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Short communication

Oxygen-doped activated carbon fiber cloth as electrode material for electrochemical capacitor

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ABSTRACT

Novel oxygen-doped activated carbon fiber cloths (OACFC), with different compositions of surface oxygen functionalities, have been prepared by direct electrooxidative/reductive methods in an undivided electrolytic cell filled with high purity water without a supporting electrolyte under high voltage conditions. The morphology and surface chemical composition of the materials have been investigated by SEM, Raman and XPS spectroscopies. They revealed an electrochemical erosion of the CF surface upon activation, concomitant with a strong change of the D/G ratio of characteristic Raman bands and the surface O/C atomic ratio, respectively. Thus pretreated material was tested as electrodes for an electrochemical capacitor by cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy measurements in 3.75 M H_2SO_4. The performance of the electrochemical capacitor based on modified carbon electrodes was compared to that of an analogous device with unmodified carbon. The measurements revealed altered electrochemical behavior of the OACFC in terms of the determined capacitances. The proposed activation method is also superior to other electrochemical activation procedures, since it uses much less energy per CF surface or mass.

1. Introduction

Generally, two types of electrochemical capacitors have been studied: (i) an electrochemical double-layer capacitor (EDLC), in which capacitance arises from the charge separation at the electrode/electrolyte interface, at materials such as activated carbons (AC); and (ii) the pseudocapacitor, in which capacitance arises from a faradic reaction occurring at the electrode surface in contact with the electrolyte. Materials showing the latter type of activity contain transition-metal oxides [1] or electroactive polymers [2]. Frequently, synergetic effects may be achieved when the capacitive charging of the double-layer overlaps with a faradic redox (pseudocapacitive) reaction(s) and the two storage mechanisms work in parallel. Such a phenomenon has been observed for instance for AC materials enriched with functional groups containing heteroatoms (mainly oxygen or nitrogen). The presence of these functionalities gives rise to an acid/base and redox activity of the carbon materials [3,4], that enhances their specific capacitances.

Various methods have been proposed to introduce oxygen or other heteroatoms to carbon materials in order to boost their capacitive properties. Recently, Raymundo-Pinero et al. [5] showed that an oxygen-rich carbon material prepared through carbonization of a seaweed biopolymer exhibited good electrochemical performance. Also Ling et al. [6] reported that oxygen-doped activated carbons prepared from bituminous coal through quick KOH activation exhibit outstanding electrochemical performances for EDLC.

Physicochemical properties of carbon materials are strongly related to their structure and chemical composition. Therefore, various modification procedures have been the subject of many researches to tailor properties of these materials for certain applications. These include for instance plasma treatment [7], laser activation [8], chemical activation [9] and electrochemical activation. The last method is superior to the other three in terms of controllability. The activation procedures reported to date are mainly based on the anodic polarization of carbons at potentials where electrolyte (water) discharge is apparent concomitantly with oxidative erosion of carbon producing CO_2 and the supporting electrolytes used contain mineral acids and bases [10] or different buffers and salts [11]. Procedures based on cathodic treatment are rarely reported [12]. On the other hand, other researchers claim that electrochemical anodization followed by cathodization yields the most active carbon materials for certain uses [13].

In this paper we propose a novel oxygen-doped activated carbon fiber cloth (OACFC) containing sufficiently high amounts of oxygen incorporated in the carbon framework, capable of participation in redox processes. Such an oxygen-rich carbon material with a hydrophilic character and pseudocapacitance properties shows high performance as an electrode material for EDLC.

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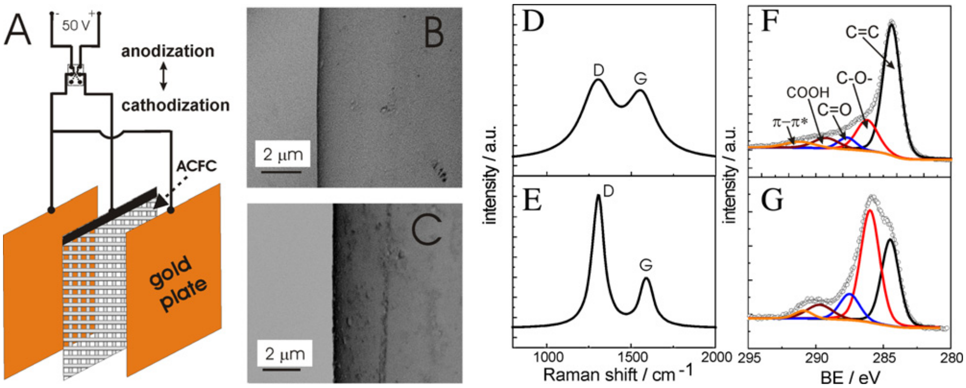

Fig. 1. Scheme of the setup used for electrochemical activation of ACFC; (B, C) SEM images of virgin and electrochemically activated ACFC, respectively; (D, E) Raman spectra of the same two samples; (F, G) XPS spectra of the same samples.

Modification of the surface of activated carbon fiber cloth (ACFC) with oxygen functionalities was attained by direct electrochemical oxidation/reduction of virgin cloth in the undivided cell filled with high purity water under high voltage conditions. To the best of our knowledge, such an activation procedure for ACFC has not yet been reported.

2. Experimental

2.1. ACFC and its electrochemical activation

The commercial ACFC of 2000 $m^2 g^{-1}$ was selected as electrode material for EDLC (Kynol® Europa GmbH, No ACC). High purity deionized water was used as the electrolyte in an undivided electrolysis cell equipped with an untreated ACFC (20 mm × 20 mm) electrode and two Au plates (20 mm × 20 mm) as counter electrodes (Fig. 1A); The distance between ACFC and Au plates was set at 2 mm. Electrochemical activation was carried out by applying a constant voltage of 50 V between electrodes, first anodic to ACFC, followed by voltage reversal (both steps 15 min long). After that ACFC was soaked with fresh deionized water for 15 min, and then dried at 40 °C for 1 h.

2.2. Materials characterization

Surface morphologies of ACFC and OACFC were investigated under a scanning electron microscope (Philips SEM 515). XPS spectra of virgin and electrochemically treated ACFC were obtained with a VSW photoelectron spectrometer (Vaccum System Workshop Ltd., England). Raman spectra of tested samples were recorded using a Bruker IFS66v/S FT-IR/Raman spectrometer with an Nd:Y laser as the light source operating at a 1064 nm wave length with a power of 10 mW. The wettability of the samples was analyzed by the simple observation method.

2.3. Electrochemical measurements

The capacitor electrodes were made in the form of discs of OACFC (1 cm^2). The EDLC was assembled by sandwiching a Fisher® separator between two electrodes, and placing them into the test vessel (the Swagelok® system with stainless steel collectors). Prior to tests the capacitor was conditioned at a temperature of *ca.* 50 °C in order to reach the equilibrium between the electrodes and the electrolyte (3.75 M H_2SO_4). Electrochemical properties of the EDLC were studied by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy, using electrochemical analyzer systems (Atlas 0461, Atlas-Solich, Poland, and μAutoLab FRA2 type III, EcoChemie, Netherlands).

3. Results and discussion

3.1. Structural characteristics

Fig. 1A presents the electric circuit used for electrochemical pretreatment of ACFC and Fig. 1B–G – general characterization data for

Table 1
Relative quantities (%) of different energy levels and atomic ratios for various OACFC samples.

Energy level or atomic ratio[a]	Sample			
	Untreated	Cathodized	Anodized	Anodized/cathodized
C 1s				
Graphite (284.6)	62.9	46.4	33.3	32.7
Alcohol, phenol, ether (286.0)	18.4	30.1	36.6	45.4
Carbonyl (287.4)	6.0	14.7	16.1	11.1
Carboxyl, ester, (289.4)	7.6	6.0	9.0	7.9
π–π^* (290,6)	5.2	2.8	4.9	3.0
O 1s				
(C=O), carbonyl O in COOR (531.5)	32.1	8.3	5.5	–
(C-OH, C-O-C) (532.4)		74.7	80.6	100
Noncarbonyl O in COOR (533.8)	50.4	16.9	10.8	–
$H_2O_{(ads)}/O_{2(ads)}$ (535.5)	17.5	–	3.0	–
N 1s				
C=N– (399.8)	–	81.7	100	100
Pyridinic N (401.0)	100	18.3	–	–
O/C	0.09	0.15	0.33	0.33
(O + N)/C	0.10	0.22	0.36	0.38
C_{ox}/C_{gr}	0.67	1.15	2.00	2.06
$C_{(C–O–)}/C_{(C=O)}$	3.07	2.05	2.28	4.10

[a] BE values are given as average values.