Sustainable porous carbons on the basis of biomaterials for supercapacitors

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Introduction: The biomass is renewable sources of energy, deriving from plants and animals. In addition, some residues of agricultural waste biomass can be considered as precursors for the production of variety of activated carbons. This approach is cheap, readily available and considered as a veritable way of combating the problems with waste disposal in the agricultural industries. Last decade, special attention is paid on the nanostructured carbon-based materials fabricated from renewable bio-resources, which have great potential in the rechargeable energy storage systems [1].

Symmetric supercapacitors are now attracting both the research and technology interest since they provide excellent stability during numerous cycling. The function of supercapacitors is based on the reversible adsorption of electrolyte ions into electrode materials. Therefore, the appropriate selection of electrode materials determines the supercapacitors' performance. The texture of the used material and its surface chemistry are the most important factors that control the electrochemical performance of carbon materials, since they ensure high energy density in such device. The modification of surface functional groups of carbon materials usually leads to changes in the double-layer properties such as wettability, capacitance, electrical conductivity, zero point charge and self-discharge characteristics [2, 3].

The present work reports new data on the application and electrochemical characterisation of "active" carbons, obtained by pyrolysis of coconuts, as electrode materials for supercapacitors.

Experimental: In the present work two activated carbons (YP-50F and YP-80F) are used as electrode materials for the assembly of supercapacitor cells. The activated carbons (ACs) are commercial products kindly provided by "Kuraray Europe" GmbH and they are obtained from coconuts used as a raw material.

Materials Characterization of the electrode materials: The samples were studied by the following physicochemical methods of analysis. The surface composition of ACs were investigated by X-ray photoelectron spectroscopy (XPS) using AXIS Supra electron- spectrometer (Kratos Analitycal Ltd.) and achromatic AlKα radiation with photon energy of 1486.6 eV and charge neutralisation system. The binding energies (BE) were determined with an accuracy of ±0.1 eV. The chemical composition in the depth of the films was determined monitoring the areas and binding energies of C1s, O1s and F1s photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd. the concentrations of the different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors. The chemical composition of the surface functional groups was determined by the Böhm method. The porous texture of the samples was examined by low-temperature (77.4 K) nitrogen adsorption using Quantachrome (USA) NOVA 1200e instrument. The specific surface area was evaluated by the BET method at a relative pressure p/p_o in the range of 0.10-0.30. The total pore volume is calculated according to Gurwitsch's rule at $p/p_o = 0.99$. The pore size distribution is estimated by using the Barett-Joyner-Halenda method.

Electrochemical tests: The activated carbon materials are used to produce electrodes for electrochemical cells for capacity measurements. The supercapacitor cell contains two identical electrodes from activated carbon (80%), graphite ABG 1005 EG-1 (10%) and binder (10%). Polytetrafluoroethylene (PTFE) as binder was previously added to activated carbon using a standardized procedure [4]. The formed sheet electrodes were dried at 140 ° C for 12 hours and pressed under 20 MPa pressure. The electrodes were soaked in the electrolyte (6M KOH) under vacuum and then mounted in a coin-cell with Viledon 700/18F separator and filled with electrolyte. The capacitor cells were subjected to galvanostatic charge-discharge cycling using an Arbin Instrument System BU-2000.

The changes of electrode materials after electrochemical test were analyzed by means of *ex-situ* XPS techniques.

Results and discussion: The specific surface area and the total pore volume of ACs are measured and their values are presented in Table 1. Both YP-50F and YP-80F ACs display high specific surface area, which is mainly due to the development of micropores.

ACs can be distinguished on the basis of their functional groups (Table 2). As one can see, the phenolic, carboxylic and basic groups present in comparable amounts for both YP-50F and YP-80F, while the lactone groups are detected for YP-50F only.

Table 1. Main texture parameters of the used carbons materials - specific surface (S_{BET}), total pore volume (V_t), micropore volume (V_{mi})

Sample	S_{BET} m^2g^{-1}	V_t cm^3g^{-1}	V_m cm^3g^{-1}
YP-50F	1756	0.80	0.62
YP-80F	2385	1.28	0.73

Table 2. Surface functional groups, determined by the Böhm method, mmol g^{-1}

Samples	Phenolic $mmolg^{-1}$	Lactone $mmolg^{-1}$	Carboxyl $mmolg^{-1}$	Basic $mmolg^{-1}$
YP-50F	0,2319	0,0276	0,0017	1,1325
YP-80F	0,2388	-	0,0014	1,1246

The symmetric supercapacitors cells were studied at constant current charge-discharge mode in the voltage range 0 -1.2V (Fig. 1). As one can see, both YP-50F and YP-80F have very close capacitance values at current load varying between 60 and 360 mA/g (Fig. 1a). The supercapacitor with carbon YP-80F demonstrate stable cycleability more than 2000 cycles, while the capacitance of the cell with carbon YP-50F drops sharply after the 600th cycle (Fig. 1b).

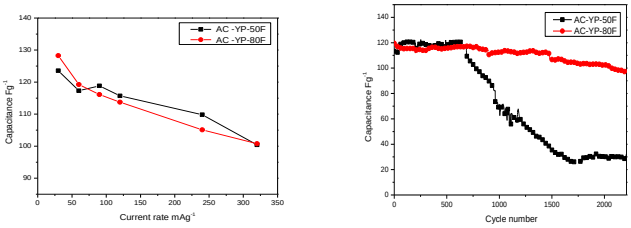

Fig. 1. Discharge capacitance as a function of the current load (a) and cycle number at 60 mAg^{-1} (b) for symmetric supercapacitors with used carbons

To understand this behaviour, Figure 2 summarizes the XPS spectra of pristine carbons and carbons after the electrochemical test. It appears that the surface YP-50F is covered with carboxylic groups in a higher extent than that of YP-80F, thus indicating the changes in the surface functionality groups during of electrode working in 6 M KOH electrolyte. The *ex-situ* XPS data can be related to the presence of lactone functional groups in YP-50F (Table 2) which generate both CO and CO_2 during decomposition [5].

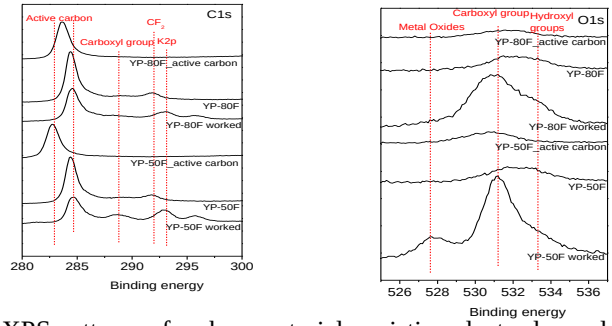

Fig. 2. XPS patterns of carbon materials, pristine electrodes and worked electrodes

Conclusions: Two commercial carbons (YP-50F and YP-80F) are tested as electrode materials in symmetric supercapacitors applying charge/discharge cycling tests. The supercapacitor with YP-80F carbon electrodes demonstrates an excellent cycleability, stable capacity at prolongs cycling (over 2000 cycles) and high efficiency of charge/discharge. The electrochemical cell with YP-50F carbon showed instability in long-term testing due to the presence of lactone groups in its composition and change in its morphology.

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