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An improved adsorption method for the characterization of water-based supercapacitor electrodes

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The specific surface area is a key characteristic of carbon materials used in supercapacitor electrodes. In this paper, the use of a methylene blue technique for specific surface area determination is presented. Values for the specific surface area, determined by a new method, provide better correlation with theoretical values for the specific electrical capacity of highly-porous carbon electrodes than the values measured by the common BET method. Additionally, the methylene blue adsorption method is thought to characterize carbon adsorption activity in relation to a supercapacitor electrolyte.

Keywords: Supercapacitors, specific surface area, methylene blue, aqueous electrolyte.

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1. Introduction

Supercapacitors, also called ionistors, or electric double layer capacitors (EDLC), are electrochemical energy storage devices. Their application area is rapidly expanding because of their unique power and energy storage properties. A common supercapacitor device contains a pair of highly-porous carbon electrodes immersed in an electrolyte solution and divided by a dielectric membrane. The commonly used electrolyte solutions are aqueous solutions of salts [1], acids [2] and alkalis [3]. Ionic liquids (either neat or dissolved in polar organic solvents) are considered to have promising electrolyte properties [4]. This electrode-electrolyte system forms an electric double layer (EDL) at the interface between conductive electrode and electrolyte. The electric capacitance of the EDL is defined by formula:

$$C = S \frac{\varepsilon \cdot \varepsilon_0}{d}, \quad (1)$$

where C is the specific electrical capacitance, S is the specific surface area, ε is the permittivity, ε_0 is the vacuum permittivity and d is the thickness of adsorption layer. Therefore, it is theoretically possible to reach significant values for the EDL capacitance using a material with larger specific surface area. However, often the real EDL specific capacitance does not correspond to a specific capacitance of the “isolated” electric double layer. This is why we tried to improve the method of measuring of the specific surface area to reach an acceptable correlation between this data and the actual EDLC capacitance.

2. Structure and properties of the used carbon materials

The carbon materials investigated in the work are the highly-porous microstructured forms derived from pyrolyzed rice straw. After the pyrolysis the product was etched in alkali solution to remove residual of SiO₂. All of these materials were prepared and partially characterized in Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk. These materials have different microstructure because of different processing conditions. The main parameters of the materials are given in Table 1, and the micrographs (obtained by SEM method) of some materials are given in Figs. 1 – 3.

TABLE 1. The main parameters of investigated carbon materials

Material (unique name)	BET surface area, m ² /g	Average pore diameter, nm
ME544	544	4.7
ME900	906	3.1
ME991	991	3.0
ME1100	1100	3.0
MI2232	2232	2.2

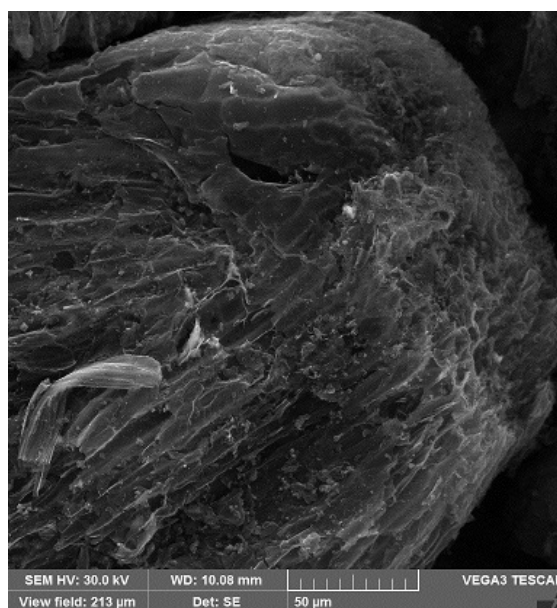


FIG. 1. SEM micrograph of ME991, scale 50 μm

Micrographs of the materials show a highly-porous structure with different pore depths and geometries. These factors, such as the average pore diameter, strongly affect the adsorptive properties of the material.

3. The method of methylene blue adsorption

The conventional method for specific surface area (SSA) measurement is the BET method, named after first letters of its inventors [5]. This method is based on a liquid nitrogen adsorption at a temperature below its boiling point [6]. However, the obtained value for SSA is strongly affected by the capillary condensation, which sometimes gives very large values

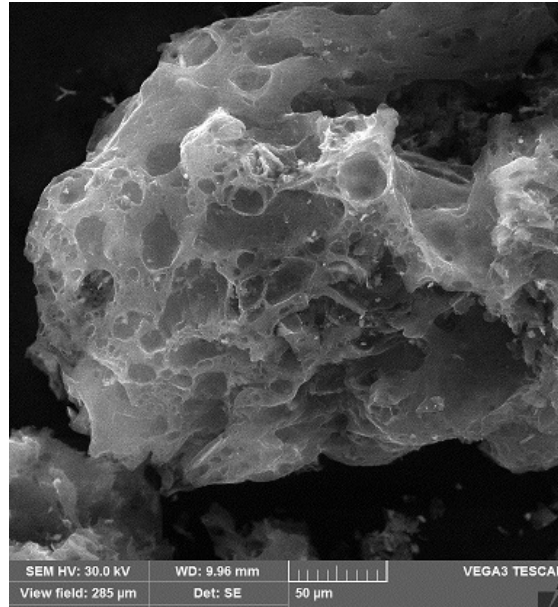


FIG. 2. SEM micrograph of ME2232, scale 50 μm

of SSA. As a result, the material MI3200 (the same type as material MI2232) has shown SSA values near 3200 m^2/g , ranging down to 2600 m^2/g , the highest theoretical value of SSA calculated for single-layer graphene [7]. However, the nitrogen molecule is non-polar, whereas all the electrolyte and solvent molecules used in supercapacitors are all polar in nature. Assuming that the polarity of the adsorbed molecules influences the amount of the material adsorbed, we decided to utilize another method for determining the specific surface area [8]. This method, which is based on the adsorption of methylene blue dye from 0.2 % aqueous solution, is called here the “MetB” method.

To define the SSA by “MetB” method, a minute amount (1 – 10 mg, depending on powder fineness) of the investigated carbon material was added to 5 ml distilled water and 1 drop (approx. 20 mg) 3 M H_2SO_4 solution in a 10 ml flask which was then sealed hermetically. Then, that flask was sonicated in ultrasound bath for 10 minutes to prevent particle agglomeration. Next, an aqueous methylene blue solution was injected into the flask slowly (approx. 0.05 g every 30 min) by a previously weighed syringe. When the suspension’s color change (blue) stopped for 15 min, the syringe was removed and reweighed. The specific surface area (SSA) is defined by the formula:

$$S = \frac{V \cdot C \cdot N \cdot A_m}{m \cdot M}, \quad (2)$$

where V is solution volume (ml), C is concentration of methylene blue (g/ml), N is Avogadro’s constant ($6.023 \cdot 10^{-23} \text{ mol}^{-1}$), A_m is the size of methylene blue adsorption site $1.06 \cdot 10^{-18} \text{ m}^2$, m is mass of carbon material, M is molecular mass of methylene blue (319.9 g/mol). Therefore, when using solution with 0.2 % concentration, the SSA can be calculated with formula:

$$S \left[\frac{\text{m}^2}{\text{g}} \right] = 4.0 \left[\frac{\text{m}^2}{\text{g}} \right] \cdot \frac{M}{m}, \quad (3)$$

where M is mass of methylene blue solution (g), m is mass of carbon material (g).

4. Preparation of the electrodes and specific capacitance measuring

To define the specific capacitance of supercapacitor electrode materials, we used a cyclic voltammetry technique which allowed us to determine the capacitance for our experimental supercapacitor electrodes. A sample supercapacitor consists of two electrodes (placed on stainless steel gauze) separated by a paper membrane and immersed in an electrolyte solution. We used 0.5 M Na_2SO_4 aqueous solution with an additional 2 wt.% ethyl alcohol as surfactant (this was necessary because of the investigated carbon materials' hydrophobicity). To make the electrode, an amount of investigating carbon material (50 mg) was mixed with 0.25 ml 1 % water suspension of PTFE as binder and transferred onto metal gauze. After that, the electrodes were dried for 1 h on an open hot plate at 95 °C to prevent water boiling, and subsequently, the electrodes were formed under 30 MPa pressure. A pair of electrodes made from the same material was assembled in supercapacitor and sealed in polyethylene to prevent electrolyte evaporation and leakage. The capacitance of these model supercapacitors was measured by a cyclic voltammetry method at 5 – 50 mV/s scan rates at 0 – 500 mV voltage window. As an example, the voltammetric curve for ME991 material is shown in Fig. 3.

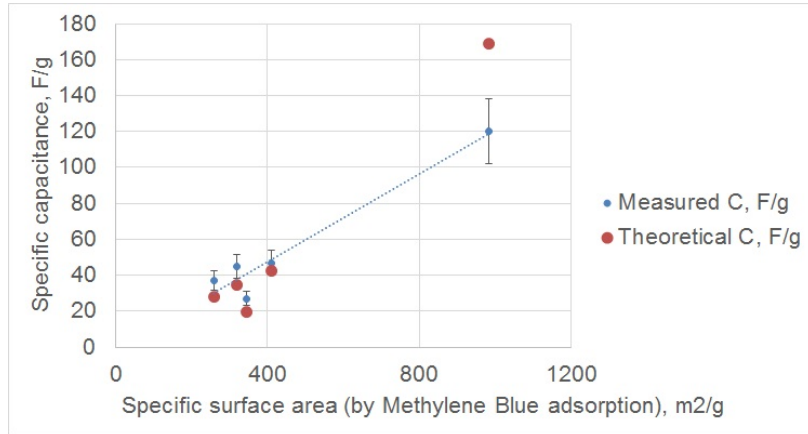


FIG. 3. Comparison of real (blue points) and theoretical (red points) capacitance values of surface area of high-porous carbon materials

To translate the capacitance of supercapacitor into the specific capacitance of the material, one can use a formula:

$$C_s = 2 \cdot \frac{C_{meas}}{m}, \quad (4)$$

where C_s is specific capacitance of material, C_{meas} is measured capacitance of model supercapacitor, and m is full mass of the both carbon electrodes.

To calculate the theoretical value for the specific capacitance of a material, one can use a cylindrical pore model, described in [9]. In this model, the authors used the geometric characteristics of the pore, such as characteristics of the cylindrical capacitor with the solvated ion's diameter as the inner diameter and the average pore diameter as the outer diameter for this cylindrical capacitor:

$$C = S \cdot \frac{\varepsilon \cdot \varepsilon_0}{b \cdot \ln\left(\frac{b}{a_0}\right)}, \quad (5)$$

where ε is permittivity of solvent, ε_0 is vacuum permittivity, b is average pore diameter, a_0 is solvated ion's diameter (0.339 nm for sodium ion), S is full surface area of electrode.

The results for the SSA measured by our “MetB” method corresponded to the measured and calculated specific capacitance of our materials, which are shown in Table 2.

TABLE 2. The measured and calculated parameters of investigated carbon materials

Material	BET surface area, m ² /g	“MetB” surface area, m ² /g	Measured specific capacitance, F/g	Theoretical specific capacitance, F/g
ME544	544	345	27	20
ME906	906	411	47	42
ME991	991	320	45	35
ME1100	1100	259	37	28
ME2232	2232	983	120	169

5. Conclusion

The measured and calculated capacitance of carbon materials with 1000 m²/g (BET) and 300 – 400 m²/g (MetB) specific surface area correlate well. However, highly-porous materials show a worse correlation between these values. We postulate that this divergence is connected either with some kinetic characteristics of the electrochemical system – low diffusion speed in pores, or with inactivation of the surface by a binder or pressure processing.

Though a BET method is fairly convenient, it is not fully appropriate for measuring the specific surface area of highly-porous carbon materials, especially those materials appropriate for supercapacitor electrodes. The method based on methylene blue adsorption yields results that are in better agreement with other experimental data.

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