Method of measuring interface area of activated carbons in condensed phase

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Abstract. In this work, we investigated the correlation between the heat of wetting of supercapacitor electrode material (activated carbon) with condensed phases (electrolytes based on homologous series of phosphoric acid esters) and the capacity of the supercapacitor. The surface area of the electrode–electrolyte interface was calculated according to the obtained correlations using the conventional formula for calculating the capacitance of a capacitor.

1. Introduction

Interphase interactions play an important role in the multitude of processes used in various technologies. Understanding of the mechanisms and knowledge of the parameters of interaction of particles with the surface are necessary for successful creation of a number of devices. Electrochemical double-layered supercapacitors (EDLC) represent a fairly intensively developing energy storage technology, widely in demand in niches associated with electric or hybrid vehicles, to recover the energy of braking or to provide rapid acceleration of the vehicle [1]. In supercapacitors, often used as an organic electrolyte are solutions of special salts in acetonitrile or propylene carbonate, because they are based on a relatively high charging voltage (about 3–3.5 V).

The development of new and improvement of existing EDLC requires an understanding of the behavior of the electrolyte on the surface of the electrode material, the processes that occur during charging and discharging. However, the properties of porous carbon materials, used because of their large specific area as electrodes, make experimental studies extremely difficult. These materials have high electrical conductivity and strong optical absorption, which practically excludes the possibility of measurements in pores of micron and submicron sizes, in which, in fact, the giant capacitance of supercapacitors is formed.

One of the most important factors determining the efficiency of a supercapacitor is the degree of use of the internal surface of the pores, which in turn is determined by the wettability of a particular porous electrode material by a specific electrolyte. A known method for characterizing the wetting from the value of the contact angle of the droplet [2] in this case. It seems to be of little use, since it can be realized only on macroscopic open surfaces. In the present work,
2. Experiment

2.1. Calorimetry

Norit (Cabot) DLC Supra 30 activated carbon was used in this work as electrode material. Model supercapacitors were fabricated in standard CR2032 cases in a dry box. The calorimetric measurements were carried out using the calorimeter shown in figure 1.

Data recording was carried out by Resistance Temperature Detector through the bridge circuit using the millivoltmeter with a recorder function. The heating resistor with a nominal value of 100 Ω was connected to the stabilized dc power supply.

The experiment is divided into three phases:

(i) Thermal stabilization of the calorimetry system.

(ii) Breaking the glass bottom. The temperature jump due to the wetting of the the activated carbon by the electrolyte. Afterwards, the system goes into the stationary mode.

(iii) Heating the system with the registration of the temperature jump to determine the heat capacity of the system [3–5].

The calorimeter was assumed to be adiabatic and its heat capacity in the temperature range of the measurement was assumed to be constant. Therefore the ratios of thermal effects to the
temperature jump of these effects are equal to each other:

\[ mC_p = \text{const} = C_{c,s} = \frac{Q_w}{\Delta T_w} = \frac{Q_h}{\Delta T_h} \] (1)

If the mass of the weighed sample is taken into account, i.e. if the specific value is used, the following formula is obtained:

\[ Q_{w,s} = \frac{Q_w}{m} = \frac{Q_h}{m} \frac{\Delta T_w}{\Delta T_h} \] (2)

where \( C_p \) is the heat capacity of the calorimetry system in J/(g K); \( Q_w \) is heat released upon wetting, J; \( Q_{w,s} \) is the integral heat evolved due to the wetting of the weighed sample, J/g; \( \Delta T_w \) is the temperature jump due to the wetting of the weighed sample, K; \( Q_h \) is the heat conveyed to the system by the heating thermoresistor, J; \( \Delta T_h \) is the temperature jump due to the forced heating of the calorimetry system, K; \( m \) is the mass of the weighed sample, g.

The series of experiments was interpreted using the weighted average method because the obtained measurements must be considered of unequal accuracy. The obtained value of specific heat of wetting (J/g) was recalculated to molar heat of wetting (J/mol) using the formula [6]

\[ Q_{w,\text{mol}} = \frac{Q_{w,s}N_a}{S_sN_s} \] (3)

where \( N_a = 6.02 \times 10^{23} \text{ mol}^{-1} \)—the Avogadro constant; \( S_s \)—specific surface area obtained in a gas phase using a method based on Brunauer–Emmett–Teller theory (BET method); \( N_s \)—the number of molecules of solvent per surface area molecules/m².

The number of molecules was calculated from the formula for approximate diameter of the molecule [4]

\[ d_{\text{mol}} \approx 3 \sqrt[3]{\frac{6M}{\pi \rho N_a}} \Rightarrow S_{\text{mol}} = \frac{\pi}{4} d_{\text{mol}}^2 \Rightarrow N_s = \frac{1}{S_{\text{mol}}} \] (4)

where \( M \)—molar mass of electrolyte, kg/mol; \( \rho \)—density of electrolyte, kg/m³.

Henceforth only molar heat of wetting \( Q_{w,\text{mol}} \) will be discussed, therefore it will be used without the index (Q).

2.2. Electrochemical measurement

Model coin cells were fabricated in standard CR2032 cases with Norit DLC Supra 30 activated carbon electrodes with the mass of 0.015 g.

An ElinsP-30SM potentiostat with recording frequency of 40 s⁻¹ was used for measurement. The measurements were performed in the classic cyclic voltammetry with different scan rates of 5, 10, and 50 mV/s in the potential range from 0 to 2.8 Volts. For each scan rate, the capacity of the supercapacitor, and the correlation of capacity and scan rate was calculated. By extrapolating to the zero value of the scan rate, the capacity was obtained, which was used in the following calculations.

3. Results and discussion

Table 1 shows the results of calorimetry measurements of integral heat of wetting of activated carbons by the series of electrolytes being studied. The values obtained point at the physical nature of the adsorption during wetting, i.e. they demonstrate the absence of explicit chemical processes [2, 7, 8].

Table 2 shows the capacity values obtained for the supercapacitors with different scan rates: \( C_1 \) is for 5 mV/s; \( C_2 \) is for 10 mV/s; \( C_3 \) is for 50 mV/s and \( C_s \) is specific capacity.

The data obtained for the homological series of alkyl phosphates was used to plot the dependence of specific capacity of the supercapacitors on the integral heat of wetting (figure 2).
Table 1. Integral heat of wetting values of Norit DLC Supra 30 of activated carbons by the series of electrolytes.

| Electrolyte Solvent | Integral heat of wetting (J/g) | Integral heat of wetting (J/mol) |
|---------------------|--------------------------------|---------------------------------|
| 1 mol/L LiBF$_4$ trimethyl phosphate | 211.5 | 25170.5 |
| 1 mol/L LiBF$_4$ triethyl phosphate | 258.0 | 39276.8 |
| 1 mol/L LiBF$_4$ tributyl phosphate | 248.8 | 50 849.7 |

Table 2. Values of electrical capacities for different scan rates for supercapacitors being studied.

| Electrolyte Solvent | $C_1$ (F/kg) | $C_2$ (F/kg) | $C_3$ (F/kg) | $C_s$ (F/kg) |
|---------------------|--------------|--------------|--------------|--------------|
| 1 mol/L LiBF$_4$ in trimethyl phosphate | 25 480 | 22 240 | 10 350 | 26 320 |
| triethyl phosphate | 21 150 | 17 000 | 6850 | 21 360 |
| tributyl phosphate | 11 220 | 9060 | 4370 | 11 230 |

Figure 2. Dependence of the specific capacity of supercapacitors on the integral heat of wetting of electrode material with electrolyte.

It is known that the capacity of the capacitor is in direct proportion to the area of the capacitor plates:

$$C_s = \frac{\varepsilon_0 \varepsilon}{d} S_s,$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m—the dielectric constant; $\varepsilon$—the dielectric permittivity of solvent and $S_s$—the specific surface area.

Due to the distance between the “plates” of the supercapacitor is approximately equal to the thickness of the double electric layer times two because the double electric layer is formed on
Table 3. Values of electrical capacities for different scan rates for supercapacitors being studied.

| Electrolyte           | δ (10 nm) | d (10 nm) | K (F/m²) | K/A (J kg mol⁻¹ m⁻²) |
|-----------------------|-----------|-----------|----------|----------------------|
| trimethyl phosphate   | 5.00      | 10.00     | 0.019    | -0.032               |
| triethyl phosphate    | 3.92      | 7.84      | 0.015    | -0.025               |
| tributyl phosphate    | 3.12      | 6.24      | 0.012    | -0.020               |

Figure 3. Dependence of adjusted integral heat of wetting $Q_*$ on the function $f(K/A)$ for 1 mol/L solution of LiBF$_4$ in alkyl phosphates using Norit DLC Supra 30 activated carbon.

Each “plate”, it is possible to calculate the $d$ value for the 1.1-valent LiBF$_4$ electrolyte in the solvents being studied as double the value for the diffuse layer $\delta$ using the formula:

$$\delta = \sqrt{\varepsilon_0 \varepsilon RT / 2Fl},$$

(6)

where $l$—ionic strength in mol/L.

Equation (5) takes the form

$$C_s = KS_s,$$

(7)

where $K = (\varepsilon_0 \varepsilon) / d$. Combining equation (7) and an approximation expression for the dependence in figure 2, the following system of equations is obtained:

$$\begin{cases} 
C_s = AQ + B, \\
C_s = KS_s, 
\end{cases}$$

(8)

where $A = -0.58$ F mol/(J kg), $B = 41894$ F/kg, are coefficients of linear approximation taken from the straight line expression shown in figure 3.

Table 3 shows calculated thickness of the double electrical layer in supercapacitors being studied.
Solving the system for the heat of wetting, the following is obtained:

\[ Q^* = \frac{K}{A} S_s, \]  \hspace{1cm} (9)

where \( Q^* = Q + B/A \) is the adjusted integral heat of wetting, J/mol. Therefore, \( S \) can be determined as the slope coefficient of the linear plot of the dependence \( Q^* = f(K/A) \) for the homological series shown in figure 3.

The slope coefficient is 2100.059 m\(^2\)/kg \((R^2 \approx 1)\), which is commensurate to the specific surface area of 1900 m\(^2\)/g (1900 000 m\(^2\)/kg) specified by the manufacturer (deviation \( \approx 11\% \)) and can be considered the true electrochemically active and available surface of the Norit DLC Supra 30 activated carbon in the supercapacitor for the given series of electrolytes.

4. Conclusion

As a result of the direct calorimetry and cyclic voltammetry studies, integral heat of wetting and electric capacity of the supercapacitor material were measured in a homological series of phosphoric acid esters. The calculated value of specific surface area of the interface of activated carbon in the condensed phase (2100 m\(^2\)/g) satisfactorily matches the value of specific surface area obtained in the gas phase using the BET method (1900 m\(^2\)/g). The method of measuring the surface area of the interface between activated carbon and the condensed phase is phenomenological and is based solely on measuring the heat of wetting of the activated carbon by condensed phase, with subsequent calculation of specific surface area. The calculation was based on the conventional dependence \( C_s = (\varepsilon_0 \varepsilon/d) S_s \). This method is of great interest to developers of new supercapacitor systems because it allows to choose electrode materials with maximum surface determined not in the gas phase (BET method) but in condensed phase. Measurements using this method can be performed faster with modern calorimetry equipment than using the BET method, and the method yields results adequate for the operating conditions of the specific supercapacitor system.

References

[1] Kiseleva E A, Lelin F V, Zhurilova M A and Shkolnikov E I 2017 Russ. J. Appl. Chem. 90 712–5
[2] Kompan M E, Agafonov D V, Bursian A E, Dmitriev D S and Mikryukova M A 2016 Phys. Solid State 58 2555–9
[3] Kostikov V I et al 1974 Uproschennaja metodika opredeleniya teplot smachiva niya uglerodnyh poroshkov organsicheskimi zhidkostjami Konstrukcionsye Materialy na Osnove Ugljera (Moscow: Metallurgiya)
[4] Dmitriev D S, Satarov A A, Mikrjukova M A, Naray V N and Agafonov D V 2014 Syuzhli fiil’nosti elektrodnyh materialov HIT s ih elektrohimicheskim povedeniem Mezhdunarodnaya Nauchno-Praktiches- kaya Konferenciya Teoriya i Praktika Sovremennyh Elektrohimicheskikh Proizvodstv (Saint Petersburg: SPbGTI(TU))
[5] Dmitriev D S, Satarov A A, Mikrjukova M A, Naray V N and Agafonov D V 2015 Issledovanie liofil’nyh harakteristik Vysokodispersnyx uglerodnyh materialov V Nauchno-Tehnickoj Konferenciya (s Mezh- dunarodnym Uchastjem) Nedelya Nauki 2015 (Saint Petersburg: SPbGTI(TU))
[6] Fridrihsberg D A 1984 Kurs Kolloidnoj Himii: Uchebnik dlya Vuzov (Leningrad: Himiya)
[7] Summ B D and Gorjunov Ju V 1976 Fiziko-Himicheskie Osnovy Smachivaniya i Rastekaniya (Leningrad: Himiya)
[8] Karnauhov A P 1999 Tekstura Dispersnyh i Poristyh Materialov (Novosibirsk: Nauka)