

НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ  
Інститут металофізики ім. Г. В. Курдюмова

НАНОСИСТЕМИ,  
НАНОМАТЕРІАЛИ,  
НАНОТЕХНОЛОГІЇ

**ЗБІРНИК НАУКОВИХ ПРАЦЬ**  
**ТОМ 6, ВИПУСК 4**

РВВ ІМФ  
КИЇВ — 2008

PACS numbers: 81.05.U-, 81.40.Rs, 82.45.Yz, 82.47.Uv, 84.32.Tt

## **Electrochemical Characteristics of Capacitor Systems Formed on Chemically Modified Carbon Base**

**B. K. Ostafiychuk, I. M. Budzulyak, V. I. Mandzyuk, and R. P. Lisovskyy**

*Vasyl Stefanyk Precarpathian National University,  
Shevchenko Str., 57,  
Ivano-Frankivsk, Ukraine*

Influence of chemical modification of the activated carbon (AC) material on its specific capacity is found out with the use of methods of impedance spectroscopy, cyclic voltammetry and chronopotentiometry. As shown, a general capacity is the sum of two components, namely, double electric-layer (DEL) capacity and pseudocapacity, thus the deposit of the last is insignificant (8–14%). The alloying with rare-earth metals and their compounds results in the rise of specific capacity of AC. Probably, the principal reason of such a growth is transformation of valence bond of carbon material due to introduction of the additional electron states from the implanted metals. As a result, the considerably greater amount of ions (especially, positive ones) will take part in DEL forming, and, consequently, will predetermine growth of specific capacity.

З'ясовано вплив хемічної модифікації активованого вуглецевого матеріалу на його питому місткість з використанням метод імпедансної спектроскопії, циклічної вольтамперометрії та хроноамперометрії. Показано, що загальна місткість є сумою двох складових — місткості подвійного електричного шару (ПЕШ) та псевдомісткості, причому, внесок останньої є незначним (8–14%). Легування рідкоземельними металами та їх сполуками призводить до збільшення питомої місткості активованого вуглецю. Ймовірно, основною причиною такого зростання є трансформація валентної зони вуглецевого матеріалу за рахунок добавляння додаткових електронних станів від втілених матеріалів, в результаті чого значно більша кількість йонів (насамперед, позитивних) буде брати участь у формуванні ПЕШ, а отже, і зумовлювати зростання питомої місткості.

Изучено влияние химической модификации активированного углеродного материала на его удельную емкость с использованием методов импедансной спектроскопии, циклической вольтамперометрии и хроноамперометрии. Показано, что общая емкость является суммой двух составляющих — емкости двойного электрического слоя (ДЕС) и псевдоемкости, причем, вклад последней незначителен (8–14%). Легирование редкоземельными метал-

лами и их соединениями увеличивает удельную емкость активированного углерода. Вероятно, основной причиной такого роста является трансформация валентной зоны углеродного материала за счет добавления дополнительных электронных состояний от внедренных материалов, вследствие чего значительно большее количество ионов (в первую очередь, положительных) будет принимать участие в формировании ДЭС, а, следовательно, и обуславливать рост удельной емкости.

**Key words:** activated carbon material, double electric layer, specific capacity, Nyquist diagram, cyclic voltamogram.

*(Received November 21, 2008)*

## 1. INTRODUCTION

The use of various methods of after-activation modification of an activated carbon (AC) is related to the necessity to improve its parameters as electrode material of electrochemical capacitors (EC). So it is not possible to attain the necessary values of given parameters in the process of activating, in particular, specific resistance and specific capacity of a double electric layer (DEL) formed by the given material and electrolyte [1].

Coming from general principles of physics and topology of the developed surface, the principle decision of the indicated problem possible both due to the increase of the electronic state density in a AC matrix [2], and due to bringing as soon as possible greater part of the developed surface in DEL forming, because, as known [3], to 50% of working pores do not wet by an electrolyte through their chemical-structural features. One of possibilities of the indicated ideas realization is modification of AC by its alloying by rare-earth metals and their compounds, that would give possibility substantially to multiply a DEL capacity, and, accordingly, the capacitors formed on the basis of thus modified AC. Er belongs to the first (its percentage in AC makes 0.1, 0.2, and 0.4 wt.%), to the second— $Tm_2O_3$ ,  $Eu_2O_3$ ,  $Dy_2O_3$ ,  $Ho_2O_3$ ,  $Pr_2O_3$ , content of which in AC made 0,1 wt.%. The addition of copper was entered in an amount 0.1 wt.% into got alloyed materials (Er,  $Tm_2O_3$ ,  $Eu_2O_3$ ) with the purpose of rise of its electronic conductivity. Therefore, the influence of introduction of the indicated metals into AC on its physical and chemical properties and operating characteristics of capacitors with a DEL formed on its base [4] was explored in a given work.

## 2. EXPERIMENTAL

AC got from fruit stone by them carbonization with a next activation in the closed reactor at high pressure was used as research objects [5].

The alloying of AC by erbium was carried out with using a nitro-acid

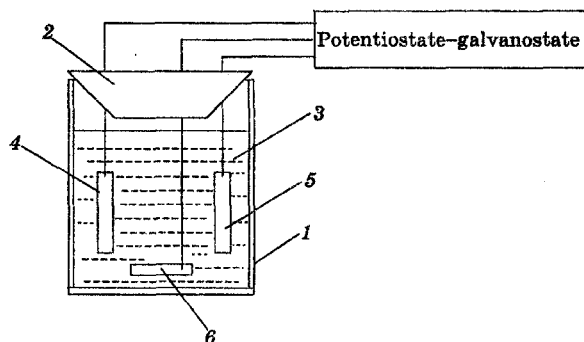


Fig. 1. Electrochemical cell: 1—glass cell; 2—pressurizing cover; 3—electrolyte; 4—working electrode; 5—reference electrode; 6—comparative electrode.

erbium. Investigation of alloying admixtures distribution in AC was carried out by the method of second ion mass spectrometry on mass spectrometer MS-7201 device.

A three-electrode electrochemical cell (Fig. 1) was used for the receipt of Nyquist diagrams. AC with the proper percentage of the alloyed material was used as working electrode, a comparative electrode was similar to working that, a silver-chlorine electrode Ag/AgCl was as a reference electrode. A potential of carbon material in relation to the reference electrode made  $-0.33$ – $-0.28$  V. 30% water solution of KOH + 0.3% water solution of LiOH was used as an electrolyte. The impedance measuring was conducted with the use of spectrometer Autolab PGSTAT/FRA-2 (Holland) in the frequency interval of  $10^{-2}$ – $10^5$  Hz.

The receipt of cyclic voltamperograms of carbon electrodes was conducted in the potential range of  $-1$ – $0.2$  V with the use of above three-electrode cell with silver-chlorine electrode reference electrode. Scan rate was 5, 8, 10, 20, 30, 40, and 50 mV/s.

### 3. RESULTS AND DISCUSSION

It is comfortably to study properties of enough wide rows of the systems, especially electrochemical ones, after response of this systems to an external sinusoidal signal. The use of impedance spectroscopy method for solving of indicated above tasks is most expedient in this plan, as it enables to conduct research in the enough wide frequency interval ( $f = 10^6$ – $10^{-3}$  Hz) [6].

For Er-modified carbon materials, a Nyquist diagram (Fig. 2) presents by itself a combination of two asymmetric semicircles in the frequencies region of  $1$ – $10^5$  Hz. Low-frequency branch tends to infinity at  $\omega \rightarrow 0$  for AC with 0.1 and 0.2 wt.% Er content that indicates on the typical behaviour of the capacitor systems. It inclines angularly  $\sim 45$  to

the actual resistance axis for material with 0.4 wt. % Er content that can specify in the presence of diffusive processes in the explored material, which are described by an Warburg impedance.

Equivalent schemes, which model electrochemical processes, flowed at the electrode-electrolyte boundary and in material, testify the in favor of indicated suppositions (Fig. 3). A relative error for each parameters of equivalent scheme does not exceed 5%; parameter  $\chi^2 = 10^{-4}$ – $10^{-5}$  that testifies to legitimacy of the offered choice.

Resistance  $R_{ct}$  corresponds to series equivalent resistance, which consists of the electrolyte resistance, resistance of lead and contacts. Two  $R||CPE$ -links can be linked to heterogeneity of DEL and fractal structure of electrode, resistance  $R_4$  is polarization or electronic resistance of material, Cdl—DEL capacity, capacity-type constant phase element CPE3 corresponds to a Faraday capacity;  $W_o$ —diffusive Warburg impedance.

The increase of Er percentage results in the insignificant increase of total resistance  $R_2 + R_3$  (from 16 to 25 Ohm). It testify that Er introduction blocks the ions  $C^+$  transport through the electrode-electrolyte boundary and hinders to them to form DEL. Except for it, a growth of Er content predetermines a forming of heterogeneous DEL and inten-

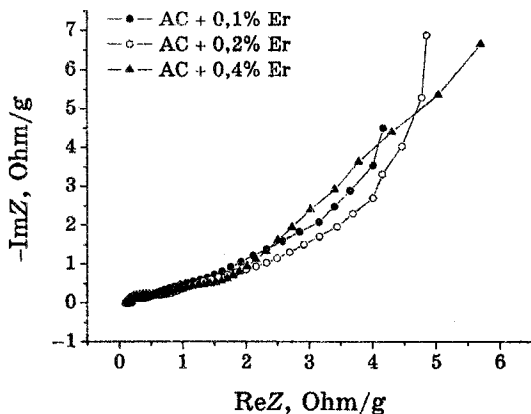


Fig. 2. Nyquist diagram of Er-modified AC.

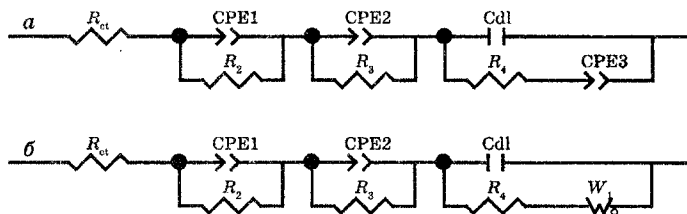


Fig. 3. Equivalent schemes for Nyquist diagrams obtained for Er-modified AC: (a) 0.1 and 0.2 wt. % Er content; (b) 0.4 wt. % Er content.

sification of diffusive processes in it—growth of CPE1 and CPE2 parameters confirm it. The first parameter is the constant phase element of capacity type ( $n \sim 0.83$ ), the second one is of diffusive type ( $n \sim 0.55$ ). The  $n$  parameter is in a formula for determination of impedance size of CPE element  $Z_{CPE} = A^{-1}(j\omega)^{-n}$  and characterize a phase deviation. A growth of erbium concentration in AC results in the increase of CPE<sub>3</sub> parameter, which presents by itself the constant phase element with the heterogeneously distributed capacity ( $n = 0.82-0.91$ ). Thanks to it, the total capacity of material is multiplied not only thanks to a DEL capacity, but also due to faraday processes. Electronic resistance of material according to impedance spectroscopy data makes 22.6, 22.7, and 24,3 Ohm, respectively. There is a maximum for DEL capacity at 0.2% Er content (Table 1). It is possible to assume that thanks to an erbium the electronic state density is multiplied at a Fermi level of carbon material, as a result greater amount  $C^+$  ions take part in DEL forming. Subsequent erbium introduction results in blocking of working pores of AC, as a result there is reduction of DEL capacity [7].

The given supposition is confirmed by the results of potentiodynamics researches (Fig. 4). There is the difference of the  $I-E$  curves especially in the region of negative potentials, at which a DEL capacity is provided by  $C^+$  ions from the electrolyte side. Dissymmetry of given curves in relation to the zero current line ( $I = 0$ ) is the characteristic feature, that specifies on the passing of processes unconnected with DEL forming (above all Faraday processes).

Introduction of copper in an amount of 0.1 and 0.4 wt.% into Er-modified material, which has a maximal specific capacity, does not

TABLE 1. Specific capacity of AC, F/g.

Material	Method		
	Impedance spectroscopy	Voltamperometry	Chronopotentiometry
AC	56	64	69
AC + 0.1% Er	71	77	73
AC + 0.2% Er	75	83	72
AC + 0.4% Er	59	66	65
AC + 0.2% Er + 0.1% Cu	61	69	68
AC + 0.2% Er + 0.4% Cu	72	81	77
AC + 0.1% $Tm_2O_3$	—	68	63
AC + 0.1% $Tm_2O_3$ + 0.1% Cu	89	101	81
AC + 0.1% $Eu_2O_3$	80	86	67
AC + 0.1% $Eu_2O_3$ + 0.1% Cu	82	84	68
AC + 0.1% $Dy_2O_3$	78	83	65
AC + 0.1% $Ho_2O_3$	80	83	70
AC + 0.1% $Pr_2O_3$	54	59	58

change the type of Nyquist diagram noticeably, predetermining the change of general impedance of the electrochemical system only (Fig. 5). According to it, an equivalent scheme, which models motion of electrochemical processes in the explored system, will have a similar kind (Fig. 3, a).

Electrochemical system made on the Er-modified material basis with 0.1 wt.% Cu content is characterized by the some greater values of  $R_2$  and  $R_3$  parameters (2.8 and 3.7 Ohm, and 19.1 and 24.9 Ohm, respectively) and practically unchanging electronic resistance  $R_4$  (22.8 and 23.2 Ohm, respectively) in comparison with the unalloyed by a copper material. However, there is the reduction of all three resistances at 0.4 wt.% Cu concentrations in carbon material, especially, electronic one  $R_4$  (14.2 Ohm) that is expressly represented on  $-\text{Im}Z = f(\text{Re}Z)$  depend-

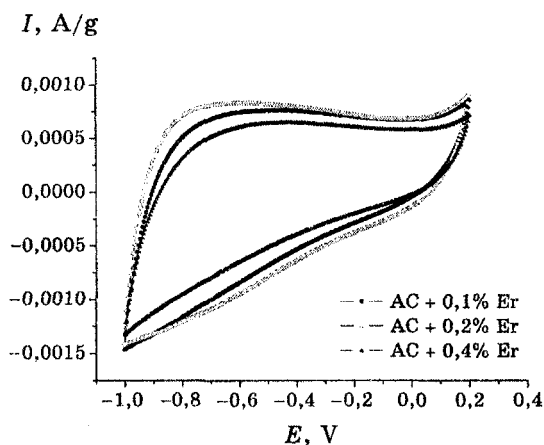


Fig. 4. Cyclic voltamperograms of Er-modified AC.

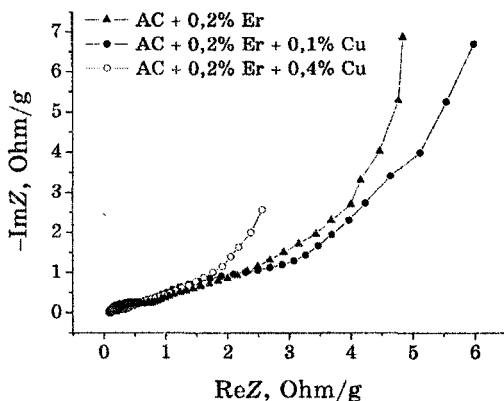


Fig. 5. Nyquist diagrams for Er- and Er + Cu-modified AC.

ence. Accordingly to Table 1, such modification by a copper does not lead the specific capacity of carbon material to the improvement, and can be used with a purpose of the increase of its electronic conductivity. Except for it, almost the identical capacity of the unalloyed and alloyed (0.4 wt.%) standards is achieved not due to DEL capacity, but due to the faraday that conditioned by the passing of mass-transfer processes (probably, redox reactions).

It is confirmed by the results of voltamperometric researches, accordingly to which there is an 'influx' in the negative potential region for a standard with 0.4 wt.% Cu contents, which is attribute to the faraday processes (Fig. 6). A horizontal plateau on the anode branch of  $I-E$ -curve of other standard indicates on that the specific capacity of material is provided mainly by DEL capacity.

The use of oxides by rare-earth metals as alloying material ( $Tm_2O_3$ ,  $Dy_2O_3$ ,  $Pr_2O_3$ ,  $Eu_2O_3$ ,  $Ho_2O_3$ ) does not change cardinally the general type of impedance curve (Fig. 7) (except for AV, alloyed by  $Tm_2O_3$ ). However, equivalent schemes, which model electrochemical processes, some differ. In particular, for AC doped by  $Dy_2O_3$  and  $Pr_2O_3$ , a scheme is similar to that on Fig. 3. There is the difference: the constant phase element  $CPE_3$  is the element of capacity type for the first material, while for the second, diffusive one.

For  $Eu_2O_3$ - and  $Ho_2O_3$ -doped materials, a scheme is the same as well as for Cr- and Mn- doped AC (Fig. 8) [2]. For AC doped by  $Tm_2O_3$ , we can not find an equivalent scheme, which would describe satisfactorily the behaviour of the electrochemical system.

As follows from Table 1, a specific capacity for  $Eu_2O_3$ -,  $Ho_2O_3$ -, and  $Dy_2O_3$ -doped material is practically identical. Taking into account the results of impedance spectroscopy and voltamperometry (Fig. 9), it is

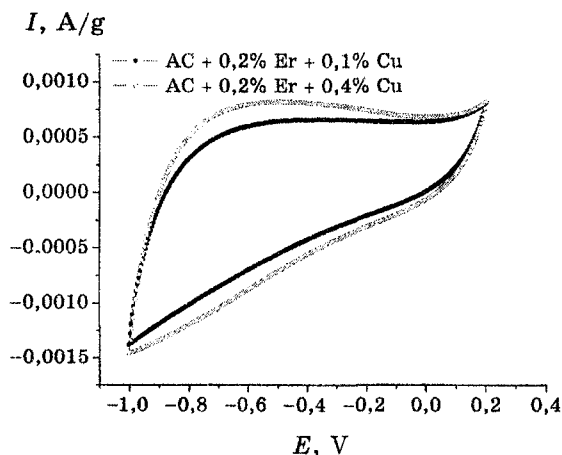


Fig. 6. Cyclic voltamperograms of Er + Cu-modified AC.



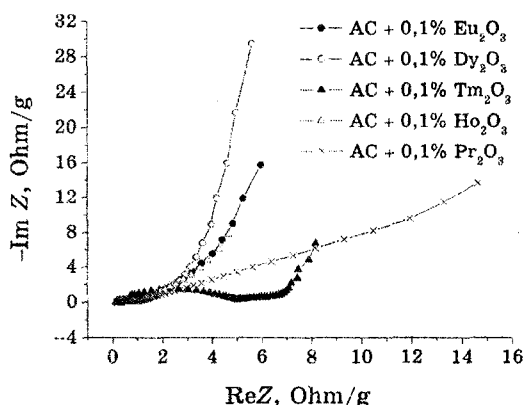


Fig. 7. Nyquist diagrams of AC doped by oxides of rare-earth metals.

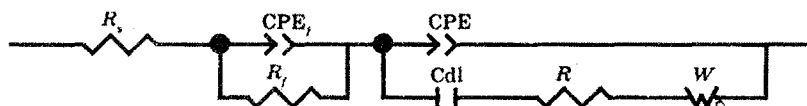


Fig. 8. Equivalent scheme for Nyquist diagram obtained for chemical modified AC.

TABLE 2. Internal resistance, Ohm.

Material	Method	
	Impedance spectroscopy	Chronopotentiometry
AC + 0.1% Er	22.6	24.3
AC + 0.2% Er	22.7	23.2
AC + 0.4% Er	24.3	29.4
AC + 0.2% Er + 0.1% Cu	23.2	25.2
AC + 0.2% Er + 0.4% Cu	14.2	17.8
AC + 0.1% Tm <sub>2</sub> O <sub>3</sub>	39.5	47.3
AC + 0.1% Tm <sub>2</sub> O <sub>3</sub> + 0.1% Cu	14.9	18.2
AC + 0.1% Eu <sub>2</sub> O <sub>3</sub>	9.2	11.3
AC + 0.1% Eu <sub>2</sub> O <sub>3</sub> + 0.1% Cu	7.4	8.4
AC + 0.1% Dy <sub>2</sub> O <sub>3</sub>	11.9	13.3
AC + 0.1% Ho <sub>2</sub> O <sub>3</sub>	11.7	13.4
AC + 0.1% Pr <sub>2</sub> O <sub>3</sub>	30.9	32.8

possible to assert that the general specific capacity of the explored material is provided by DEL capacity and pseudocapacity. For two other materials, in which Pr<sub>2</sub>O<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub> are as alloying additions, the deposit of pseudocapacity is unimportant.

Additional alloying of the given materials by copper in an amount of

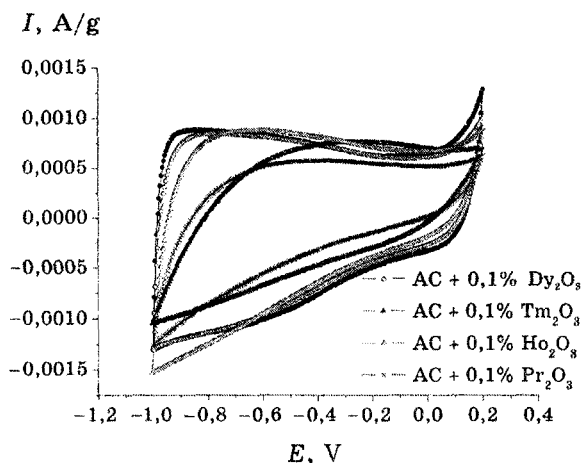


Fig. 9. Cyclic voltamperograms of AC doped by oxides of rare-earth metals.

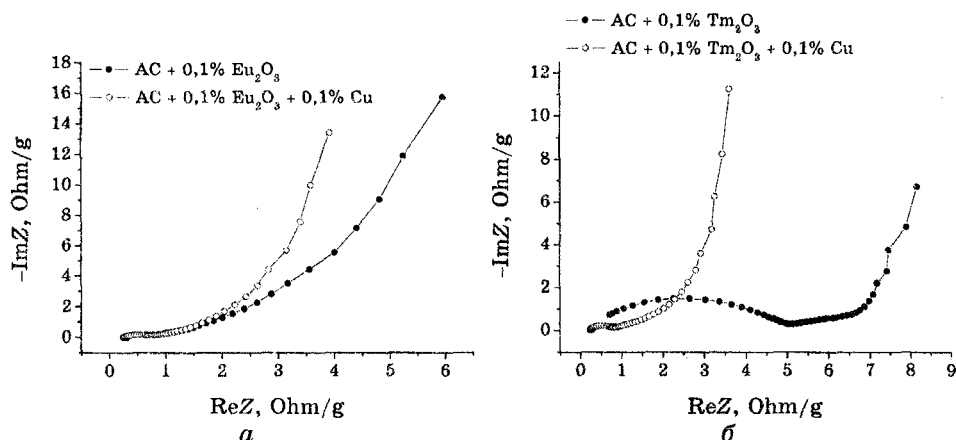


Fig. 10. Nyquist diagrams of AC doped by oxides of rare-earth metals and copper.

0.1 wt. % results not only in growth of specific capacity, but also in reduction of general impedance of the system (Fig. 10).

Internal resistance, which characterizes electro-physical properties of electrode carbon material, is no less important parameter. Its determination was conducted by the methods of impedance spectroscopy and chronopotentiometry. In the first case, the size of internal resistance was got from the results of model, and in the second, with the use of formula  $R = \Delta U / (2I)$ , where  $\Delta U$ —voltage drop on a discharge curve (Fig. 11),  $I$ —discharge current.

The values of internal resistance of the explored materials, got both methods, are resulted in Table 2.

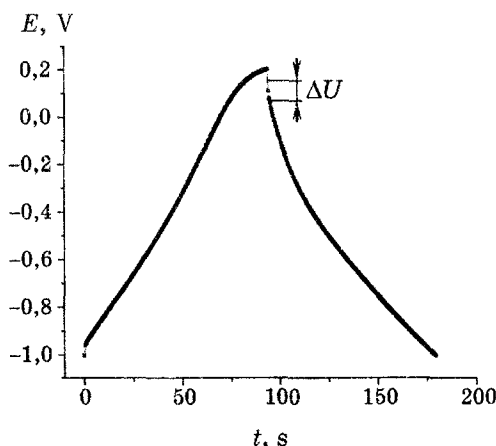


Fig. 11. A typical shape of charge-discharge curve.

It is necessary to remark that a difference between the got values is not very substantial (it does not exceed 7%). However, the chronopotentiometry method is more exact thanks to the simplicity.

Thus, chemical modification of AC by rare-earth metals and their compounds results in the rise of specific capacity AC. The principal reason of such growth, accordingly to previous researches, is transformation of valence area of carbon material due to bringing of the additional electronic states from the inculcated metals, as a result the considerably greater amount of ions (first of all, positive ones) will take part in DEL forming, and, consequently, to predetermine a growth of specific capacity.

## CONCLUSIONS

The equivalent schemes of capacitor system on modified AC bases are proposed, which describe satisfactorily electrochemical processes both on electrode-electrolyte boundary and in AC-matrix.

The general capacity of explored system is the sum of two components—DEL capacity and pseudocapacity, thus the deposit of the last is insignificant (8–14%).

The alloying by rare-earth metals and their compounds can results in the rise of specific capacity of AC up to 17%.

## REFERENCES

1. V. V. Nemoshkalenko, *X-Ray Emission Spectroscopy of Metals and Alloys* (Kiev: Naukova Dumka: 1972).

2. I. M. Budzulyak, V. I. Mandzyuk, R. P. Lisovskyy, R. I. Merena, and M. V. Berkeshchuk, *Nanosistemi, Nanomateriali, Nanotehnologii*, **4**, No. 3: 569 (2006).
3. A. Yu. Rychagov, N. A. Urinson, and Yu. M. Vol'fkovych, *Electrochemistry*, **37**, No. 11: 1348 (2001).
4. I. M. Budzulyak, I. I. Grigorchak, I. F. Myronyuk, and B. K. Ostafiychuk, *Molecular Energy Storage* (Patent No. 45576A. Ukraine MKII<sup>7</sup> H01G2/00, H01G4/00, H01G5/00, H01C7/00. Declared 23.01.2001. Published 15.04.2002. Bull. No. 4).
5. R. P. Lisovsky and R. I. Merena, *The IV-th International Conference NEET (21-24 June, 2005, Zakopane, Poland)*.
6. Z. B. Stoynov, B. M. Grafov, B. Savova-Stoynova, and V. V. Yolkin (Moscow: Nauka: 1991).
7. R. P. Lisovsky, R. I. Merena, and Ye. R. Luchkevych, *The X-th International Conference on Physics and Technology of Thin Films (2005, Yaremcha)*, vol. 2, p. 80.