Short communication

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

Grzegorz Milczarek*, Aleksander Ciszewski, Izabela Stepniak

*Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Piotrowo 3, 60-965 Poznan, Poland*

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.

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## 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.

* Corresponding author. Tel.: +48 616652158.
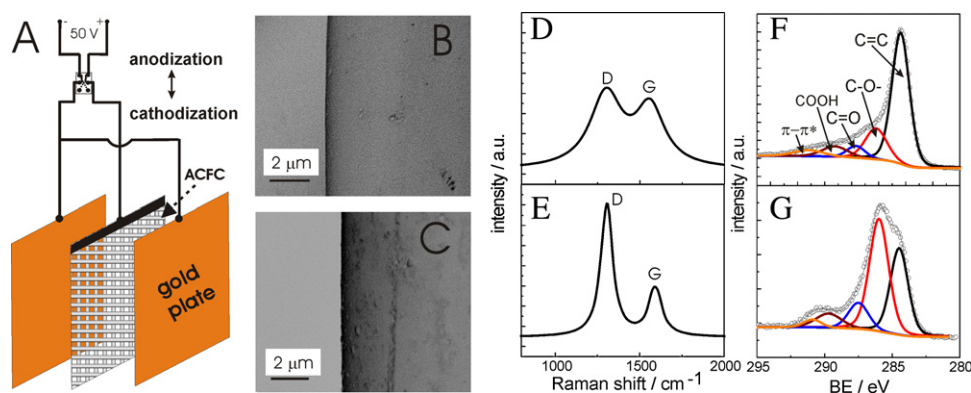  *E-mail address:* grzegorz.milczarek@put.poznan.pl (G. Milczarek).

**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 spec-

tra 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$_2$SO$_4$). 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 |
| $\pi$–$\pi^*$ (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$_2$O$_{(ads)}$/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.

**Table 2**
A comparison of energy consumption during electrochemical pretreatment of OACFC in different electrolytes.

| Carbon material | Electrolyte | $j_{act}$/A m$^{-2}$ | $Q_{act}$/C m$^{-2}$ [a] | O/C | Ref. |
|---|---|---|---|---|---|
| PAN CF | Ammonium carbonate | 50 | $1.73 \times 10^3$ | 0.18 | [18] |
| PAN CF | Ammonium oxalate | 6 | $0.564 \times 10^3$ | 0.15 | [19] |
| KYNOL® ACFC | H$_2$O | $\sim 1.04 \times 10^{-4}$ | 0.094 (188 C g$^{-1}$) | 0.33 | This work |

[a] Calculated from modification current, time and real surface area of CFs in contact with the electrolyte.

parent and modified samples. These data show that: (i) the surface of individual fibers becomes roughened after the electrochemical pretreatment most probably due to the erosion of the material accelerated by massive gases evolution, (ii) the ratio of two main Raman bands (D/G) significantly increases after activation, meaning that it disrupts the graphitic structure of ACFC, (iii) the XPS analysis reveals the introduction of significant amounts of different oxygen functionalities during the activation procedure. The detailed analysis of XPS data for an unmodified material and after a high voltage treatment at different polarizations is presented in Table 1.

Untreated ACFC samples were originally hydrophobic and repelled a drop of water. However, after the anodization/cathodization treatment their character changed. Drops of water put on the modified surface changed their volume very slowly at the beginning and disappeared completely after *ca.* 3 s. This qualitative observation indicates a hydrophilization process of the tested samples owing to the introduction of some polar groups onto their surface by the procedure in question.

### 3.2. Electrochemical characteristics

A detailed analysis of electrochemical performance of the tested capacitors with parent and electrochemically modified ACFC electrodes is presented in Fig. 2. Fig. 2A shows cyclic voltammograms (CVs) of two electrode cells with tested materials in 3.75 M H$_2$SO$_4$ as the electrolyte; scan rate of potential 10 mV s$^{-1}$. The CV profiles were nearly rectangular in shape, suggesting good capacitive devices in both cases. In addition to the current due to the charge/discharge of the electrical double-layer, cathodic and anodic humps are observed. The humps are more pronounced in the case of OACFC. For activated carbons, these peaks are traditionally ascribed to redox reactions of oxygenated surface functionalities, such as the quinone/hydroquinone (Q/HQ) pair or pyrone-like structures [14,15]. This interpretation fits well with XPS results showing increased amounts of quinone-like and pyrone-like functionalities (bands C=O and C–O in Table 1) for modified ACFC. According to Nian and Teng [16], the effect of surface functional groups on the capacitance was contingent on the type of functional groups in a way that C–OH and C=O were believed to increase the specific capacitance, while COOH behaved in the opposite way. This speculation could support our XPS results that revealed only a minute increase of the COOH component of the C 1s band, while C–OH and C=O components increased significantly after electro-

chemical activation. Due to the presence of a high population of these groups, specific capacitance determined from the CV measurements increased from 161 F g$^{-1}$ to 172 F g$^{-1}$, when comparing unmodified and modified electrodes.

AC impedance spectroscopy, which distinguishes resistance and capacitance of devices, was further employed to analyze the performance of the capacitor cells. The impedance spectra of these cells, as the Nyquist plots, are shown in Fig. 2B (after 10 cycles of the charge/discharge test at the current of 10 mA). The determined capacitances were 144 F g$^{-1}$ and 169 F g$^{-1}$ for unmodified and modified electrodes, respectively. For each sample there is a semi-circle intersecting the real axis in the high frequency region, and the plot transforms to almost a vertical line with decreasing frequency. From the point of intersecting with the real axis in the range of high frequency, resistance of the cell was estimated to be 0.8 Ω for the OACFE electrodes under these experimental conditions, which is a little bit lower to that for the unmodified electrodes, i.e. 0.9 Ω. In the low frequency region, where a nearly complete penetration into pores would be allowed, the vertical line exhibits the domination of the capacitance behavior at the electrolyte/carbon interface.

For a more detailed capacitance analysis we relied on the approach by Taberna et al. [17] to separate the real part of capacitance C′ from its imaginary part C″ and to plot them as a function of frequency. From these relationships it is possible to deduce the relaxation time constant that defines the frontier between capacitive behavior and resistive behavior of the capacitor. The data show (Fig. 2C) that time constants are very different, i.e. 11.9 and 5.9 s for ACFC and OACFC electrodes, respectively. Thus we can speculate that the capacitor with modified electrodes is capable of delivering its stored energy over two times faster than the capacitor with unmodified electrodes, i.e. at a higher power. Preliminary stability tests performed at galvanostatic charging/discharging mode at current density of 0.5 A g$^{-1}$, revealed that after 4000 cycles, the modified material retained 97% of its initial capacity, which is similar to the stability observed for untreated ACFC.

The excellent electrochemical performance of OACFC could be ascribed to the following characteristics: (i) a large surface area for OACFC provides sufficient electrode/electrolyte interfaces for charge accommodation, (ii) the presence of oxygen enhances surface wettability of OACFC to ensure an adequate utilization of the exposed surface for charge storage, and (iii) the presence of oxygen in the carbon network may yield a stable pseudo-capacitance through faradic charge-transfer reactions. The proposed activation
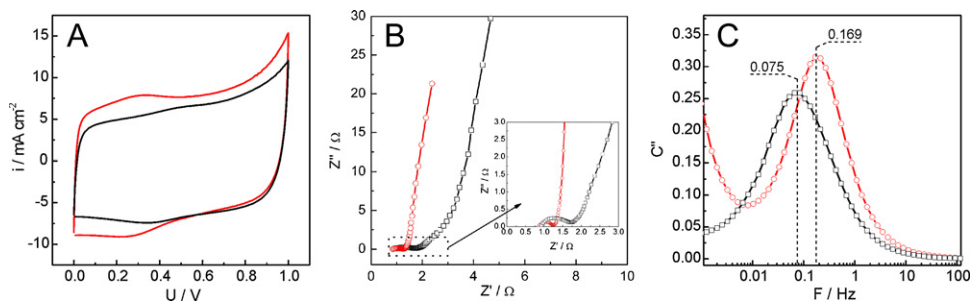


**Fig. 2.** (A) Cyclic voltammetry of a symmetrical capacitor utilizing virgin and modified ACFC; (B) electrochemical impedance spectra of the same capacitors; (C) a comparison of C″ derived from electrochemical impedance spectra. Data plotted in black refer to virgin material and those plotted in red to the modified counterpart.

method is also superior to other electrochemical activation procedures, since it uses much less energy per carbon surface or mass (Table 2).

## 4. Conclusion

A straightforward strategy was developed to activate electrochemically ACFC for the application in an electrochemical capacitor. It is based on a high voltage treatment of the parent ACFC in deionized water in the absence of any supporting electrolyte.

The obtained activated samples were found to be effective electrode materials for electrochemical capacitors, superior in specific capacitance and charge/discharge time constants, owing to their high specific surface area, high oxygen content and good wettability. The activation method is assumed to be general and will be further applied for the activation of other carbon materials.

## Acknowledgment

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