INTERCALATION PSEUDO-CAPACITANCE IN CARBON SYSTEMS OF ENERGY STORAGE

B.P. Bakhmatyuk¹, B.Ya. Venhryn¹, I.I. Grygorchak¹, M.M. Micov² and S.I. Mudry³

¹Lviv Polytechnic National University, 1 Kotliarevskyi Str., Lviv, 79013, Ukraine
²Concern “Hefra”, 16 Stanicna Str., Bratislava, 84103, Slovak Republic
³Ivan Franko Lviv National University, 8 Kyrylo and Mefodiy Str., Lviv, 79005, Ukraine

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Abstract. The contribution of intercalative pseudo-capacitance of K⁺ and Cs⁺ 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⁺ 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 m²/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/cm² [1-4]. Consequently, the maximum capacitance of a material whose surface area equals $S=1000$ m²/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:

Corresponding author: S.I.Mudry, e-mail: mudry@physics.wups.lviv.ua

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Li⁺ + e⁻ + [C] ↔ [Li⁺δ-C⁻δ], \hspace{1cm} (1)
where δ 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, \( C_{DL} \), is as follows:

\[
\frac{1}{C_{DL}} = \frac{1}{C_{G-Ch}} + \frac{1}{C_{H}} + \frac{1}{C_{sc}}, \hspace{1cm} (2)
\]

where \( C_{G-Ch} \) is the capacitance of the Gouy-Chapman diffusive layer, \( C_{H} \) – the capacity of the Helmholtz layer and \( C_{sc} \) – 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 HNO₃ 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 5.10⁻³⁻¹⁰⁴ 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 \( C = (2πfZ')^{-1} \) formula as an average value within the 5.10⁻³⁻¹⁰⁴ 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, \( \phi_{st} \), 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]:

\[
E = E_0 + \frac{RT}{nF} \ln (a_r/a_o), \hspace{1cm} (3)
\]

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.

<table>
<thead>
<tr>
<th>Material</th>
<th>Area of pores (d&lt; 4.4 Å) m⁻²•g⁻¹</th>
<th>Area of pores (4.4&lt;d&lt;19 Å) m⁻²•g⁻¹</th>
<th>Area of pores (d&gt;19 Å) m⁻²•g⁻¹</th>
<th>Electrochemical potential, eV</th>
<th>Initial potential in 7.6m KOH (3.2m CsBr), ( \phi_{st} ), (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBC</td>
<td>576</td>
<td>332</td>
<td>120</td>
<td>-4.08</td>
<td>0.05 (0.23)</td>
</tr>
<tr>
<td>FS1</td>
<td>448</td>
<td>498</td>
<td>181</td>
<td>-4.3</td>
<td>0.2</td>
</tr>
<tr>
<td>FS2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.28</td>
</tr>
</tbody>
</table>
Table 2. Porometric data for SBC.

<table>
<thead>
<tr>
<th>Maxima positions in function of pores' diameter distribution, Å</th>
<th>Pore volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>0.52</td>
</tr>
<tr>
<td>11</td>
<td>0.017</td>
</tr>
<tr>
<td>15</td>
<td>0.66</td>
</tr>
</tbody>
</table>

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

\[ \mu_s = \mu_{s, \text{stand}} + RT \ln a_s. \]

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.

<table>
<thead>
<tr>
<th>Ion (solution)</th>
<th>Potential of ion separation (relative to standard hydrogen electrode), V</th>
<th>Chemical potential of ions in the solution, eV</th>
<th>Ion hydration energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺ (7.6m KOH)</td>
<td>-2.84</td>
<td>-1.55</td>
<td>-5.35</td>
</tr>
<tr>
<td>Cs⁺ (3.16m CsBr)</td>
<td>-2.913</td>
<td>-1.39</td>
<td>-4.21</td>
</tr>
<tr>
<td>Br⁻ (3.16m CsBr)</td>
<td>1.065</td>
<td>-3.33</td>
<td>-3.65</td>
</tr>
<tr>
<td>OH⁻ (7.6m KOH)</td>
<td>0.32</td>
<td>-2.85</td>
<td>-5.29</td>
</tr>
</tbody>
</table>
C_{sc}^{-2} = \left(\frac{\epsilon_{sc}/kT}{e}\right)^{-1}\times2L_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-
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Table 4. Parameters of EEC interface FS2 for 7.6m KOH at $E=-0.7V$.

<table>
<thead>
<tr>
<th>CPE-T $10^{-4}$, F</th>
<th>CPE-P, r.u.</th>
<th>R1, Ohm</th>
<th>C1, F</th>
<th>R2, Ohm</th>
<th>C2, F</th>
<th>R3, Ohm</th>
<th>C3, F</th>
<th>R4, Ohm</th>
<th>C4, F</th>
<th>R5, Ohm</th>
<th>C5, F</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7788</td>
<td>0.54</td>
<td>1.317</td>
<td>12.72</td>
<td>0.6085</td>
<td>0.3783</td>
<td>2.297</td>
<td>2.615</td>
<td>11.55</td>
<td>7.566</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$^2$/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$^+$ and Cs$^+$ cations in intercalative pores about 4.8 Å in diameter. The equivalent electric circuit of the
electrode-electrolyte interface developed in this work has allowed us to determine the intercalative pseudo-capacitance charge for K⁺ ions in intercalative pores of FS2 from \( C = 490 \, \text{F/g} \) at the initial potential of \( \phi_{st} = -0.28 \, \text{V} \) up to \( C = 996 \, \text{F/g} \) at the maximum electrode charge potential \( (E = -0.7 \, \text{V}) \).

REFERENCES


