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HIGH-ENERGY-DENSITY ELECTRODE ON THE BASIS OF ACTIVATED CARBON MATERIAL FOR HYBRID SUPERCAPACITORS

B.P. Bakhmatyuk [*]

Lviv Polytechnic National University, 12 St. Bandera Street, Lviv 79013, Ukraine

ABSTRACT

The "Norit DLC Supra 30" commercial activated carbon material (NS commercial ACM) has been investigated as a polarized electrode for a hybrid supercapacitor (HS) in aqueous ZnI_2 solution. Energy-dispersive X-ray spectroscopy and Raman spectroscopy have shown that there is considerable increase in response of iodine atoms of the electrochemically adsorbed material as compared to that of the initial material. Thermodynamic functions of the process of the $C_x{}^*I$ formation have been determined; they indicate that the entropy-related contribution to Gibbs free energy dominates there. The drawn theoretical Langmuir isotherm and capacity-voltage characteristic were compared with corresponding experimental ones. One-electron transfers of the process of iodine electrosorption and the reversibility of this process have been experimentally shown. The obtained experimental value of the specific pseudocapacitive discharge (C^f) is equal to 7376 F g^{-1} at the efficiency of the cycle of 93 %. Practical discharge has the following parameters: specific power (P) is 2.28 W g^{-1}, specific energy (W) is 1426 J g^{-1}, specific capacity (C) is 1254 C g^{-1}. The obtained practical values of specific energy and capacity are equal to 82 % and 87 % of the theoretical values respectively.

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1. Introduction

Activated carbon material (ACM) whose total specific surface (S_{total}) according to BET is equal to or greater than 1000 m^2 g^{-1} are used for fabrication of easily polarized electrodes of electrochemical supercapacitors (ES) [1,2]. Nowadays, the electrochemical supercapacitors have considerable advantage over batteries as to their specific power and the number of cycles, but they are of less specific energy. The double electric layer capacitor (DELC) of symmetric configuration, which work on charge–discharge of highly-developed charge-blocking surface of ACM, cannot solve the problem of considerable reduction of the difference in energy density in comparison with modern batteries. Their energy density does not exceed 30 Wh kg^{-1} [3–5]. During last years, the ES of asymmetric configuration with an easily polarizable electrode on the basis of ACM and with a weakly polarizable electrode (for example PbO_2 of a lead-acid cell or NiOOH of an alkaline cell) is being dynamically developed [6–8]. Due to the use of asymmetric configuration, a 5-times increase in capacitance in comparison, for example, with DELC of symmetric configuration can be achieved

[9]. Besides, the use of pseudocapacitance of carbon electrode enables us to considerably increase specific (per unit mass) energy indices of ACM.

Processes of electrodeposition of lead on gold and those of hydrogen on platinum under underpotential relative to the main reaction (the densities of charge are 410 μC cm^{-2} and 210 μC cm^{-2} for lead and hydrogen respectively, i.e. they are high) are well investigated. Such quasi-reversible pseudocapacitive processes are of 10–100 times greater specific capacitances than those on blocking electrodes [10].

As shown elsewhere [11,12], the ability of microporous ACM with a total specific surface of about 1000 m^2 g^{-1} to gain a charge greater than 2000 F g^{-1} under positive polarization in iodide aqueous solutions without reaching the potential of iodine release into free state is investigated. Pseudocapacitive process is characterized by the surface gating potential, which is characterized by Fermi level of ACM [11]. According to a model which does not take into account interatomic interaction in the adsorptional layer (g = 0), the Langmuir isotherm can be represented by the well-known relation from [10]:

$$\theta_I \times (1 - \theta_I)^{-1} = (Kc_{I^-}) \times \{\exp(EF) \times (RT)^{-1}\}, \tag{1}$$

here $0 < \theta < 1$; K is the constant of adsorptional equilibrium; c_{I^-} is the concentration of iodine ions in the solution. In the work [10]

[*] Tel. : +38 0937045031.
  E-mail address: bakhmatyukb@gmail.com (B.P. Bakhmatyuk).

Table 1
Physico-chemicalparameters of "Norit DLC Supra 30".

Parameter	Value
Total specific surface, $m^2 g^{-1}$	1900
Specific surface micropores, $m^2 g^{-1}$	1810
Micropore volume, $cm^3 g^{-1}$	0.61
Specific surface mesopore, $m^2 g^{-1}$	90
Mesopore volume, $cm^3 g^{-1}$	0.25
Salt content, %	2
Humidity, %	3
Particle size, μm	13–20

the following formula is obtained:

$$C_F = (q_I F) \times (RT)^{-1} \times \{\theta_I (1 - \theta_I)\}, \tag{2}$$

which indicate the maximum of the pseudocapacitance at $\theta = 0.5$, and the electrode potential of the maximum is considered as equilibrium electrode potential E^0. The ability of ACM to make the monolayer adsorption, which is used for determination of the iodine index NI, is well-known [13].

According to the works [14,15], in which the correlation between NI and S_{total} is made according to BET, under normal condition, from iodide aqueous solution 1 mg of iodine can be adsorbed per $1 m^2$ of ACM surface. The influence of ACM nanocomposites with iodine on the increase in energy density of a supercapacitor in non-aqueous electrolyte is investigated in the works [16–19]. In the works [20–24], the increase in the capacitance of a supercapacitor in iodide solution is stated.

In our opinion, the determination of the theoretical data of electrosorption of iodine and comparison of practical and theoretical data of capacitance and energy density of NS commercial ACM in the system of HS is of considerable interest. Just this is considered in this work.

2. Experiment

2.1. Materials

The "Norit DLC Supra 30"commertial material (Table 1) and Zn foil (99.999%, Aldrich) were used for our experiments. All the chemicals were of analytical grade, and they were used without further purification.

2.2. Material characterization

The morphology and elemental chemical composition of the film-like electrodes have been investigated by means of PEM-1061 transmission electron microscope (TEM) with EDAR attachment. Raman spectroscopy was performed with a help of T64000

Jodin Jvon Raman spectrometer having $1 cm^{-1}$ instrumental resolution. For each test, about 20 mg of carbon sample was used. Only 0.01% (0.1 mW) of the laser power at 488 nm wavelength with exposure time of 200 s was used to avoid possible laser-induced damage.

2.3. Electrode preparation and electrochemical measurements

For investigations, there were used film-like electrode materials whose active mass $m_a = 10–40$ mg with the added binder 5–10 wt.% of Teflon and 10–20 wt.% of acetylene carbon black or graphite for increase in electric conductance. The electrodes were assembled by means of pressing film-like electrode materials to a net of stainless steel. Electrochemical investigations were carried out in a two-electrode glass cell with a Zn foil counter electrode ($16 cm^2$) and in a three-electrode glass cell with a $AgCl1/2Cl^-$ reference electrode. As the electrolyte, 25% ZnI_2 aqueous solution was used. All measurements were taken at room temperature. The electrode potentials E are referred to the standard hydrogen electrode. The electrochemical properties of the supercapacitor were investigated by cyclic voltammetry (CV), by galvanostatic charge–discharge (GCD), by method of electromotive force (EMF) measurement; the investigations have been carried out with the use of an AUTOLAB PGSTAT 30 measuring complex made in Netherlands by "ECO CHEMIE". The temperature coefficient of electromotive force in the temperature range 20–60 °C was measured with the use of TW2 thermostat. Galvanostatic investigations of the galvanic element

$$Zn|25\%ZnI_2|NS \text{ commerical ACM}, \tag{3}$$
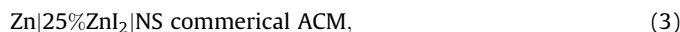
were also carried out with the use of a measuring module of the prototype of an HS. Here electrodes of NS commercial ACM and electrodes of Zn foil, whose area was $16 cm^2$, were used. C_f, W, P, Coulomb efficiency (η), and electrochemical equivalent of iodine (ε_I) from GCD and CV were determined according to the following known formulas:

$$C_d = (I_d \times t_d) \times (\Delta U \times m_a)^{-1} (a),$$
$$C_c = (I_c \times t_c) \times (\Delta U \times m_a)^{-1} (b),$$
$$C_d = I_d \times (v \times m_a)^{-1} (c), \tag{4}$$

$$W = U_{av} \times I_d \times t_d \times m_a^{-1} (a),$$
$$P = I_d \times U_{av} \times m_a^{-1} (b),$$
$$\eta = (C_d) \times (C_c)^{-1} 100\%,$$
$$\varepsilon_I = m_I \times (I_d \times t_d)^{-1} (c), \tag{5}$$
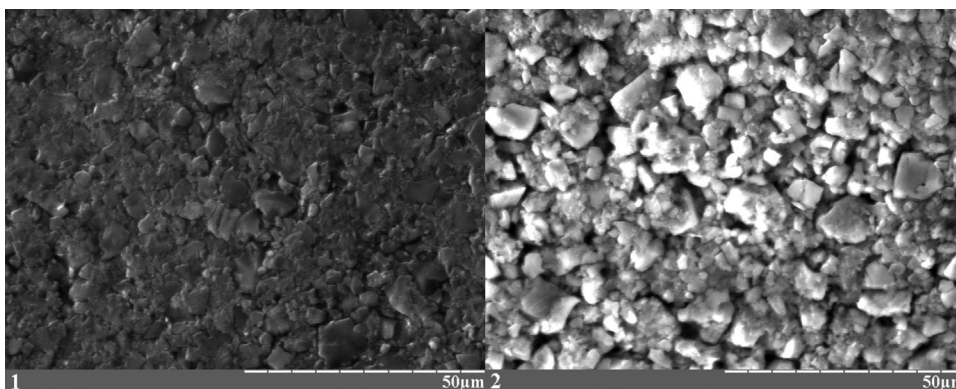
Fig. 1. TEM images: 1–initial material; 2–electrochemically charged electrode.