

UDC 544.018/544.6.018.2/544.636

PACS numbers: 61.43.Gt, 81.07.Wx, 88.80.F, 82.47.Uv

doi: 10.15330/jpnu.3.1.80-85

THE INFLUENCE OF MODIFICATION OF THE SURFACE OF NANOPOROUS CARBON MATERIAL BY THE OXIDES OF METALS

B.I. RACHYI, M.M. KUZYSHYN, M.O. NYKOLIUK, R.I. MERENA, R.P. LISOVSKY

Abstract. Nitrogen containing carbon materials with metal of oxides (Fe, Ni, Co) prepared by the chemical precipitation method have been shown to be outstanding novel materials for electrochemical capacitors. The electrochemical properties of the electrodes have been studied by considering the effect of the mole ratio of metals. Cyclic voltammetric measurements indicate that nickel, cobalt and iron oxides increase specific capacity of electrochemical capacitors up to 260 F/g in 30% KOH electrolyte. Impedance studies show that the enhanced electrical properties and high frequency response are attributed to the presence of Fe oxides.

Keywords: electrochemical capacitor, pseudocapacitance, oxide of metal, nanoporous carbon material, surface modification.

1. INTRODUCTION

It is known that the energy storage in the electrochemical capacitors can be carried out by the electrostatic charge-discharge of the electric double layer realized in electrodes of the nanoporous carbon; or as the result of fast reversible faraday reactions which tend to occur when using oxides of ruthenium and iridium. However, the carbon materials with the large specific area of surface do not yield the high values of specific power and capacity. So promising is the combination of modification of the available electrode materials by heat treatment and chemical treatment with the implementation of metals and their oxides on the surface of the porous carbon to improve its electrochemical properties [1, 2].

2. MATERIALS AND METHODS

The combination of modifications by the heat treatment and chemical treatment with the introduction of oxides of metals on the surface of nanoporous carbon material (NCM) can increase the pseudocapacitance properties of the electrodes of electrochemical capacitors (EC). For this purpose, 3 g of N-containing NCM [3] is mixed with the aqueous metal nitrate 0.005 M and ammonia water 0.01 M. The mixture is moved for 3 hours at 333 ± 5 K, then washed with distilled water to obtain a neutral pH. As a result of chemical reactions on the surface of NCM the metal hydroxides were formed. Prepared

material was dried at 353 K for 12 hours, then it was subjected to thermal treatment at $T = 673 \pm 10$ K in air for forming the metal oxides. As a result, there were received the samples of NCM with the metal content of 0.5; 1; 2 and 5 (in % of weight). Doped metals were iron, nickel and cobalt.

Electrochemical studies of behavior electrode materials in an aqueous electrolyte solution with the three-electrode cell. The basic composition for the working electrodes served mix included N-containing NCM precipitated with oxides of nickel, iron and cobalt and thermal expanded graphite. The resulting mixture was pressed into the nickel mesh with the size 5×5 mm². After the drying the shaped electrodes were soaked in an electrolyte solution. As subsidiary served platinum electrode and exemplary served chloride-silver electrode (Ag/AgCl), which is placed into the aqueous solution of KCl 3.5 M and combined with the working chamber via Agar-agar salt bridge. As the electrolyte was used the 33% aqueous KOH. Electrochemical studies are conducted using spectrometer Autolab PGSTAT100 with the cyclic voltammetry and chronopotentiometry, electrochemical impedance spectroscopy method in the frequency range of $10^{-2} \dots 10^5$ Hz and the following modulation of the equivalent electrical circuit (EEC). The calculation of parameters was made with the way of minimizing the standard deviation of measured impedance modulus and impedance modulus, automatically calculated for present EEC, using the installed software ZView-2 (Kramers-Kroning coefficient not more than 10^{-4} , difference between experimental and model curves is not more than 10%).

3. RESULTS AND DISCUSSION

For the detailed analyze of physic-chemical processes on the border between the carbon electrode and electrolyte the Nyquist Plot were made (Fig. 1). All the impedance hodographs are the same far from the origin, that is modeled by frequency-independent resistance.

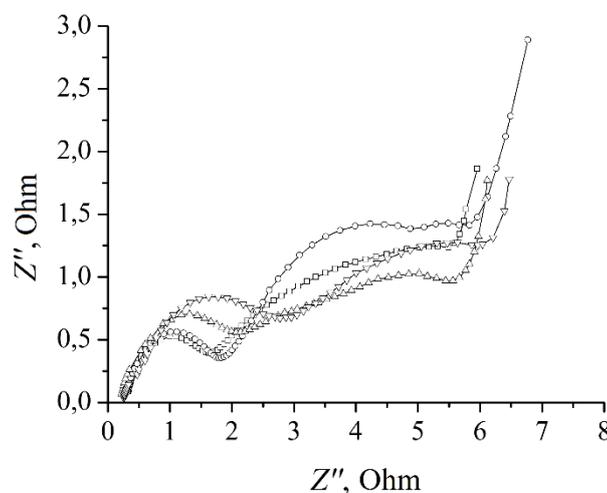


Fig. 1. Nyquist Plot for carbon electrodes with different consistence of iron:
 \square – 0,5; \circ – 1; Δ – 2 and ∇ – 5 % of weight.

Impedance spectrum in the high frequency range is an arch which probably accords to a barrier created during transfer of the charge from the wire way to nanosponge carbon [4]. In the middle-frequency range there is an arch that indicates the pseudocapacitance accumulation of charge. The quick reversible Faraday reactions which are going together with the capacitance charge storage demands additional energy for chemical connections creation. In the low frequency range in all cases there is a linear part which has different angles and associated with the accumulation of the charge by the dual electric layer. The angle of the curve increases according to the iron content, that indicates the dominance of diffusion limitations over the kinetic ones.

Based on the arguments above to approach experimental curves (Fig. 1), that describe pseudocapacitance accumulation of the electric energy process, there is EEC on the Fig. 2.

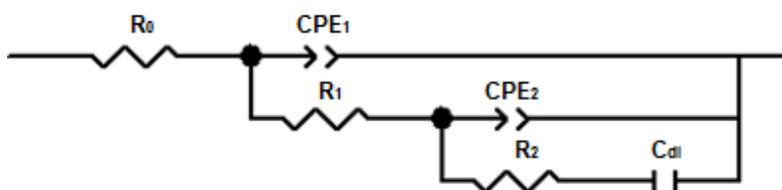


Fig. 2. EEC to make model Nyquist Plot, which we got for carbon electrodes doped with iron oxide.

At this scheme R_0 considers resistance of electrolyte, contacts and wire ways. The following elements indicate diffusion processes of the accumulation of electric charges in the sponges of carbon material on the border between electrode and electrolyte. So the link $CPE_1 \parallel R_1$ describes the forwarding of the charge through the border of electrolyte and electrode, which are caused by electrode material fractal structure. The link $CPE_2 \parallel R_2 - C_{dl}$ is responsible for diffusion processes that are caused by faraday reactions in transport ports and for kinetic processes of the double layer formation in micro ports, where R_1 and R_2 are the faraday resistance and polarize resistance, C_{dl} is the capacity of charge on the border (in this case it could be regarded as the capacity of double layer). This model of EEC gave us the possibility to approach the experimental spectrum to the calculated one and to get the parameters values for the scheme above (Tab. 1).

Sample	R_0 , Ohm	CPE_{1-T} , mF	CPE_{1-P}	R_1 , Ohm	CPE_{2-T} , Ohm	CPE_{2-P}	R_2 , Ohm	C_{dl} , F
CFe-0.5	0.329	0.454	0.929	1.092	0.164	0.458	5.896	8.866
CFe-1	0.314	0.590	0.895	1.287	0.209	0.580	5.253	8.256
CFe-2	0.265	0.511	0.873	1.845	0.119	0.324	7.885	7.694
CFe-5	0.272	0.411	0.732	2.226	0.203	0.458	8.147	5.031

Tab. 1. EEC parameters in disconnected circuit potential.

In the model Nyquist Plots for EEC there were included elements of the constant phase CPE . Their impedance is determined with the formula: $Z_{CPE} = CPE_T(j\omega)^{-CPE_P}$, where the CPE_P parameter considers the phase deviation and, accordingly type modeled process. When the CPE_P value approaches to 1, this element defines the capacitance behavior of the system; but when $CPE_P \sim 0,5$ it defines diffusion behavior of the system. It should be noted, that the physical content of item CPE is not finally determined yet. In general it is considered as the result of the diffusion to uneven available surface, which formally attributed fractional dimension, or as accumulation of charge directly on this surface. In this case there is unevenly distributed capacitance, that is often associated with the surface roughness of the material [5].

Based on the above and data modeling analysis (Tab. 1) could argue that CPE_1 is the element of constant phase capacitive, which describes the spatially distributed capacitance carbon matrix ($CPE_1 - P$ approaches to 1). The volume of R_1 increases with increasing iron content and, the volume of $CPE_1 - P$ decreases from 0.9 to 0.7 with its increase. This fact is probably caused by decrease of active surface area, which is involved in the formation of double layer and by decrease in electrical conductivity of the carbon electrode. Significant changes characterize the CPE_2 . According to table 1 it can be attributed as the steady phase diffusion type element. It is responsible for the diffusion of charge carriers, which is caused by quick reversible Faraday reactions.

Features and morphology of carbon electrodes which we have got are reflected in a kind of changes of EEC parameters during varying the electrode potential. For example for sample CFe-1 there are Nyquist Plots with different potentials of electrodes (Fig. 3).

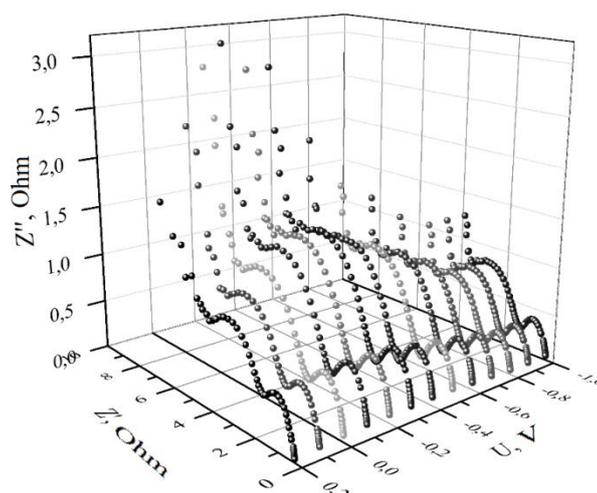


Fig. 3. Nyquist Plots with different potentials of electrodes for CFe-1.

Hodographs of impedance of electrodes have two well defined semicircle arches in ranges of high-frequency and middle-frequency, which can register under processes, accordingly, of transport of ions to the border of two phases and of pseudocapacitance accumulation of electric charge. After analysis of the data (Tab. 2) which we have got by modeling EEC (Fig. 2) it is possible to notice that resistances R_0 and R_1 are almost independent of the applied potential. The behavior of the element C is similar to changing of the electrode potential whereby its value increases sharply at potentials -0.4 V and -0.8 V. When the potential is -0.3 V is seen an increase in midrange arc, that is caused by faraday reaction: Fe_3O_4 goes into FeOOH [6]. With further growth of potential, as the result, carriers, which are formed in the charge trying to get the border of two phases. The same way when the potential is -0.7 V there is another reaction: FeOOH goes into FeO_2 , and it caused the electrons released [6]. This in turn increases the electronegativity of the material, thus improving the availability of ions of K^+ to surface of the electrode. With the next potential growth the capacity reaches its maximum value.

So, potential dependence of parameters of EEC, which defines the behavior of the carbon electrode that is modified with the iron oxide depends on its content and on the area of the material which is involved to electrostatic accumulation of the electric power.

Fig. 4 demonstrates cyclic voltammograms for the N-containing NCM with different content of iron (scan rate 1 mV/s), received by three-electrode cell regarding chlorine-silver comparing electrode.

E, V	R_0, Ohm	CPE_{1-T}, mF	CPE_{1-P}	R_1, Ohm	CPE_{2-T}, Ohm	CPE_{2-P}	R_2, Ohm	C_{dl}, F
0.2	0.302	2.608	0.859	1.057	0.215	0.462	5.848	11.570
0.1	0.305	1.794	0.856	1.229	0.173	0.534	5.194	5.612
0	0.309	1.072	0.875	1.331	0.149	0.572	5.367	4.723
-0.1	0.313	0.704	0.894	1.365	0.149	0.577	5.739	4.837
-0.2	0.314	0.598	0.896	1.375	0.160	0.583	5.828	5.611
-0.3	0.314	0.598	0.896	1.375	0.160	0.583	5.828	5.611
-0.4	0.314	0.590	0.895	1.287	0.209	0.580	5.253	8.256
-0.5	0.313	0.703	0.885	1.227	0.236	0.585	4.718	10.19
-0.6	0.313	0.881	0.878	1.160	0.266	0.593	4.208	11.30
-0.7	0.311	1.234	0.863	1.088	0.298	0.600	3.666	12.87
-0.8	0.308	1.933	0.846	1.017	0.329	0.607	3.112	13.22
-0.9	0.308	1.933	0.846	1.017	0.329	0.607	3.112	13.22
-1	0.308	1.933	0.846	1.017	0.329	0.607	3.112	13.22

Tab. 2. Parameters of EEC, which have been received by modeling of hodographs of impedance for the sample CFe-1 with different potentials of electrodes.

Getting cyclic voltammograms for carbon electrodes makes possible to calculate their specific capacitance relative to the chlorine-silver electrode compared by the formula: $C_{sp} = I / (2 \cdot s \cdot m)$, where I – is the current of anodic or cathodic branches in voltammograms; s – is the scanning rate; m – the active weight of the electrode.

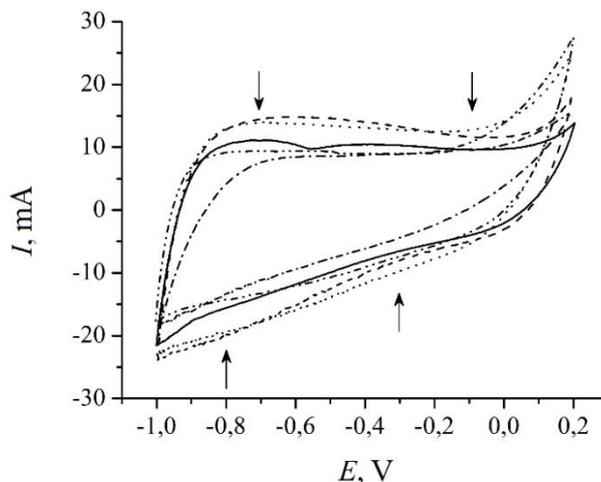


Fig. 4. Cyclic voltammograms for the N-containing NCM with different content of iron (scan rate 1mV/s): — 0.5; - - - 1, - - - - 2, ·····5 (in % of mass).

The calculated values of the specific capacity are shown in table 3. The cyclic voltammograms are symmetric that evidence of reversible electrochemical behavior of existing cells. Additionally, the potential-dynamic curves demonstrate peaks, caused by the occurrence of the fast redox reactions.

Sample	Specific capacity, F/g		Effectiveness, %
	charging	discharging	
CKN-4	196.3	165.6	84.4
CFe-0,5	170.8	169.9	99.5
CFe-1	273.3	259.4	94.9
CFe-2	210.8	197.4	93.7
CFe-5	134.4	129.6	96.5

Tab. 3. Capacitance characteristics of iron-containing samples.

As shown in the (Tab. 3) with an increase in the percentage of iron, the capacity of the iron-modified NCM increases up to a maximum of 260 F/g with the iron content of 1%, that is caused by the combination of the capacity double layer on the border between carbon electrode and electrolyte with the pseudocapacitance, caused by iron oxide. Further increase of the share doped reduces the value of specific capacity by excess coating of surface of nanoporous carbon by the iron oxide. Thus, reducing the capacity of double layer is caused by the limiting of surface of NCM by iron oxide [2].

At fig. 4 for the sample CFe-0.5 it is possible to notice two anode peaks and two cathode peaks, which are caused by redox reactions. First Fe_3O_4 converts to $FeOOH$, then $FeOOH$ goes to $FeO_2 \cdot FeOOH$ and FeO_2 , which transform back to Fe_3O_4 and $FeOOH$ accordingly [6]. As shown in the tab. 4, deposition of iron increases the capacity of nanoporous carbon electrode, and iron content of 1% provides the maximum specific capacity (260 F/g). It should be noted that with increasing of the iron oxide content, the intensity peaks at potentials -0.3 V and -0.7 V decrease. This shows the dominance of process of electrostatic accumulation of electrical energy.

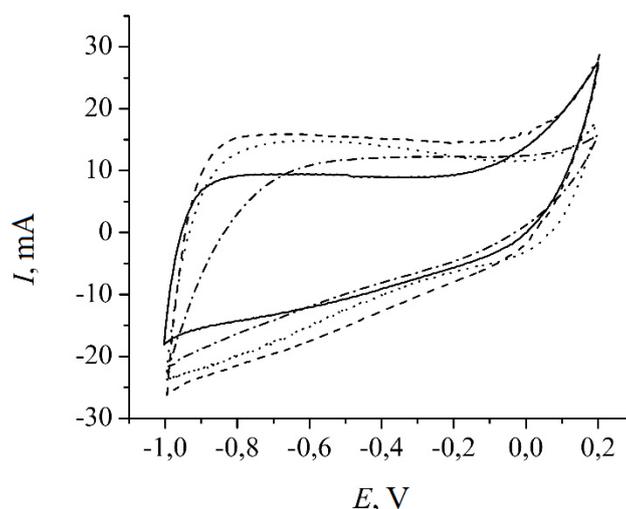


Fig. 5. Cyclic voltammograms for metal-containing NCM: — CNi-1; --- CFe-1, CCo-1, -.- NCM.

Based on the results of studies were received voltammograms of samples with the deposited metals of nickel, iron and cobalt with the mass content of 1%, scanning speed was 1 mV/s (fig. 5). Find the peaks of redox reactions at voltammograms of the samples with the oxide nickel and oxide cobalt is impossible, that is caused by large values of capacitance double layer [7].

Galvanostatic measuring of the cells, whose electrodes were formed based on NCM with the different oxides of metals showed almost symmetrical behavior of the charge/discharge processes (fig. 6). Slight deviations asymmetry of the curves of charge/discharge observed for the sample CFe-1, which showed the highest value of specific capacitance of 260 F/g.

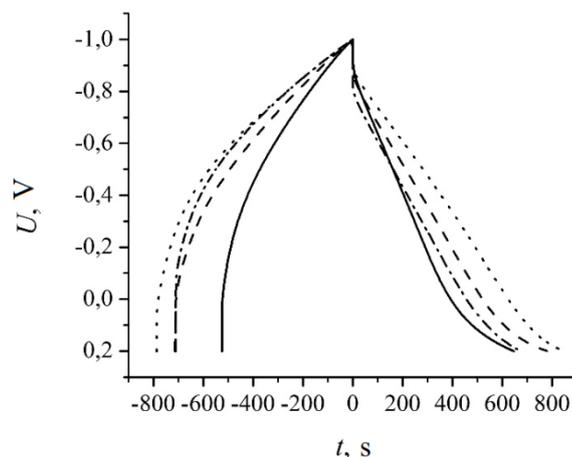


Fig. 6. Chronopotentiograms for the samples — CKN-4; --- CNi-1, -.- CFe-1, CCo-1.

The result is absolutely consistent with the data of the cyclic voltammetry (Tab. 3). It should be noted that such carbon electrodes exhibit greater capacitance value than N-containing NCM (Tab. 4).

Sample	CKN-4	CCo-1	CFe-1	CNi-1
C_{sp} , F/g	165.6	195.6	259.4	201.5

Tab. 4. Specific capacity of metal-containing NCM.

In addition, at the curves of charge/discharge of investigated materials it is possible to mark two areas with different slope: from -1 V to -0.3 V and from -0.3 V to 0.2 V (Fig. 6). According to [8, 9], some surfactants can promote the adsorption of anions or of cations or of both by the electrostatic forces and specific chemical absorption. In the first area dominates the process of electrostatic charge/discharge of double layer; in the second area there is an influence of the quick reversible Faraday processes to the accumulation of the electric power.

4. CONCLUSIONS

Developed the method for the deposition of metal oxides on the surface of the nitrogenous NCM. Found that if the content of a metal is 1%, so nickel, cobalt and iron oxides increase specific capacity of EC up to 260 F/g with the current discharge 0.3 A/g.

The contribution of the pseudocapacitance to overall capacity of EC which include nitrogenous NCM makes 30%. The deposition of the oxides of nickel, cobalt and iron on the surface of the N-containing NCM further increase this contribution respectively by 18, 22 and 60%, that is caused by the occurrence of redox reactions on the surface of NCM with the participation of the surface functional groups, OH⁻ ions and metal oxides.

REFERENCES

- [1] Lee Y.J., Jung J.C., Park S., Seo J.G., Baek S.-H., Yoon J.R., Yi J., Song I.K. Preparation and characterization of metal-doped carbon aerogel for supercapacitor. *Current Applied Physics*, **10** (2010), 947-951.
- [2] Lee Y.J., Park S., Seo J.G., Yoon J.R., Yi J., Song I.K. Nano-sized metal-doped carbon aerogel for pseudocapacitive supercapacitor. *Current Applied Physics*, **11** (2011), 631-635.
- [3] Ostafiychuk B.K., Budzulyak I.M., Rachiy B.I., Kuzyshyn M.M., Shyyko L.O. Nanoporous nitrogen-containing coal for electrodes of supercapacitors. *Nanoscience and nanotechnology research*, **1** (2) (2013), 17-22.
- [4] Macdonald J.R., Cook G.B. Reply to comments by almond and west on Na β -alumina immittance data analysis. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **193** (1-2) (1985), 57-74.
- [5] Pajkossy T., Nyikos L. Diffusion to fractal surfaces – II. Verification of theory. *Electrochimica Acta*, **34** (2) (1989), 171-179.
- [6] Liu X.M., Zhang Y.H., Zhang X.G., Fu S.H. Studies on Me/Al-layered double hydroxides (Me = Ni and Co) as electrode materials for electrochemical capacitors. *Electrochimica Acta*, **49** (19) (2004), 3137-3141.
- [7] Lang J.W., Yan X.B., Liu W.W., Wang R.T., Xue Q.J. Influence of nitric acid modification of ordered mesoporous carbon materials on their capacitive performances in different aqueous electrolytes. *Journal of Power Sources*, **204** (2014), 220-229.
- [8] Qu D. Studies of activated carbons used in double layer supercapacitors. *Journal of Power Sources*, **109** (2002), 403-411.
- [9] Cottineau T., Toupin M., Delahaye T., Brousse T. Nanostructured transition metal oxides for aqueous hybrid electrochemical supercapacitors. *Applied Physics A*, **82** (2006), 599-606.

Address: B.I. Rachiy, M.O. Nykoliuk, R.P. Lisovsky, Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine;
M.M. Kuzyshyn, R.I. Merena, Ivano-Frankivsk National Medical University, 2, Halytska Str., Ivano-Frankivsk, 76018, Ukraine.

E-mail: bogdan_rachiy@ukr.net.

Received: 18.04.2016; **revised:** 20.05.2016.

Рачій Б.І., Кузишин М.М., Николюк М.О., Мерена Р.І., Лісовський Р.П. Вплив модифікації поверхні нанопористого вуглецевого матеріалу оксидами металів. *Журнал Прикарпатського університету імені Василя Стефаника*, 3 (1) (2016), 80–87.

Азотовмісні нанопористі вуглецеві матеріали з оксидами металів (Fe, Ni, Co), що осаджені хімічним методом є перспективним електродним матеріалом для електрохімічних конденсаторів. В залежності від вмісту металів вивчено електрохімічні властивості електродів. Методом циклічної вольтамперометрії встановлено, що осаджені оксиди нікелю, кобальту та заліза сприяють зростанню питомої ємності електрохімічних конденсаторів до 260 Ф/г у 30% водному розчині КОН. Імпедансні дослідження показують, що покращені електричні властивості і високий частотний відгук зумовлені наявністю оксиду заліза.

Ключові слова: електрохімічний конденсатор, псевдоємність, оксид металу, нанопористий вуглецевий матеріал, модифікація поверхні.