

On the hierarchy of the influences of porous and electronic structures of carbonaceous materials on parameters of molecular storage devices

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Abstract

The relation between porous structure, electronic properties of carbonaceous material and the capacitance of its interface with an electrolyte is discussed. It is shown that, in an electric double-layer, the contribution of pseudocapacitive charge accumulation is determined, mainly, by the position of Fermi level in the carbonaceous material and depends on thermodynamic parameters of ions in the electrolytic solution. The sizes of the pores in which the processes of capacitive and pseudocapacitive charge accumulation dominate are determined. Theoretical analysis of the processes taking place on the nanoporous carbon|electrolyte interface has made it possible to recognize the intercalative nature of pseudocapacity and to find the criterion of its manifestation in the form of the formation of a continuous series of stable valency phases.

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1. Introduction

Molecular energy storage devices (MESD) occupy an intermediate position between electrochemical accumulators and "electrostatic" capacitors, in conventional classification. Their specific power and specific capacitances exceed by several orders the formers and the latters, respectively [1,2] and in general case, they combine principles of action of both of them. It means that they can accumulate and store energy not only by means of capacitance (in electric double-layer of "blocking electrode-electrolyte" interface; usually called "supercapacitor charge") but also by reversible faradaic processes such as ion absorption or redox reactions which cause a pseudocapacitance different from that of electric double-layer (EDL) [3–5]. For the known kinds of activated carbon, nowadays there is no reason to neglect any component of capacitance. Besides, it is pseudocapacitance that most probably causes the discrepancy between experimentally obtained values of specific capacitance [6,7] and the theoretically calculated value for EDL which even beyond

the BDM (Bockris, Devanathan and Muller) [8] cannot exceed ~140–150 F/g, because maximal possible value of porous area is 3000 m²/g; for the known classes of carbon and electrolytic systems, at this value differential capacitance does not exceed 15–17 μF/cm² [9] due to the increase in Thomas–Fermi screening length, and electrochemical accessibility amounts to ~30% [10]. Unfortunately, nowadays not only the hierarchy of contribution of the aforesaid capacitance into the general capacitance but also different from the contribution of functional surface groups mechanisms of redox processes are not sufficiently elucidated; the criteria of their emergence connected with the porous structure of nanoporous carbon are not determined either. Just these issues are discussed in this paper.

2. Experimental investigation

Different kinds of activated carbon used in experiments were obtained by means of activational carbonization of initial raw materials of different nature: styrenebenzene copolymer (SBC), phenolic resin (PhR) and fruit stones (FS). Method of precisional porometry and small angle X-ray scattering method [11] were applied to investigate their porous structure, respectively, ASAP 2000 M porometer and DRON-3 diffractometer were used. The

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electrochemical measurements were carried out according to the three-electrode setup with chlorine–silver reference electrode. The surface area of the working electrode exposed to electrolyte was 0.5 cm^2 . Galvanostatic, potentiodynamic, farad–volt and impedance (within the frequency range 10^{-2} to 10^5 Hz) dependences have been determined with a help of equipped with FRA-2 and GPES programs “AUTOLAB” device manufactured by “ECO CHEMIE” firm (Netherlands). The values of the capacitance that were used to plot farad–volt dependences have been determined through impedance measurements with an accuracy 2–8% (Kramers–Kronig tests were in the range 10^{-6} to 10^{-5}) according to the formula $C = (j2\pi fZ'')^{-1}$ as mean values in the frequency range of 10^{-1} to 1 Hz. Kramers–Kronig test is fully described in article [12]. As a rule of thumb, value between 10^{-6} and 10^{-5} is reasonable. An ac amplitude of 5 mV was used.

All measurements were taken at room temperature. Potentials E are referred to the standard hydrogen electrode. Aqueous solutions of KOH (7.6 m), KBr (5.8 m), CsBr (3.16 m), KI (4 m) were used as electrolytes. These aqueous solutions were made sufficiently concentrated in order to ensure high capacitance of diffuse layer in electrolyte (Gouy–Chapman layer) $> 100 \mu\text{F}/\text{cm}^2$ as well as sufficient electric conductance.

3. Results and discussion

It is pertinent to all the aforesaid carbonaceous materials that their functional dependences of pore area distribution with respect to the diameter of pores are of optimal forms [13] as to the accumulation of capacitance charge; these curves have their maxima in the neighbourhood of the point $d = 20 \text{ Å}$; the behaviour of these curves is similar in the range of micro- and mesopores. However, they essentially differ as to the total surface area of the pores in which the formation of dense screened electric double-layer is problematic ($d \lesssim 4.4 \text{ Å}$) and also as to the total surface of electrolytic micro ($4.4 < d < 19 \text{ Å}$) and mesopores ($d > 19 \text{ Å}$) (Table 1). As it follows from this table, the carbonaceous materials investigated also differ in their electronic structure visualized by different positions of Fermi level measured according to experimental technique [14]. In the case of sharp expansion of spatial charge region in a solid, under positive polarization of the investigated material in 7.6 m solution of KOH, the dependence between the capacitance C_{sc} and the potential φ_{sc} of the spatial charge region can be represented by the known relation:

$$C_{\text{sc}}^{-2} = \frac{2L_D}{(\varepsilon_0 \varepsilon_{\text{sc}})^2 (|e\varphi_{\text{sc}}/kT| - 1)}, \quad (1)$$

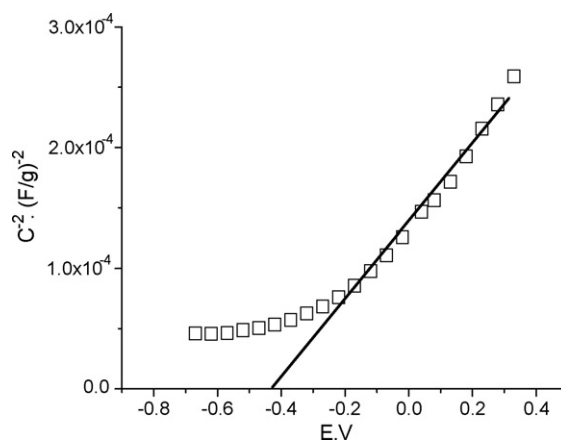


Fig. 1. Dependence C^{-2} – E for SBC in 7.6 m KOH.

here L_D is Debye width, ε_0 and ε_{sc} are dielectric constants. In this coordinate system, the experimental data take their positions in a straight line (Mott–Shotky lines), Fig. 1; and thus we can assume that the conditions $C_{\text{sc}} \ll C$ (Helmholtz’s layer) and $\varphi_{\text{sc}} \gg E$ hold true. Then, the intersection of a Mott–Shotky line with x -axis at $C^{-2} = 0$ gives us the value of electrochemical potential (flat zone potential). We assume that for the investigated carbonaceous materials (like for metals) the value of electrochemical potential μ_C can be chosen equal to E_F – energy of an electron on Fermi surface, the reference being from the bottom of the conductivity zone [14]. Typical impedance as well as Bode dependences and capacitive behaviours for the electric double-layer charge, from which the capacitance for farad–volt dependences were determined, are shown in Figs. 2–4 [15]. The measured data of farad–volt characteristics (FVC) in different (KOH, KBr, CsBr) electrolytic solutions (see Fig. 5a) show that, for all the materials investigated, these FVC are essentially asymmetric, when capacitance charge is accumulating in electric double-layer. Low values of specific capacitance in the positive range of potentials are pertinent to practically all known materials, at least, for aqueous solutions of potassium hydroxide [16]. It is caused, mainly, by shunting the capacitance of Helmholtz’s layer because of essential expansion of space charge layer in a solid when the latter is positively polarized [17]. This shunting unambiguously indicate that it is necessary for practical purposes to symmetrize FVC, first of all, at the expense of ensuring high density of states in the vicinity of Fermi level of activated carbonaceous material [18–21]. The position of Fermi level plays an exclusively important role for the processes which take place at the electrode|electrolyte interface, especially in the positive range of potentials for a certain kind of anions. And really, as it

Table 1
Porometric and thermodynamic characteristics of investigated carbonaceous materials

Material	Area of the pores, $d \lesssim 4.4 \text{ Å}$ (m^2/g)	Area of the pores, $4.4 < d < 19 \text{ Å}$ (m^2/g)	Area of the pores, $d > 19 \text{ Å}$ (m^2/g)	Value of electrochemical potential, μ_F (eV)	Value of stationary potential in 4 m KI, E_{st} (V)
SBC	576	332	120	–4.08	0.24
PhR	316	480	174	–4.1	0.3
FS	448	498	181	–4.3	0.32

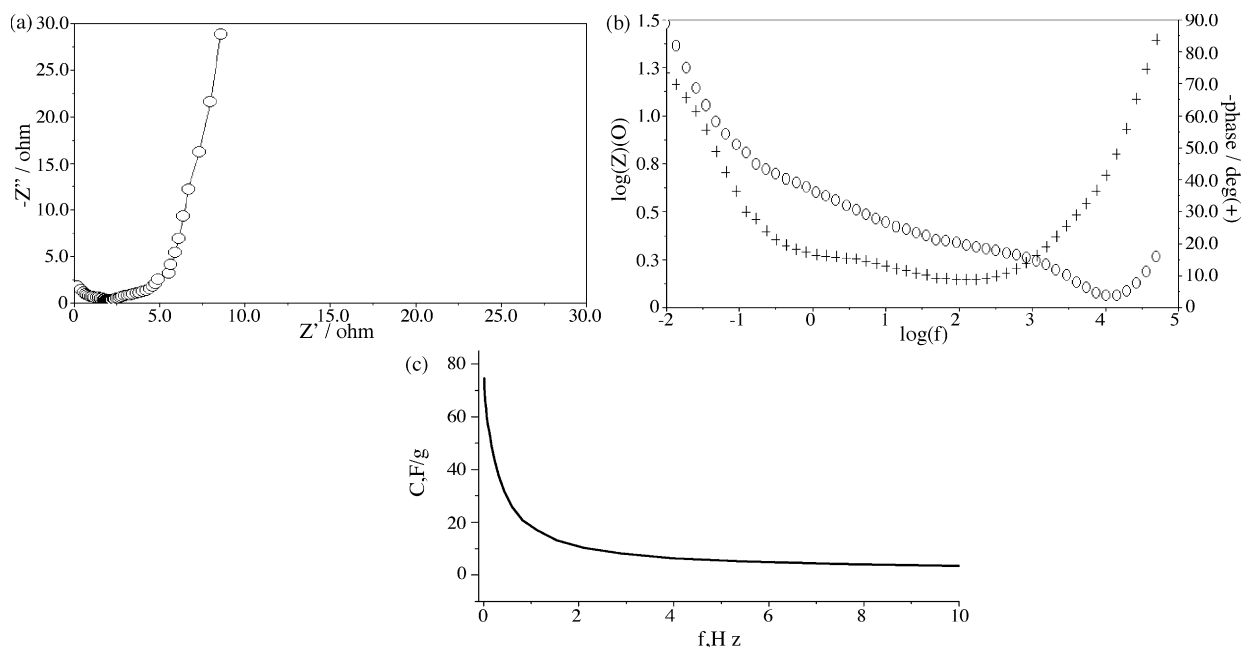


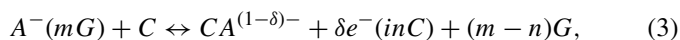
Fig. 2. Typical impedance as well as Bode dependences and capacitive behaviour for SBC in 7.6 m KOH at $E_{st} = 0.05$ V.

follows from Table 1 and Table 2, the latter contains the known data concerning the energy of ion hydration [22–26] and the calculated values of the chemical potential and the potential of getting them into loose state in solutions. The sharp rise of the positive part of FVC curve takes place only for iodine anions, whose values of chemical potentials and energies of hydration are less among the electrolyte systems investigated; in anode region, the degree of increase in capacitance values being determined just by the position of Fermi level in activated carbon, it is easily seen in Fig. 5b. From the values of Fermi energies μ_F obtained for the investigated materials and from the chemical potentials μ_{el} of the ions in aqueous solution given in eV (see Tables 1 and 2) with references to the energy of an electron in vacuum near the surface of the material, we can draw charts of energies. According to them, for example, for materials in 4 m aqueous solution of KI, the galvanic-potential φ_{cr} of C|electrolyte interface:

$$\varphi = \frac{\mu_{I^-} - \mu_C}{e} \quad (2)$$

(e is elementary charge). This can serve as an energetical criterion for pseudocapacitive charge accumulation with iodine ions

according to the scheme [3]:



here m and n are the numbers of hydration ion in solution and in sorptive state, respectively; C is the positively charged carbonaceous material. Calculated values of φ_{cr} for SBC, PhR and FS are equal to 0.2, 0.22, 0.41 V, respectively, and experimentally measured ones are $E_{st} = 0.24, 0.3, 0.32$ V, respectively. Comparing these data, we can draw the conclusion that pseudocapacitive charge of SBC, PhR takes place as early as during the initial potential of the electrode, and that the polarization of the electrode towards the potential of free state iodine formation is equal to 0.24 and 0.18 V, respectively.

These regularities as well as small polarization during the charging with iodine ions ($0.48 - 0.41 = 0.07$ V) make it impossible for FS material to take great values of pseudocapacitance.

In the negative range of potentials, charge accumulation is, mainly, without faradaic process in EDL. In this case, the increase of charge capacity when changing from K^+ to Cs^+ fairly correlates with the decrease of hydration energy of the ion in this electrochemical series and with the greatest polarization of Cs^+ (-0.85 V).

Table 2
Thermodynamic parameters of ions in different electrolyte solutions

Ion (solution)	Potential of ion separation, with reference to standard hydrogen electrode V (eV)	Chemical potential of ion in solution, μ_{el} (eV)	Free energy of ion hydration, according to Born (eV)
K^+ (7.6 m KOH)	−2.84	−1.55	−5.35
Cs^+ (3.16 m CsBr)	−2.913	−1.39	−4.21
Br^- (3.16 m CsBr)	1.065	−3.33	−3.65
I^- (4 m KI)	0.511 (−5.011)	−3.89	−3.3
OH^- (7.6 m KOH)	0.32	−2.85	−4.9 to −5.0 [24,25]

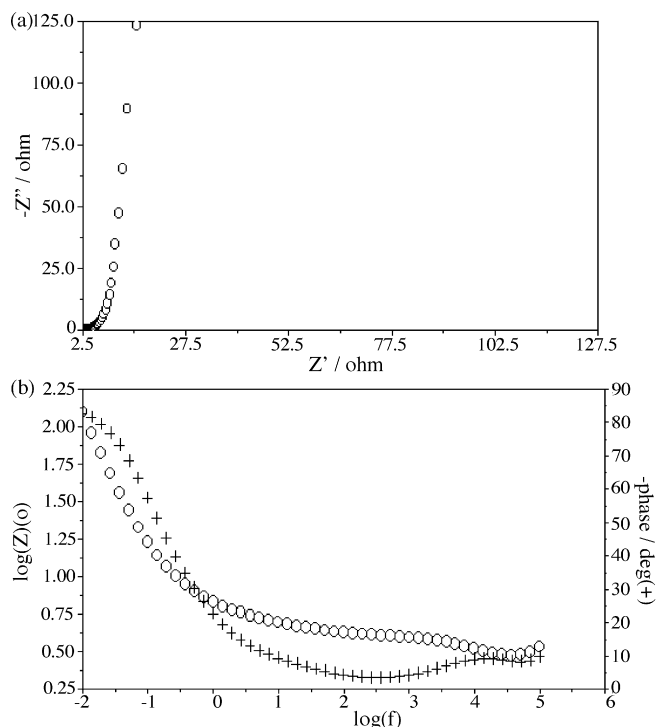


Fig. 3. Typical impedance dependence as well as Bode and capacitive dependence for SBC material in 4 m KI at $E = 0.24$ V.

It is noteworthy, that the values of specific capacitance for cesium cations are determined not only by promoted by low value of hydration energy capacitive contribution but by faradaic contribution as well; the nature of the latter being, in all probability, bound up with intercalation processes. Also as a confirmation of such mechanism of pseudocapacity, first of all in the positive

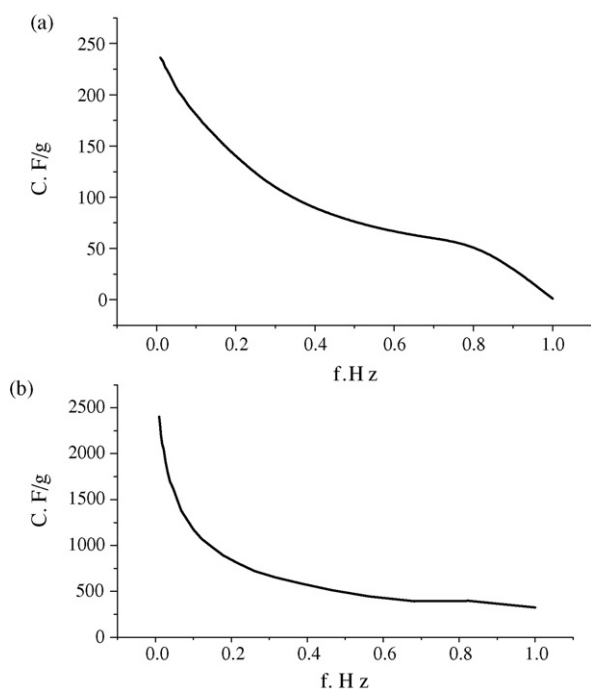


Fig. 4. Capacitive dependences for SBC material in 4 m KI at $E = 0.28$ V (a) and $E = 0.43$ V (b).

range of potentials, we can consider the data of potentiodynamic investigation in 4 m solution of KI (Fig. 6a) under high contribution of faradaic current into the charge-discharge process for example cycle 4 (1.85–1.44 A/g); this current being determined according to the technique and (for comparison) in 7.6 m KOH, for which $i_f = 0.21$ A/g (Fig. 6b) [27].

To ascertain the peculiarities of intercalative pseudocapacitance and the criteria of its emergence, consider the following quantummechanic model.

The total (specific) capacitance of an electrode can be represented as follows:

$$C = C_{EDL} + C_{int}, \quad (4)$$

where C_{EDL} is the capacitance of the double electric layer, C_{int} is the pseudocapacitance of intercalation process into nanopores of carbonaceous materials. In general case (taking into account ion association effects) this pseudocapacitance can be written as follows:

$$C_{int} = \frac{ed(\langle m_+ \rangle - \langle m_- \rangle)\xi}{d\varphi}, \quad (5)$$

where $\langle m_+ \rangle$ and $\langle m_- \rangle$ are mean numbers of adsorbed guest species in a pore, ξ is the density of pores, e is electron charge. It is obvious that $\langle m_+ \rangle$ and $\langle m_- \rangle$ are functions of electric potential φ (the potential being applied to an electrode) and of adsorption energy of ions in the material of the electrode— U_a :

$$\langle m_+ \rangle = f(\varphi, U_a). \quad (6)$$

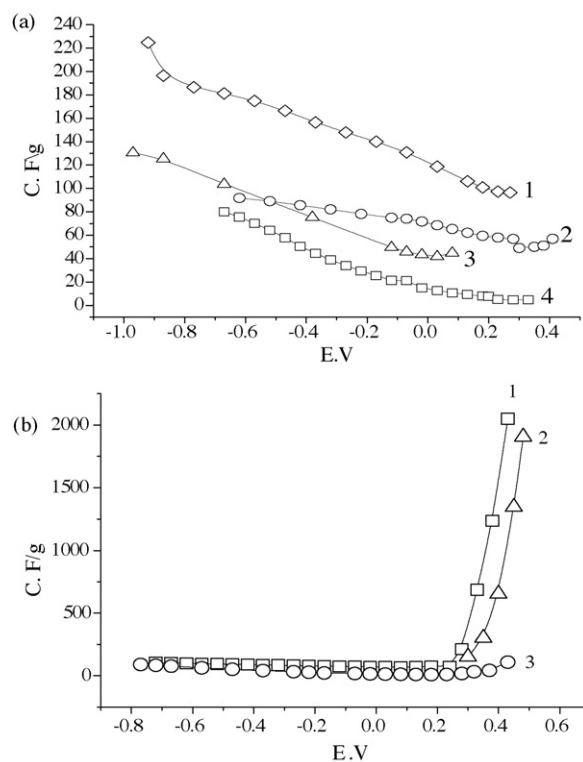


Fig. 5. FVC of electrode|electrolyte interface for (a) SBC in: 3.16 m CsBr (1), 5.8 m KBr (2), 7.6 m KOH (3), FS in: 7.6 m KOH (4); (b) SBC (1), PhR (2), FS (3) in: 4 m KI.

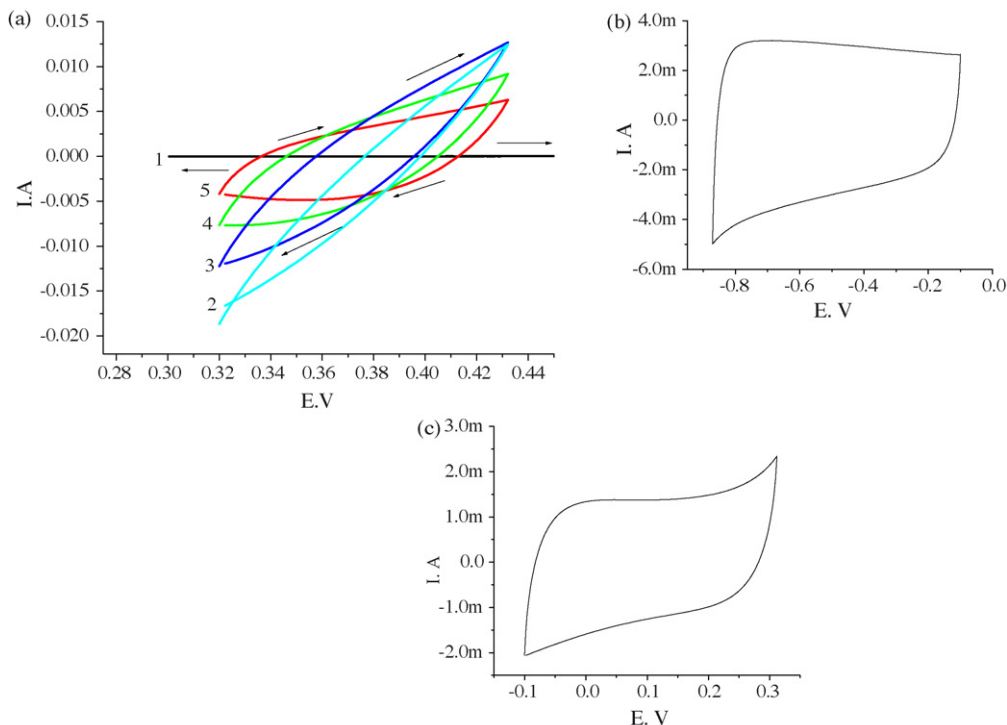


Fig. 6. Potentiodynamic curves SBC: (a) in 4 m KI (1: Ni background $v_p = 0.01$ V/s, 2: $v_p = 0.005$ V/s, 3: $v_p = 0.002$ V/s, 4: $v_p = 0.001$ V/s) in the positive range of potentials which prevent I_2 release and (b, c) 7.6 m KOH ($v_p = 0.01$ V/s).

It is clear that the introduction of an ion from the electrolyte into the material (i.e. disblockation of electrode) is possible only when the adsorption energy in the solid does not exceed the value of its chemical potential in the electrolyte μ_{el} :

$$U_a \leq \mu_{el}. \quad (7)$$

The latter indicates that a certain critical potential φ_{cr} (see 2) can exist at which the blocked electrode becomes faradaic relatively to a certain kind of ions whose value is μ_{el} in the electrolyte investigated. The inverse relation corresponds to the condition of blocked electrode.

Statistic thermodynamics of ion intercalation into carbon material pores can be qualitatively “approximately” described by means of “lattice gas” model excluding two ions “+” and “-” in the same intercalation pore (node). For this model, the Hamiltonian function is the following:

$$H = \sum_f [U_{+m_f}(1 - m_{-f}) + U_{-m_f}(1 - m_{+f})]. \quad (8)$$

It is easy to see that, in the approximation of non-interacting guest atom, the expressions for the mean values of occupation numbers are the following:

$$\langle m_+ \rangle = \frac{\exp[(\mu_+ - U_{a+})/kT]}{\{2 + \exp[(\mu_+ - U_{a+})/kT] + \exp[(\mu_+ - U_{a-})/kT]\}}. \quad (9)$$

The expression for $\langle m_- \rangle$ is analogical.

In Relation (9), the only unknowns are adsorption energies U_{a+} and U_{a-} . To determine U_a , the simplified “jellium” model [28] is used; in this model, the Hamiltonian of the system may

be written in the form:

$$H = \sum_{\sigma} E_a \hat{n}_{a\sigma} + \sum_{\sigma,k} E_{k\sigma} \hat{n}_{k\sigma} + U n_{a\downarrow} n_{a\uparrow} + V \sum_{k,a} (a_{\sigma} c_{k\sigma} + h e) + W(1 - \sum_{\sigma} \hat{n}_{a\sigma}) \sum_{\sigma,k,p} (c_{k\sigma}^+ c_{p\sigma} - \langle c_{k\sigma}^+ c_{p\sigma} \rangle_0), \quad (10)$$

where $\hat{n}_{a\sigma} = a_{a\sigma}^+ a_{a\sigma}$, $\hat{n}_{k\sigma} = c_{k\sigma}^+ c_{k\sigma}$, $a_{a\sigma}^+$, $a_{a\sigma}$ are operators of the emergence and annihilation of localized state of guest atom on ions, $c_{k\sigma}^+$, $c_{k\sigma}$ are operators of the emergence and annihilation of free electrons in carbon, E_a is adsorption energy of ions in the material of the electrode at E_{st} .

In this Hamiltonian, the first term describes the energy of electrons on positive implanted ions, the second term describes the energy of free non-disturbed by intercalation electrons in the material, the third term describes the energy of (exchanging) interaction of electrons on guest atoms, the fourth term describes the hybridization energy of the s -level of the guest atom, the fifth term describes the electrostatic interaction between the implanted and disturbed charges in the electron subsystems.

The Hamiltonian (10) can be with good approximation applied to the positive and negative ions.

From the mathematical point of view, the last term of Hamiltonian (10) is the biggest troublemaker. To avoid this trouble, we use ideas of continuum model of ion solvation in polar liquids. Such models (Thomassi–Scroco) fairly describe the processes of ion solvation in polar liquids.

The model is constructed so that the medium into which the ion penetrates is described by continuum. In the location

of an ion, a pole is made in which the ion is located. With its electric field, the ion induces a so called reactive field in its neighbourhood; the reactive field influences the ion itself.

To determine this field, Poisson equation should be applied:

$$\nabla^2 \varphi = -4\pi\rho = -\lambda^{-1}v(r). \quad (11)$$

The solution of (11) is expression (12)

$$W_{\text{cav}} = \left(\frac{q^2}{r}\right) [e^{-r/\lambda} - 1], \quad (12)$$

where q is the ion charge, r is the radius of the pore, λ is the length of Thomas–Fermi screening.

Generally speaking, the ion charge q can be altered. In our case it is of the form:

$$q = e \left(1 - \sum_{\sigma} \langle n_{a\sigma} \rangle\right),$$

where

$$\langle n_{a\sigma} \rangle = \langle \Psi | \hat{n}_{a\sigma} | \Psi \rangle.$$

By means of varying W_{cav} , we obtain the cavitation energy operator:

$$\begin{aligned} \delta_{\Psi^*} W_{\text{cav}} &= \frac{\partial W_{\text{cav}}}{\partial q} \delta_{\Psi^*} q, \\ \delta W_{\text{cav}} &= \delta \left\{ \left(\frac{q^2}{r}\right) [e^{-r/\lambda} - 1] \right\} \\ &= - \left(\frac{2e^2}{r}\right) \left(1 - \sum_{\sigma} \langle n_{a\sigma} \rangle\right) [e^{-r/\lambda} - 1] \sum_{\sigma} \hat{n}_{a\sigma}. \end{aligned} \quad (13)$$

In this way, having reduced this problem to a one-electron problem we transform (10) into the approximative Hamiltonian:

$$\begin{aligned} H_{\sim} &= \sum_{\sigma} \left(E_a - \left(\frac{2}{r}\right) \left[1 - \sum_{\sigma} \langle n_{a\sigma} \rangle\right] [e^{-r/\lambda} - 1] \right) \hat{n}_{a\sigma} \\ &+ \sum_{k,\sigma} E_{k\sigma} \hat{n}_{k\sigma} + U n_{a\downarrow} n_{a\uparrow} + V \sum_{k,\sigma} (a_{\sigma} c_{k\sigma} + h e), \end{aligned} \quad (14)$$

from which, on the basis of Anderson's approach [29] we have,

$$\langle n_{a\uparrow} \rangle = \left(\frac{1}{\pi}\right) \arctg \left[\left(\frac{1}{\Delta_a}\right) (E_a + \lambda + U \langle n_{a\downarrow} \rangle - e\varphi - E_F) \right]. \quad (15)$$

Here Δ_a is the width of hybridized level, E_F is the situation of Fermi level.

The mean number of electrons per one positive ion $\langle n_a \rangle$ reflects the physical nature of the dissolution of a “guest” component; i.e. either solution through the formation of stable valency phases with the monotoneous variable $\langle n_a \rangle = f(\varphi)$ or through jump-like change of this function; the latter corresponds to phase transformation of the 1st kind in stable valency compounds. In the first case, we have pseudocapacitance and, in the second case we have a two-phase system with an infinite discontinuity in x -interval of concentration. Using Eq. (15) and taking the

derivative of the chemical potential μ_{el} with respect to $\langle n_a \rangle$, we find the criteria of the satisfaction of the first and the second conditions: $W_{\text{cav}} = (q^2/r)[e^{-r/\lambda} - 1] < \pi \Delta_a$ corresponds to pseudocapacitance, and $W_{\text{cav}} = (q^2/r)[e^{-r/\lambda} - 1] > \pi \Delta_a$ corresponds to two-phase system. For Thomas–Fermi screening radius these criteria can be written, respectively,

$$\lambda > r \left\{ \ln \left[\left(\frac{\pi}{2}\right) \Delta_a \left(\frac{r}{q^2}\right) - 1 \right] \right\}^{-1}, \quad (16)$$

$$\lambda < r \left\{ \ln \left[\left(\frac{\pi}{2}\right) \Delta_a \left(\frac{R}{q^2}\right) - 1 \right] \right\}^{-1}. \quad (17)$$

Now, supposing that the introduced electron is always in paramagnetic state, the expression for its adsorption energy in a solid can be found:

$$\begin{aligned} U_a &= \int_{-\infty}^{E_F + e\varphi} \omega N(\omega) d\omega - \int_{-\infty}^{E_F + e\varphi} \omega N_0(\omega) d\omega \\ &= E_a \langle n_a \rangle + e\varphi - e\varphi \langle n_a \rangle - E_F \langle n_a \rangle, \end{aligned}$$

where $N_0(\omega)$ is the density of the states of the unperturbed electronic subsystem (free electrons).

Thus,

$$U_a = \langle n_a \rangle (E_a - e\varphi - E_F) + e\varphi. \quad (18)$$

Having found U_a , pseudocapacity can be calculated on the basis of (5) and (9).

4. Conclusions

The measurement data of farad–volt dependences in different electrolytes (KOH, KBr, CsBr, KI) show their sharp asymmetry in cathode and anode regions because of the formation of great pseudocapacitance up to 2000 F/g in anode region (KI); they also show very small capacitive charge accumulation (no more than 5.4 F/g) in anode region (KOH). In the former case, this asymmetry is, mainly, connected with shunting of Helmholtz's layer capacitance by great faradaic capacitance (pseudocapacitance); in the latter case, this is connected with sharp expansion of spatial charge region in a solid.

The formation of great capacitance (225 F/g) for the Cs^+ ion in negative region and supergreat pseudocapacitance (2000 F/g) for the I^- ion is caused by the ability of these ions to intercalate nanopores of activated carbon ($d \lesssim 4.4 \text{ \AA}$) that requires minimal value of chemical potential and hydration energy of the ion in a solution.

The influence of electronic structure on the charge accumulation in EDL is discussed in this paper; mathematical relations for calculating adsorption energy an ion in intercalative pores of activated carbon are deduced; mathematical relations which can serve as criteria for the formation of pseudocapacitance are obtained.

References

- [1] A.K. Shukla, S. Sampath, K. Vijayamohan, Curr. Sci. 79 (2000) 1656.
- [2] R. Kötz, M. Carlen, Electrochim. Acta 45 (2000) 2483.

- [3] B.E. Conway, *Electrochemical Supercapacitors*, Plenum Publishing, New York, 1999.
- [4] Yu.M. Volfkovich, T.M. Serdjuk, *Electrochimica Acta* 38 (2002) 1043.
- [5] B.E. Conway, H. Andreas, W.G. Pell, *Proceedings of the 14th International Seminar on Double Layer Capacitor and Hybrid Energy Storage Devices*, Deerfield Beach, USA, 2004, p. 155.
- [6] S. Dietz, V. Nquen, *Proceedings of the 10th International Seminar on Double Layer Capacitor and Similar Energy Storage Devices*, Deerfield Beach, USA, 2000.
- [7] H. Shi, *Electrochim. Acta* 41 (1996) 1633.
- [8] J.O'M. Bockris, M.A. Devanathan, K. Muller, *Proc. R. Soc. A* 274 (1963) 55.
- [9] G. Gryglewicz, J. Machnikowski, E. Lorenc-Grabowska, G. Lota, E. Frackowiak, *Electrochim. Acta* 50 (2005) 1197.
- [10] A.D. Little, *Proceedings of the 4th International Seminar on Double Layer Capacitor and Similar Energy Storage Devices*, Deerfield Beach, USA, 1994.
- [11] R.N. Kyut, E.A. Smorgonskaya, S.K. Gordeev, A.B. Grechinskaya, A.M. Danishevskiy, *Fizika tverdogo tela* 41 (1999) 1484.
- [12] B.A. Boukamp, *J. Electrochem. Soc.* 142 (1995) 1885.
- [13] M. Endo, T. Takeda, Y.J. Kim, K. Koshiba, K. Ishii, *Carbon Sci.* 1 (2001) 117.
- [14] Yu. Ya. Gurevich, Ju.B. Pleskov, *Photoelectrochemistry of Semiconductors*, Nauka, Moskva, 1983.
- [15] J.R. Scully, D.C. Silverman, M.W. Kending, *Electrochem. Impedance: Anal. Interpret.*, STP 1188 ASTM, ISBN 0-8031-1861-9.
- [16] A. Beliakov, A. Brintsev, N. Khodyrevskaya, *Proceedings of the 14th International Seminar on Double Layer Capacitor and Hybrid Energy Storage Devices*, Deerfield Beach, USA, 2004, p. p.84.
- [17] M. Hahn, M. Baertschi, O. Barbieri, J.-C. Sauter, R. Kotz, R. Gally, *Electrochem. Solid St. A* 33 (2004) 7.
- [18] J.P. Randin, E. Yeager, *J. Electrochem. Soc.* 118 (1971) 711.
- [19] J.P. Randin, E. Yeager, *J. Electroanal. Chem.* 36 (1972) 257.
- [20] H. Gerischer, *J. Phys. Chem.* 89 (1985) 4249.
- [21] H. Gerischer, R. McIntyer, D. Scherson, W. Storck, *J. Phys. Chem.* 91 (1987) 1930.
- [22] A.M. Suhotin, *The Directory in Electrochemistry*, Himiya, Leningrad, 1981.
- [23] K.P. Mischenko, G.M. Poltoratsiy, *Thermodynamics and Structure of Water and Not Water Solutions of Electrolytes*, Himiya, Leningrad, 1976.
- [24] G.B. Naumov, B.N. Rygenko, N.L. Hodakovskiy, *The Directory of Thermodynamic Sizes*, Atomizdat, Moskva, 1971.
- [25] J.V. Coe, *Chem. Phys. Lett.* 229 (1994) 161.
- [26] M.D. Tissandier, K.A. Cowen, W.Y. Feng, *J. Phys. Chem. A* 102 (1998) 7787.
- [27] Weng To-Chi, Teng Hsiusheng, *J. Electrochem. Society*, 148 (2001) A368.
- [28] N.D. Lang, W. Kohn, *Phys. Rev. B* 1 (1970) 4555.
- [29] P.W. Anderson, *Phys. Rev. Lett.* 34 (1975) 953.