Journal of The Electrochemical Society, **153** (9) A1655-A1671 (2006)
0013-4651/2006/153(9)/A1655/17/$20.00 © The Electrochemical Society

Mathematical Model of Heterogeneous Electrochemical Capacitors and Calculation of Their Parameters

S. A. Kazaryan,[a] S. N. Razumov,[a] S. V. Litvinenko,[a] G. G. Kharisov,[a] and V. I. Kogan[b,z]

[a]*Joint Stock Company ESMA, Troitsk, Moscow, Russia*
[b]*American Electric Power, Columbus, Ohio 43215, USA*

A mathematical model of heterogeneous electrochemical supercapacitors (HES) is proposed which makes it possible to develop capacitors with optimal designs and make calculations of their energy, capacity, and power parameters. Special attention is paid to the processes which occur in electrodes with double electric layer (DEL) of HES capacitors during their charge and discharge by different currents. It is demonstrated theoretically that in the efficiency of HES capacitors' operation, an important role is played by distribution of the potential along the thickness of electrodes with DEL. In order to build capacitors with improved parameters and optimal design, it is of paramount importance to take account of the type and value of conductivity of the material of the electrode with DEL and conductivity of the electrolyte in its pores. Analysis is performed to determine the efficiency of $PbO_2|H_2SO_4|C$ system capacitors' operation subject to thickness, conductivity, and specific capacitance of the electrode with DEL. It is established that energy and capacity parameters of the capacitors depend to a great extent on conductivity of their negative electrodes and electrolytes. It is demonstrated that there are different mechanisms of losses of energy and charge of the capacitors during their charge, discharge, and storage.

[DOI: 10.1149/1.2212057]

Manuscript submitted November 17, 2005; revised manuscript received April 20, 2006. Available electronically June 29, 2006.

In recent years the development of new, more efficient technologies of synthesis of various carbon materials has gained momentum, most of which are used in double electric layer (DEL) electrochemical capacitors. The new technologies of synthesis make it possible to control physical, electrical, electrochemical, structural, and crystallographic properties of the carbon materials (which are important for use in electrochemical capacitors) and improve their parameters. Some unique parameters of numerous new carbon materials[1,2] have drawn attention and increased the number of scientists who are involved in fundamental research of different properties of carbon materials, development, and theoretical and experimental research of the processes which occur in the capacitors. This has resulted in considerable improvement of energy, power, and operation parameters and creation of new electrochemical capacitors, which have better prospects.

The modeling of electrochemical capacitors and theoretical research of various processes which take place in the capacitors are of great scientific interest and are the basis for the understanding, control of the parameters, and for practical proposals aimed at building capacitors with advanced energy and power parameters. Despite this fact, the bulk of the research on capacitors and their components are experimental works. The results of multiple experimental efforts and their detailed review are set forth in the referenced book.[3] The currently obtained, quite reliable experimental results and their increasing number have created the necessary prerequisites for the development of a modern theory of electrochemical capacitors, which will promote developing electrochemical capacitors with the parameters that meet modern requirements and launch them in mass commercial production.

Numerous characteristics of DEL capacitors and parameters of the processes which occur therein are closely interconnected. They depend on the physical, electrical, electrochemical and crystallographic parameters of electrode materials, electrolyte, as well as on the design of the electrodes, separator, and capacitor as a whole. Therefore, the modeling of capacitors for the calculation of their energy, capacity, and other operation characteristics and precise description of various electrode processes is inconceivable without due account of the capacitor component parameters.

When modeling and calculating the capacitor parameters, the bulk of the researchers do not consider the physical, electrical, and structural properties of their electrode materials and components, which causes discrepancy between the results of theoretical calculations and experimental measurements of the parameters of real-life capacitors.

In the work[4] research is performed (within the framework of a model of capacitors having positive and negative electrodes with DEL) with regard to the stability of electrolyte and energy and Coulombic efficiency of capacitors at high levels of the state of their charge. It is shown that operation and storage of the capacitors at the voltages within the limits of thermodynamic equilibrium of electrolytes does not warrant low losses of energy and charge of the capacitors. Besides, the dynamics of energy losses of the capacitors is shown when the number of their charge–discharge cycles is increased.

The authors of the work[5] also put forward a model of the capacitors having two electrodes with DEL and performed analytical solutions of the dependences of energy and power parameters, and energy and Coulombic efficiencies of the capacitors on certain parameters of their electrodes, separators, and electrolytes. Despite the fact that this model provides for high accuracy of the calculated parameters of symmetric capacitors, particularly in the case of small electrode thicknesses, it is not suitable for calculations of the parameters of heterogeneous capacitors with adequate accuracy required for practical application. Within the framework of this model, in which neither the type of conductivity of the electrode materials nor any change of conductivity during the charge and discharge of the capacitors are taken into account, making a correct choice of electrical and physical parameters of the electrode materials for the manufacture of capacitors with different electrolytes and optimal designs is a most difficult task. Besides, the model proposed in the work[5] does not allow doing research of the behavior of the potentials of individual electrodes of the capacitors during their charge and discharge. The dependences of the potentials of individual electrodes of the capacitors on their different parameters play an important role in any research, development, and operation of the capacitors, particularly in the case of the capacitors having a high state of charge, whose electrolyte's stability may significantly depend on the electrode's thickness and the value of the charge currents.[4]

A model of the capacitor having positive and negative electrodes with DEL[6] allows doing research of the dependence of the energy and capacity parameters on the ionic and electronic conductivity of liquid and solid phases of the electrodes. Besides, within the framework of this model no account was taken of the type and changes of conductivity of the solid phase of the electrodes and electrolyte in the process of charge and discharge of the capacitors.

The capacitance of DEL electrodes of the capacitors is also sig-

---

[z] E-mail: vikogan@aep.com

nificantly related to the properties of their electrode materials. Therefore, taking account of the properties of the electrode materials during the capacitor modeling makes it possible to more accurately characterize parameters of a wider range of the capacitors within the framework of a single, more comprehensive model of DEL electrochemical capacitors.

The referenced book[3] describes various models of DEL structure and contains a detailed analysis of their parameters and features. In the interface of the conducting solid body and ion-conducting liquid electrolyte, DEL is formed, which is capable of storing electric charge of great density, and such a system is regarded as a primary electrochemical capacitor. Both the energy of the conventional electric capacitors and the energy stored in DEL is the potential energy.

In the case of serial connection of the two primary capacitors to ensure that their liquid electrolytes are in direct contact, such combination of the two capacitors becomes serviceable in the range of the electrolyte stability voltages and has been widely used in practice. The aggregate capacitance (C) of the serially connected primary capacitors is expressed by the formula as follows

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \qquad [1]$$

where C_1 and C_2 are the capacitance of the first and second primary capacitors, respectively.

When the liquid electrode (electrolyte) of both primary capacitors is common and the solid electrodes are identical, the combination of the two primary capacitors is called a *symmetric* electrochemical capacitor.

Electrochemical capacitors with DEL, in which one of the electrodes is polarizable, i.e., an electrode with DEL, and the other one is nonpolarizable, represent a new class of capacitors. In the reference materials the capacitors with polarizable and nonpolarizable electrodes are called "asymmetric," "hybrid," and "heterogeneous" capacitors.[7-9] Capacitors are called "asymmetric," given the fact that the nonpolarizable electrode has quite great capacitance as compared with the capacitance of the polarizable electrode, i.e., there is asymmetry which brings about asymmetry of the capacitance of the capacitor. Capacitors are called "hybrid" because one of the electrodes of the capacitor of this type is a "battery" electrode, i.e., it is used for the manufacture of batteries, and the capacitor as a whole is made as a *hybrid* of a "battery" electrode and an electrode with DEL. It is obvious that the name of a "hybrid" capacitor is not quite suitable, because when a nonpolarizable electrode is used in the capacitor, which is not used in batteries, the notion of "hybrid" becomes indefinite, vague, and ceases to be a characterizing name of this capacitor.

The energy, stored or delivered by the polarizable electrode with DEL during the charge and discharge of the capacitor with polarizable and nonpolarizable electrodes, is potential energy, i.e., energy of interaction of the dissimilar DEL electric charge. The delivered or stored energy of the nonpolarizable (Faraday) electrode of this capacitor is of chemical nature. Nonequilibrium electrons (holes) from the side of the solid body and ions from the side of the electrolyte in DEL of the polarizable electrode are in a free state. The electrons (holes) of the nonpolarizable electrode, which are transferred to the negative electrode during the charge and discharge, are in a bound state, i.e., only after the phase transition of the second order of the active material of the Faraday electrode does there emerge charge carriers which participate in the process of the charge and discharge of the capacitors.

The purpose of this work is to build a theoretical basis for the calculations, control, and improvement of the energy, capacity, power, and other parameters (important for safe and long operation) of various types and designs of DEL heterogeneous electrochemical supercapacitors (HES) with simultaneous account of physical, electrical, electrochemical properties of electrode materials, designs, and spatial structures of electrodes and separator. The concentration of nonequilibrium electrical charge in DEL of the modern capacitors may reach high values, which will be shown below, and this causes strong interaction of the electrical charge of DEL from the side of the electrolyte and the near-surface layers of the walls of the electrode's pores. Besides, the power of interaction changes in the process of the charge and discharge of the capacitor. Therefore, when making calculations of the parameters of DEL capacitors, it is important to take account of the effect of strong interactions on the conductivity of the pore walls and the capacitance of DEL.

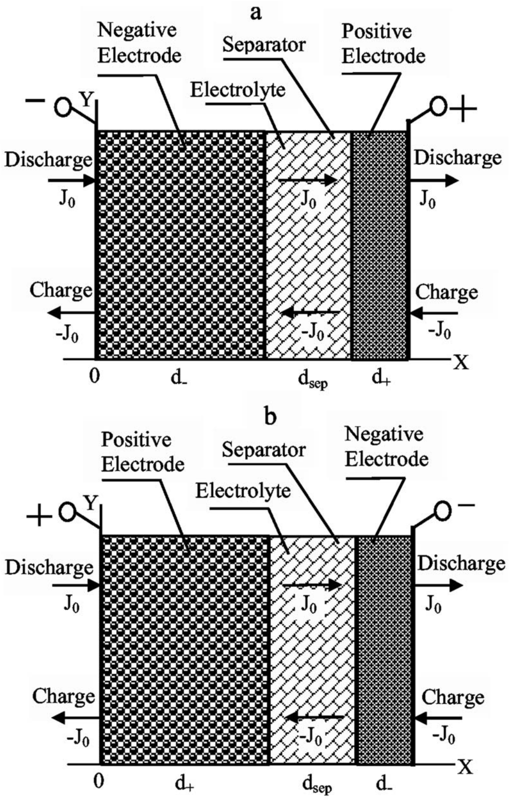

Figure 1. Schematic design of HES capacitor with (a) negative and (b) positive polarizable electrode.

Model of Heterogeneous Electrochemical Capacitors and the Theoretical Basis for Calculation of Their Parameters

As it was pointed out above, one of the electrodes of HES capacitors is an electrode with DEL while the other one is a Faraday electrode. Besides, the electrolyte of the electrode with DEL and the electrolyte of the Faraday electrode may be either similar or different. In this paper we review HES capacitors which have similar electrolyte in the pores of the positive, negative electrodes and separator. The design of the HES capacitors is shown in Fig. 1.

Let us consider HES capacitors having designs as shown in Fig. 1. The first HES capacitor consists of a negative electrode with DEL, positive Faraday electrode, and a separator which separates the electrodes (Fig. 1a), while the capacitor electrolyte is in the pores of the electrodes and separator. The HES capacitor of the $PbO_2|H_2SO_4|C$ system is an example of such a capacitor. In 1997,[10] experts of JSC ESMA were the first to develop and patent this capacitor. Currently it has the highest value of the specific discharge energy (18–24 Wh/kg, subject to the mode of operation), low cost, and in the near future this capacitor may become a commercial product. Figure 2 shows the dependence of the voltage on the time of the HES capacitor of the $PbO_2|H_2SO_4|C$ system with a capacitance of 282 kF at 5 h charge and discharge by constant current of different values.

High energy parameters, great cycle life, and low price of the HES capacitor of $PbO_2|H_2SO_4|C$ systems have drawn the attention of other experts who have been also actively involved in the re-

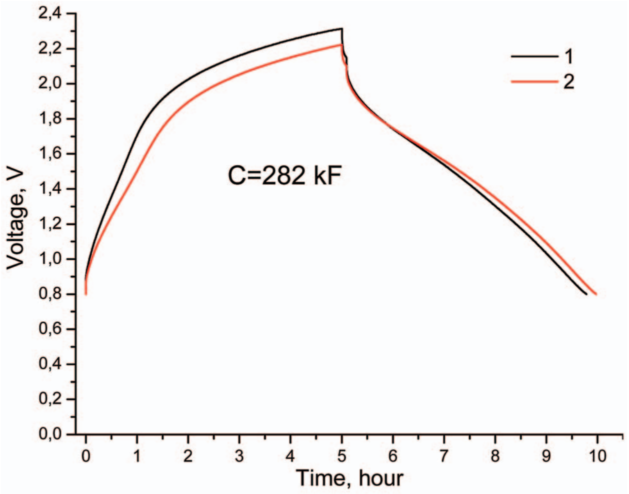

Figure 2. HES capacitor dependence of voltage on time with capacitance of 282 kF at 5 h charge and 5 h discharge by constant current of (1) 20 and (2) 15 A.

search work of its electrode processes and design features in recent years[7,11-15] with a view of further improving the energy and operation parameters. Lead dioxide is an active material of the positive nonpolarizable electrode of HES capacitor of $PbO_2|H_2SO_4|C$ system, while the negative electrode with DEL is made on the basis of activated carbon materials or conducting organic polymers.[9] Aqueous solution of the sulfuric acid is used as the capacitor's electrolyte.

The second HES capacitor consists of a positive electrode with DEL, negative Faraday electrode, and separator which separates the electrodes (Fig. 1b). The capacitor's electrolyte is also in the pores of its electrodes and separator, and the HES capacitor of the $Pb|H_2SO_4|C$ system[15] is an example of this capacitor.

The potential of the nonpolarizable electrodes of HES capacitors during their charge and discharge does not, in fact, change. Unlike the nonpolarizable electrode, during the charge and discharge of the capacitor, in a wide range, the potential of the electrode with DEL is polarized and depolarized, i.e., a change of the voltage of the HES capacitor during its charge and discharge is, in fact, determined by a change of the potential of the polarizable electrode only.[9] In DEL of the capacitor's polarizable electrode, the charge carriers exist in a free or loosely coupled state. Besides, the carriers of nonequilibrium charge have the following spatial arrangement: the nonequilibrium ions of the electrolyte are localized in the interface of the polarizable electrode and electrolyte from the side of the electrolyte, and the nonequilibrium electrons or holes are localized in the near-surface layer of the polarizable electrode from the side of the solid body.

Let us assume that the HES capacitor consists of two volume electrodes: positive and negative electrodes. The polarizable electrode is a solid electron conductor with porous spatial structure, while the electrolyte is a liquid ion conductor and is in the pores of the solid matrix. The spatial porous structure of the solid matrix of the polarizable electrode is designed in such a way that all the pores are communicated, while the electrolyte is in all the pores of the matrix and creates in its porous space an imbedded spatial structure with ion conductivity, i.e., the polarizable electrode of the capacitor consists of mutually imbedded spatial structures of the porous solid matrix and liquid matrix. Besides, the solid and liquid matrixes have electron (hole) and ion conductivity, respectively, and the electrode's capacitance is determined by the double electric layer, which is formed in the interface of the two matrixes.

Let us assume that the polarizable electrode is a negative electrode of a HES capacitor. Inasmuch as during the charge and discharge of the capacitor only its negative electrode is polarized and the parameters of the negative electrode play a prevailing role in the capacity and energy parameters of the capacitor, let us consider the distribution of $\varphi^{-}(x,t)$ potential of the negative electrode along its thickness and the dependence of the potential on different parameters of the negative electrode during the charge and discharge of the capacitor by constant current.

Inasmuch as a real-life electrochemical capacitor has three-dimensional spatial structure, the potentials of the electrodes and the energy of the capacitor during its charge and discharge depend on the geometric shape of the capacitor and paths of the charge carriers' movement. Bearing in mind that in the efficiency of the operation of the porous electrodes a specially important role is played by the conductivity of the solid, liquid phases, and distribution of the currents in the electrodes,[16] let us perform a detailed analysis of the dependence of the energy and capacity parameters on the electrical, physical, and electrochemical properties, and spatial structure of the negative electrode with DEL.

In order to facilitate calculation of the capacitor's parameters, let us consider the capacitor with a flat configuration (Fig. 1a). The charge and discharge of the capacitor is performed by constant current through the current collectors which are located on the surfaces of the polarizable and nonpolarizable electrodes, and the densities of electron and ion currents in the capacitor's volume are collinear to the "x" axis. The current collectors of the negative and positive electrodes are arranged, respectively, at $x = 0$ and at $x = d_c$ (thickness of the capacitor). The densities of the charge and discharge currents on the surfaces of the negative electrode at $x = 0$ and $x = d_-$ are identical and have the value of J_0.

The changes of the density of the electric charges $\rho_-(x,t)$ and $\rho_+(x,t)$ by the volume of the negative electrode during the charge and discharge of the capacitor are determined by the following equations of continuity

$$\begin{cases} \dfrac{\partial\, \rho_-(x,t)}{\partial\, t} = \operatorname{div} J_-(x,t) - G_-(x,t) + R_-(x,t) & [2] \\[2ex] \dfrac{\partial\, \rho_+(x,t)}{\partial\, t} = \operatorname{div} J_+(x,t) + G_+(x,t) - R_+(x,t) & [3] \end{cases}$$

where $\rho_-(x,t)$ and $\rho_+(x,t)$ are the densities of the charges of the free carriers, respectively, in the solid matrix of the negative electrode and in the electrolyte, which is in the pores of the negative electrode; $J_-(x,t)$ and $J_+(x,t)$ are the densities of the currents, respectively, in the solid matrix of the negative electrode and in the electrolyte which is in the pores of the negative electrode; and $G_-(x,t)$ and $R_-(x,t)$ are the rates, respectively, of the spontaneous generation and recombination of nonequilibrium charge carriers in the solid matrix of the negative electrode; $G_+(x,t)$ and $R_+(x,t)$ are rates, respectively, of the spontaneous generation and recombination of nonequilibrium charge carriers in the electrolyte, which is in the pores of the negative electrode.

It follows from Eq. 2 and 3 that $G_-(x,t) = J_{VG_-}(x,t)$ and $R_-(x,t) = J_{VR_-}(x,t)$; $G_+(x,t) = J_{VG_+}(x,t)$ and $R_+(x,t) = J_{VR+}(x,t)$. Here $J_{VG_-}(x,t)$, $J_{VR_-}(x,t)$, and $J_{VG+}(x,t)$, $J_{VR_+}(x,t)$ are volume densities of the currents of the spontaneous generation and recombination of nonequilibrium charge carriers, respectively, in the solid matrix and electrolyte of the negative electrode of the capacitor.

Inasmuch as the electric charge in any point of the volume of the negative electrode with DEL should be compensated, it is obvious that $J_{VG_-}(x,t) = J_{VG_+}(x,t) = J_{VG}(x,t)$ and $J_{VR_-}(x,t) = J_{VR_+}(x,t) = J_{VR}(x,t)$, i.e., the rates of the spontaneous generation of nonequilibrium charges in the solid matrix and in the electrolyte of the negative electrode are identical. The rates of the spontaneous recombination of nonequilibrium charges in the solid matrix and in the electrolyte of the negative electrode are also identical. As a rule, in electrochemical capacitors the rates of the spontaneous generation (spontaneous charge) of nonequilibrium carriers is much lower as compared with the rates of the spontaneous recombination (self-discharge) of nonequilibrium carriers. Therefore, in our subsequent calculations we shall assume that $J_{VG}(x,t) = 0$.

Let us consider the following instances of the design of HES capacitors.

Instance 1.— The negative electrode of the capacitor is a *polarizable electrode* and the solid matrix has *electron conductivity*, i.e., DEL (e/Z^+) consists of electrons (e) and positive ions (Z^+). In this instance, the densities of the currents $J_-(x,t)$ and $J_+(x,t)$ are determined by the following formula

$$J_-(x,t) = \sigma_-^m E_-(x,t) - D_{e(p)} \nabla \rho_-(x,t) \qquad [4]$$

$$J_+(x,t) = \sigma_-^{\mathrm{el}} E_+(x,t) - D_+ \nabla \rho_+(x,t) \qquad [5]$$

where D_e and D_+ are the coefficients of diffusivity, respectively, of the main nonequilibrium charge carriers of the matrix and the positive ions of DEL; σ_-^m and σ_-^{el} are the conductivity of the solid matrix and electrolyte, respectively, of the negative electrode of the capacitor; and $E_-(x,t)$ and $E_+(x,t)$ are the electric field intensity in the solid matrix and in the electrolyte of the negative electrode, respectively.

It is clear that during the charge and discharge of HES capacitors, the potential of the polarizable electrode may assume both higher and lower values as compared with the potential of zero charge (pzc) of the solid matrix. When, during the charge and discharge of the capacitor, the potential of the polarizable electrode becomes higher than the pzc potential, the majority charge carriers of the solid matrix are compensated by nonequilibrium charge carriers, and in Eq. 4 the coefficient of diffusivity D_e should be replaced by the coefficient of diffusivity of holes, D_p. The particular features and conditions of emergence of such a situation are considered below in greater detail.

Instance 2.— The negative electrode of the capacitor is a *polarizable electrode* and the solid matrix has *hole conductivity*, i.e., DEL (e/Z^+) consists of electrons (e) and positive ions (Z^+). In this instance, the densities of the currents $J_-(x,t)$ and $J_+(x,t)$ are determined by the following formulas

$$J_-(x,t) = \sigma_-^m E_-(x,t) - D_{p(e)} \nabla \rho_-(x,t) \qquad [6]$$

$$J_+(x,t) = \sigma_-^{\mathrm{el}} E_+(x,t) - D_+ \nabla \rho_+(x,t) \qquad [7]$$

When, during the charge and discharge of the capacitor, the potential of the polarizable electrode becomes lower than the pzc potential, the majority charge carriers of the solid matrix are compensated by nonequilibrium charge carriers and in Eq. 6, the coefficient of diffusivity D_p should be replaced by the coefficient of diffusivity D_e.

Instance 3.— The positive electrode of the HES capacitor is a *polarizable electrode*, and the solid matrix has *electron conductivity*, i.e., DEL (p/Z^-) consists of holes (p) and negative ions (Z^-). In this instance, the densities of the currents $J_-(x,t)$ and $J_+(x,t)$ are determined by the following formula

$$J_-(x,t) = \sigma_+^{\mathrm{el}} E_-(x,t) - D_- \nabla \rho_-(x,t) \qquad [8]$$

$$J_+(x,t) = \sigma_+^m E_+(x,t) - D_{e(p)} \nabla \rho_+(x,t) \qquad [9]$$

where D is the coefficient of diffusivity of the negative nonequilibrium ions of the electrolyte; σ_+^{el} and σ_+^m are the conductivity of the electrolyte and solid matrix of the positive polarizable electrode, respectively.

When, during the charge and discharge of the capacitor, the potential of the polarizable electrode becomes higher than pzc potential, the majority charge carriers of the solid matrix are compensated by nonequilibrium charge carriers, and in Eq. 9 the coefficient of diffusivity D_e should be replaced by the coefficient of diffusivity D_p.

Instance 4.— The positive electrode of the capacitor is a *polarizable electrode* and the electrode material has *hole conductivity*, i.e., DEL (p/Z^-) consists of holes (p) and negative ions (Z^-). In this instance, the densities of the currents $J_-(x,t)$ and $J_+(x,t)$ are determined by the following formula

$$J_-(x,t) = \sigma_+^{\mathrm{el}} E_-(x,t) - D_- \nabla \rho_-(x,t) \qquad [10]$$

$$J_+(x,t) = \sigma_+^m E_+(x,t) - D_{p(e)} \nabla \rho_+(x,t) \qquad [11]$$

When during the charge and discharge of the capacitor the potential of the polarizable electrode becomes lower than pzc potential, the majority charge carriers of the solid matrix are compensated by nonequilibrium charge carriers, and in Eq. 11 the coefficient of diffusivity D_p should be replaced by the coefficient of diffusivity D_e.

$E_-(x,t)$ and $E_+(x,t)$ are related to potentials $\varphi_-(x,t)$ and $\varphi_+(x,t)$ by the following expressions

$$E_-(x,t) = -\nabla \varphi_-(x,t) = -\frac{\partial \varphi_-(x,t)}{\partial x} \qquad [12]$$

$$E_+(x,t) = -\nabla \varphi_+(x,t) = -\frac{\partial \varphi_+(x,t)}{\partial x} \qquad [13]$$

where $\varphi_-(x,t)$ is the potential (in relation to pzc) of the matrix; and $\varphi_+(x,t)$ is the potential (in relation to pzc) of the electrolyte in the area of DEL.

Let us consider the dependences of parameters of HES capacitors with polarizable negative electrodes, whose solid matrix has electron or hole conductivity, on the value of the potential of the polarizable electrodes. For this purpose, let us represent conductivity of the solid matrix of the negative electrode (σ_-^m) as

$$\sigma_-^m = en_0\mu_n + ep_0\mu_p \qquad [14]$$

Here n_0 and p_0 are the equilibrium concentrations, respectively, of free electrons and holes of the solid matrix (in the area of the pore walls); μ_n and μ_p are the effective mobilities, respectively, of electrons and holes of the solid matrix, which depend on the parameters of the porous structure and electrophysical properties of the pore walls.

Conductivity of the liquid matrix (electrolyte) of the negative electrode (σ_-^{el}) should be represented as

$$\sigma_-^{el} = eZ^+n_0^+\mu_+ + eZ^-n_0^-\mu_- \qquad [15]$$

Here n_0^+ and n_0^- are the equilibrium concentrations of the positive and negative ions, respectively, of the electrolyte in the pores of the negative electrode; eZ^+ and eZ^- are the values of the charges of the positive and negative ions, respectively, of the electrolyte; μ_+ and μ_- are effective mobilities of the positive and negative ions, respectively, which depend on the porous structure of the solid matrix of the negative electrode and electrophysical and electrochemical properties of the electrode.

During the charge of HES capacitor with a negative polarizable electrode, a negative nonequilibrium charge (electrons) is accumulated in the near-surface layers of the walls of the pores of the negative electrode's solid matrix, which is transferred to the volume of the electrode from an external source. Similarly, a positive nonequilibrium charge (holes) is accumulated in the near surface layers of the pore walls of the solid matrix of the positive electrode with DEL of the HES capacitor. Bearing in mind that the change of conductivity of the solid matrix of the electrodes based, in fact, on all nonmetal materials, during the charge and discharge of the capacitor, is one of the parameters which determine the power of the capacitors and the capacitance is also related to the conductivity, let us consider the change of conductivity in greater detail.

Let us assume that a carbon plate based on activated carbon powders with p-type conductivity is used in an HES capacitor with a negative polarizable electrode. The equilibrium concentration of the free holes in the walls of the pores of the porous carbon materials is in the range of 10^{19}–10^{20} cm^{-3}.[17] The intrinsic concentration of the free holes in the pure graphite at room temperature is about 6×10^{18} cm^{-3}.[1] Bearing in mind that during the charge of the HES capacitor there occurs accumulation of nonequilibrium DEL electrons in the near-surface layers of the walls of the carbon electrode pores, it would not be difficult to assume that as long as the capacitor is charged, a partial compensation of the holes by nonequilibrium electrons takes place in the walls of the pores of the carbon electrode. Inasmuch as the thickness of the walls of the pores of the carbon powders having a specific developed area of 1200–1500 m^2/g (which are usually used for the manufacture of electrodes of electrochemical capacitors) is about 8–10 Å, a partial compensation of the holes takes place, in fact, along the entire thickness of the walls. Consequently, the process of compensation will continue until the hole concentration goes down to 6×10^{18} cm^{-3} (inherent concentration of holes), and, subsequently, the concentration of electrons will grow. Besides, the carbon plate conductivity will change. This process may often be observed in the electrodes of different electrochemical capacitors, which results in a considerable change of the conductivity during their charge and discharge, as shown in the operation[18] of the capacitor with nonaqueous electrolyte.

If, during a full charge of an HES capacitor, the potential of the negative electrode shifts by the value of 0.5 V (in relation to pzc) toward lesser values, and the value of the potential, and the value of the specific capacitance of the carbon powder is $C_m = 600\ F/g$, the maximum concentration of nonequilibrium electrons in the pore walls has the value of 4.24×10^{21} cm^{-3}, subject to the fact that the weight density of the walls has the value of 2.26 g/cm^3. When the value of the equilibrium concentration of the holes in the walls of the carbon powder is equal to 1×10^{20} cm^{-3}, the walls after the polarization of the carbon plate acquire electron conductivity and the concentration of electrons will be 4.14×10^{21} cm^{-3}. Besides, it is not difficult to show that when there is a shift of the potential by 0.5 V (in relation to pzc) toward greater values (which takes place during the discharge of the HES capacitor), growth of the concentration of holes occurs.

Subject to high density of the states of the electron levels of the carbon materials, it is not difficult to suppose that the nonequilibrium charge carriers of the pore walls will take part in the process of the charge transfer, and accordingly, during the charge and discharge of capacitor, there will be a change of conductivity of the carbon plate (in relation to the conductivity of the zero charge). Bearing in mind that pzc potential of the activated carbon materials varies in the range of 0.0–0.2 V (in relation to SHE),[19] subject to the technology of synthesis and parameters of the source materials, the following should be taken into account in order to calculate the parameters of electrochemical capacitors of a particular system: range of the operating potentials of the electrodes with DEL, type of conductivity, and concentration of the majority charge carriers of the polarizable electrodes.

This effect causes a considerable change of ohmic resistance of the HES capacitor of the $PbO_2|H_2SO_4|C$ system during charge and discharge in the voltage window of 2.3–0.8 V. More detailed study of this process (which is very important for the development of electrochemical capacitors, and, in particular, $PbO_2|H_2SO_4|C$ capacitor) is beyond the scope of this paper, but later on a separate experimental and theoretical paper will be devoted to this issue.

The conductivity in the walls of the pores of the solid matrix of the negative and positive electrode with DEL during the charge and discharge of the capacitor shall be determined by the following formulas, respectively

$$\sigma_-^m = e\mu_n(n_0 + \Delta n) + e\mu_p p_0 \qquad [16]$$

$$\sigma_+^m = e\mu_n n_0 + e\mu_p(p_0 + \Delta_p) \qquad [17]$$

where Δn and Δp are the nonequilibrium concentrations, respectively, of free electrons and holes.

The conductivity of the electrolyte, in the pores of the solid matrix of the polarizable negative and positive electrodes, respectively, are determined by the following formulas

$$\sigma_-^{\mathrm{el}} = eZ^+\mu_+(n_0^+ + \Delta n^+) + eZ^-\mu_- n_0^- \qquad [18]$$

$$\sigma_+^{\mathrm{el}} = eZ^+\mu_+ n_0^+ + eZ^-\mu_-(n_0^- + \Delta n^-) \qquad [19]$$

where Δn^+ and Δn^- are the nonequilibrium concentrations of the positive and negative ions of the electrolyte, respectively, in the pores of the polarizable electrodes.

Despite the fact that the electric charge is accumulated in the polarizable electrode during the capacitor's charge, it is, in general, an electrically neutral system. The compensation of the positive and negative DEL charges of the polarizable electrode takes place in localized volume ν_τ, whose overall dimensions are limited by the aggregate thickness of DEL (thickness of DEL layer from the side of the electrolyte + thickness of the layer of the volume spatial charge from the side of the solid matrix). Therefore, in the elementary unit ν_τ of the capacitor the electric neutrality is always retained, i.e.

$$\int_{\nu_\tau}\int\int [\rho_-(x,t) + \rho_+(x,t)]dv = 0 \qquad [20]$$

The capacitance of DEL depends on the form and dimensions of the pores; physical, chemical, and crystallographic properties of the solid matrix of the polarizable electrode; as well as on the dimensions and electron structure of the electrolyte's ions and the electrolyte's properties in general. According to numerous experiments, the capacitance of DEL may be quite adequately characterized by the formula of the capacitance of the capacitor having flat plates (C_{fc})

$$C_{fc} = \varepsilon\varepsilon_0 S/d \qquad [21]$$

where ε is dielectric permittivity of the medium between the plates; ϵ_0 is the dielectric constant ($\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm); S is the surface area of the capacitor's plate, and d is the distance between the plates.

In order to evaluate the capacitance of the unit area ($S = 1\ cm^2$) of the developed surface of the electrode with DEL of the electrochemical capacitor, let us assume that $\varepsilon = 78$ and $d = 3.1$ Å. According to Eq. 21, the electrode's capacitance is 199.8 μF. However, the experimental measurements show that in many metal electrodes the value of the specific capacitance of DEL in aqueous electrolyte is in the range of 23–125 $\mu F/cm^2$,[3] which is substantially different from the theoretical values. The main divergence of the theoretical and experimental values of DEL capacitance is related to the value of ϵ in the area of DEL and DEL structure.

The value of ε, as a macroscopic characteristic of the medium, cannot characterize, with adequate accuracy, the dielectric permittivity of the space by the value of order of atomic sizes (the thickness of DEL), especially in strong electric fields. In order to determine the values, the behavior of solvent ε in DEL, and describe the different electrode processes, it is appropriate to use a quantum mechanics approach to DEL structure, as shown in Ref. 20. Besides, DEL should be modeled subject to: (*i*) electronic, atomic, and molecular polarization of the solvent; (*ii*) deformation of external electron shells of ions and molecules of the electrolyte in DEL, (*iii*) changes of conductivity and density of electron levels on the surface of the solid matrix of the electrode subject to the potential; and (*iv*) formation of the volume spatial charge in the near-surface layers of the electrode's solid matrix.

The increase of the density of the quasi-free electrons (holes) and ions in the volume of the spatial charge of the solid matrix of the electrode and electrolyte, respectively, during the capacitors' charge brings about the occurrence of strong interactions. The value of the capacitance of DEL becomes a function of its electric charge, properties of the electrolyte, and solid electrode materials. Therefore, Eq. 21 makes it possible to evaluate only the maximum expected value of DEL capacitance, and in order to obtain a more precise value of the capacitance it is appropriate to take account of the aforementioned conditions in Eq. 21.

It follows from Eq. 16, 18, and 20 that the density of nonequilibrium charges and the potentials of the solid matrix and electrolyte of the negative polarizable electrode are related to each other by the following formula

$$d\rho_-(x,t) = 2C_V d\varphi_-(x,t) \qquad [22]$$

$$d\rho_+(x,t) = 2C_V d\varphi_+(x,t) \qquad [23]$$

where C_V (F/cm^3) is the specific (by volume) capacitance of the negative electrode; $\varphi_-(x,t)$ is the potential (in relation to the pzc) of the matrix of the negative electrode; and $\varphi_+(x,t)$ is the potential (in relation to the pzc) of the electrolyte in the area of DEL.

It follows from Eq. 22 and 23 that $\Delta n(x,t)$, $\Delta p(x,t)$, $\Delta n^+(x,t)$, and $\Delta n^-(x,t)$ are related to each other by the following formulas

$$\Delta n = -2C_V\varphi_-(x,t)/e \qquad [24]$$

$$\Delta p = 2C_V\varphi_+(x,t)/e \qquad [25]$$

$$\Delta n^+ = 2C_V\varphi_+(x,t)/(eZ^+) \qquad [26]$$

$$\Delta n^- = -2C_V\varphi_-(x,t)/(eZ^-) \qquad [27]$$

By inserting the values of the nonequilibrium charge carriers from Eq. 24-27 to Eq. 16-19 and taking into account Eq. 12 and 13, we obtain expressions for the conductivity of the solid matrix and electrolyte in the pores of the matrix of the polarizable electrodes for the above-mentioned instances:

Instance 1.

$$\begin{cases} \sigma_-^m = e\mu_n[n_0 - 2C_V\varphi_-(x,t)/e] + e\mu_p p_0 & [28] \\ \sigma_-^{\mathrm{el}} = eZ^+\mu_+[n_0^+ + 2C_V\varphi_+(x,t)/(eZ^+)] + eZ^-\mu_- n_0^- & [29] \end{cases}$$

Instance 2.

$$\begin{cases} \sigma_-^m = e\mu_n n_0 + e\mu_p[p_0 + 2C_V\varphi_-(x,t)/e] & [30] \\ \sigma_-^{\mathrm{el}} = eZ^+\mu_+[n_0^+ + 2C_V\varphi_+(x,t)/(eZ^+)] + eZ^-\mu_- n_0^- & [31] \end{cases}$$

Instance 3.

$$\begin{cases} \sigma_+^m = e\mu_n n_0 + e\mu_p[p_0 + 2C_V\varphi_+(x,t)/e] & [32] \\ \sigma_+^{\mathrm{el}} = eZ^-\mu_-[n_0^- - 2C_V\varphi_-(x,t)/(eZ^-)] + eZ^+\mu_+ n_0^+ & [33] \end{cases}$$

Instance 4.

$$\begin{cases} \sigma_+^m = e\mu_n n_0 + e\mu_p[p_0 + 2C_V\varphi_+(x,t)/e] & [34] \\ \sigma_+^{\mathrm{el}} = eZ^+\mu_+ n_0^+ + eZ^-\mu_-[n_0^- - 2C_V\varphi_-(x,t)/(eZ^-)] & [35] \end{cases}$$

Now let us consider a solution of the system of Eq. 2 and 3 for the solid negative electrode with double electric layer. Let us assume that the conductivity of the solid matrix of the negative electrode under review is electron one (Instance 1). Let us also assume that $G = 0$. By inserting appropriate expressions from Eq. 28, 29, 22, and 21 into Eq. 4 and 5 in place of σ_-^m, σ_-^{el}, $d\rho_-(x,t)$, and $d\rho_+(x,t)$, we will have expressions for $J_-(x,t)$ and $J_+(x,t)$

$$J_-(x,t) = -\{e\mu_n[n_0 - 2C_V\varphi_-(x,t)/e] + e\mu_p p_0\}\frac{\partial\,\varphi_-(x,t)}{\partial x} - 2D_e C_V\frac{\partial\,\varphi_-(x,t)}{\partial x} \qquad [36]$$

$$J_+(x,t) = -\{eZ^+\mu_+[n_0^+ + 2C_V\varphi_+(x,t)/(eZ^+)] + eZ^-\mu_- n_0^-\}\frac{\partial\,\varphi_+(x,t)}{\partial x} - 2D_+C_V\frac{\partial\,\varphi_+(x,t)}{\partial x} \qquad [37]$$

In Eq. 36 and 37 the specific capacitance C_V at great deviations of the potential of the capacitor electrodes from the potential of pzc becomes a function of the potential, i.e., $C_V = C_V(\varphi)$. However, the results of research of the capacitances of different types of electrochemical capacitors with DEL show that at small deviations of the potential of the electrodes, the value of $C_V(\varphi)$ depends very little on the value of the potential. As an example, the capacitances of the capacitors having their electrodes based on activated carbon materials and different types of electrolytes do not, in fact, depend on the electrode potential when C_V is in the range of 1–50 F/cm^3 and specific developed surface of the electrodes is not more than 1200 m^2/g. Henceforth, we model DEL electrochemical capacitors subject to a strong dependence of the capacitance of the polarizable electrodes on their potential. This allows increasing the accuracy of the theoretical calculations of the parameters and interpretation of the experimental results of different capacitors in a wide range of operating voltages.

By inserting expressions of $J_-(x,t)$ and $J_+(x,t)$ from Eq. 36 and 37 into Eq. 2 and 3, subject to Eq. 22 and 23, after the transformation we have the following system of differential equations

$$\frac{\partial\,\varphi_-(x,t)}{\partial t} = \frac{1}{2C_V(\varphi^-)}\mathrm{div}\left\{\{e\mu_n[n - 2C_V(\varphi^-)\varphi_-(x,t)/e] + e\mu_p p + 2C_V(\varphi^-)D_c\}\frac{\partial\,\varphi_-(x,t)}{\partial x}\right\} + \frac{J_{VR}}{2C_V(\varphi^-)} \qquad [38]$$

$$\frac{\partial\,\varphi_+(x,t)}{\partial t} = \frac{1}{2C_V(\varphi^-)}\mathrm{div}\left\{\{eZ^+\mu_+[n^+ + 2C_V(\varphi^-)\varphi_+(x,t)/(eZ^+)] + eZ^-\mu_- n^- + 2D_+C_V(\varphi^-)\}\frac{\partial\,\varphi_+(x,t)}{\partial x}\right\} - \frac{J_{IR}}{2C_V(\varphi^-)} \qquad [39]$$

where φ^- is specified as $\varphi^- = \varphi_-(x,t) - \varphi_+(x,t)$.

Analytical solution of this equation system generically is a difficult task; therefore, in order to facilitate a solution, let us consider a number of particular cases which are of high practical value. For this purpose, let us assume that the capacitance $C_V(\varphi)$ does not depend on the potential of the capacitor electrodes, and the concentrations of nonequilibrium charge carriers in the walls and in the electrolyte of DEL negative electrode pores, respectively, is considerably lower than the equilibrium concentrations, i.e.

$$n_0 \gg 2C_V\varphi_-(x,t)/e \qquad [40]$$

$$n^+ \gg 2C_V\varphi_+(x,t)/eZ^+ \qquad [41]$$

Let us introduce the notations

$$\alpha_- = \sigma_-^m + 2D_eC_V \qquad [42]$$

$$\alpha_+ = \sigma_-^{\mathrm{el}} + 2D_+C_V \qquad [43]$$

Subject to the accepted approximations, Eq. 40 and 41, and notations, 42 and 43, the system of Eq. 38 and 39 is as follows

$$\begin{cases} \dfrac{\partial\,\varphi_-(x,t)}{\partial t} = \dfrac{\alpha_-}{2C_V}\dfrac{\partial^2\varphi_-(x,t)}{\partial x^2} + J_{VR_-}(x,t)/(2C_V) & [44] \\ \dfrac{\partial\,\varphi_+(x,t)}{\partial t} = \dfrac{\alpha_+}{2C_V}\dfrac{\partial^2\varphi_+(x,t)}{\partial x^2} - J_{VR_+}(x,t)/(2C_V) & [45] \end{cases}$$

Now let us multiply Eq. 44 by α_+, and Eq. 45 by α_-, and subtract, term by term, Eq. 45 from Eq. 44. As a result we will have one differential equation for the potential $\varphi^-(x,t)$ of the negative electrode

$$\frac{\partial\,\varphi^-(x,t)}{\partial t} = \gamma^2\frac{\partial^2\varphi^-(x,t)}{\partial x^2} + \frac{J_{VR}(x,t)}{C_V} \qquad [46]$$

where

$$\gamma^2 = \frac{\alpha_+\alpha_-}{C_V(\alpha_+ + \alpha_-)} \qquad [47]$$

$$J_{VR} = J_{VR_+} = J_{VR_-} \qquad [48]$$

Therefore, the solution of the differential equation, 46, makes it possible to obtain the dependence $\varphi^{-}(x,t)$ of the negative electrode with DEL on its overall dimensions and physical, electrochemical, and capacitance parameters at any point of time t during the charge and discharge of the capacitor. In order to facilitate a solution of the differential equation, 46, let us assume that the negative electrode does not have self-discharge, i.e., $J_{VR} = 0$. However, all electrochemical capacitors have self-discharge, which is determined by different mechanisms and in many cases is an important parameter of the capacitors. A solution of Eq. 46, subject to a specific mechanism or a combination of different mechanisms of self-discharge, makes it possible to study and control the effect of the mechanisms and parameters of self-discharge on the electric and capacitance parameters of capacitors.

The boundary conditions of this task during the capacitor discharge are as follows

$$J_{-}(0,t) = -\alpha_{-}\left.\frac{\partial\varphi^{-}(x,t)}{\partial x}\right|_{x=0} = J_0 \quad [49]$$

$$J_{+}(d,t) = \alpha_{+}\left.\frac{\partial\varphi^{-}(x,t)}{\partial x}\right|_{x=d_{-}} = J_0 \quad [50]$$

and the initial condition is as follows

$$\varphi^{-}(x,t)|_{t=0} = \varphi^{-}_{0_{-}} \quad [51]$$

The boundary conditions of this task during the capacitor charge are as follows

$$J_{-}(0,t) = \alpha_{-}\left.\frac{\partial\varphi^{-}(x,t)}{\partial x}\right|_{x=0} = J_0 \quad [52]$$

$$J_{+}(d,t) = -\alpha_{+}\left.\frac{\partial\varphi^{-}(x,t)}{\partial x}\right|_{x=d_{-}} = J_0 \quad [53]$$

and the initial condition is as follows

$$\varphi^{-}(x,t)|_{t=0} = \varphi^{-}_{0^{+}} \quad [54]$$

Let us consider distribution of $\varphi^{-}(x,t)$ along the thickness of the negative polarizable electrode during the charge and discharge of the capacitor. The solution of the differential equation, 46, referred to in the reference material[21] by the methods of solution of similar equations, subject to the boundary conditions Eq. 49, 50, 52, and 53, and initial conditions 51 and 54, leads to the following analytical expression of the potential $\varphi^{-}(x,t)$

$$\varphi^{-}(x,t) = \varphi^{-}_{0^{+}_{-}} \pm \frac{J_0}{d_{-}C_V}\left\{t + C_V\left[\frac{\alpha_{+}+\alpha_{-}}{2\alpha_{+}\alpha_{-}}x^2 - \frac{d_{-}x}{\alpha_{-}} + \frac{d_{-}^2(2\alpha_{+}-\alpha_{-})}{6\alpha_{+}\alpha_{-}} - \frac{2d_{-}^2}{\pi^2}\sum_{n=1}^{\infty}\left(\frac{1}{\alpha_{-}} + \frac{(-1)^n}{\alpha_{+}}\right)\frac{e^{-(\pi n\gamma/d_{-})^2 t}}{n^2}\cos\frac{\pi n x}{d_{-}}\right]\right\} \quad [55]$$

where sign $(J_0/d_{-}C_V) < 0$ (sign "−") corresponds to the process of charge and sign $(J_0/d_{-}C_V) > 0$ (sign "+") to the process of the capacitor discharge. Therefore, we have dynamic dependences of the potential $\varphi^{-}(x,t)$ on such parameters of the negative electrode with DEL as: d_{-}, C_V, J_0, α_{-}, and α_{+} during the charge and discharge of the capacitor.

Note that it follows from Eq. 55 that if the current collectors of the negative and positive electrodes of the primary electrochemical capacitor are in YZ plane at the values of «x» coordinates, respectively, $x = 0$ and $x = d_{-}$, the difference of the potentials of the liquid positive and solid negative electrodes shall be expressed by the formula

$$V(d_{-},t) = -\varphi^{-}(d_{-},t)/2 - \varphi^{-}(0,t)/2 \quad [56]$$

and it is obvious that $V(d\_t)$ is the voltage of this capacitor as a function of its thickness and time of charge and discharge.

By inserting the values of $x = d_{-}$ and $x = 0$ in Eq. 55, Eq. 56 will be as follows

$$V(d_{-},t) = V_{0^{+}_{-}} \pm \frac{J_0}{d_{-}C_V}\left\{t + \frac{C_V d_{-}^2(\alpha_{+}+\alpha_{-})}{2\alpha_{+}\alpha_{-}} \times\left[\frac{1}{6} - \frac{1}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-(2\pi n/d_{-})^2[\alpha_{+}\alpha_{-}t/C_V(\alpha_{+}+\alpha_{-})]}\right]\right\} \quad [57]$$

where $V_{0^{+}_{-}} = -\varphi^{-}_{0^{+}_{-}}$, sign $(J_0/d_{-}C_V) > 0$ corresponds to the process of charge, and sign $(J_0/d_{-}C_V) < 0$ to the process of the capacitor discharge. Provided $\alpha_{+} = \alpha_{-} = \alpha$, Eq. 57 has the following expression

$$V(d_{-},t) = V_{0^{+}_{-}} \pm \frac{J_0}{d_{-}C_V}\left\{t + \frac{C_V d_{-}^2}{\alpha} \times\left[\frac{1}{6} - \frac{1}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-(2\pi n/d_{-})^2(\alpha t/2C_V)}\right]\right\} \quad [58]$$

Let us now consider the distribution of the potential $\varphi(x,t)$ along the thickness of the HES capacitor of the $PbO_2|H_2SO_4|C$ system during its charge and discharge by a constant current. The positive electrode of this HES capacitor is a nonpolarizable electrode and it consists of PbO_2 active material, and the negative electrode is a polarizable electrode based on porous carbon materials. Aqueous solution of the sulfuric acid is used as electrolyte. We should note that real-life positive electrodes in HES capacitors during their charge and discharge are polarized in narrow ranges of potentials (as compared with the negative electrode). In order to facilitate calculations, we assume that the potential of the positive electrode (φ^{+}) does not change during the charge and discharge and does not depend on the coordinates in the range of $d_{\text{sep}} \le x \le d_{+}$ (Fig. 1).

During the charge and discharge of this capacitor, there is a change of the concentration and, accordingly, of the electrolyte's conductivity. Besides, there is a change in the conductivity of the active material of the positive electrode and conductivity of the matrix of the carbon polarizable electrode. A change of the conductivity of the positive electrode's active material depends on the depth of its charge and discharge. Inasmuch as in practice Coulombic capacity of the nonpolarizable electrode of the heterogeneous capacitor is selected (to provide for as great a cycle life as possible), to ensure that it is several times higher than Coulombic capacity of the polarizable electrode, we may disregard, to a first approximation, any changes in the conductivity of $PbO_2/PbSO_4$ positive electrode in the process of the charge and discharge.

As was pointed out previously, subject to the specific capacitance parameters, the type of conductivity, and electrophysical parameters of the polarizable electrode, its conductivity during the charge and discharge may change in a wide range. These changes have a considerable effect both on the capacitance and other parameters of electrochemical capacitors. Consequently, in order to obtain more precise results, in the calculations we also consider the parameter changes.

Figure 3 shows the distribution of the electric charge and potentials in the walls of the pores and in the electrolyte which is inside the pores of the negative carbon electrode with p-type conductivity. During strong polarization of the negative electrode there occurs a change of the conductivity type in the near-surface layer of the walls of the pores. This results in emergence of physical p-n transition. The thickness and distribution of the volume spatial charge of p-n transition depends on the electrophysical parameters of the solid electrode, material, electrolyte, and potential of the electrode.

The activated carbon powders which are used for the manufacture of polarizable electrodes of electrochemical capacitors are, in general, degenerate semiconductors of p-type conductivity in which Fermi level (E_F) is in the valence band. When there is strong polar-

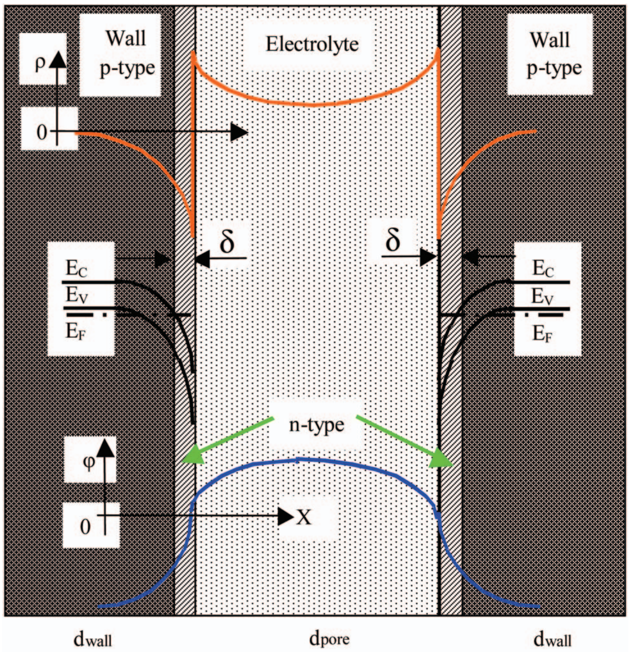

Figure 3. Distributions of electric charge and potentials in the walls of cylindrical shaped pores and in the electrolyte which is inside the pores of the negative electrode with p-type conductivity.

ization of these electrodes, the surface layers of the wall pores play an extremely important role in DEL parameters. As may be seen in Fig. 3, when there is a strong bend of the bands in the near-surface layers of the wall pores by δ thickness, Fermi level E_F is above the conductivity band bottom, i.e., the material in this area is a degenerate material with p-type conductivity. Subject to anisotropy of the carbon materials as well as different dimensions and forms of the pores, numerous nonlinear effects should be expected both in the near-surface layers of the walls and in the wall pores. The capacitance of DEL from the side of the electrolyte and from the side of the solid body are serially connected with each other, and the parameters of the wall pores[18] play a major role in the change of the DEL total capacitance.

If we assume that during the charge and discharge of the capacitor the concentration of ions of the electrolyte and conductivity of the positive and negative electrode change in a narrow range and the type of conductivity of the walls of the polarizable electrode pores does not change, the value of potential $\varphi(x,t)$ as a function of HES capacitor position will have the following expression

$$\varphi(x,t) = \begin{cases} \varphi^{-}_{0\pm} \pm \dfrac{J_0}{d_- C_V}\left\{t + C_V\left[\dfrac{\alpha_+ + \alpha_-}{2\alpha_+\alpha_-}x^2 - \dfrac{d_- x}{\alpha_-} + \dfrac{d_-^2(2\alpha_+ - \alpha_-)}{6\alpha_+\alpha_-} - \dfrac{2d_-^2}{\pi^2}\sum_{n=1}^{\infty}\left(\dfrac{1}{\alpha_-} + \dfrac{(-1)^n}{\alpha_+}\right)\dfrac{e^{-\left(\frac{\pi n\gamma}{d_-}\right)t_2}}{n^2}\cos\dfrac{\pi n x}{d_-}\right]\right\} & \text{at } 0 \le x \le d_- \\ \pm J_0\rho_{sep}x & d_- \le x \le (d_- + d_{sep}) \\ \varphi^+ & \text{at } (d_- + d_{sep}) \le x \le (d_- + d_{sep} + d_+) \end{cases} \quad [59]$$

where φ^{+}_{0+} and φ^{-}_{0-} are the potentials of the negative electrode of the HES capacitor before the charge and before the discharge, respectively, ρ_{sep} is the specific electric resistance of the separator; and d_-, d_{sep}, and d_+ are the thickness, of the negative electrode, separator, and positive electrode, respectively. Besides, sign $(J_0/d_-C_V) < 0$ corresponds to the process of charge, and sign $(J_0/d_-C_V) > 0$ corresponds to the process of the capacitor discharge.

Therefore, subject to the fact that electromotive force (emf) of the HES capacitor is determined as

$$U_C(d_-, d_{sep}, \gamma, C_V, t) = \varphi^+ - \varphi^-(0,t) \quad [60]$$

from Eq. 59 we obtain an analytical expression for emf of the capacitor during its charge and discharge by constant current

$$U_C(d,t) = U_{C0} \pm \frac{J_0}{d_- C_V}\left\{t + C_V d_-^2\left[\frac{2\alpha_+ - \alpha_-}{6\alpha_+\alpha_-} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\left(\frac{1}{\alpha_-} + \frac{(-1)^n}{\alpha_+}\right)\frac{e^{-(\pi n\gamma/d_-)^2 t}}{n^2}\right]\right\} \quad [61]$$

where $U_{C0} = \varphi^+ - \varphi^{-}_{0\pm}$ is the emf of the capacitor at $t = 0$; sign $(J_0/d_-C_V) > 0$ corresponds to the process of charge, and sign $(J_0/d_-C_V) < 0$ to the process of the capacitor discharge.

Subject to the fact that the capacitor has the specific internal resistance ρ_{int} (Ω cm^2), which is determined by the resistances of the current collectors of the negative and positive electrodes, by the resistance of the active material of the positive electrode and resistance of the separator (whose pores are filled by the electrolyte and which was not taken into account during the calculations) then the capacitor voltage during the charge and discharge is expressed by the formula

$$U(d_-,t) = U_0 \pm J_0\rho_{int} \pm \frac{J_0}{d_- C_V}\left\{t + C_V d_-^2\left[\frac{2\alpha_+ - \alpha_-}{6\alpha_+\alpha_-} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\left(\frac{1}{\alpha_-} + \frac{(-1)^n}{\alpha_+}\right)\frac{e^{-(\pi n\gamma/d_-)^2 t}}{n^2}\right]\right\} \quad [62]$$

Similarly, it is possible to obtain analytical expressions for the potentials of the electrodes and voltages of both homogeneous (symmetric) capacitors and of HES capacitors having a positive electrode with DEL.

Calculations and Analysis of Energy, Capacity, and Power Parameters of HES Capacitors

A.— Let us perform parameter analysis of an HES capacitor having a negative electrode with DEL. Let us assume that the capacitor does not have self-discharge and has the area of the visible surface of the plates of the positive and negative electrodes $S = 1$ cm^2. The negative electrode is on one side of the plate of the positive electrode (as shown in Fig. 1a). The positive electrode is an electrode based on PbO_2, whose equilibrium electrode potential is $\varphi^+ = 1.7$ V [in relation to standard hydrogen electrode (SHE) potential], and it does not change during the charge and discharge of the capacitor. The capacitor in fully discharged and charged states has equilibrium voltage 0.8 and 2.0 V, respectively, i.e., the potential of the negative electrode of the discharged and charged capacitor has equilibrium values of $\varphi^{-}_{0+} = +0.9$ V and $\varphi^{-}_{0-} = -0.3$ V, respectively, in relation to SHE potential.

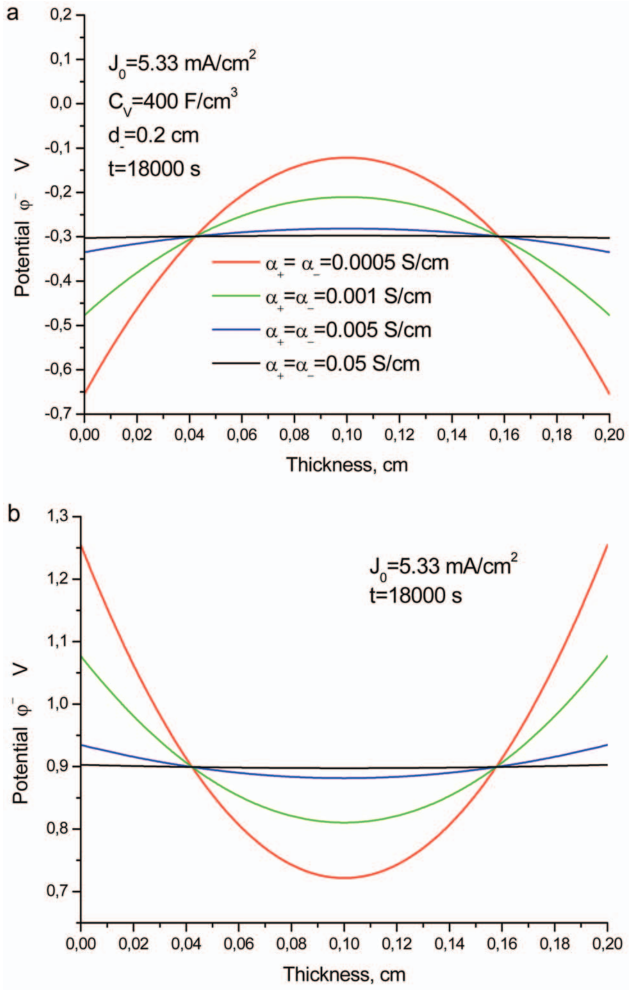

Figure 4. Distribution of potential (in relation to SHE) of the negative electrode as a function of position after (a) 5 h charge and (b) 5 h discharge by constant current of HES capacitor with different parameters of α_+ and α_-.

Let us consider a capacitor with different values of the following parameters: (*i*) specific capacitance of the negative electrode C_V; (*ii*) thickness of the negative electrode d_-; (*iii*) surface density of the charge and discharge currents J_0; (*iv*) parameters α_+ and α_-. The capacitor with the following numerical values of the parameters is charged and discharged by constant current: $C_V = 400$ F/cm^3; $d_- = 0.2$ cm; $J_0 = 5.33$ mA/cm^2; and $\alpha_+ = \alpha_-$, equal to 0.0005, 0.001, 0.005, and 0.05 S/cm. The time of charge and discharge is 5 h each.

It is obvious from the above data that the capacitor capacitance has the value of $C = 80$ F, and charge and discharge current is 5.33 mA, i.e., during the charge of the capacitor which is discharged to 0.8 V, the amount of electric charge delivered to the capacitor is $Q_{\text{ch}} = 96$ C. Besides, during the discharge of the capacitor, which is charged to 2.0 V, the amount of the electric charge delivered to the external circuit is $Q_{\text{dis}} = 96$ C.

First let us consider the distribution of the potential of the negative electrode with DEL as a function of position during the charge and discharge. By using the Eq. 59, it is possible to plot dependences of the potential of the negative electrode on its thickness during the charge and discharge and different values of the parameters α_+ and α_- (Fig. 4). Figure 4 shows that the value of the potential of the negative electrode varies considerably as a function of position during 5 h charge (a) and 5 h discharge (b) by constant current. Besides, the distribution of the negative electrode potential of an HES capacitor depends greatly on the values of the parameters α_+ and α_-.

Provided $\alpha_+ = \alpha_-$, the potential of the negative electrode $\varphi^-(x)$ after the capacitor charge has a symmetric distribution along its thickness, irrespective of the parameters α_+ and α_-. The value $\varphi^-(x)$ has a minimum value at $x = 0$ and $x = d_-$, and a maximum value at $x = d_-/2$ (Fig. 4a). Such distribution of potential shows that during the charge of the capacitor the surface layers of the negative electrode with DEL are charged more efficiently than its central part. As an example, when the value of the parameters $\alpha_+ = \alpha_- = 0.0005$ S/cm, then $\varphi^-(0) = \varphi(d_-) = -0.655$ V and $\varphi^-(d_-/2) = -0.122$ V, i.e., $\varphi^-(d/2) - \varphi^-(0) = 0.533$ V. It is obvious that such distribution of the potential $\varphi^-(x)$ brings about uneven distribution of the potential energy of DEL along thethickness of the polarizable electrode. At the end of the charge process, the emf of the capacitor (U_C) has the value of $U_C = 1.7\ \text{V} - (-0.655\ \text{V}) = 2.355$ V.

When the values of the parameters α_+ and α_- ($\alpha_+ = \alpha_- = 0.05$ S/cm) are high, the value of the potential $\varphi^-(x)$ changes, in fact, very little along the thickness of the negative electrode after the capacitor charge, and at the end of the charge process U_C of the capacitor reaches 2.03 V.

It is clear from the example that a pause after the capacitor charge results in the leveling of the electric charge of DEL along the thickness of the negative electrode, i.e., depolarization of the potential of the negative electrode occurs. The time of the potential leveling along the thickness of the negative electrode depends on the capacitor parameters and modes of charge. Some portion of energy of the negative electrode during depolarization is lost. The amount of energy loss also depends on the parameters of the negative electrode and the mode of the capacitor charge. As an example, after the charge of the capacitor with the parameters $\alpha_+ = \alpha_- = 0.0005$ S/cm to the value of $U_C = 2.32$ V, the value of U_C decreases to the equilibrium value of 2.0 V in the process of depolarization.

The discharge of the capacitor charged to the value of $U_C = 2.0$ V by constant current of 5.33 mA during 5 h also causes an uneven distribution $\varphi^-(x)$ along the thickness of the negative electrode (Fig. 4b). It is obvious that the surface layers of the negative electrode are discharged more effectively. It also follows from Fig. 4b that right after the discharge of the capacitor with the values of $\alpha_+ = \alpha_- = 0.0005$ S/cm, the value of the potential $\varphi^-(0) = \varphi^-(d_-) = 1.255$ V and $\varphi^-(d_-/2) = 0.721$ V, i.e., $\varphi^-(d_-/2) - \varphi^-(0) = 0.534$ V, and after a long pause there is depolarization of the negative electrode and leveling of its potential along its thickness.

The value of U_C after the discharge of the capacitor with the parameters $\alpha_+ = \alpha_- = 0.0005$ S/cm is 0.425 V, and after depolarization U_C grows to the equilibrium value of 0.8 V. As a result of depolarization of the negative electrode after its discharge, there occurs a partial loss of capacitor energy. However, the value of the depolarization losses during the discharge also depends on the parameters of the capacitor and modes of its discharge. Both during the charge and under similar conditions of charge and discharge, depolarization loss of energy is lower during capacitor discharge than the charge.

At high values of parameters α_+ and α_-($\alpha_+ = \alpha_- = 0.05$ S/cm), the value of the potential $\varphi^-(x)$ right after the capacitor discharge changes very little along the thickness of the negative electrode (Fig. 4b). The U_C value of this capacitor at the end of discharge reaches $U_C = 0.797$ V and grows to $U_C = 0.8$ V after a long pause. It is obvious that depolarization losses of energy after the discharge of this capacitor are insignificant.

B.— Now let us consider the dependences $\varphi^-(x)$ of the capacitor set forth in section A, with different values of the parameters α_+ and α_- and different densities of the charge and discharge currents.

Figure 5 shows distributions of the potentials of the negative electrode as a function of position during 5 h charge (a) and 5 h

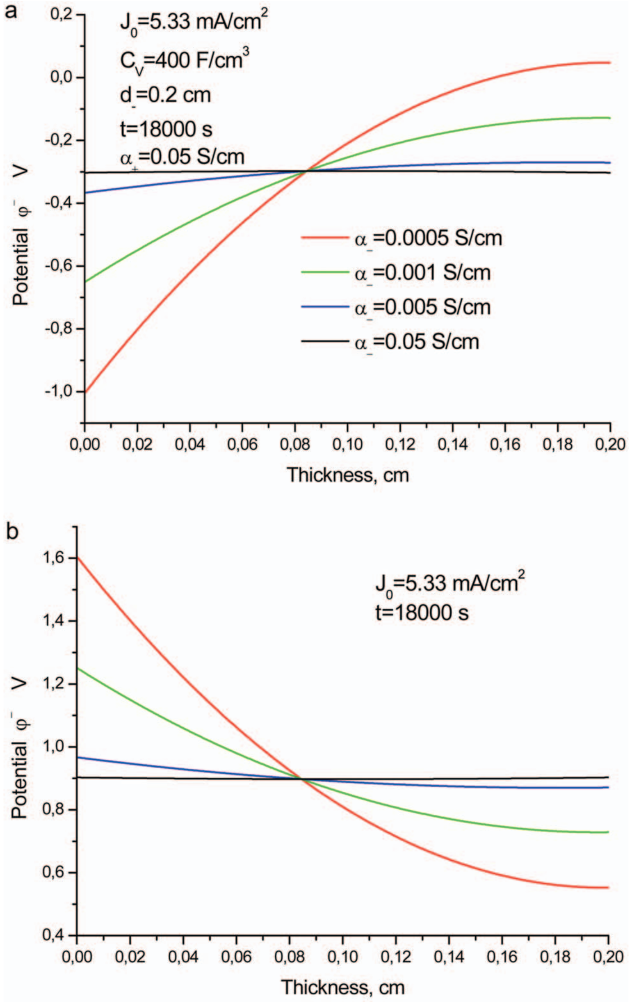

Figure 5. Distribution of potential (in relation to SHE) of the negative electrode as a function of position after (a) 5 h charge and (b) 5 h discharge by constant current of HES capacitor with different parameters of α_-.

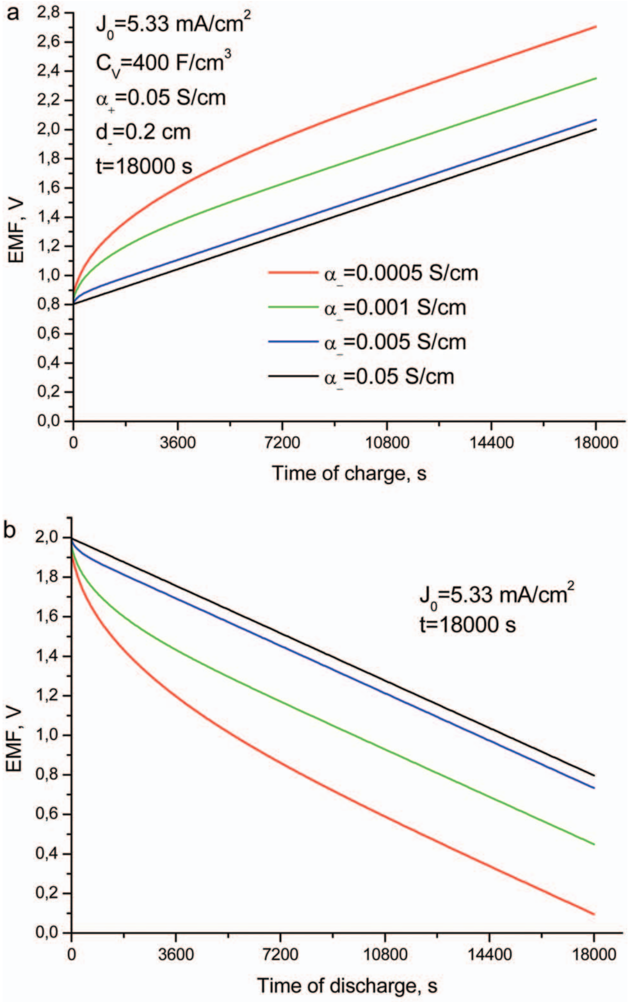

Figure 6. Capacitor dependence of emf on time during (a) 5 h charge and (b) 5 h discharge with different α_- and constant current.

discharge (b) by constant current of the HES capacitor with the parameters $\alpha_+ = 0.05$ S/cm; and $\alpha_- = 0.0005$, 0.001, 0.005, and 0.05 S/cm. Figure 5 shows that during the charge of the capacitors with different values of α_-, the surface layer (from the side of the current collector) of the negative electrode is charged and discharged more effectively. Along with the growth of the value of α_-, there is a growth of the even pattern of potential distribution along the thickness of the negative electrode of the capacitor.

During the charge of the capacitor with the value of the parameter of $\alpha_- = 0.0005$ S/cm, the values of the negative electrode potentials, right after the charge process, are as follows: $\varphi^-(0) = -1.0$ V; $\varphi^-(d_-) = 0.047$ V. Consequently, the U_C value of this capacitor at the end of the charge process reaches $U_C = 2.70$ V and decreases to the value $U_C = 2.0$ V after a long pause. As it follows from Fig. 5b, after the discharge of the capacitor, the potential of the negative electrode on the surface from the side of the current collector increases to the value of 1.6 V, i.e., the emf value of the capacitor at the end of discharge is $U_C = 0.1$ V and increases to 0.8 V after a long pause. Along with the increase of α value, both during capacitor discharge and charge, there is growth of the even pattern of distribution of the negative electrode potential along the thickness. The values of α_+ and α_- have a great influence on the time dependence of emf and voltage of the capacitor during charge and discharge (Fig. 6).

Figure 6 shows the influence of growth of α_- on the U_C pattern during charge and discharge of the capacitor by constant current. Along with the decrease of α_- value there occurs a nonlinear time dependence $U_C(t)$. Besides, the nonlinear pattern of $U_C(t)$ is rather strong at the initial phase of the charge and discharge and decreases along with the increase of the time of charge and discharge.

This example clearly shows the importance of parameters α_+ and α_- of the negative electrode (which also determine the energy parameters and modes of charge and discharge of the capacitors). Therefore, the optimal mode of charge and discharge of electrochemical capacitors is closely related, in particular, to these parameters of the polarizable electrodes of the capacitors.

Now let us consider the dependences $\varphi^-(x)$ of the capacitor with the parameters $\alpha_+ = 0.05$ S/cm and $\alpha_- = 0.005$ S/cm and time periods of charge and discharge 5, 4, 3, and 1 h. The charge and discharge current values of the capacitor are shown in Fig. 7a and b, respectively.

It follows from Fig. 7 that when the time of charge and discharge decrease and the charge and discharge currents increase, the distribution of the potential $\varphi^-(x)$ changes considerably along the thickness of the polarizable electrode. During the capacitor charge by constant current at 5.33 mA for 5 h, the value of U_C at the end of the charge process reaches 2.066 V. During the capacitor charge by constant current at 26.67 mA for 1 h, the value of U_C at the end of the charge process reaches 2.338 V. During the constant current discharge of 5.33 and 26.67 mA for 5 and 1 h, respectively, the emf value at the end of discharge is 0.734 and 0.465 V, respectively.

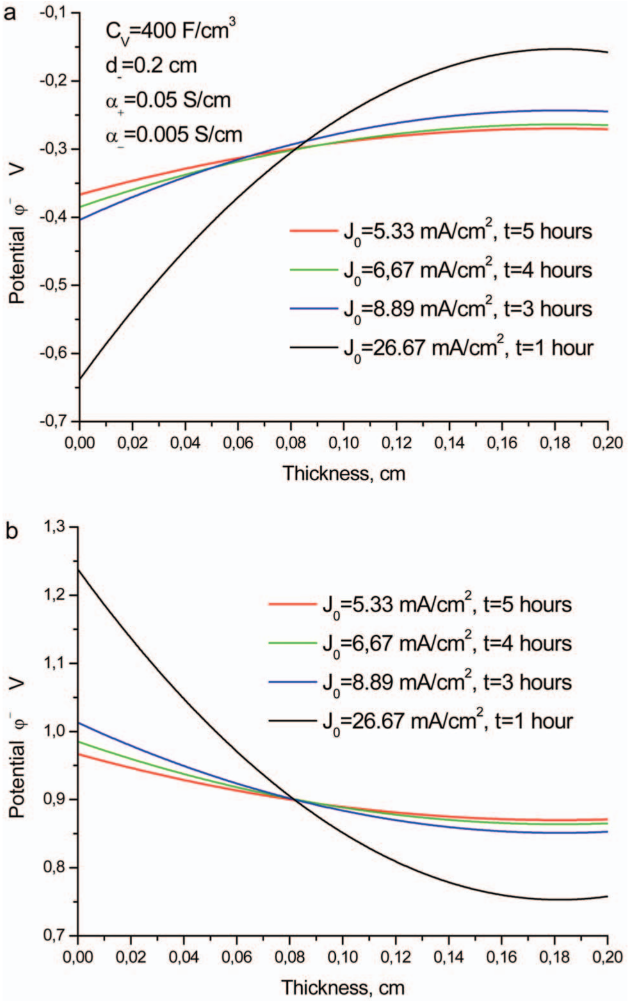

Figure 7. Distribution of potential (in relation to SHE) of negative electrode as a function of position during (a) charge and (b) discharge of HES capacitor by constant current of different densities.

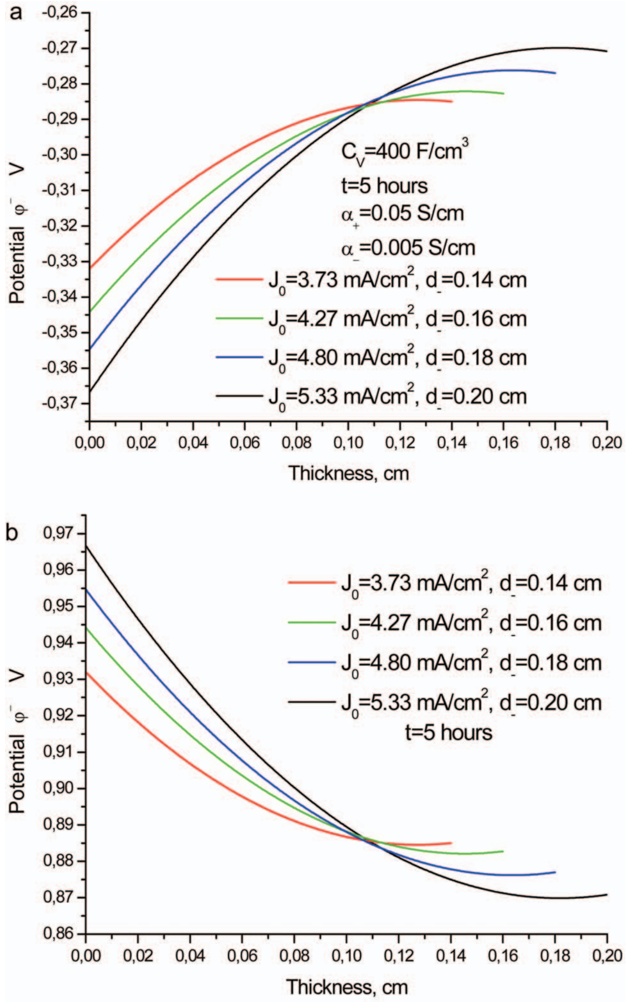

Figure 8. Distribution of potential (in relation to SHE) of negative electrodes as a function of position at (a) 5 h charge and (b) 5 h discharge by constant current of HES capacitors with different thickness of negative electrode.

Therefore, a decrease of the duration of charge and an increase of charge currents of the capacitors results in a change of the energy parameters and operating range of the capacitor voltages. The rate of change of the energy parameters and operating range of voltages is related to the parameters of the polarizable electrode and the values of the charge and discharge currents of the capacitors.

C.— Because, according to Eq. 59 the distribution of the potential $\varphi^-(x)$ of the negative electrode along its thickness, except for other parameters, is also a function of specific capacitance and thickness of the polarizable electrode, let us consider the dependences $\varphi^-(x)$ of the capacitor with different C_V values and thickness of the polarizable electrode.

Let us assume that the capacitor parameters α_+ and α_- have the values $\alpha_+ = 0.05$ and $\alpha_- = 0.005$ S/cm. The capacitors with polarizable negative electrode thicknesses equal 0.14, 0.16, 0.18, and 0.20 cm are charged and discharged by constant currents of 3.73, 4.27, 4.80, and 5.33 mA, respectively. The time of the charge and discharge is 5 h each.

The thicknesses of the polarizable electrode and charge and discharge currents are selected to ensure that all the capacitors are subject to the following condition: during the charge of the capacitors discharged to 0.8 V and discharge of the capacitors charged to 2.0 V, the volume current density has a similar value and is 2.665 mA/cm^3. Such approach makes it possible to perform a more correct comparison of the parameters of the capacitors with different thicknesses of the polarizable electrode.

Figure 8 shows the distribution of the potential $\varphi^-(x)$ of the negative electrodes along their thickness during 5 h charge (a) and 5 h discharge (b) of HES capacitors by constant currents. As it follows from Fig. 8a and b, when the thickness of the polarizable electrode decreases, there is an increase of the uniformity of the distribution of the potential $\varphi^-(x)$ along the electrode thickness during charge and discharge of the capacitor. It is obvious that the energy losses during the depolarization of the potential of the negative electrode after charge and discharge decrease along with a thickness decrease of the polarizable electrode. Therefore, selection of the thickness of the capacitor electrodes is of practical importance, and this parameter has a considerable effect both on the energy and operation parameters of electrochemical capacitors.

Let us perform comparison of U_C capacitors with polarizable electrodes having thickness of 0.14 and 0.2 cm during 5 h charge and discharge by constant currents of 3.73 and 5.33 mA. It follows from Fig. 8 that the capacitors with a polarizable electrode having thickness of 0.14 and 0.2 cm, right after charge, have emfs of 2.032 and 2.067 V, respectively. Right after the discharge of these capacitors, their U_C values are 0.733 and 0.768 V, respectively.

It follows from the results that the operating emf range of the

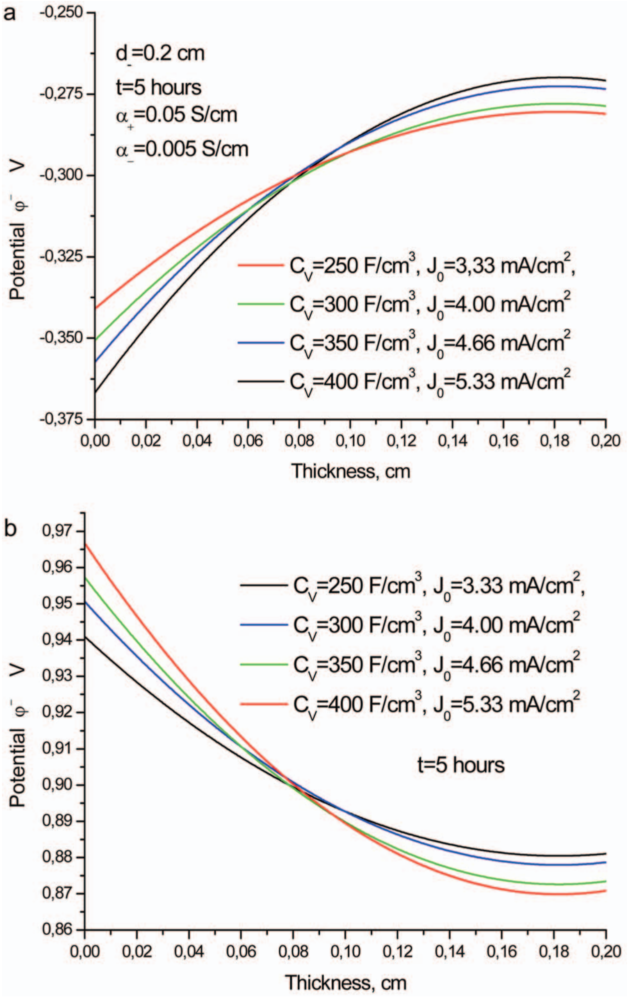

Figure 9. Distribution of potential (in relation to SHE) of negative electrode as a function of position at (a) 5 h charge and (b) 5 h discharge of HES capacitor with different values of specific capacitance by constant current of different densities.

capacitor with the 0.14 cm thick polarizable electrode is 2.032–0.768 V, and with the 0.2 cm thick polarizable electrode it is 2.067–0.733 V, i.e., when the thickness of the capacitor's polarizable electrode changes, there is a change of its operating range of voltages.

Figure 9 shows the distribution of the potentials along the thickness of the negative electrodes with different values of the specific capacitance during 5 h charge (a) and 5 h discharge (b) of the HES capacitor by constant current. The specific capacitance of the polarizable electrode and charge and discharge currents of the capacitors are selected to ensure that all the capacitors during the charge and discharge (discharged to 0.8 V before charge and charged to 2.0 V before discharge) were subject to the following conditions: $(I_{\text{ch/dis}} \cdot t_{\text{ch/dis}})/C_V = \text{const} = 240\ \text{mV cm}^3$, where $I_{\text{ch/dis}}$ is the value of the charge or discharge current, and $t_{\text{ch/dis}}$ is the time of charge or discharge.

As it follows from Fig. 9, the distribution of $\varphi^-(x)$ potential along the thickness of the polarizable electrodes during the charge and discharge of HES capacitors depends on the value of the specific capacitance (C_V) of the active material of the capacitor negative electrode. Besides, this uneven pattern of $\varphi^-(x)$ along the thickness of the polarizable electrode grows with an increase of the value of C_V, both during the charge and during the discharge of the capacitor. It follows from this that an increase of the specific energy parameters of the capacitor brings about growth of energy losses of the capacitor during depolarization of the potential of the polarizable electrode after charge and discharge of the capacitor. Subject to Eq. 47, it also follows from Eq. 55 that an increase of C_V is accompanied by growth of the polarization losses of energy during the charge and discharge of the capacitor, even when other parameters of the polarizable electrode remain unchanged.

Therefore, the growth of the specific (by volume) capacitance of the polarizable electrode results in an increase of the specific energy parameters of the capacitors and growth of polarization and depolarization energy losses.

D.— Let us perform analysis of the parameters of the HES capacitor with a design of the capacitor set forth in section A. Let us assume that the capacitor is charged by constant current until emf $U_{\text{Cch}} = 2.0$ V is reached and discharged by constant current to the emf value $U_{\text{Cdis}} = 0.8$ V. The potential of the negative electrode at the end of the charge process and at the end of the discharge process of the capacitor has the following values, respectively: $\varphi_{0-}^- = -3.0$ V and $\varphi_{0+}^- = +0.9$ V (in relation to SHE potential). Let us also assume that there is no self-discharge of the capacitor.

Let us consider two modes of charge and discharge of the capacitors with the following parameters: (*i*) specific capacitance of the negative electrode $C_V = 400\ \text{F/cm}^3$; (*ii*) visible surface area of the plates of the positive electrode $S = 6290\ \text{cm}^2$; (*iii*) thickness of the carbon plate of the negative electrode $d_- = 0.2$ cm; (*iv*) specific ohmic internal resistance $\rho_{\text{int}} = 12\ \Omega\ \text{cm}^2$; and parameter $\alpha_+ = 0.05$ S/cm. Parameter α_- has the following values: 0.0005, 0.001, 0.005, and 0.05 S/cm.

Mode I.— The capacitor discharged to 0.8 V is charged by constant current to the emf value $U_{\text{Cch}} = 2.0$ V and the time of the charge process (t_{ch}) is 5 h. There is a pause after the charge during which the potential is leveled along the thickness of the negative electrode. Thereafter the capacitor is discharged by constant current to the emf value of the negative electrode $U_{\text{Cdis}} = 0.8$ V. The time of the discharge process (t_{dis}) is 5 h. There is a pause after the discharge during which the potential is leveled along the thickness of the negative electrode to an equilibrium value.

Mode II.— The capacitor discharged to 0.8 V is charged by constant current to the emf value $U_{\text{Cch}} = 2.0$ V and the time of the charge process (t_{ch}) is 1 h. There is a pause after the charge during which the potential is leveled along the thickness of the negative electrode. Thereafter the capacitor is discharged by constant current to the emf value of the negative electrode $U_{\text{Cdis}} = 0.8$ V. The time of the discharge process (t_{dis}) is 5 h. There is a pause after the discharge during which the potential is leveled along the thickness of the negative electrode.

Charge and discharge of the capacitor in mode I.— Let us perform analysis of the energy and capacity parameters of the HES capacitor during the charge and discharge in this mode. It is obvious from the above-mentioned data that the capacitance of the HES capacitor (hereafter referred to as HES-503.2) of the said design has the value of $C = 503.2$ kF. The maximum stored energy of the HES-503.2 capacitor in the emf operating range of 2.0–0.8 V is as follows

$$E = \frac{C(U_{\text{Cch}}^2 - U_{\text{Cdis}}^2)}{2} = 845.375\ \text{kJ} = 234.827\ \text{Wh} \qquad [63]$$

The maximum value of the electric charge of HES-503.2 in the emf operating range of 2.0–0.8 V is as follows

$$Q = C(U_{\text{Cch}} - U_{\text{Cdis}}) = 603.84\ \text{kC} = 167.733\ \text{Ah} \qquad [64]$$

By using Eq. 61 we can build an emf dependence on the 5 h charge and discharge time of the capacitors with different parameters (Fig. 10). It follows from Fig. 10a that the dependence of emf on time with an increase of parameter α_- from the value of α_-

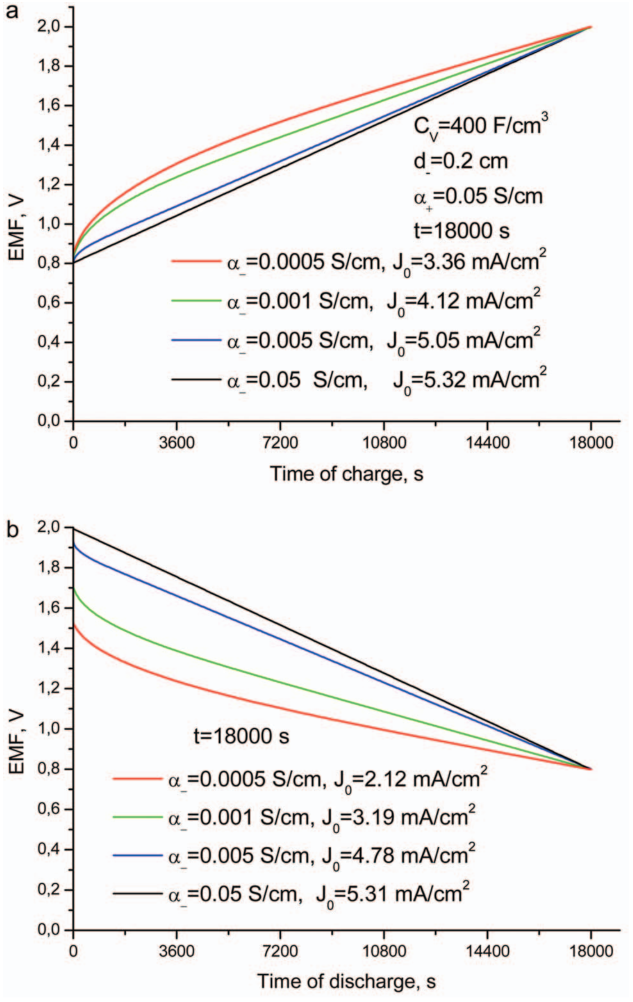

Figure 10. Capacitor emf dependence on time of (a) 5 h charge and (b) 5 h discharge with different parameters during charge to emf =2 V and discharge to emf = 0.8 V.

= 0.0005 to 0.05 S/cm changes considerably. Besides, the density of the charge current J_0 for the capacitor with the parameters α_- = 0.05 and 0.0005 S/cm is $J_0 = 3.36$ and 5.32 mA/cm^2, respectively. It is obvious that the value of the stored electric charge (Q_{ch}) of the capacitors (subject to the fact that the time of charge is 5 h) grows with an increase of the parameters α_- (Table I). It follows from Table I that when the parameter α_- increases 100 times, the value Q_{ch} grows 1.583 times (from 105.67 to 167.31 Ah).

By using the above-mentioned method, it is not difficult to show that Q_{ch} of the capacitor has a similar dependence on the value of the parameter α_+. Consequently, the values of the parameters α_+ and α_- have a considerable effect on capacitor capacity and energy parameters. Equations 42 and 43 show that parameters α_+ and α_- are determined by the conductivity of the carbon plates, conductivity of the electrolyte in the pores of the carbon plates, coefficient of diffusivity of electrons and ions in the carbon plate, and specific capacitance of the carbon plate. This example shows that the parameters α_+ and α_- have an effect on the capacitor parameters and by controlling these parameter values, it is possible to control the capacitor parameters in general.

The calculations show that the energy (E_{Cch}) required for the capacitor charge (with no account of ohmic internal resistance losses) to the emf value of 2.0 V also depends considerably on the values of α_+ and α_-. During the capacitor charge with α_- = 0.0005, 0.001, 0.005, and 0.05 S/cm, E_{Cch} is 165.99, 196.83, 227.32, and 234.576 Wh, respectively (Table I). A 100 times increase of α_- brings about growth of E_{Cch} by 1.413 times. A portion of the charge energy E_{Cch} is stored in the capacitor during the charge process, called effective charge energy ($E_{\mathrm{ch}}^{\mathrm{eff}}$), and some portion of the energy is dissipated at the polarization resistance of the capacitor ($E_{\mathrm{ch}}^{R\mathrm{pol}}$). In these examples we consider only polarization resistance of the negative electrode.

The value of ($E_{\mathrm{ch}}^{\mathrm{Rpol}}$) is determined by the formula

$$E_{\mathrm{ch}}^{\mathrm{Rpol}} = E_{\mathrm{Cch}} - E_{\mathrm{Cch}}^{\mathrm{eff}} \qquad [65]$$

The calculated E_{Cch} values and the capacitors with different values of α_- are set forth in Table I, from which it follows that along with the growth of α_-, there is a growth of E_{Cch}, while the value of $E_{\mathrm{ch}}^{R\mathrm{pol}}$ decreases. A 100 times increase of α_- brings about a decrease of $E_{\mathrm{ch}}^{R\mathrm{pol}}$ by 66.05 times.

Inasmuch as during the charge of the capacitor the potential of the negative electrode along the thickness has different values, a pause after the charge causes redistribution of the potential and leveling of the value along the thickness of the polarizable electrode of the capacitor, i.e., during a pause after the charge, depolarization of the capacitor negative electrode occurs. As a result, emf of the capacitor decreases to the value of U_{Cch}^{ap}. After a pause, the value of U_{Cch}^{ap} of the capacitors with the parameters of α_- equal to 0.0005, 0.001, 0.005, and 0.05 S/cm are 1.556, 1.727, 1.936, and 1.997 V, respectively. This process is accompanied by a decrease of the capacitor energy, and the value of the capacitor energy (E_{Cch}^{ap}) with the above-mentioned parameters of α_-, after a pause, i.e., after the completion of the depolarization, is 124.48, 163.71, 217.22, and 233.987 Wh, respectively.

Therefore, during depolarization of the charged capacitor some portion of the stored energy ($E_{\mathrm{ch}}^{\mathrm{dpol}}$) changes into heat. This mechanism of the energy losses manifests itself in a more express manner in the capacitors with lower values of the parameters of α_+ and α_-, and what is important for choosing an optimal mode of the capacitor charge, during the capacitor charge by high currents. The value of $E_{\mathrm{ch}}^{\mathrm{dpol}}$ is calculated by the following formula

$$E_{\mathrm{ch}}^{\mathrm{dpol}} = E_{\mathrm{Cch}}^{\mathrm{eff}} - E_{\mathrm{Cch}}^{\mathrm{ap}} \qquad [66]$$

and, as it is shown in Table I, changes considerably along with a change of the value of α_-. A 100 times increase of α_- brings about a 1370 times decrease of $E_{\mathrm{ch}}^{\mathrm{dpol}}$ energy. Table I also shows that when the values of $\alpha_+ = \alpha_- = 0.05$ S/cm in 5 h mode of the capacitor charge, the negative electrode of the capacitor does not, in fact, depolarize. After the charge process, emf of the capacitor decreases by only 3 mV, which does not, in fact, influence the capacitor energy parameters.

Because the capacitor has internal ohmic resistance, a portion of the charge energy (E_{ch}^{R}) dissipates at the internal resistance during the capacitor charge. The value of E_{ch}^{R} during the charge by constant current (I_{ch}) is calculated by the following formula

$$E_{\mathrm{ch}}^{R} = I_{\mathrm{ch}}^{2} R t_{\mathrm{ch}} \qquad [67]$$

The E_{ch}^{R} values of the capacitors with different α_- values is set forth in Table I. It follows from this data that along with the growth of α_-, there is a growth of Coulombic capacity of the capacitors and the value of E_{ch}^{R}.

Therefore, the value of the aggregate charge energy (E_{ch}) during the capacitor charge is as follows

$$E_{\mathrm{ch}} = E_{\mathrm{Cch}} + E_{\mathrm{ch}}^{R} \qquad [68]$$

Table I shows that the value E_{ch} of the capacitors with the α_- parameters equal to 0.0005, 0.001, 0.005, and 0.05 S/cm are 170.25, 203.24, 236.94, and 245.26 Wh, respectively.

Both during the charge and discharge, emf of the capacitors has a nonlinear dependence on time of charge and discharge (Fig. 10). Besides, this nonlinear dependence of emf on time decreases along with an increase of the α_- parameter. Inasmuch as the discharge of

Table I. Parameters of the HES-503.2 capacitor during charge and discharge in modes I and II.

			α, S/cm							
			Mode I				Mode II			
Par.	Parameters	Unit of measurement	0.0005	0.001	0.005	0.05	0.0005	0.001	0.005	0.05
1.	I_{ch}	A	21.134	25.915	31.76	33.46	50.13	70.89	130.83	165.427
2.	Q_{ch}	Ah	105.67	129.574	158.82	167.31	50.13	70.89	130.83	165.427
3.	E_{Cch}	Wh	165.99	196.83	227.32	234.576	80.258	113.26	198.2	233.12
4.	$E_{\mathrm{Cch}}^{\mathrm{eff}}$	Wh	127.22	164.736	217.24	233.989	56.617	80.797	166.793	230.237
5.	$E_{\mathrm{ch}}^{\mathrm{Rpol}}$	Wh	38.77	32.094	10.08	0.587	23.641	32.463	31.407	2.883
6.	U_{Cch}^{ap}	V	1.556	1.727	1.936	1.997	1.159	1.307	1.736	1.9835
7.	E_{Cch}^{ap}	Wh	124.48	163.71	217.22	233.987	49.15	74.66	165.89	230.23
8.	$E_{\mathrm{ch}}^{\mathrm{dpol}}$	Wh	2.74	1.026	0.02	0.002	7.467	6.137	0.903	0.007
9.	E_{ch}^{R}	Wh	4.26	6.406	9.6246	10.68	4.7945	9.587	32.655	52.208
10.	E_{ch}	Wh	170.25	203.24	236.94	245.26	85.053	122.847	230.855	285.328
11.	I_{dis}	A	13.33	20.065	30.066	33.4	6.32	10.976	24.78	30.02
12.	Q_{dis}	Ah	66.67	100.3	150.33	167.0	31.6	54.88	123.91	165.11
13.	E_{Cdis}	Wh	71.319	117.40	201.21	233.15	29.346	55.014	154.082	229.486
14.	E_{Cadlis}	Wh	37.728	27.07	7.068	0.252	16.337	13.886	5.7386	0.3082
15.	$E_{\mathrm{dis}}^{\mathrm{Rpol}}$	Wh	15.433	19.24	8.942	0.585	3.467	5.760	6.0694	0.4358
16.	U_{Cdis}^{ap}	V	1.079	1.0094	0.8607	0.8022	0.9325	0.9145	0.8495	0.80226
17.	E_{dis}^{ap}	Wh	36.64	26.48	7.045	0.246	16.04	13.72	5.706	0.254
18.	$E_{\mathrm{dis}}^{\mathrm{dpol}}$	Wh	1.087	0.59	0.023	0.006	0.297	0.166	0.0326	0.0544
19.	$E_{\mathrm{dis}}^{\mathrm{R}}$	Wh	1.696	3.84	8.479	10.64	0.381	1.149	5.857	8.596
20.	E_{dis}	Wh	69.62	113.56	192.73	222.51	28.965	53.865	148.225	220.89
21.	Q_{Cadis}	Ah	39.0	29.27	8.49	0.31	18.53	16.01	6.92	0.317
22.	η_{E1}	%	40.89	55.87	81.34	90.72	34.055	43.847	64.207	77.416
23.	η_{E2}	%	62.41	68.9	84.315	90.71	52.914	55.024	66.678	77.505
24.	δ_{ERpol}	%	31.83	25.24	7.9	0.477	31.87	31.114	16.246	1.163
25.	δ_{ER}	%	3.498	5.04	7.51	8.6928	6.085	8.740	16.683	21.31
26.	δ_{Edpol}	%	2.247	0.795	0.422	0.003	9.128	5.126	0.405	0.02

the capacitors is performed after a pause which follows the charge of the capacitors, then (as it was pointed out above) the emf values of the capacitors at the start of the discharge are different. Such calculations show that for 5 h discharge the values of the discharge currents (I_{dis}) of the capacitors with the parameters α_- equal to 0.0005, 0.001, 0.005, and 0.05 S/cm, should be 13.33, 20.065, 30.066, and 33.4 A, respectively, and Coulombic discharge capacity (Q_{dis}) should have the values 66.67, 100.3, 150.33, and 167.0 Ah, respectively.

Calculation of the delivered energy (E_{Cdis}) during discharge of the capacitors is made by means of the Eq. 61 and shows that E_{Cdis} grows along with an increase of α_- (Table I). Equation 61 also makes it possible to calculate the energy which is stored in the capacitor after its discharge, E_{Cadis}. During the discharge of the capacitor, the potential of the polarizable electrode has a different value along the thickness of the carbon plates, so a portion of the capacitor energy is not delivered during discharge. The value of E_{Cadis} is determined by the polarization properties of the capacitor and is closely related to the parameters α_+, α_-, and to the discharge current I_{dis}. The table shows a decrease of E_{Cadis} along with growth of α_-.

During discharge, a portion of the stored energy of the capacitor is dissipated at the internal polarization resistance ($E_{\mathrm{dis}}^{\mathrm{Rpol}}$) and is determined by the following formula

$$E_{\mathrm{dis}}^{\mathrm{Rpol}} = E_{\mathrm{Cch}}^{ap} - E_{\mathrm{Cdis}} - E_{\mathrm{Cadis}} \qquad [69]$$

As it follows from Table I, despite the fact that the densities of the discharge currents are small, the value of $E_{\mathrm{dis}}^{\mathrm{Rpol}}$ depends considerably on the parameter α_-. It also follows from Eq. 61 that the $E_{\mathrm{dis}}^{\mathrm{Rpol}}$ value, in fact, similarly depends on α_+. During the discharge of the capacitors with α_- equal to 0.0005, 0.001, 0.005, and 0.05 S/cm, $E_{\mathrm{dis}}^{\mathrm{Rpol}}$ is 15.433, 19.24, 8.942, and 0.585 Wh, respectively.

A pause after the discharge of the capacitors brings about an even distribution of the potential along the thickness of the carbon plate of the negative electrode. Along with an increase of the pause's duration after discharge, emf of the capacitor gradually grows and reaches the maximum equilibrium value (U_{Cdis}^{ap}). The U_{Cdis}^{ap} values of the capacitors are set forth in Table I. During redistribution of the electric charge of the double electric layer along the thickness of the carbon plate after the discharge of the capacitors, some portion of the residual energy is lost and the energy (E_{dis}^{ap}) is retained in the capacitor, whose value is set forth in Table I, and which is calculated by the following formula

$$E_{\mathrm{dis}}^{ap} = \frac{C({U_{\mathrm{Cdis}}^{ap}}^2 - 0.8^2)}{2} \qquad [70]$$

The energy ($E_{\mathrm{dis}}^{\mathrm{dpol}}$) which is dissipated at the polarization resistance during depolarization of the potential of the negative electrode after the capacitor discharge is determined by the formula

$$E_{\mathrm{dis}}^{\mathrm{dpol}} = E_{\mathrm{Cadis}} - E_{\mathrm{dis}}^{\mathrm{ap}} \qquad [71]$$

and the obtained values of $E_{\mathrm{dis}}^{\mathrm{dpol}}$ of the capacitors are also set forth in Table I. During capacitor discharge by constant current (I_{dis}) some portion of the charge energy (E_{dis}^{R}) is dissipated at the internal resistance. The value of the energy E_{dis}^{R} is calculated by the formula

$$E_{\mathrm{dis}}^{R} = I_{\mathrm{dis}}^{2} R t_{\mathrm{dis}} \qquad [72]$$

The value of the energy released to the load (E_{dis}) during the capacitor discharge is determined by the formula

$$E_{\mathrm{dis}} = E_{\mathrm{Cdis}} - E_{\mathrm{dis}}^{R} \qquad [73]$$

and the obtained results are set forth in Table I. It is seen that E_{dis} grows considerably along with the growth of α_-.

The amount of the electric charge (Q_{Cadis}), which is retained in the capacitor after the discharge, also depends on the value of the discharge current and α_-, and is determined by the formula

$$Q_{\mathrm{Cadis}} = C(U_{\mathrm{Cdis}}^{\mathrm{ap}} - 0.8) \quad [74]$$

The values of Q_{Cadis} are also set forth in Table I, from which it follows that along with the growth of α_- there occurs a considerable decrease of Q_{Cadis}, i.e., the capacitor discharges more efficiently.

Now let us consider the energy efficiency of the charge–discharge cycle of the capacitor. Subject to the fact that during the capacitor charge the energy E_{ch} is spent and the value of the energy delivered to the load during the discharge is E_{dis}, the energy efficiency of the first charge–discharge cycle (η_{E1}) can be determined by the formula as follows

$$\eta_{E1} = \frac{E_{\mathrm{dis}}}{E_{\mathrm{ch}}} 100\% \quad [75]$$

The values of the energy efficiency calculated as per Eq. 75 are set forth in Table I. It follows from this data that the values of the energy efficiency (η_{E1}) of the capacitors with α_- equal to 0.0005, 0.001, 0.005, and 0.05 S/cm during 5 h charge and 5 h discharge are 40.89, 55.87, 81.34, and 90.72%, respectively. However, some portion of the energy stored during the capacitor charge is retained in the capacitor during discharge. Consequently, it is possible to introduce a new parameter of the energy efficiency of the charge–discharge cycle (η_{E2}) which takes account of the value of the energy E_{dis}^{ap} that is retained in the capacitor after the discharge and pause. The value η_{E2} is determined by the expression

$$\eta_{E2} = \frac{E_{\mathrm{dis}} + E_{\mathrm{dis}}^{ap}}{E_{\mathrm{ch}}} 100\% \quad [76]$$

The η_{E2} values are set forth in Table I. As it follows from this data, the difference of η_{E1} and η_{E2} decreases considerably along with an increase of α_-.

We should also note an aspect which is important for the analysis of capacitor parameters and which often occurs in practice, i.e., the values of the charge energy E_{ch} and Coulombic charge capacity Q_{ch} during the second charge of the capacitor are smaller compared to similar capacitor parameters during the first charge. This is determined by the fact that after the first discharge the capacitors remain partially charged. Because the time of charge is 5 h, one may easily see that for the second charge of the capacitors to emf = 2.0 V, it is necessary to decrease the charge currents as compared with the currents of the first charge process. In order to perform discharge of the capacitors after the second charge process during 5 h it is also required to change the values of the discharge currents. This trend goes on in several subsequent charge–discharge cycles until it reaches equilibrium. In this process a monotonic decrease of the energy and capacity parameters of the capacitors is observed. From Eq. 59 and 61, it is seen that the occurrence of this effect is inherent in all the capacitors and depends on the parameters of the polarizable electrode.

This effect is very common in practice, and in order to obtain stable energy parameters of the capacitors it is necessary to perform several charge–discharge cycles. The practice shows that when the parameters of HES-282 capacitors (with electric capacitance of 282 kF) change in the said mode, it is sufficient to perform 3–5 charge–discharge cycles to obtain reliable results.

The self-discharge current plays an important role in the stabilization of the capacitor parameters during each selected mode of charge and discharge when the time periods of charge and discharge are rather great. The record of the self-discharge current makes it possible to more accurately calculate the energy parameters of the capacitors during long charge and discharge. From the obtained results it is also obvious that the method of the charge process plays an important role in obtaining optimal energy parameters.

Therefore, during both the charge and discharge of the capacitors there occur energy losses. These energy losses are determined by the following: polarization resistance ($E_{\mathrm{ch}}^{\mathrm{Rpol}}, E_{\mathrm{dis}}^{\mathrm{Rpol}}$); ohmic resistance ($E_{\mathrm{ch}}^{R}, E_{\mathrm{dis}}^{R}$); and depolarization of the polarizable electrode ($E_{\mathrm{ch}}^{\mathrm{dpol}}, E_{\mathrm{dis}}^{\mathrm{dpol}}$) after the capacitor charge. The aggregate values of the polarization losses of energy (δ_{ERpol}) during the charge and discharge are set forth in Table I and are determined by the formula

$$\delta_{\mathrm{ERpol}} = \frac{E_{\mathrm{ch}}^{\mathrm{Rpol}} + E_{\mathrm{dis}}^{\mathrm{Rpol}}}{E_{\mathrm{ch}}} 100\% \quad [77]$$

The energy losses at the internal ohmic resistance and depolarization losses during charge and discharge of the capacitor are determined by the formulas

$$\delta_{\mathrm{ER}} = \frac{E_{\mathrm{ch}}^{R} + E_{\mathrm{dis}}^{R}}{E_{\mathrm{ch}}} 100\% \quad [78]$$

and

$$\delta_{\mathrm{Edpol}} = \frac{E_{\mathrm{ch}}^{\mathrm{dpol}} + E_{\mathrm{dis}}^{\mathrm{dpol}}}{E_{\mathrm{ch}}} 100\% \quad [79]$$

Table I shows that during the charge and discharge of the capacitor with $\alpha_- = 0.0005$ S/cm the energy losses are 37.59%, and the bulk portion of the energy (31.83%) is lost at the polarization resistance. The energy losses at the internal ohmic resistance are 3.498%, and during depolarization of the polarizable electrode of the capacitor, 2.247% of energy is lost. When the value of α_- decreases, the polarization and depolarization losses are reduced and the share of ohmic losses grows. The growth of ohmic losses of energy is determined by the growth of Coulombic capacity and the capacitor's stored energy.

Therefore, this example shows the importance of the carbon plate parameters for the manufacture of electrochemical capacitors with high energy parameters and high efficiency of charge–discharge cycle.

Charge and discharge of capacitors in mode II.— Similarly, the dependences of emf on the time of charge and discharge of the capacitors with different values of α_- (Fig. 11) were plotted. Figure 11a shows that the nonlinear dependence of emf on time at 1 h capacitor charge grows as compared with the dependence of emf on time at 5 h charge. On the contrary, the nonlinear dependence of emf on time during the capacitor discharge decreases (Fig. 11b) as compared with the emf dependence during discharge in mode I, which is related to lower densities of the charge currents in mode II.

The value of Coulombic capacity of the capacitors considerably decreases when the time of charge of the capacitors decreases from 5 to 1 h. Besides, the rate of Coulombic capacity decrease depends on the value of parameter α_-. When $\alpha_- = 0.0005$ S/cm in the case of 5 h charge, Coulombic capacity (Q_{ch}) is 105.67 Ah, and in the case of 1 h charge $Q_{\mathrm{ch}} = 50.13$ Ah, i.e., the difference of Coulombic capacities is 55.54 Ah. When $\alpha_- = 0.05$ S/cm in the case of 5 h charge $Q_{\mathrm{ch}} = 167.31$ Ah, and in the case of 1 h charge $Q_{\mathrm{ch}} = 165.427$ Ah. The difference of Coulombic capacities in this case is only 1.883 Ah. The energy parameters and energy efficiency of the charge–discharge cycle also decrease insignificantly when the capacitor is charged for 1 h. The said data shows that for the manufacture of the capacitors designed for a fast charge, it is necessary to ensure that the parameters α_+ and α_- have high values. It is also obvious that when the time of the charge of the capacitors, designed for long charge and discharge, is reduced, a considerable decrease of the energy of the capacitors occurs and the energy efficiency of their charge–discharge cycle goes down.

The results of calculations of the energy and capacity parameters of the capacitors during the charge and discharge in mode II are set forth in Table I. The table shows that U_{Cch}^{ap} has a low value when the values of α_- are small. This causes considerable growth of depolarization energy losses in such mode of charge. The fivefold reduction of the time of charge of the capacitor with $\alpha_- = 0.0005$ S/cm brings about a growth of δ_{ERpol} from 2.247 to 9.128%.

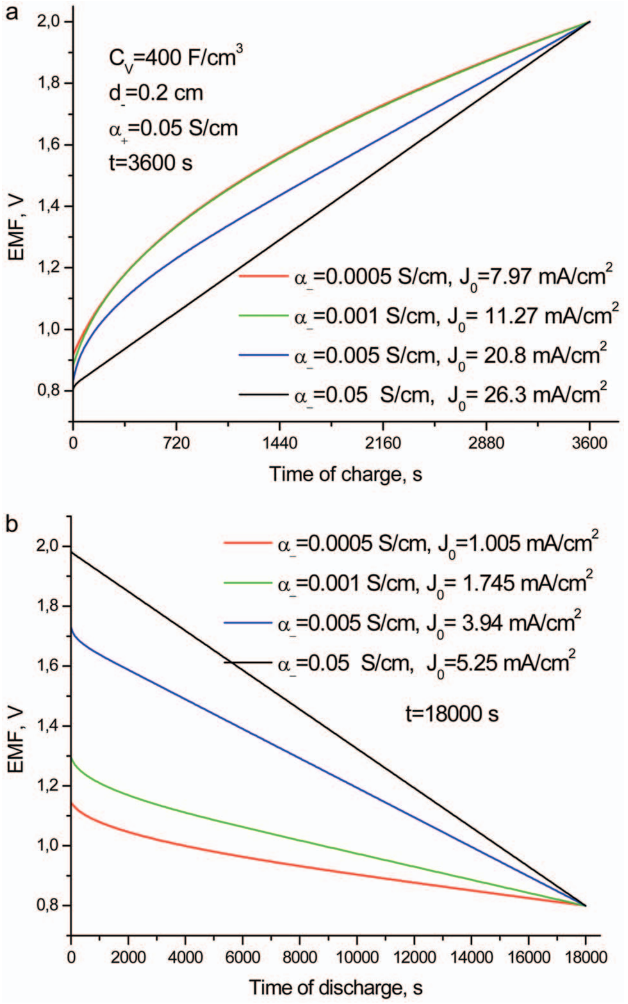

Figure 11. Capacitor emf dependences on the time of (a) 1 h charge and (b) 5 h discharge with different parameters during charge emf =2 V and discharge to emf = 0.8 V.

Reduction of the energy efficiency of the charge–discharge cycle of the capacitors during operation in mode II is determined, mostly, by considerable energy losses during capacitor charge. For the purposes of development and manufacture of electrochemical capacitors which are capable of being charged and discharged in a fast manner, it is appropriate to select efficient thickness of the electrodes, subject to their other parameters and parameters of the mode of charge and discharge of the capacitors.

The measurements of energy, capacity parameters, energy and Coulombic efficiency, as well as other parameters of HES capacitors of $PbO_2|H_2SO_4|C$ systems with different parameters of the negative electrode with DEL based on activated carbon powders show that in the voltage range of 0.8–2.2 V the experimental and calculated values of the said parameters are quite consistent. When the capacitor voltage increases over 2.2 V, there is a slight divergence between the calculated and experimental results. This is determined by the fact that at the charge voltage which is more than 2.1 V the capacitance of the electrode with DEL becomes dependent on the voltage of the capacitors (Fig. 2), and along with the increase of the charge voltage the said dependence becomes greater. However, the capacitance of the capacitors during the discharge depends very little on their voltage, which makes it possible (within the framework of the model of HES capacitors) to calculate (with adequate accuracy) the discharge parameters of the capacitors with high state of charge.

Conclusions

The model of HES capacitors and the obtained analytical expressions make it possible to calculate energy, capacity, power parameters, energy efficiency of charge–discharge cycles of the capacitors subject to the type and value of conductivity of the solid matrixes of electrodes with DEL, conductivity of electrolyte, thickness and specific capacitance of electrodes, and values of charge and discharge currents of the capacitors.

During the charge and discharge of HES capacitors by constant current, the potential of the electrode with DEL has uneven distribution along its thickness. The rate of unevenness of the potential depends on the density of the current, thickness, conductivity of the solid matrix and electrolyte, as well as on specific capacitance of the electrode and state of charge and discharge of the capacitor. At low conductivity values of the solid matrix of the electrode with DEL and electrolyte, its near-surface layers are charged and discharged more effectively. At high state of charge of the HES capacitor of $PbO_2|H_2SO_4|C$ systems, a physical p-n transition is formed on the near-surface layers of the walls of its negative electrode pores.

The voltage of HES capacitors changes in a nonlinear manner subject to the time of charge and discharge by constant current of the capacitors with constant capacitance. The rate of nonlinearity grows along with the thickness of the electrodes with DEL, currents, and conductivity of the solid matrix of the electrode and electrolyte.

An increase of the rate of charge and discharge of HES capacitors by means of increasing currents and/or decreasing the time of charge and discharge (during the charge by constant Coulombic capacitance and discharge to the assigned value) brings about a decrease of the energy, capacity parameters, and increase of the operating window of the capacitor voltages. The rate of change becomes higher along with the decrease of conductivity of the solid matrix, electrolyte, and increase of the thickness and specific capacitance of the electrode with DEL. In the invariable parameters mode of the algorithm of continuous charge–discharge cycles in the initial cycles, the energy, and capacity parameters of the capacitors decrease and thereafter become stable.

The energy efficiency of the charge–discharge cycles of HES capacitors depends significantly on the conductivity of the solid matrix of the electrode with DEL and of the electrolyte, thickness of the electrode, and value of charge–discharge currents. The major portion of the energy losses of the HES capacitor is determined by the polarization resistance of the electrodes. Some portion of the losses is determined by the depolarization of the potentials of the electrodes with DEL during pauses after the charge and discharge of the capacitors. Along with the increase of the conductivity of the solid matrix of the electrode and electrolyte, the polarization and depolarization losses of energy during the charge and discharge of the capacitors decrease nonlinearly.

Acknowledgments

The authors thank John Miller (United States) for his well-intentioned comments and constructive suggestions, which have contributed to the manuscript's improvement. We also express our appreciation to Vladimir Kazarov for fruitful discussions of the results and for valuable assistance in the article's appropriate formatting. We appreciate valuable help from Paul Toomey (AEP) in submission of the manuscript for publication in JES.

The work on this manuscript has been fulfilled with financial support of JSC ESMA (Russia) and AEP (United States) under a joint program "Heterogeneous Electrochemical Supercapacitors."

American Electric Power assisted in meeting the publication costs of this article.

List of Symbols

C	capacitance, F
C_m	mass specific capacitance, F/g
C_V	volume specific capacitance, F/cm^3

d_-	thickness of negative electrode, cm
d_+	thickness of positive electrode, cm
d_C	thickness of capacitor, cm
d_{sep}	thickness of separator, cm
D_+, D_-	diffusivity of the positive and negative ions of the electrolyte, m^2/s
D_e, D_p	diffusivity of electrons and holes of the solid matrix, cm^2/s
eZ^+, eZ^-	electric charge of positive and negative ions, C
$E_-(x,t)$, $E_+(x,t)$	intensity of electric field in the solid matrix and in electrolyte, V/cm
E_{ch}, E_{dis}	charge and discharge energy, Wh
$E_{\mathrm{ch}}^{\mathrm{dpol}}$, $E_{\mathrm{dis}}^{\mathrm{dpol}}$	depolarization loss of energy during the charge and discharge, Wh
E_{ch}^{R}, E_{dis}^{R}	ohmic loss of energy during the charge and discharge, Wh
E_{Cadis}	residual energy after the discharge, Wh
E_{Cch}, E_{Cdis}	charge and discharge energy with no account of ohmic losses, Wh
E_{Cch}^{ap}, E_{dis}^{ap}	energy of the charged and discharged capacitor after a pause, Wh
$E_{\mathrm{Cch}}^{\mathrm{eff}}$	effective charge energy, Wh
$E_{\mathrm{ch}}^{\mathrm{Rpol}}$, $E_{\mathrm{dis}}^{\mathrm{Rpol}}$	loss of energy in polarization resistance, Wh
$G_-(x,t)$, $R_-(x,t)$	rate of spontaneous generation and recombination of charge in the solid matrix, $\mathrm{C}/(\mathrm{cm}^3\ \mathrm{s})$
$G_+(x,t)$, $R_+(x,t)$	rate of spontaneous generation and recombination of the electrolyte's ions, $\mathrm{C}/(\mathrm{cm}^3\ \mathrm{s})$
I_{ch}, I_{dis}	charge and discharge current, mA or A
J_0	surface density of current, $\mathrm{mA}/\mathrm{cm}^2$
$J_-(x,t)$, $J_+(x,t)$	density of current in the solid matrix and in electrolyte, $\mathrm{mA}/\mathrm{cm}^2$
$J_{VG_-}(x,t)$, $J_{VR_-}(x,t)$	volume density of current of spontaneous generation and recombination of charge of the solid matrix, $\mathrm{mA}/\mathrm{cm}^3$
$J_{VG_+}(x,t)$, $J_{VR_+}(x,t)$	volume density of current of spontaneous generation and recombination of the electrolyte's ions, $\mathrm{mA}/\mathrm{cm}^3$
n	integer
n_0, p_0	equilibrium concentrations of free electrons and holes of the solid matrix, cm^{-3}
n_0^+, n_0^-	equilibrium concentration of positive and negative ions of electrolyte in the pores of electrolyte, cm^{-3}
Q_{ch}, Q_{dis}	Coulombic capacity of charge and discharge, C or Ah
S	area of visible surface of electrodes, cm^2
t	time, s
Q_{Cadis}	residual Coulombic capacity after the discharge, Ah
R	ohmic resistance of the capacitor, Ω
t_{ch}, t_{dis}	time of charge and discharge, h or s
U	voltage of capacitor, V
U_C	emf of capacitor, V
U_{Cch}, U_{Cdis}	emf during charge and discharge, V
U_{Cch}^{ap}	emf of the charged capacitor after a pause, V
U_{Cdis}^{ap}	emf of discharged capacitor after a pause, V
$V(d,t)$	voltage of primary capacitor, V

Greek

α_-, α_+	effective conductivity of the solid matrix and electrolyte of the negative electrode, S/cm
δ_{Edpol}	depolarization loss of energy of charge–discharge cycle, %
δ_{ER}	ohmic loss of energy of charge–discharge cycle, %
δ_{ERpol}	polarization loss of energy of charge–discharge cycle, %
Δn, Δp	nonequilibrium concentration of free electrons and holes of the solid matrix, cm^{-3}
Δn^+, Δn^-	nonequilibrium concentration of positive and negative ions of electrolyte in the pores of electrolyte, cm^{-3}
ε	dielectric permittivity of medium
ε_0	dielectric constant ($\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm)
η_{E1}	energy efficiency of the first charge–discharge cycle, %
η_{E2}	energy efficiency of the stationary charge–discharge cycle, %
μ_+, μ_-	effective mobility of positive and negative ions of electrolyte, $\mathrm{cm}^2/(\mathrm{V\ s})$
μ_n, μ_p	effective mobility of electrons and holes of the solid matrix, $\mathrm{cm}^2/(\mathrm{V\ s})$
ν_τ	elementary volume of integration, cm^3
$\rho_-(x,t)$, $\rho_+(x,t)$	density of charge of free carriers in the solid matrix and in electrolyte which is in the pores of the negative electrode, C/cm^3
ρ_{int}	specific internal resistance, $\Omega\ \mathrm{cm}^2$
ρ_{sep}	specific resistance of separator, Ω cm
σ_-^{el}, σ_+^{el}	conductivity of electrolyte in the pores of the negative and positive electrodes with DEL, S/cm
σ_-^{m}, σ_+^{m}	conductivity of walls of the pores of the solid matrix of the negative and positive electrodes with DEL, S/cm
$\varphi^-(x,t)$	potential of the negative electrode, V
$\varphi_-(x,t)$, $\varphi_+(x,t)$	potential (in relation to pzc) of the solid matrix and electrolyte, V
φ_{0+}^-, $\varphi_{0\_}^-$	potential of negative electrode of the capacitor before the charge and before the discharge, V

References

1. *Science of Fullerenes and Carbon Nanotubes*, M. S. Dresselhaus, G. Dresselhaus, and P. C. Eclund, Editors, Academic Press, New York (1995).
2. T. L. Makarova, *Fiz. Tekh. Poluprovodn.*, **38**, 641 (2004).
3. B. E. Conway, *Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications*, Kluwer Academic Plenum Publishers, New York (1999).
4. B. Pillay and J. Newman, *J. Electrochem. Soc.*, **143**, 1806 (1996).
5. D. Dunn and J. Newman, *J. Electrochem. Soc.*, **147**, 820 (2000).
6. C. J. Farahmandi, in *Electrochemical Capacitors II*, F. M. Delnick, D. Ingersoll, X. Andrieu, and K. Naoi, Editors, PV 96-25, p. 167, The Electrochemical Society Proceedings Series, Pennigton, NJ (1996).
7. B. E. Conway and W. G. Pell, in *The 12th International Seminar on Doublelayer Capacitor and Similar Energy Storage Devices*, Dec 9–11, 2002, Deerfield Beach, FL (2002).
8. *Chemical Current Sources*, Moscow (2003).
9. S. Kazaryan, S. Razumov, G. Harisov, and S. Litvinenko, U.S. Pat. 6,842,331 B1(2005).
10. A. I. Belyakov, O. G. Dashko, V. A. Kazarov, S. A. Kazaryan, S. V. Litvinenko, I. I. Kutyanin, P. A. Schmatko, V. I. Vasechkin, and J. M. Volfkovich, Pat. PCT/RU97/00353 (1997).
11. A. Burke, T. Kershaw, and M. Miller, UC Davis, Report no. USD-ITS-RR-03-2, June 2003.
12. Yu. M. Volfkovich and P. A. Shmatko, in *Proceedings of the 8th International Seminar on Doublelayer Capacitor and Similar Energy Storage Devices*, Dec 7–9, 1998, Deerfield Beach, FL (1998).
13. A. Burke, in *The 10th International Seminar on Doublelayer Capacitor and Hybrid Energy Storage Devices*, Dec 8–10, 2003, Deerfield Beach, FL (2003).
14. E. R. Buiel, in *Advanced Capacitor World Summit*, Washington, DC, July 14–16, 2004.
15. S. Razumov, A. Klementov, S. Litvinenko, and A. Beliakov, U.S. Pat. 6,222,723 B1 (2001).
16. A. I. Masliy, N. P. Poddoubniy, and A. V. Korolyuk, *Electrochemistry (Tokyo, Jpn.)*, **37**, 261 (2001).
17. V. V. Popov, S. K. Gordeyev, A. V. Gerchinskaya, and A. M. Danishevskiy, *Solid State Phys.*, **44**, 758 (2002).
18. R. Kotz, M. Hahn, O. Barbieri, J.-C. Sauter, and R. Gallay, in *The 13th International Seminar on Doublelayer Capacitor and Hybrid Energy Storage Devices*, Dec 8–10, 2003, Deerfield Beach, FL (2003).
19. D. Dobosh, *Electrochemical constants*, Moscow (1980).
20. R. R. Nazmudtinov, *Electrochemistry (Tokyo, Jpn.)*, **38**, 131 (2002).
21. N. S. Koshlyakov, E. B. Gliner, and M. M. Smirnov, *Equations in Partial Derivatives of Mathematical Physics*, "The Higher School" Publishing House, Moscow (1970).