operating voltage. The change of internal stress was reported by Takeuchi *et al.* (5).

These results indicate the interface of alkaline activated graphitizing carbon is different in morphology from those of conventional activated carbons. It was ascertained from TEM observation that the microstructures of alkaline activated graphitizing carbon consisted of a network structure that was formed by frames of graphene layers (Fig. 6). It has been found that Electric double-layer interface of alkaline activated mesophase carbon existed as high density per unit volume, it was dominated by edge plane of hexagonal lattice, compared with those of conventional activated carbon materials. The differential electrode capacitance of the edge plane to basal

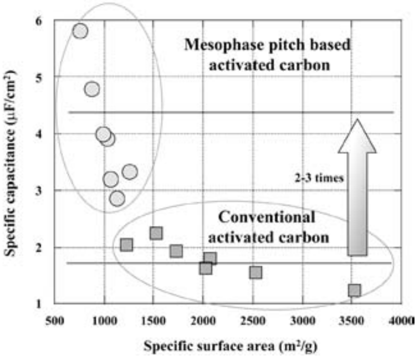

FIGURE 4 A relationship between specific capacitance per specific surface area which derived by a calculation (μF/cm^2) and specific surface area (m^2/g) of activated carbons (See Color Plate XI).

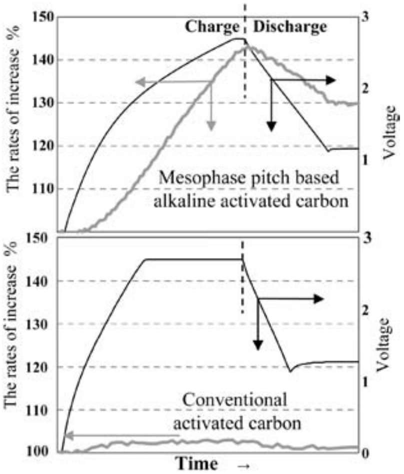

FIGURE 5 Change of thickness of electrodes assembly and 1st charge-discharge curves (See Color Plate XII).

plane is referred to the other literature (6). According to the report, the capacitance of edge plane of HOPG (highly oriented pyrolytic graphite) was strongly dependent on the electrode potential. Accordingly, the authors should suppose that capacitance of the edge plane activated by KOH may be greatly variable by shift of Fermi level in graphene layers which is induced by charge/discharge. It is suggested that the reason why thickness of activated carbon electrodes changes in the novel method was

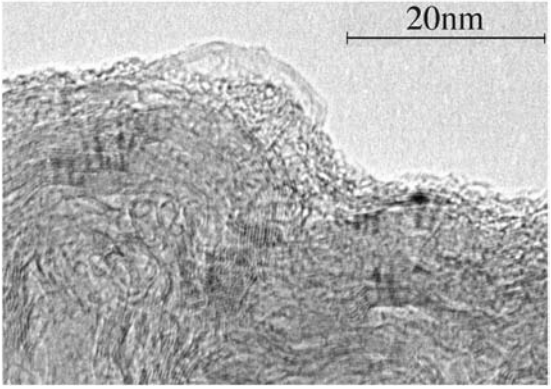

FIGURE 6 TEM micrograph. Several stacked graphene layer was observed. Pore structure of activated graphitizing carbon with KOH activation was imaged by contrast of a photograph.

attributed to an increase of adsorbed ion on the edge plane activated by KOH.

4. CONCLUSION AND MECHANISM OF ALKALINE ACTIVATION

The reason why activated graphitizing carbon prepared by chemical activation showed high capacitance in spite of lower specific surface area was

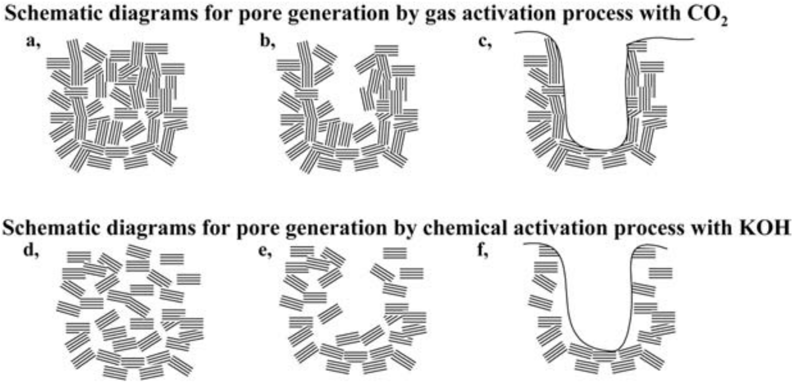

FIGURE 7 The schematic model for suggested structural change with gas activation in conventional activated carbon (a–c) and with chemical activation in novel method by KOH (d–f).

attributed to a difference in activation mechanism. Figure 7 shows the schematic model for suggested structural change with gas activation in conventional activated carbon (a–c) and with chemical activation in novel method by KOH (d–f). For chemical activation, KOH is impregnated to the site of functional groups and unstable Electron state on edge plane, the edge carbon atoms in graphene react with potassium peroxide derived from KOH decomposition. For gas activation, edge recession by preferred reaction on edge plane stops in the place which contact with basal plane of carbon layer. Therefore, all the inside of the pore wall almost consists of basal plane. However, inside of the pore wall with the novel method was dominated by edge plane.

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