

A hybrid supercapacitor activated carbon/LiBF₄/activated carbon–biogenic Fe₂O₃ composite

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Two types of electrode material are used in the assembly of supercapacitor cells - activated carbons and electrochemically active α -Fe₂O₃ (hematite). The activated carbon with nanosized particles (specific surface area 1500 m²g⁻¹) is a product of TDA Research, USA. The nanosized hematite (bio-Fe₂O₃) is produced by thermal treatment (400 °C/2 h in an argon atmosphere) of biogenic α -FeOOH (goethite) obtained by laboratory cultivated *Leptothrix* bacteria. The oxide is structurally and morphologically characterized by XRD, SEM, TEM and tested as an electrode material in hybrid lithium battery-double layer supercapacitors. The hybrid cell is assembled from an electrode of activated carbon, a composite electrode with an activated carbon matrix, the addition of 50 % bio-Fe₂O₃ and an organic electrolyte - LiBF₄ with a solvent ethylene carbonate/dimethyl carbonate mixture (EC/DMC) 1:1. A symmetric supercapacitor cell composed of two identical electrodes from activated carbon and the same organic electrolyte is also assembled and tested for comparison. The cells are subjected to galvanostatic charge/discharge cycling at different current loads and both demonstrate a high specific capacity (50 Fg⁻¹ for the symmetric and about 50% higher capacity for the hybrid supercapacitor), a high efficiency (above 95%) and stable capacity behavior at prolong cycling. The results prove the possibility of application of bio-Fe₂O₃ as an electrochemically active material for hybrid lithium battery – supercapacitor systems.

Key words: biogenic hematite, electrode materials, hybrid supercapacitors, charge/discharge cycling

INTRODUCTION

The increased interest in electrochemical double-layer capacitors (supercapacitors) is largely stimulated by the growing needs of technology for the storage of energy produced by renewable energy sources, such as solar stations and wind generators, as well as by heeding the advantages of supercapacitors in comparison with conventional electrochemical power sources. As well known, batteries and the fuel cells show a high energy density but they have a low power density and a limited lifecycle. Supercapacitors tend to have a lower energy density compared to batteries, but they can provide a much higher power capability, high efficiency and excellent cycling characteristics [1-3].

The electrochemical double-layer supercapacitors are usually symmetrical with two identical carbon electrodes. In order to improve the energy density while keeping a long lifecycle, hybrid electrochemical systems involving the hybridization of a faradaically rechargeable battery-type electrode with an electrochemical double-layer

capacitor-type electrode (e.g. asymmetric supercapacitors), are introduced. Thus, various hybrid capacitor configurations consisting of activated carbon as a positive electrode and a negative electrode based on metal oxides (nickel, lead or manganese oxides) [4–6], conducting polymers [7] or Li intercalation oxides [8, 9], are suggested.

Porous carbons are among the most attractive materials for preparation of electrodes for electrochemical capacitors. The main advantage of these materials is the possibility to produce highly porous structures with a high specific surface area as well as to develop various composite electrodes by adding electrochemically active materials to the carbon matrix [10].

Fe₂O₃ is a promising electrode material for the Li-ion battery because of its low cost, simple manufacturing process, wide range of sources, environmental friendliness and mainly – a large theoretical specific capacity. The cycling performance of this material however is not satisfactory because of the partial destruction of the electrode that may take place upon repetitive cycling reactions between the Fe₂O₃ and Li-ions [11].

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Our previous studies [12-15] were devoted to the synthesis of activated carbon materials suitable for electrodes for electrochemical double-layer capacitors as well as to the development of carbon-based composite electrodes for hybrid lithium battery-supercapacitor systems. It was shown that nanoporous carbon materials can be synthesized from waste biomass (apricot stones and spent ground coffee) or by carbonization of mixtures of coal tar pitch and furfural with subsequent hydrothermal treatment. The capacitance values of up to 70 Fg⁻¹ are obtained for a symmetric carbon-based supercapacitor with Et₄NBF₄ – propylene carbonate electrolyte and about a twice higher capacitance for the asymmetric supercapacitor, composed of an activated graphitized carbon electrode and an activated carbon-Li₄Ti₅O₁₂ oxide composite electrode in a LiPF₆ – DMC/EC (1:1) electrolyte, with high efficiency and very good cycleability of both supercapacitors.

The objective of the present work is to develop a hybrid lithium battery - supercapacitor using activated carbon and activated carbon-bio-Fe₂O₃ composite with an organic electrolyte as electrodes, as well as to compare the capacitance behavior of the hybrid supercapacitor with that of a symmetric carbon-based supercapacitor.

EXPERIMENTAL

Synthesis of electrode materials: Two types of electrode materials are used for the assembly of supercapacitor cells - activated carbon (AC) and electrochemically active α -Fe₂O₃ (hematite). The nanosized hematite (bio-Fe₂O₃) is produced by thermal treatment (400°C for 2 hours in an argon atmosphere) of biogenic iron oxide/hydroxides (goethite) obtained by laboratory cultivated *Leptothrix* bacteria [15]. The activated carbon with nanosized particles is a product of TDA Research (USA).

Morphological and structural characterization of the electrode materials: The biogenic iron oxide/hydroxide precursor and the obtained oxide material are structurally characterized by X-diffraction (XRD). 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 on a Bruker D8 Advance diffractometer with Cu K α radiation and a LynxEye detector. The phase identification was performed with a DiffraPlus EVA using the ICDD-PDF2 Database. The mean crystallite size is determined with the Topas-4.2 software package using the fundamental parameters peak shape description including appropriate

corrections for the instrumental broadening and the diffractometer geometry.

The morphology of the electrode materials is examined by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) using a JEOL Superprobe 733.

The pore structure of the carbon used are investigated by nitrogen gas adsorption [13]. 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.

Electrochemical tests. The activated carbon and bio-Fe₂O₃ materials are used to fabricate electrodes for two types of electrochemical cells for capacity measurements. The first type is a symmetric supercapacitor cell using two identical electrodes from activated carbon and an organic electrolyte - lithium tetrafluoroborate (LiBF₄) with organic solvent - ethylene carbonate and a dimethyl carbonate (EC/DMC) mixture in the ratio 1:1. The symmetric supercapacitor is denoted as AC/(LiBF₄-EC/DMC (1:1))/AC.

The second one is an asymmetric (hybrid) supercapacitor cell with a composite electrode and an activated carbon electrode. The composite (negative) electrode is assembled from an activated carbon matrix with the addition of bio-Fe₂O₃ (50%). The positive electrode is made from the same AC and the same organic electrolyte - LiBF₄-EC/DMC (1:1) as used in the symmetric cell. This asymmetric supercapacitor is denoted as (AC+bio-Fe₂O₃)/(LiBF₄-EC/DMC (1:1))/AC.

By adding a binder - polyvinylidene difluoride (PVDF) to the electrode materials, a paste is formed, which is glued to Cu foil discs (surface area 1,75 cm²). The formed sheet electrodes are dried at 70 °C for 2 hours and pressed under a pressure of 200 kg cm⁻². The electrodes obtained are soaked in organic electrolyte under a vacuum and then mounted in a coin-type cell with a Glassmat separator and filled with an electrolyte in a dry box and argon atmosphere. The capacitor cells were subjected to galvanostatic charge-discharge cycling using an Arbin Instrument System BU-2000 [14, 15]. The test program is carried out at a constant current mode at different current loads (from 10 to 500 mA g⁻¹) at 10 cycles and room temperature. Some cell are subjected to continuous cycling charge/discharge at a current of 60 mA g⁻¹ for up to 1000 cycles.

RESULTS AND DISCUSSIONS

Physicochemical characterization of the electrode materials. Fig.1 (a and b) represents the powder X-ray diffraction patterns of the biogenic

FeOOH (goethite) precursor and the α -Fe₂O₃ oxide phase obtained after thermal treatment. It is seen that the oxide product (bio-Fe₂O₃) is a single phase hematite with the unit cell parameters: $a = 5.0388 \text{ \AA}$ and $c = 13.774 \text{ \AA}$. The mean crystallite size of bio-Fe₂O₃ is estimated to be about 10 nm. The TEM observations have shown that the bio-Fe₂O₃ particles (cf. Fig.2) are nanosized and form clusters, while the biogenic FeOOH consists of nanotube particles, which cover the bacterium structure in the form of a sheath.

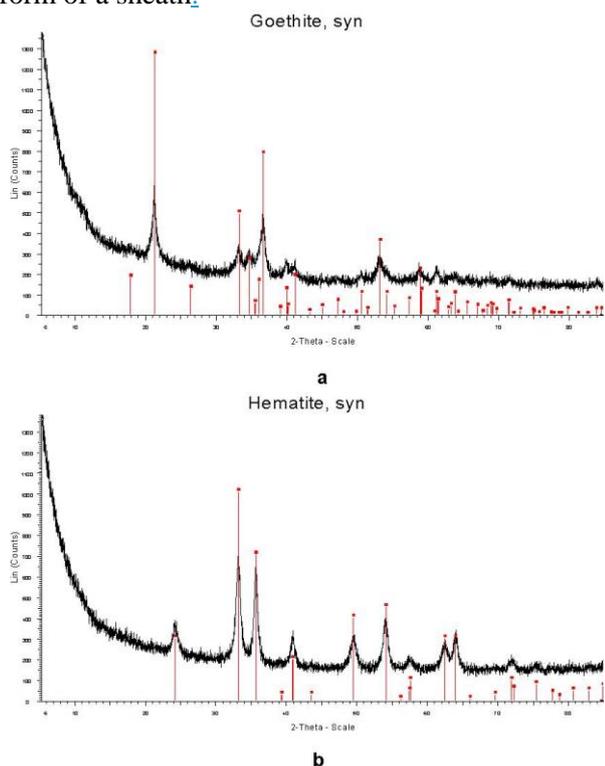


Fig. 1. XRD powder patterns of biogenic FeOOH (a) and bio-Fe₂O₃ (b).

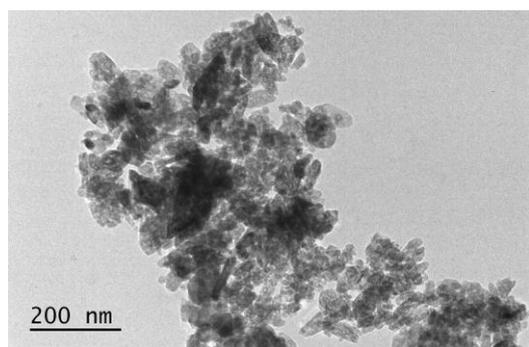


Fig. 2. TEM image of bio-Fe₂O₃.

The examination of the samples of activated carbon have shown that the specific surface area is 1520 m²g⁻¹, the total volume of the pores is 0,68 cm³g⁻¹, the volume of the micropores - 0,55 cm³g⁻¹ (i.e. 80% of the total pore volume) and the volume of the mesopores - 0,13 cm³g⁻¹.

Electrochemical performance of the supercapacitor cells. The electrochemical performance of the two-electrode symmetric and asymmetric (hybrid) capacitor cells are studied by charge-discharge cycling test.

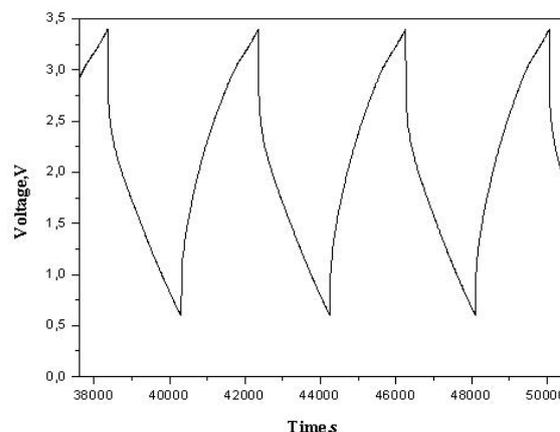


Fig. 3. Charge-discharge behavior of a hybrid battery-supercapacitor (AC+bio-Fe₂O₃)/(LiBF₄ - EC/DMC (1:1))/AC at a current load of 60 mA g⁻¹.

Fig. 3 illustrates the charge–discharge behaviour of a hybrid supercapacitor cell assembled by the composite electrode (AC+bio-Fe₂O₃), the AC electrode and the electrolyte LiBF₄ – EC/DM (1:1) at a current load of 60 mA g⁻¹. As seen the hybrid lithium battery-supercapacitor cell shows a reproducible charge-discharge behavior and indicates very stable and high specific capacity values at a relatively high current load. The processes on the composite anode are obviously lithiation/delithiation of Fe₂O₃ (i.e. a typical Faradaic process) together with the adsorption/desorption of the Li-ion on the AC surface of the electrode, while on the AC cathode only the process of electrostatic adsorption/desorption of BF₄⁻¹ takes place.

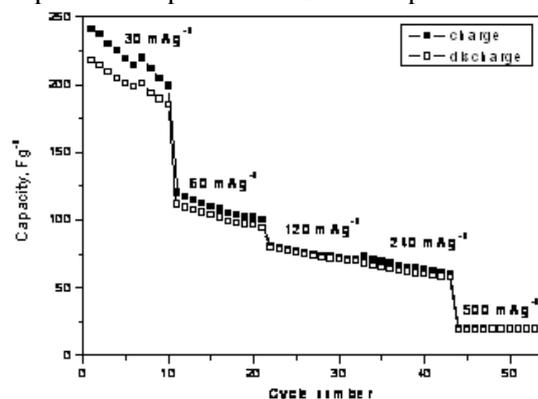


Fig. 4. Dependence of the charge and discharge capacity of hybrid battery-supercapacitor (AC+bio-Fe₂O₃)/(LiBF₄ - EC/ DMC (1:1))/AC on the number of cycles at different current loads.

The electrochemical test of the hybrid supercapacitor cells includes 10 charge/discharge cycles at each current load – from 30 to 500 mA g⁻¹ (Fig. 4). As expected both the charge and discharge capacity decrease with the increase of the current rate but the efficiency of the process (expressed as the ratio of the discharge and charge capacity) increases – from an average of 90% at 30 mA g⁻¹ to 98% at 500 mA g⁻¹. It should be noted however that the capacitor cell retains a relatively high specific capacity even at a very high current load (above 100 mA g⁻¹).

Fig. 5 illustrates the dependence of the charge and discharge capacity on the number of cycles for the symmetric and the hybrid supercapacitors at a current load of 60 mA g⁻¹ for both the capacitor cells. It is worth noting that the symmetric cell represents typical electric double-layer supercapacitors for energy storage. Both capacitors demonstrate high efficiency (about 95%) and high stability of their capacity during cycling, especially for the symmetric supercapacitor cell. The hybrid supercapacitor shows up to two times higher capacity values than the symmetric one (50 Fg⁻¹).

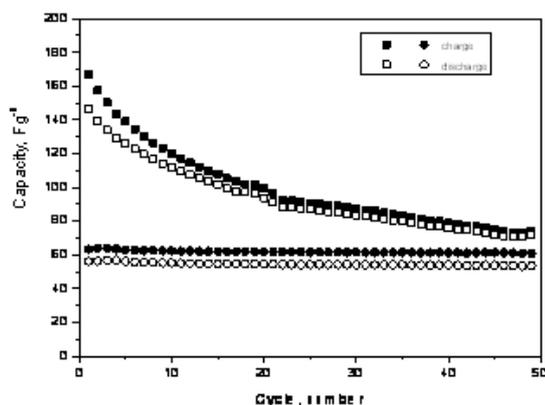


Fig. 5. Dependence of the charge and discharge capacity of hybrid battery- supercapacitor (AC+bio-Fe₂O₃)/(LiBF₄ - EC/ DMC (1:1)) /AC (■, □) and symmetric capacitor AC/(LiBF₄ - EC/ DMC (1:1))/AC (○, ●) on the number of cycles at a current load of 60 mA g⁻¹.

A comparison of the dependence of the discharge capacity on the current load for the symmetric and hybrid supercapacitors is made on Fig. 6. The value of the discharge current affects much more strongly the capacity of the hybrid battery-supercapacitor cell which is obviously related to the much stronger effect of the current on the faradaic reaction on the composite electrode, i.e. on its pseudocapacity. The results illustrate also the higher capacity values of the hybrid supercapacitor, especially at low current loads (below 50 - 100 mA g⁻¹).

In the course of electrochemical testing it is also established that the capacity loss of the hybrid supercapacitor does not exceed 8-10% after prolonged cycling (above 1000 cycles) and the supercapacitor works satisfactorily even at a high current load (above 200 mA g⁻¹).

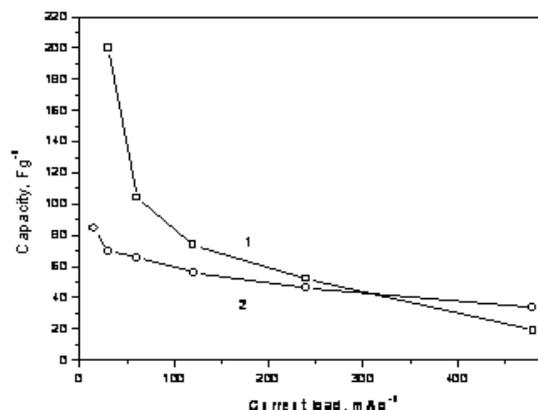


Fig. 6. Dependence of the discharge capacity of a hybrid battery-supercapacitor (AC+bio-Fe₂O₃)/(LiBF₄ - EC/ DMC (1:1)) /AC (1) and a symmetric capacitor AC/(LiBF₄ - EC/ DMC (1:1))/AC (2) on the current load.

The work on the synthesis of activated carbon with an appropriate pore structure and morphology as well as on the optimization of the composition and structure of the composite electrode is in progress and the results will be reported soon.

CONCLUSIONS

On the basis of the results in the present study, the following conclusions are made:

1) Nanosized hematite (bio-Fe₂O₃) can be produced by thermal treatment of biogenic α -FeOOH (goethite), obtained by laboratory cultivated *Leptothrix* bacteria and used as an electrochemically active additive in the composite electrode with an activated carbon matrix for lithium battery - supercapacitor systems.

2) The hybrid supercapacitor thus developed (AC+bio-Fe₂O₃) / (LiBF₄-EC/DMC (1:1)) / AC demonstrates high reproducibility of the charge/discharge processes, a high specific capacity (80 Fg⁻¹), high efficiency (above 95 %) and stable cycleability at prolong cycling.

The results prove the possibility of application of bio-Fe₂O₃ as an electrochemically active material for hybrid lithium battery – supercapacitor systems.

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ХИБРИДЕН СУПЕРКОНДЕНЗАТОР - АКТИВЕН ВЪГЛЕН / LiBF₄ / КОМПОЗИТ ОТ АКТИВЕН ВЪГЛЕН И БИОГЕНЕН Fe₂O₃

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(Резюме)

Използвани са два вида електродни материали за асамблиране на суперкондензаторни клетки - активен въглен и електрохимично активен α -Fe₂O₃ (хематит). Активният въглен с наноразмерни частици (специфична повърхност 1500 m²g⁻¹) е търговски продукт на TDA Research, САЩ. Наразмерният хематит (био-Fe₂O₃) е синтезиран чрез термична обработка (400 °C / 2 ч в атмосфера на аргон) на биогенен α -FeOOH (гъотит), получен чрез лабораторно култивирана *Leptothrix* бактерия. Био-Fe₂O₃ е структурно и морфологично охарактеризиран с помощта на рентгеновата дифракция (XRD), сканираща електронна микроскопия (SEM) и трансмисионна електронна спектроскопия (ТЕМ) и изследван като електроден материал в хибридна литиева батерия-електрохимична суперкондензаторна система. Хибридната клетка е съставена от електрод от активен въглен, композитен електрод с матрица от активен въглен и добавка на 50% био-Fe₂O₃. Използван е органичен електролит LiBF₄, с разтворител смес от етилен карбонат / диметил карбонат (EC/DMC) 1:1. За сравнение е съставена и симетрична суперкондензаторна клетка от два идентични електрода от активен въглен и същият органичен електролит. Клетките са подложени на галваностатични зарядно/разрядни циклични тестове при различно токово натоварване и показват висока специфичен капацитет (50 Fg⁻¹ за симетричен и с около 50% по-висок капацитет за хибридният суперкондензатор), висока токова ефективност (над 95%) и стабилен капацитет при продължително циклиране. Резултатите показват възможността за прилагане на био-Fe₂O₃ като електрохимично активен материал за хибридна литиева батерия - суперкондензаторна система.