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Activated carbon obtained by pyrolysis of coconut shells as electrode material for hybrid non-aqueous supercapacitor cells

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Introduction: Hybrid supercapacitors employ one electrode storing charge by Faradaic reactions and another by capacitive double layer formation. The aim is to synergistically combine the merits of battery and supercapacitor technologies, to produce cells that show higher specific energy than supercapacitors and higher specific power and longevity than batteries (Béguin*et al*, 2014).

Biomass is biological material from living, or recently living organisms, most often referring to plants or plant-derived materials, which can be converted to higher value products or energy. Such are the carbon materials whose surface area and porosity characteristics re influenced by the nature of the original biomass feedstock and the process conditions of pyrolysis and activation (Heschel*et al.* 1995).

The coconut shell produces nanostructured carbon with a relatively low internal resistance and good electrical conductivity properties, which determines their potential in the rechargeable energy storage systems. Therefore, in recent years the efforts of many researchers are focused on the use of various methods, including pyrolysis, to improve their pore properties with a combination of superior ion and electron transfer properties (Zhang *et al*, 2017). In our previous studiesthe relations between texture structure, functional groups and surface compositions of activated carbons obtained from coconut pyrolysis and their electrochemical performance as electrodes in symmetric supercapacitors are investigated. The results obtained showed very high and stable capacitive properties of in 6 M KOH (Karamanova et al, 2019).

The present work reports new data on the performance of “active” carbons, obtained by pyrolysis of coconuts, as electrode materials in hybrid supercapacitor systems. As a “battery-like” electrode, nanotube sodium titanate $Na_2Ti_2O_4(OH)_2$ is selected. This oxide has been shown to display high performance in sodium-ion hybrid capacitor (Babu and Shaijumon 2017). For the sake of comparison, lithium titanate $Li_4Ti_5O_{12}$ is also used as “battery-like” electrode. The capacitive performance of carbon and oxide electrodes is determined by galvanostatic experiments in non-aqueous lithium and sodium electrolytes.

Experimental: In the present work two types of electrode materials are used for assembly of supercapacitor cells - activated carbons and electrochemically active Na- and Li-titanate. The activated carbons (YP-50F and YP-80F) having large surface area (>1700 m^2g^{-1}) and a basic character are commercial products kindly provided by “Kuraray Europe” GmbH and they are obtained from coconuts used as a raw material. The sodium titanate with nanotube morphology is synthesized hydrothermally using NaOH and TiO_2. Commercial product of nano-sized lithium titanate, $Li_4Ti_5O_{12}$ (Sigma Aldrich, USA), is utilized. The lithium and sodium electrolytes comprise $LiBF_4$, $NaBF_4$, $LiPF_6$ and $NaPF_6$ salts desolved in mixed EC/DEC and PC solutions.

To get inside into surface and bulk electrode changes during electrode cycling the physicochemical characterization of activated carbons and composites are carried out before and after electrochemical tests by XPS spectroscopy, SEM and BET analyses. The X-ray photoelectron spectroscopy (XPS) was conducted using AXIS Supra electron- spectrometer (KratosAnalitycal 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 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/po in the range of 0.10-0.30. The total pore volume is calculated according to Gurwitsch's rule at p/po = 0.99. The pore size distribution is estimated by using the Barett-Joyner-Halenda method.

The activated carbons and titanates are used to fabricate composite electrodes for electrochemical measurements. The symmetric supercapacitor cells contain two identical electrodes from activated carbons (80%), graphite ABG

1005 EG-1 (10%) and polyvinylideneflyoride (10%) as binder. The hybrid cells are assembled by an electrode of activated carbon *versus* electrode containing mechanical mixture between activated carbon and Na- or Li-titanate in different amount wt.%. The formed sheet electrodes were dried at 140 ° C for 12 hours and pressed under 20 MPa pressure. The electrodes were soaked in the different organic electrolytes: 1M $LiBF_4$ and 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (mixture 1:1), 1M $NaBF_4$ and 1M $NaPF_6$ in propylene carbonate. The electrochemical cells were subjected to galvanostatic charge-discharge cycling using an Arbin Instrument System BU-2000. The test program is carried out at constant current mode at different current load (from 30 to 600 mAg^{-1}) at 25 cycles and room temperature. Some cells are subjected to continuous cycling charge/discharge cycles.

Result and discussion:

Recently, we have demonstrated that both YP-50 and YP-80 are suitable as electrodes in symmetric supercapacitors working in aqueous electrolytes (Karamanova et al, 2019). In this study, we replace the aqueous with non-aqueous electrolyte. The results show that the symmetric supercapacitors display stable capacitance and high efficiency. It is noticeable that the texture characteristics of the materials affect much more strongly the capacitance compared in alkaline medium.

Figure 1 illustrates the typical hybrid behavior of a supercapacitor assembled by composite electrode (YP-50 + 25 wt.% $Na_2Ti_2O_4$), YP-50 electrode and electrolyte $NaPF_6$ - PC at a current load of 30 mAg^{-1}.

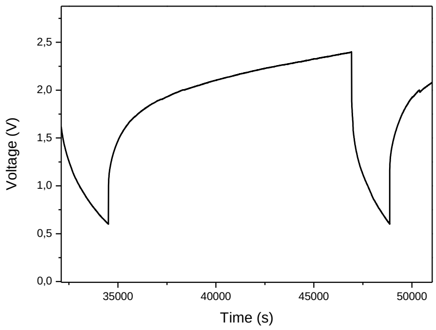

Fig. 1 Galvanostatic charge/discharge curves for hybrid supercapacitor cell with composite electrode YP-50 + 25 wt.% $Na_2Ti_2O_4(OH)_2$ in $NaPF_6$ - PC at a current load of 30 mAg^{-1}

The hybrid supercapacitors using electrodes of Na- or Li-titanates and activated carbon are characterized with high capacitance and stable capacitance behaviour at prolong cycling in comparison with the symmetric supercapacitors. This can be related to faradaic reaction occurring on Na- and Li-titanates. The contribution of the morphology of titanates (i.e. varying from nanotube to nano-sized particles) to their electrochemical characteristics should also be taken into account.

The obtained results show, that the activated carbons obtained by pyrolysis of coconut shells are suited for utilization as electrode materials in both symmetric and hybrid supercapacitors. The work on optimization of compositions and structure of the “battery-like” electrodes, as well the composition of the non-aqeous electrolytes is in progress.

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