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**BIOGENIC MAGNETITE/ACTIVATED CARBON COMPOSITE ELECTRODES FOR  
ELECTROCHEMICAL CAPACITORS IN AQUEOUS ELECTROLYTE**

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**Svetlana Veleva**

Institute of Electrochemistry and Energy Systems  
Bulgarian Academy of Sciences, BG  
E-mail: svetlana.veleva@iees.bas.bg

**Christian Girginov**

Department of Physical Chemistry  
University of Chemical Technology and Metallurgy, BG  
E-mail: girginov@uctm.edu

**Antonia Stoyanova**

Institute of Electrochemistry and Energy Systems  
Bulgarian Academy of Sciences, BG  
E-mail: antonia.stoyanova@iees.bas.bg

***Abstract:** Biogenic magnetite/activated carbon electrodes for electrochemical capacitors in aqueous electrolyte are composed. The biogenic  $Fe_3O_4$  material is obtained by laboratory cultivated *Sphaerotilus* bacteria. Two types of supercapacitors were investigated: a hybrid (asymmetric)supercapacitor (+)(AC+bio- $Fe_3O_4$ )/(6M KOH)/(AC)(-) and a symmetric supercapacitor (+)(AC)/(6M KOH)/(AC)(-), at room temperature. The electrochemical charge/discharge cycling test (500x) behavior of the hybrid supercapacitor has shown higher specific charge/discharge capacity (over  $220 \text{ Fg}^{-1}$ ) at different current densities (30 -  $480 \text{ mAg}^{-1}$ ). The addition of active bio- $Fe_3O_4$  species within the AC-matrix improved the overall electrocapacitive performance of the carbon electrode. Furthermore, this composite electrode material exhibits low porosity and high density. The electrochemical tests showed that these (AC/bio- $Fe_3O_4$ )-electrodes are suitable for the assembly of high-power supercapacitors.*

***Keywords:** hybrid supercapacitors, biogenic magnetite, carbon electrode materials, galvanostatic charge/discharge cycling*

## INTRODUCTION

Porous carbon-based materials with various additives are a very important family of electrode materials for assembly of supercapacitors [1]. These devices find increasing implementation for electrochemical energy storage (as power back-up systems) in various industrial installations. Different carbon-based materials have been designed and synthesized for the development of high-power supercapacitor with long cycle life. A promising electrode material can be achieved by addition of bio- $Fe_3O_4$  to activated carbon (AC).

The synthesis of nano-sized materials by bacteria is a process which commonly occurs in nature. An example is the oxidation of soluble  $Fe^{2+}$  ions into insoluble  $Fe^{3+}$  ions. This reaction is part of the metabolism of so-called iron bacteria and its products are slightly hydrated iron oxides, especially  $\alpha$ - $FeOOH$  and  $\gamma$ - $FeOOH$  [2]. They have nano-size particles and high surface area. The uniform size and structure, as well as the high specific surface area are of great interest aiming possible application of these materials for groundwater cleaning, in electronics, as catalysts and anode composites for lithium-ion batteries and supercapacitors.

The objective of the present work is to develop a supercapacitor cell, having electrodes of activated carbon and activated carbon/(bio- $Fe_3O_4$ )-composite. Furthermore, the aim is to compare the capacitance behavior of the hybrid supercapacitor with that of symmetric carbon-based one.

## EXPERIMENTAL

### Electrode materials

Two types of electrode materials are used for the assembly of supercapacitor cells: activated carbon (AC) and bio-Fe<sub>3</sub>O<sub>4</sub>(magnetite). The AC with nano-sized particles (1600 m<sup>2</sup>g<sup>-1</sup>) is a commercial product of TDA Research (USA). The biogenic iron oxide/hydroxide material is obtained by laboratory cultivated *Sphaerotilus* bacteria [3]. The Fe<sub>3</sub>O<sub>4</sub> nano-sized powder material has been produced by thermal treatment of biogenic  $\gamma$ -FeOOH (lepidocrocite) precursor and characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM).

### Supercapacitor cells

Using these materials, two types of supercapacitor cell were assembled. The positive electrodes were composed of AC matrix with addition of biogenic Fe<sub>3</sub>O<sub>4</sub> (25 wt. %). The negative electrode was made from the same AC. Polytetrafluorethylene (PTFE) as a binder was added previously to the activated carbon using standardized procedure. The formed sheet electrodes (surface area 1.75 cm<sup>2</sup>) were dried a 100°C for 2 hours and pressed (20 MPa). The obtained electrodes were soaked in the electrolyte (6M aqueous solution of KOH) and then mounted in a coin-type cell with Viledon FS2108 separator and filled with electrolyte. The electrolyte in both cases is a 6M KOH. Two types of supercapacitors were investigated, at room temperature:

hybrid(asymmetric)supercapacitor: (+)(AC+ bio-Fe<sub>3</sub>O<sub>4</sub>)/(6M KOH)/(AC)(-);

symmetric supercapacitor: (+)(AC)/(6M KOH)/(AC)(-).

### Electrochemical tests

The hybrid supercapacitor cells were subjected to galvanostatic charge/discharge cycling using an Arbin Instrument System (BU-2000). The test program was carried out at constant current mode at different current load (from 30 to 480 mA g<sup>-1</sup>) at 20 cycles and room temperature. Some cells are subjected to continuous cycling charge/discharge at current rate of 60 mA g<sup>-1</sup> up to 350 cycles. For comparison a symmetric supercapacitor cell is also assembled using two identical AC-electrodes [4,5].

## RESULTS AND DISCUSSION

The electrochemical test of the charge/discharge cycling behavior of the hybrid supercapacitor: (+)(AC+bio-Fe<sub>3</sub>O<sub>4</sub>)/(6M KOH)/(AC)(-) has shown higher specific discharge capacity under different current rate (Fig.1).

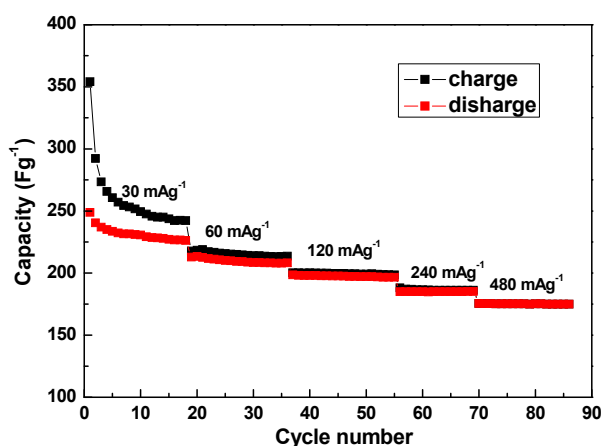


Fig.1 Specific capacity vs the number of charge/discharge cycles of hybrid supercapacitor (+)(AC+bio-Fe<sub>3</sub>O<sub>4</sub>)/(6M KOH)/(AC)(-), under different current rate.

It was of interest to investigate the dependence of the hybrid supercapacitor capacity on the applied current rate. These  $C(i)$ -dependencies are plotted and are presented in Fig. 2. For

comparison identical measurement is performed and plotted for a symmetric supercapacitor: (+)(AC)/(6 M KOH)/(AC)(-). Furthermore, Fig.2 demonstrates the excellent cycleability, stable capacity at prolonged cycling and high efficiency of charge/discharge of the studied supercapacitor under constant current rate.

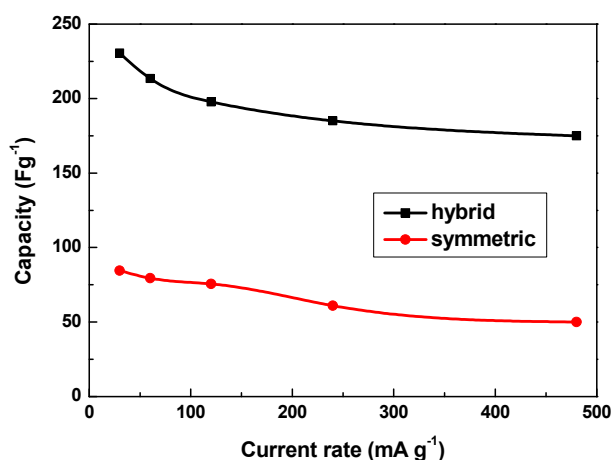


Fig.2 Specific capacity vs. number of charge/discharge cycles of hybrid supercapacitor and symmetric supercapacitor under constant current rate (60 mA g<sup>-1</sup>).

The asymmetric supercapacitor using biogenic Fe<sub>3</sub>O<sub>4</sub> in the composite electrode showed the higher capacity and efficiency and also a very stable capacity behavior at prolonged cycling (up to 500 cycles) in comparison to the symmetric one. Moreover, the addition of biogenic Fe<sub>3</sub>O<sub>4</sub> in the AC matrix increased significantly (more than twice) the specific capacity of the hybrid supercapacitor compared to the symmetric one.

Fig. 3 presents the dependency of the specific capacity versus the number of charge/discharge cycles of hybrid supercapacitor under constant current rate.

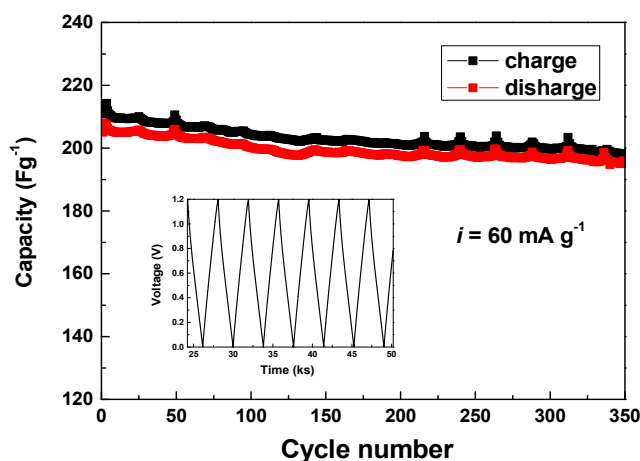


Fig. 3 Specific capacity vs. the number of charge/discharge cycles (+)(AC+ bio-Fe<sub>3</sub>O<sub>4</sub>)/(6M KOH)/(AC)(-) under 60 mA g<sup>-1</sup> current rate

From Fig. 3 it can be seen, that over 90% of the original capacitance was retained after 350 cycles, showing this hybrid supercapacitor cell has good cycle ability and efficiency. This result is most probably due to the assumption that the presence of bio-Fe<sub>3</sub>O<sub>4</sub> composite materials leads to the formation of structures with regularly distributed pores (in nano-tubular form), suitable for application in supercapacitors.

## CONCLUSIONS

Carbon composite materials with nano-sized bio-Fe<sub>3</sub>O<sub>4</sub> oxide particles homogeneously dispersed into the (AC)-porous structure is an effective electrode for high-power supercapacitors. The addition of active bio-Fe<sub>3</sub>O<sub>4</sub> species в AC-matrix improves the overall electro-capacitive performance of a carbon electrode. The electrochemical tests showed that these electrodes are effective to facilitate fast electron and ionic transfer.

The total specific capacitance of the composite materials exhibits a satisfactory specific capacity (over 220 Fg<sup>-1</sup>) after adding of bio-Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Furthermore, this electrode material has a low porosity and high density, which presents it as very suitable for the development of compact electric power sources.

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## About the authors

Res. Assist. Svetlana Veleva, Ph.D. student, Institute of Electrochemistry and Energy Systems- BAS, Acad. G. Bonchev Street, bl.10, 1113 Sofia, Bulgaria, e-mail: svetlana.veleva@iees.bas.bg

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

Assoc. prof. Antonia Stoyanova, Ph.D., Institute of Electrochemistry and Energy Systems- BAS, Acad. G. Bonchev Street, bl.10, 1113 Sofia, Bulgaria, e-mail: antonia.stoyanova@iees.bas.bg