

Study on adsorption properties of carbon electrode materials for electrochemical supercapacitors

Christian Girginov, Lozan Stoyanov, Stephan Kozhukharov,
 Antonia Stoyanova, Mladen Mladenov, Raicho Raicheff

Study on adsorption properties of carbon electrode materials for electrochemical supercapacitors. Two carbons (commercial products "TDA-Research" and "Norit-CGP") are characterized structurally and morphologically, and tested as electrode materials for electrochemical supercapacitors applying XRD, TEM, nitrogen gas adsorption methods in conjunction with electrochemical cycling voltammetry and impulse chronopotentiometry techniques. The results suggest for a higher adsorption capability of the TDA-Research carbon and the charge/discharge cycling tests of symmetric capacitors cells assembled with the carbon electrodes studied and an organic electrolyte (1M LiBF₄/ethylene carbonate and dimethyl carbonate) demonstrate an excellent cycleability, stable capacity (about 60 Fg⁻¹) at prolong cycling and high efficiency of charge – discharge (about 95%) of the supercapacitor assembled with those type carbon electrodes.

Keywords: carbon, electrode materials, adsorption properties, supercapacitors, charge/discharge cycling

INTRODUCTION

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, are relatively new generation of energy storage devices. They are rapidly gaining more attention because, of their simple principle, pulse power supply, long cycle life, and high dynamics of spreading charge [1-4]. With many thousands of times higher power density than lithium ion batteries and much larger energy density than conventional capacitors, supercapacitors offer a promising approach to meeting the increasing power demands of energy storage systems.

A supercapacitor stores energy using either ion adsorption (electrical double layer capacitors) or fast and reversible faradic reactions (pseudo-capacitors). These two mechanisms can function simultaneously depending on the nature of the electrode material.

The supercapacitors require porous and stable electrodes. Carbon-based active materials (AC) are the most widely used electrode materials for supercapacitor systems because of the often-cited desirable physical and chemical properties. These properties include low cost, various forms of carbon (powers, fibers, aerogels, composites, sheets, monoliths, tubes), easy process ability, relatively inert electrochemistry, controllable porosity and electrocatalytic active sites for a variety of redox reactions [5-7]. Carbon materials possess peculiar properties (especially: electrical conductivity and adsorption ability), predetermined by their structural (e.g. crystalline lattice, presence of defects, amorphous fraction content, etc.) and morphological (e.g. particle size, porosity and surface roughness) features, as consequence of the method and conditions applied for their synthesis.

Activated carbons can be produced using either physical activation or chemical activation or a combination of both with various carbonaceous precursors. Physical activation refers to the treatment of a carbon precursor at elevated temperatures in the presence of an oxidizing gas. Chemical activation is usually carried out at relatively low temperatures with an activating agent. Depending on the activation methods as well as the carbon precursor used, numerous AC materials with various physicochemical properties have been used as supercapacitor electrodes [8].

In previous papers [9-12] are reported some results of the research carried out in IEES-BAS for synthesis of activated carbon materials as well for development of different supercapacitor systems. It is shown that nanoporous carbon materials (specific surface area in the range 700 – 1600 m² g⁻¹) and various pore structure (partial micropore volume 0,15 – 0,60 cm³ g⁻¹) can be produced from waste biomass (apricot stones and spent

coffee grounds) or by carbonization of mixtures of coal tar pitch and furfural with subsequent hydrothermal treatment. Two types of supercapacitors (SC) are developed: Symmetric double-layer SC cells assembled with two identical electrodes made by activated carbon materials and a non-aqueous electrolyte (LiPF₆ – DMC/EC (dimethyl carbonate/ethylene carbonate mixture 1:1), Et₄NBF₄ – PC (propylene carbonate) or LiBF₄ – PC) and asymmetric SC cells – hybrid lithium battery-double layer supercapacitors composed by an electrode of nanosized activated graphitized carbon, a composite electrode with activated carbon matrix and additions of an electrochemically active nanosized oxide (Li₄Ti₅O₁₂ or Fe₂O₃), and organic electrolyte (LiPF₆ – DMC/EC 1:1 or LiBF₄ - DMC/EC 1:1). Both the symmetric and hybrid SC cells demonstrate excellent cycleability, high power capability at discharge (up to 600 mA g⁻¹) as well as high current efficiency and stable capacity behavior at prolong cycling. It is also shown that the conductivity, pore size distribution and chemical surface properties of the carbon materials contribute greatly on charge storage behavior of the electrodes in the supercapacitor systems. The capacitance values up to 70 F g⁻¹ for the symmetric carbon-based SC, depending on the electrolyte and microstructure of the carbon material used, and capacitance up to 2 times higher for the hybrid lithium battery-supercapacitors were obtained.

The objective of the present work is an electrochemical study on adsorption properties of two carbons – available commercial products “TDA-Research” and “Norit-CGP” as electrode materials for supercapacitor systems.

EXPERIMENTAL

Two types commercial activated carbon (TDA-Research and Norit-CGP) are used for the assembly of the supercapacitor cells. These materials were structurally and morphology characterized by X-diffraction (XRD) method, using a Bruker D8 Advance diffractometer with Cu K α radiation and LynxEye detector and accordingly Transmission electron microscopy (TEM), using JEOL Superprobe 733. The powder X-ray diffraction patterns are collected within the range from 5.3 to 80° 2 θ with a constant step of 0.02° 2 θ angle.

The pore structure of the carbon used is investigated by nitrogen gas adsorption [11]. The adsorption isotherm of the sample at -196 °C is recorded and used to calculate the specific surface area, pore volumes and pore size distributions.

The activated carbon materials were used to fabricate electrodes for supercapacitor cells for electrochemical measurements. The symmetric supercapacitor cell contain two identical coin type electrodes from AC and an organic electrolyte - LiBF₄ with organic solvent - ethylene carbonate and dimethyl carbonate (EC/DMC) mixture in ratio 1:1. By adding a binder – polytetrafluorethylene (PTFE) to the electrode materials, a paste is formed, which is glued to Al foil discs (surface area 1.75 cm²). The formed sheet electrodes were dried in vacuum at 140 °C for 12 hours and pressed under pressure of 200 kg cm⁻². The obtained electrodes were mounted in the electrochemical cell with Glassmat separator and filled with electrolyte in a dry box under argon atmosphere. The reference electrode was Li/Li⁺. All measurement were performed at room temperature according to the experimental procedure already published [9].

The electrochemical measurements were carried out on universal galvanostat/potentiostat “Autolab-30/2” of Ecochemie (the Netherlands) applying cycling voltammetry (CV) and impulse chronopotentiometry (ICP).

The CV measurements were carried out at different scan rate – from 0.050 V s⁻¹ up to 0.001 V s⁻¹. The starting potential at all measurements was the open circuit potential (OCP) of the carbon samples and the scan was performed at potentials up to OCP +2.40 V. The ICP measurements were performed at galvanostatic conditions at different current

rates (0.1 – 10.0 mA), the pulse were with duration of 40s both in cathodic and anodic direction.

RESULTS AND DISCUSSIONS

Physicochemical characterization of the carbon electrode materials

The TDA-Research and Norit-CGP carbon material are structurally characterized by X-diffraction (XRD) method. Figure 1 shows the powder diffraction pattern of the samples.

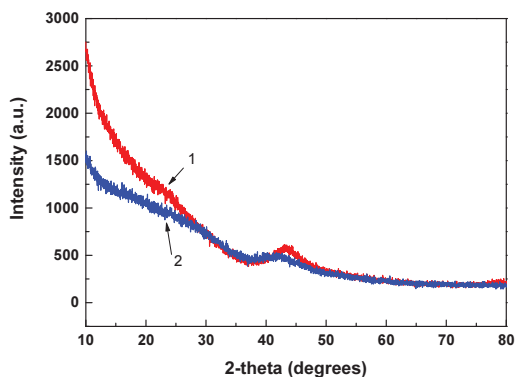


Fig.1 XRD patterns of the carbons: TDA-Research (1) and Norit-CGP(2)

On the powder patterns of both materials typical amorphous humps are observed. The first one in the range 20 – 25 degrees corresponds to (001) reflections of the graphite – type structural. The second peak in the range 38 - 48 degrees corresponds to (101) diffraction of graphite. The pattern of Norit-CGP sample shows lower value of graphitization in comparison to the TDA-Research sample.

The pore texture studies are performed by taking the nitrogen adsorption/desorption isotherms of the samples. The values of pore parameters are summarized in Table 1.

Table 1. Pore parameters of the TDA-Research and Norit-CGP samples: S_{BET} (specific surface area), S_{mi} (surface area of the micropores), V_{total} (total pore volume), V_{micro} (micropore volume), D_{av} (average pore size)

Sample	S_{BET} , [$m^2 g^{-1}$]	S_{mi} , [$m^2 g^{-1}$]	V_{total} , [$cm^3 g^{-1}$]	V_{micro} , [$cm^3 g^{-1}$]	D_{av} [nm]
TDA-Research	1524	1385	0.68	0.55	1.8
Norit-CGP	1825	889	1.40	0.38	3.1

It is seen that the both carbons have very high specific surface area but TDA-Research possesses much higher specific surface area (S_{mi}) and volume of the micropores (V_{micro}) nevertheless the smaller total pore volume (V_{total}).

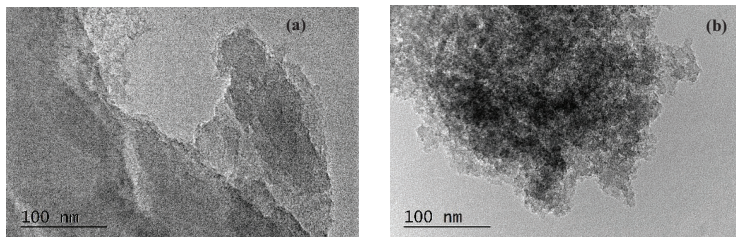


Fig.2 TEM image of the carbons: TDA-Research (a) and Norit-CGP (b)

The TEM images (Fig.2) show that the particles in both carbons are nanosized but in TDA-Research samples (Fig.2a) dominate large formations, separated by layers and small clusters, while the Norit-CGP carbon consists mainly of small particles clusters.

Electrochemical measurements

Typical CV and ICP curves for both carbon electrodes are represented on Fig. 3 and Fig. 4. The considerable differences in the CV curves of the electrodes in the same electrolyte obviously reflect the significant differences on the capacity behavior of the carbons and suggest for much higher adsorption capability of the TDA-Research carbon (Fig. 3), confirm indirectly by the results of galvanostatic impulse potential response of the electrodes in the same solution (Fig. 4).

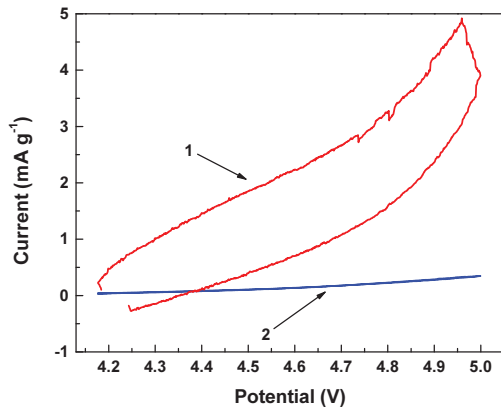


Fig.3 Cyclic voltammetric curves of the carbon electrodes in LiBF_4 electrolyte and potential scan rate 0.050 V s^{-1} : TDA-Research (1) and Norit-CGP (2)

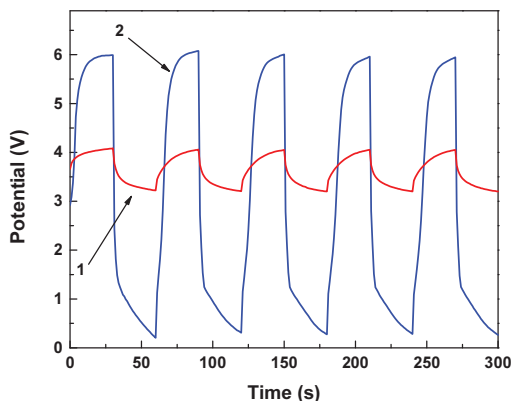


Fig.4 Galvanostatic impulse potential response of the carbon electrodes in LiBF_4 electrolyte and current 2 mA g^{-1} : TDA-Research (1) and Norit-CGP (2)

The electrochemical test of the charge – discharge cycling behavior of the symmetric capacitors assembled with the carbon electrodes studied has shown higher specific discharge capacity of the supercapacitor with TDA-Research electrodes. On Fig. 5 is demonstrated the excellent cycleability, stable capacity at prolong cycling and high efficiency of charge – discharge (about 95%) of this supercapacitor.

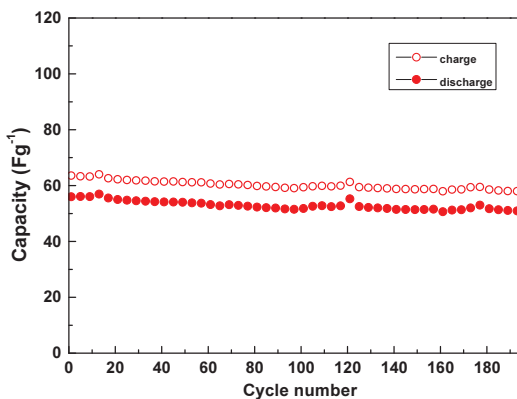


Fig.5 Dependence of the specific capacity of symmetric supercapacitor cell with TDA-Research carbon electrodes at current rate 60 mA g^{-1}

CONCLUSION

Two commercial carbons - TDA-Research and Norit-CGP are tested as electrode materials of symmetric supercapacitors applying different electrochemical methods in conjunction with structural and morphological characterizations of the materials. The pore textures study show that both carbons have very high specific surface area (1500 – 1800

m^2g^{-1}) but TDA-Research carbon possesses much higher micropore volume and micropore surface area.

The considerable differences in the CV curves and galvanostatic potential response of the electrodes suggest for a higher adsorption capability of the TDA-Research carbon. The electrochemical test of the charge – discharge cycling of the behavior of the symmetric capacitors with carbon electrodes studied confirms the adsorption capability of TDA-Research carbon material and demonstrates an excellent cycleability, stable capacity at prolong cycling and high efficiency of charge – discharge (about 95%) of the supercapacitor assembled with TDA-Research carbon electrodes.

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About the authors:

Assist. prof. Christian Girginov, Ph.D., Dept. of Physical Chemistry, University of Chemical Technology and Metallurgy, 8 "Kliment Ohridski" bld., 1756 Sofia, Bulgaria; e-mail: girginov@uctm.edu

Lozan Stoyanov, Institute of electrochemistry and energy systems (IEES), Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria; e-mail: stoyanov_lozan@abv.bg

Stephan Kozhukharov, Ph.D., Dept. of Analytical Chemistry, University of Chemical Technology and Metallurgy, 8 "Kliment Ohridski" bld., 1756 Sofia, Bulgaria; e-mail: stephko1980@abv.bg

Assoc. Prof. Antonia Stoyanova, Ph.D., Institute of electrochemistry and energy systems (IEES), Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria; e-mail: antonia.stoyanova@gmail.com

Assoc. Prof. Mladen Mladenov, Ph.D., Institute of electrochemistry and energy systems (IEES), Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria; e-mail: mladen47@bas.bg

Prof. DSc. Raicho Raicheff. Ph.D., Institute of electrochemistry and energy systems (IEES), Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria; e-mail: raicheff@bas.bg

This paper has been reviewed