

# INTERCALATION PSEUDO-CAPACITANCE IN CARBON SYSTEMS OF ENERGY STORAGE

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**Abstract.** The contribution of intercalative pseudo-capacitance of K<sup>+</sup> and Cs<sup>+</sup> ions to the total capacitance of activated carbons' aqueous solutions of KOH (7.6m) and CsBr (3.16m) electrolyte interface has been studied. It is shown on the basis of experimental and calculated porometric, thermodynamic parameters, and capacitive dependences that the measured values of specific capacity (160–260 F/g) exceeding the characteristic value of 150 F/g (for the capacitance of a double electric layer) are due to intercalative pseudo-capacitance. A computer simulation of impedance data for an equivalent electric circuit of a double electric layer and using the Stern model allowed us to determine the increase of pseudo-capacitance during K<sup>+</sup> ions' cathode intercalation process in activated carbon from the initial potential to the maximum charge, i.e. from C=490 F/g to C=996 F/g.

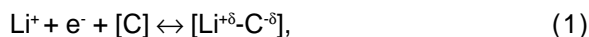
## 1. INTRODUCTION

Activated carbons (AC) of large specific surface,  $S$ , exceeding 1000 m<sup>2</sup>/g, are mostly studied with respect to their practical use as storage electrodes in supercapacitors, due to their capacity to store large electric charge in their porous structure at voltage of not less than 1.0 V [1-4]. The value of charge that can be accumulated by an AC surface in an absorption process has been calculated theoretically and found to equal 25 μF/cm<sup>2</sup> [1-4]. Consequently, the maximum capacitance of a material whose surface area equals  $S=1000$  m<sup>2</sup>/g can reach 250 F/g. However, due to a significant contribution of narrow pores for which the Thomas-Fermi screening length is commensurable with their radius, the obtained specific capacitance actually

does not exceed 150-160 F/g [5,6]. Such pores can be considered as "guest" positions for intercalated components [7,8]. We propose that AC pores for which the Thomas-Fermi screening length is commensurable with radius be referred to as intercalated pores. Certainly, occupation of these pores by ions from the electrolyte solution occurs according to the intercalation mechanism, which is Faradaic in nature and is associated with capacitive charge showing a linear dependence of voltage on the charge transferred through the interface. Such energy storage may be referred to as pseudo-capacitive. The intercalation of Li ions from non-aqueous aprotic electrolytes in graphite and graphitized porous carbon inter-layers is discussed in [9,10]. This process can be described by the following equation:

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where  $\delta$  is the Li charge [11].

There have been no studies published so far of the ions' intercalation process into AC, especially from aqueous solutions. Thus, the present paper is the first study of intercalation's pseudo-capacitive contribution into the total capacity of interface between AC and an aqueous electrolyte. The double electric layer (DL) is considered in the framework of the Stern mode, according to which the total capacitance of DL,  $C_{\text{DL}}$ , is as follows:

$$1/C_{\text{DL}} = 1/C_{\text{G-Ch}} + 1/C_{\text{H}} + 1/C_{\text{sc}}, \quad (2)$$

where  $C_{\text{G-Ch}}$  is the capacitance of the Gouy-Chapman diffusive layer,  $C_{\text{H}}$  – the capacity of the Helmholtz layer and  $C_{\text{sc}}$  – the capacitance of the bulk charge.

## 2. EXPERIMENTAL

Activated carbons used for our experimental studies were produced by carbonization of the styrene-benzene copolymer (SBC) and fruit stones (FS1, FS2). FS2 was obtained by means chemical treatment of FS1 in concentrated HCl, HF and  $\text{HNO}_3$  acids at elevated temperatures. The porous structure's characteristic was studied with the precessional porometry and small angle X-ray scattering methods (an ASAP 2000 M porometer and a DRON-3 diffractometer). The electrochemical measurements were carried out with a three-electrode setup, using a silver-silver chloride Ag/AgCl reference electrode. The  $5 \cdot 10^{-3}$ - $10^4$  Hz impedance and potentiodynamic dependences were determined with an AUTOLAB measuring complex (ECO CHEMIE, Netherlands) and the FRA-2 and GPES programs. A computer simulation of the processes enabled us to create the corresponding equivalent electric circuits (EEC) with the help of Zview-2 programs. The capacitances necessary to

obtain the capacitance–frequency dependence were obtained from impedance measurements (with accuracy 4-9%) according the  $C=(2\pi fZ'')^{-1}$  formula as an average value within the  $5 \cdot 10^{-3}$ - $10^4$  Hz frequency region. All measurements were carried out at room temperature. KOH (7.6m) and CsBr (3.16m) aqueous solutions were used as electrolytes. Potentials,  $E$ , refer to the standard hydrogen electrode. The energetic levels in eV units are represented with respect to the near-surface electron energy in vacuum.

## 3. RESULTS AND DISCUSSION

The data on precision porometry obtained for the SBC material (see Table 1) show that, contrary to FS, most of the surface has pores about 4.8 Å in diameter. Considering that these pores occupy most of the porous structure volume (see Table 2), it may be supposed that in order to obtain capacitances in excess of ~150 F/g the pores with high energy from the region near 4.8 Å (i.e. intercalation pores) should be active in the charge storage process. This follows from analysis of capacitance dependences for the studied materials at their cathode polarization (see Figs. 1 and 2). Taking into account the different porous and electron (Fermi-level position) structures and thermodynamic characteristics (the initial electrode potential,  $\varphi_{\text{st}}$ , of a non-polarized electrode in an electrolyte) of the investigated materials and the thermodynamic constants of the electrolytes used (see Tables 1, 2, and 3), different capacitive dependences should be expected for the corresponding systems. The potentials of dedication for one kind of charge ions (see Table 3) were calculated by means of a known nernstian relation [13]:]

$$E = E_0 + (RT/nF) \ln (a_o/a_r), \quad (3)$$

where  $a_o$  and  $a_r$  were the oxidation and reduction activities of potential-dependent components.

**Table 1.** Porometric and thermodynamic characteristics of the investigated carbons.

Material	Area of pores ( $d \leq 4.4$ Å), $\text{m}^2/\text{g}$	Area of pores ( $4.4 < d < 19$ Å), $\text{m}^2/\text{g}$	Area of pores ( $d > 19$ Å), $\text{m}^2/\text{g}$	Electro-chemical potential, eV	Initial potential in 7.6m KOH (3.2m CsBr), $\varphi_{\text{st}}$ , (V)
SBC	576	332	120	-4.08	0.05 (0.23)
FS1	448	498	181	-4.3	0.2
FS2	-	-	-	-	-0.28

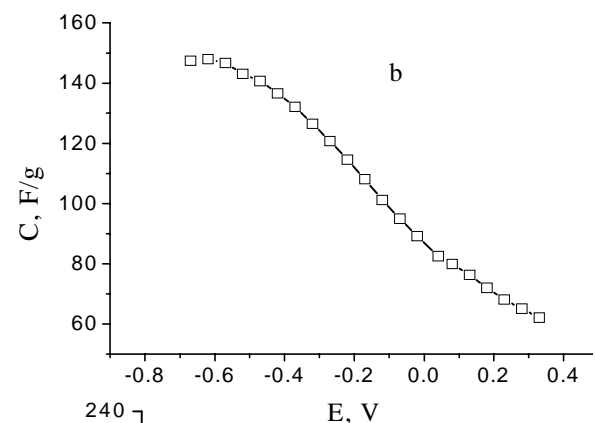
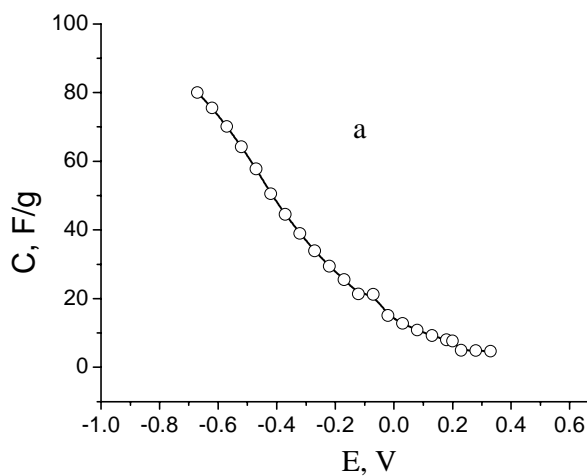
**Table 2.** Porometric data for SBC.

Maxima positions in function of pores' diameter distribution, Å	Pore volume, cm <sup>3</sup> /g
4.8	3
7	0.52
11	0.017
15	0.66

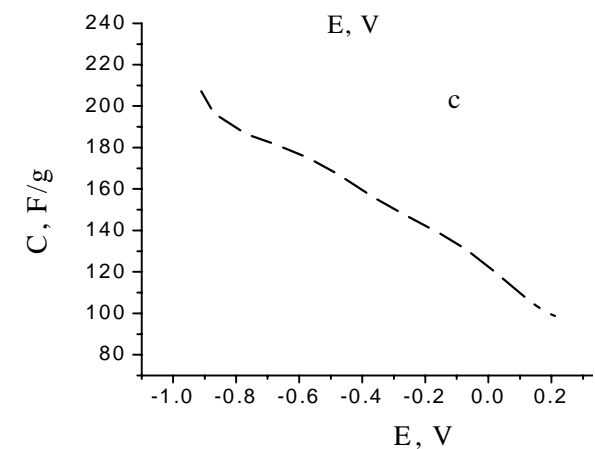
The initial electrode potential (see Table 1) was determined experimentally, while the chemical potential was determined according to the following relation [14]:

$$\mu_s = \mu_s^{\text{stand}} + RT \ln a_s \quad (4)$$

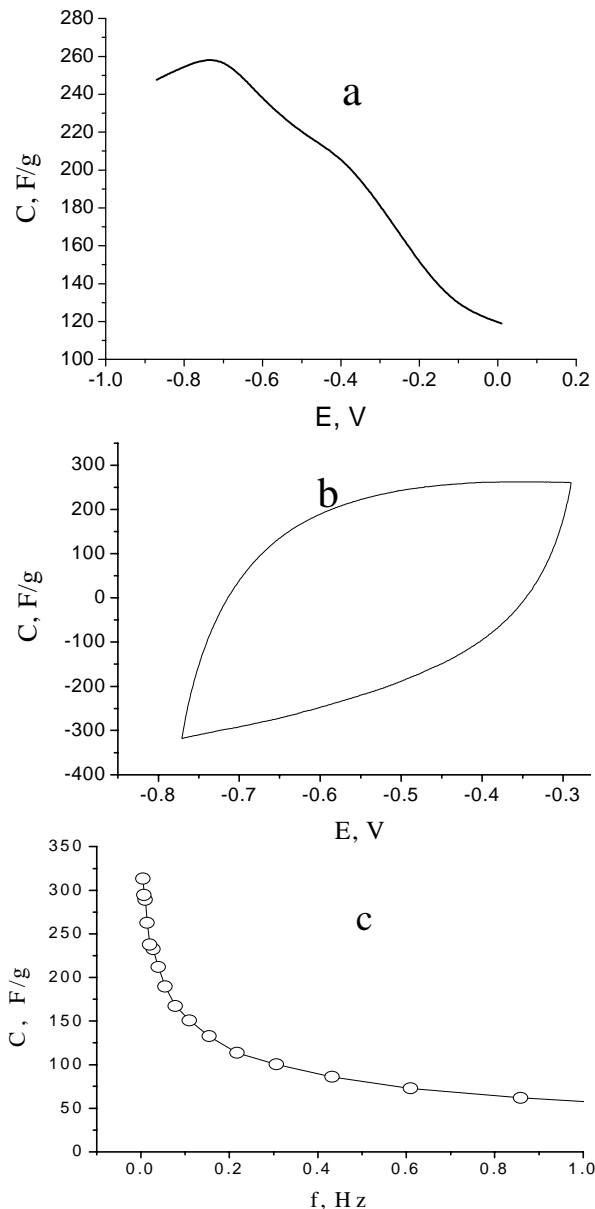
The changes in hydration free energies of the Born approach were taken from [15]. The Fermi-level position (Table 1) was determined using known experimental methods [16] and the following formula:



**Fig. 1.** Capacitive dependences of (a) FS1 and (b) SBC electrodes in 7.6m KOH and (c) an SBC electrode in 3.16m CsBr solutions.

**Table 3.** Thermodynamic parameters of ions in different electrolyte solutions.

Ion (solution)	Potential of ion separation (relative to standard hydrogen electrode), V	Chemical potential of ions in the solution, eV	Ion hydration energy, eV
K <sup>+</sup> (7.6m KOH)	-2.84	-1.55	-5.35
Cs <sup>+</sup> (3.16m CsBr)	-2.913	-1.39	-4.21
Br <sup>-</sup> (3.16m CsBr)	1.065	-3.33	-3.65
OH <sup>-</sup> (7.6m KOH)	0.32	-2.85	-5.29



**Fig. 2.** Capacitive dependences of electrode potential for FS2 measured under (a) potentiostatic conditions and (b) potentiodynamic conditions with sweep rate of  $v=10^{-2}$  V/s, where the capacities were calculated according formula  $C=I/v$  ( $I$  - current) and (c) the frequency dependence in the 7.6m KOH solution.

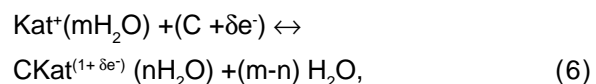
$$C_{sc}^{-2} = (|e \phi_{sc}/kT| - 1) \times 2L_D / (\epsilon_0 \epsilon_{sc})^2, \quad (5)$$

where  $L_D$  was the Debye length,  $\epsilon_0$  and  $\epsilon_{sc}$  – the electric constant and dielectric permeability for the region of volume charge, respectively. The obtained results are correct for the region of anode polar-

ization of the FS1 (0.2 – 0.3 V) and SBC (0.05 – 0.3 V) electrodes in 7.6m KOH solution (Figs. 1a and b). Within these regions the capacitance increase is not observed. Such potential regions attributed to semiconducting properties of AC surface due to sharp increasing  $L_D$  – region in electrode's volume charge, what was noted for instance in [17].

Nayquist's diagrams, as dependences of impedance' imaginary part ( $-Z''$ ) on its real part ( $Z'$ ) and Bode dependences (impedance and phase shift's dependence on frequency), have shown a typical profile for double electric layer charge. The dependences for FS2 are shown in Figs. 3a and 3b as examples.

Comparing the capacitive dependences of the SBC and FS1 electrodes in the 7.6m KOH solution (Figs. 1a and 1b), the former yields significantly greater specific capacity (80 F/g for FS1, 150 F/g for SBC) at a cathode polarization 0.15 V less than that for SBC. It may be due to the more suitable distribution of porous and electron structures in the SBC material, in which case the charging occurs without the pseudo-capacitance contribution. A comparison of the capacitive dependences of the SBC electrode in 7.6m KOH and 3.16m CsBr (Figs. 1b and 1c) illustrates a significant increase in charging capacitance for  $Cs^+$  ions (up to 210 F/g). We attribute such increase in specific capacitance to intercalative pseudo-capacitance upon introduction  $\tilde{N}s^+$  ions into pores about 4.8 Å in diameter, as illustrated by the following equation:

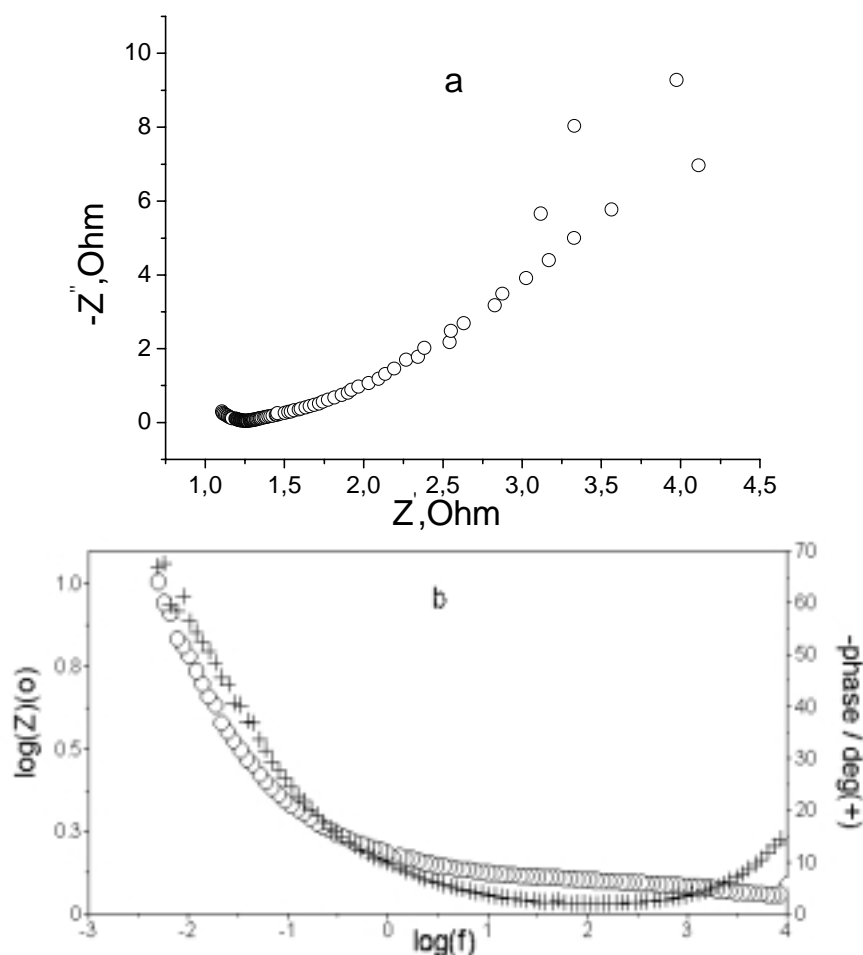


where  $Kat^+$  is the cation,  $H_2O$  – the molecule of the hydrate shell;  $(m-n)$  – the number of molecules removed from the hydrate shell during the ion dehydration process, and  $\delta e^-$  – the charge fraction. This process occurs due to the thermodynamic properties of the 3.16m CsBr solution, which suppose greater polarization of the electrode at a significantly lower hydration energy of the  $Cs^+$  ion (see Table 3).

The measured capacitive and potentiodynamic dependences for the FS2 material in the 7.6m KOH solution (Figs. 2a and 2b) have yielded values about 260 F/g, while the low frequency dependence (for  $5 \cdot 10^{-3}$  Hz, see Fig. 2c) has yielded a value above 300 F/g, in excess of the theoretical prediction. An asymmetry in the positions of negative and positive branches in the potentiodynamic dependence (Fig. 2c) is most probably due to slower kinetics of the intercalation process in comparison with the

**Table 4.** Parameters of EEC interface FS2 for 7.6m KOH at  $E=-0.7V$ .

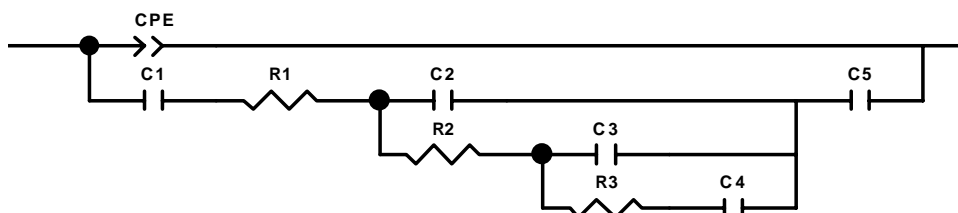
CPE-T·10 <sup>-4</sup> , F	CPE-P, r.u.	R1, Ohm	C1, F	R2, Ohm	C2, F	R3, Ohm	C3, F	C4, Ohm	C5, F
6.7788	0.54	1.317	12.72	0.6085	0.3783	2.297	2.615	11.55	7.566

**Fig. 3.** (a) Nyquist's diagram and (b) Bode dependence for FS2 in the 7.6m KOH solution at  $E=-0.7V$ .

simple capacitive charge accumulation. The model investigation of impedance data in the region of cathode polarization of the electrode to the EEC electrode-electrolyte interface (see Fig. 4) allows each of its parameters to be determined with an accuracy of 2-7% (see Table 4). The pseudo-capacitances increase from  $C=490$  F/g at the initial potential of  $\varphi_{st}=-0.28$  V up to  $C=996$  F/g at the  $E=-0.7$  V potential of the maximum electrode charge.

#### 4. CONCLUSIONS

An analysis of measured capacitive dependences for activated carbons of about 1000 m<sup>2</sup>/g active surface in 7.6m KOH and 3.16m CsBr aqueous solutions has demonstrated that the high value of specific capacitance (>150 F/g) of the activated carbons-electrolyte aqueous solution interface depends on the intercalative pseudo-capacitance of K<sup>+</sup> and Cs<sup>+</sup> cations in intercalative pores about 4.8 Å in diameter. The equivalent electric circuit of the



**Fig. 4.** EEC of the FS2-7.6m KOH interface at the maximum charge potential,  $E=-0.7\text{V}$ , with the electrode' active mass of  $m_a=11.6\cdot 10^{-3}\text{g}$ . CPE means an element of constant phase, C1 - the capacity of the Gouy-Chapman layer; R1 and C2 – the resistivity and capacity of mesopores ( $d>19\text{ \AA}$ ); R2 and C3 – the resistivity and capacity of micropores ( $4.4<d<19\text{ \AA}$ ); R3 and C4 – the resistivity and capacity of intercalative porous ( $d\leq 4.4\text{ \AA}$ ); C5 - the capacity of volume charge in the material.

electrode-electrolyte interface developed in this work has allowed us to determine the intercalative pseudo-capacitance charge for  $\text{K}^+$  ions in intercalative pores of FS2 from  $C=490\text{ F/g}$  at the initial potential of  $\varphi_{st}=-0.28\text{ V}$  up to  $C=996\text{ F/g}$  at the maximum electrode charge potential ( $E=-0.7\text{ V}$ ).

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