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Short communication

Structures and electrochemical performances of pyrolized carbons from graphite oxides for electric double-layer capacitor

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Abstract

The structural features and the electrochemical performances of pyrolized needle cokes from oxidized cokes are examined and compared with those of KOH-activated needle coke. The structure of needle coke is changed to a single phase of graphite oxide after oxidation treatment with an acidic solution having an $NaClO_3$/needle coke composition ratio of above 7.5, and the inter-layer distance of the oxidized needle coke is expanded to 6.9 Å with increasing oxygen content. After heating at 200 °C, the oxidized needle coke is reduced to a graphite structure with an inter-layer distance of 3.6 Å. By contrast, a change in the inter-layer distance in KOH-activated needle coke is not observed.

An intercalation of pyrolized needle coke, observed on first charge, occurs at 1.0 V. This value is lower than that of KOH-activation needle coke. A capacitor using pyrolized needle coke exhibits a lower internal resistance of 0.57 Ω in 1 kHz, and a larger capacitance per weight and volume of $30.3\,\mathrm{F\,g^{-1}}$ and $26.9\,\mathrm{F\,ml^{-1}}$, in the two-electrode system over the potential range 0–2.5 V compared with those of a capacitor using KOH-activation of needle coke. This better electrochemical performance is attributed to a distorted graphene layer structure derived from the process of the inter-layer expansion and shrinkage.

Keywords: Electric double-layer capacitor; Activation procedure; Graphite oxide; Pyrolized carbon; Specific capacitance; Needle coke

1. Introduction

Electric double-layer capacitors (EDLCs) have been widely used as energy storage devices for memory back-up systems, and are receiving considerable attention as a promising high-power energy source for electric devices and hybrid electric vehicles [1–3]. The energy storage mechanism of EDLCs is based on the fact that an electric double-layer is formed at the boundary between the electrode and an electrolyte. In electronic devices requiring higher energy density due to their smaller size, the higher specific volume capacitances of EDLCs is an important factor. However, conventional physically/chemically activated carbons possess a micro-porous structure with a moderately high specific surface area, which has limited the specific volume capacitance to less than $20\,\mathrm{F\,ml^{-1}}$, due to low electrode density, in two-electrode systems [4].

In recent years, an alkali-activation procedure has been investigated to obtain larger specific volume capacitance from graphitizable carbons. These carbons, activated with alkaline solutions such as KOH, NaOH, and K_2CO_3 at 700–900 °C, exhibit larger specific volume capacitances of $20–30\,\mathrm{F\,ml^{-1}}$ [5–7]. It is reported that the first cycle, that is, electric field activation, makes the electrolyte ions intercalate into the graphene layers of the carbons, which introduces the small pore structure of the electrode. Such structural changes during the first cycle are irreversible and provide larger specific volume capacitance. However, it has been also reported that this process has several problems, such as a high activation cost, corrosion of the activation vessel and the rapid degradation of capacitance during charge–discharge cycling. This electrochemical

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performance may be associated with a high diffusion resistivity of the electrolyte ions to penetrate the graphene units.

In general, the activated carbons that have been developed up to now have a pore structure that is generated by partial etching in the interior of the carbon material. They have different electrochemical characteristics, according to the microstructure of the pores that is adjusted by diverse methods.

As an activation procedure, in this study, the oxidation of graphitizable carbon with dilute nitric acid and sodium chlorate ($NaClO_3$), combined with heat treatment, is attempted to achieve an electrochemically stable active material with a large capacitance. The structural features and the electrochemical performances of pyrolized carbons from graphite oxides are examined in terms of the weight ratio of $NaClO_3$ and carbon, together with the heating temperature. A comparison is made with KOH-activated carbon.

2. Experimental

2.1. Oxidation and heat-treatment conditions of needle cokes

Needle coke derived from coal tar pitch and calcinated at 1100 °C was supplied by Nippon Steel Chemical Co. Ltd. For the oxidation of needle coke, needle coke (5 g) and sodium chlorate (in the range 12.5–50 g) were put in 70 wt.% nitric acid (150 ml), and then stirred at room temperature for 24 h. For comparative purposes, activation of the same needle coke was carried out with KOH (KOH/coke = 4/1, w/w) at 700 °C for 2 h under an argon atmosphere. After oxidation or activation, the needle cokes were washed thoroughly with distilled water and heated under vacuum at 100 and 200 °C. The rate of increase in temperature was 3 °C min^{-1}.

2.2. Preparation of electrode and cell capacitor

Needle cokes, pyrolized from oxidized needle cokes by heating at 200 °C were used as active materials for EDLC. The electrodes were composed of pyrolized needle coke, carbon black as an electric conductor and polytetrafluoroethylene emulsion (PTFE) as a binder in a weight ratio of 80:10:10. The components of the electrode were mixed at 2000 rpm in the solvent to make a slurry. A paste, obtained by drying the slurry, was repeatedly roll-pressed for modification of the sheet-type electrode.

Cell capacitors were constructed with an electrolyte impregnated in the separator sandwiched between the electrodes, whose size was 2 cm × 2 cm. These assemblages were housed in Al-laminated film cells. After an organic electrolyte solution of 1.2 M Et_4NBF_4 (tetraethylammonium-tetrafluoroborate) in acetonitrile solution was introduced, the capacitors were sealed, taking out the leads.

2.3. Structural and electrochemical analyses

The structural changes of the needle cokes were measured by X-ray diffraction using Cu Kα radiation. The micrographs of the polished needle cokes were observed with a field emission scanning electron microscope (SEM). Surface area and pore volume of the needle coke were measured according to the BET method by physical adsorption of nitrogen at 77 K, using an automatic absorption system. Crystal structure analysis was undertaken by Raman spectroscopy. The capacitors were charged and discharged at a constant current of 2 mA cm^{-2} between 0 and 2.5 V with a MACCOR (model no. MC-4) test system. The capacitance was calculated from:

$$C = \frac{it}{V} \quad (1)$$

where t is the time period, V is the voltage change, and I is the constant discharge current.

3. Results and discussion

3.1. Structures of needle cokes oxidized with $NaClO_3 + HNO_3$ and activated with KOH

Table 1 shows the preparation conditions and the properties of needle cokes oxidation-treated with dilute nitric acid and sodium chlorate (the N samples), and activated with KOH (sample K1). The values of O/C for the N samples after 100 °C-heating increase with increase in the ratio of $NaClO_3$/needle coke, and lower values of H/C and O/C in a N sample after 200 °C-heating are obtained. However, the H/C and O/C for the K1 sample have far much lower values, and it is assumed that the heating condition has almost no influence on KOH-activation of needle coke. The data in Table 1 show that the N3 sample after 200 °C-heating has a larger surface area and pore volume of 14 $\text{m}^2\,\text{g}^{-1}$ and 0.02 $\text{cm}^3\,\text{g}^{-1}$ compared with the K1 sample after 200 °C-heating.

Table 1
Preparation and properties of needle cokes oxidation-treated with $NaClO_3 + HNO_3$ and activated with KOH

Sample	Chemical	Reaction condition	Reagent/coke	E.A. (after 100 °C-heating)		E.A. (after 200 °C-heating)		Sp ($\text{m}^2\,\text{g}^{-1}$)	Vpore ($\text{cm}^3\,\text{g}^{-1}$)
				H/C	O/C	H/C	O/C		
N1	$NaClO_3 + HNO_3$	24 h at 25 °C	$NaClO_3$/coke = 2.5/1	0.16	0.10				
N2	$NaClO_3 + HNO_3$	24 h at 25 °C	$NaClO_3$/coke = 5.0/1	0.09	0.16				
N3	$NaClO_3 + HNO_3$	24 h at 25 °C	$NaClO_3$/coke = 7.5/1	0.10	0.30	0.04	0.22	14	0.02
N4	$NaClO_3 + HNO_3$	24 h at 25 °C	$NaClO_3$/coke = 10/1	0.11	0.40				
K1	KOH	2 h at 700 °C	KOH/coke = 4/1	0.02	0.2×10^{-3}	0.03	0.3×10^{-3}	4.3	2×10^{-5}