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CHARACTERIZATION OF SPECIFIC ELECTRODE MATERIALS FOR SUPERCAPACITORS

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In this paper is presented a brief overview of investigation of electrode materials for supercapacitors, which the authors dealt with for years. In addition to the standard electrode material (graphite and ruthenium), other materials were examined, particularly sulfides of copper. Different electrochemical methods (galvanostatic, potentiostatic, cyclic voltammetry and electrochemical impedance spectroscopy) have been used.

Keywords: supercapacitors, electrode materials, electrochemical investigations.

In addition to the standard electrode materials (graphite and ruthenium) some other materials are recently used, mainly oxides and sulfides of certain metals. Some of these materials have been studied long time ago, but recently the use of new technologies (especially nanotechnology) achieved a significant improvement in energy efficiency. On the other hand, these materials are much more acceptable for their cost, therefore new solutions have been intensively explored worldwide. More dominant requirements with energy sources to be cleaner and more economical led to intensive research related to alternative electrode materials [1].

SUPERCAPACITOR ELECTRODE MATERIALS

Supercapacitors are a relatively new type of capacitors distinguished by a phenomenon of electro-chemical double-layer, diffusion and large effective area, which leads to extremely large capacitance per unit of geometrical area (many times higher than that of conventional capacitors). They occupy the place between lead batteries and conventional capacitors. In terms of specific energy (accumulated energy per mass unity or volume) and in terms of specific power (power per mass unity or volume) they take place in the area that covers the order of several magnitudes. Supercapacitors fulfill a very wide area between accumulator batteries and conventional capacitors taking into account specific energy and specific power [2, 3]. Batteries and fuel cells are typical devices of small specific power, while conventional capacitors can have specific power higher than 1 MW/dm^3, but at a very low specific energy. Electrochemical capacitors improve batteries characteristics considering specific power or improve capacitors characteristics considering specific energy in combination with them. In relation to other capacitor types, supercapacitors offer much higher capacitance and specific energies [4—10].

It was found that different natural sulfide minerals such as pyrite (FeS_2) [11] and chalcocite (Cu_2S) [4], as well as metal sulfides obtained by chemical precipitation, like cobalt sulfide [12] or nano SnS [13] and ZnS [14], exhibit capacitance characteristics in aqueous solutions of some acids and alkaline. Compound CuS appears as an intermediary product or a final product in electro-chemical oxidation reactions of chalcocite which exhibits supercapacitor characteristics. The common characteristic of sulfides exhibiting high capacitances is that their metal constituent can appear in two or more valence states. Also, while modeling anodic oxidation reaction of covellite, it was established that the equivalent electrical circuit has to contain one relatively high capacitor [8]. Those facts were the reason for examination of the mineral covellite capacitive characteristics.

The applied standard electrochemical methods, such as galvanostatic, cyclic voltammetry, potentiostatic method and electrochemical impedance spectroscopy (EIS), and other methods of material characterization (optical and scanning electron microscopy) were described in [7—10].

The electrochemical characterization was carried out by a standard three-electrode system consisting of saturated calomel electrode (SCE) as a reference electrode, platinum as a counter electrode and a number of working electrodes the active part of which is the tested material. The contact between the copper wire and the electrode material was achieved using conducting silver glue, and then mounted in acrylic mass for cold mounting. The working electrodes (five of them) occupied 18—49 mm^2 and the counter electrode — 200 mm^2 of active surface area. The optical microscopy of the electrode material was carried out by using a LOMO MIN9 microscope with digital camera JENOPTIK ProgRes C10+ for the immediate records transfer into the computer. The electronic microscopy was performed by using a JSM 35 microscope. The X-ray analysis was done by Siemens difractometer Kristaloflex 810.

System for the electrochemical characterization consisted of hardware — PC, AD-DA Converter NI-6251 (National Instruments), analog interfaces (Technical Faculty, Bor) — and software for measurement (LabVIEW platform and application software, developed at the Technical Faculty in Bor) [15]. Electrochemical characterization was performed using a standard system with three electrodes. System with three electrodes consisted of: copper (steel, platinum) electrode as the working electrodes, saturated calomel electrode as the reference electrode and the platinum counter electrode.

The starting material was samples of natural copper mineral covellite (CuS). The first series of experiments was done in unimolar aqueous solutions of sulfuric acid with or without the addition of copper sulfate. The experiments in the second series were performed in strong alkaline solution (6 M KOH). The next material for building the supercapacitor was activated carbon (Aktivkohle (zur Analyse), MERCK). In order to prepare supercapacitor electrodes, a mixture of activated carbon and polymer binder — polyvinylidene difluoride (PVDF) — in mass ratio 10:1 was prepared in an automatic mill for 30 min. The mixture was then soaked with acetone in order to produce a paste.

The next electrochemical methods have been used: galvanostatic, cyclic voltammetry, potentiostatic method and impedance spectroscopy. In order to determine the main parameters, the investigated electrochemical system was modeled by a simplified equivalent circuit which consisted of a main capacitance, a serial resistance and leakage resistance [9].

A. Galvanostatic examination

Classic galvanostatic method assumes that the system is excited by the constant current between working and the system response. Besides the classical, the modified method [12, 14] with prolonged duration of current impulse is applied in order to allow the overwhelming system analysis. All the prepared electrodes were first examined in the unimolar solution of pure sulfuric acid (1 M H_2SO_4). Galvanostatic investigations with the same electrodes have been performed in a strong alkaline solution as well. Galvanostatic curve for the covellite electrode (surface area 0.42 cm^2) subjected to excitation of 1 mA for the duration of 80 s in the solution of 6 M KOH is given in fig. 1. Serial resistance of about 80 $\Omega \cdot cm^2$ has been determined from the diagram.

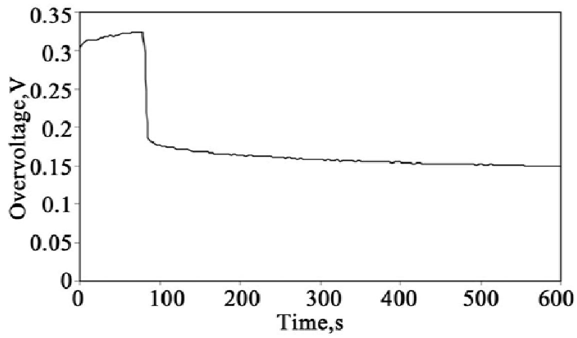

Fig. 1. Galvanostatic curve of covellite in 6 M KOH aqueous solution (excitation 1 mA, 80 s; active surface area 0.42 cm^2)

B. Cyclic voltammetry

Since the standard cyclic voltammetry method is very convenient for capacitance measurements, a series of experiments was carried out in various electrolytes. Fig. 2 shows voltammetric curves of covellite electrode in 6 M KOH solution obtained using a sweep rate of $5mVs^{-1}$. Capacitance calculated from the third loop is around 6.7 $F{\cdot}cm^{-2}$ (electrode active surface area 0.42 cm^2).

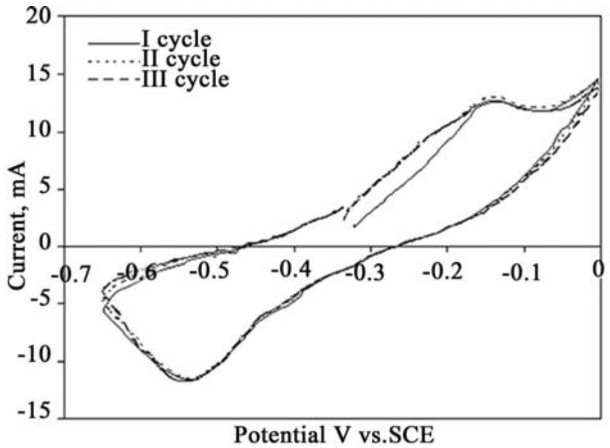

Fig. 2. Consecutive voltammograms of covellite in 6 M KOH at $5mVs^{-1}$

C. Electrochemical impedance spectroscopy

Since EIS, if applied on the systems containing high capacitances, demands long duration of experiments [14] just few characteristic electrochemical systems were examined by this method. Fig. 3 shows the impedance diagram of covellite electrode in the solution of 6 M KOH. The alternate excitation voltage was V_{ACmax} = 7 mV, without the DC off-set (V_{DC} = 0 mV). From the EIS diagram it was obtained a capacitance of 9.3 $F{\cdot}cm^{-2}$, which is in agreement with the value obtained from the cyclic voltammetry measurement. Also, from the same diagram were obtained the serial resistance of 82 $\Omega{\cdot}cm^2$ and the leakage resistance of 380 $\Omega{\cdot}cm^2$.

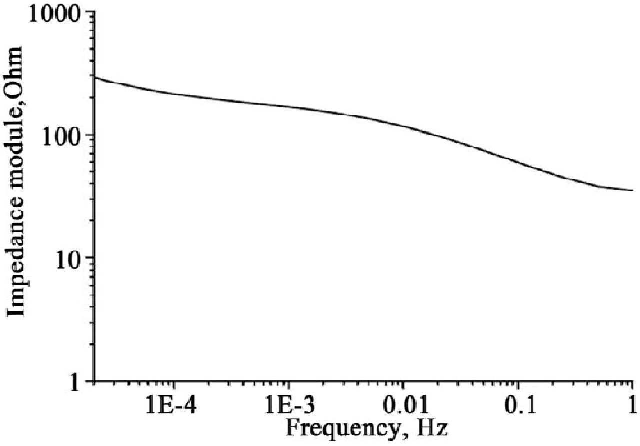

Fig. 3. Impedance diagram for covellite electrode in 6 M KOH

The supercapacitors investigations using different electrochemical methods showed that natural copper mineral covellite exhibits relatively high capacitivity in order of magnitude of 20 $F{\cdot}cm^{-2}$. In alkaline solution covellite exhibits a capacitance of the same order of magnitude, although for about three times lower; at the same time leakage, i. e. self-discharge is bigger. The investigations on covellite in acidic and alkaline solutions had a goal to enable optimization of the electrochemical systems in the sense to obtain as high performance as possible (usually the lowest serial and biggest parallel resistance at the same time). A number of chalcocite electrodes were examined in various electrolytes and the preliminary optimization of the system was performed from the aspect of its application for electrochemical supercapacitors considering two key parameters: capacitance and leakage current. All the methods applied pointed out at high value of capacitance (approximately 110 and 200 F·cm^{-2}, depending on electrolyte) which implies that chalcocite is likely to be a new material for supercapacitors. The presented results are comparable with the testing results on standard electrode materials (AC and RuO_2).

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Стевич З., Райжич-Вуясинович М., Радованович И., Бугаринович С., Грекулович Б.
Характеристика некоторых электродных материалов для суперконденсаторов.

Представлен краткий обзор исследования электродных материалов для суперконденсаторов, с которыми авторы работали в течение многих лет. Кроме стандартных электродных материалов (графита и рутения), рассмотрены и другие материалы, в частности сульфиды меди. Для исследований использовались различные электрохимические методы (гальваностатический, потенциостатический, метод циклической вольт-амперометрии и электрохимической импедансной спектроскопии).

Ключевые слова: *суперконденсаторы, электродные материалы, электрохимические исследования..*