

The Study of Operating Parameters of a Graphene Electrode-Based Supercapacitor by the Voltmeter-Ammeter Method

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Abstract

In current practice of developing supercapacitors, graphene appears to be a promising electrode material due to its unique physico-mechanical properties. Using graphene-based electrodes in supercapacitors opens up new prospects, primarily, the range expansion of operating and design parameters to enable the realization of higher operating voltage levels and to ensure thermal stability and an increase in the number of charge/discharge cycles.

In the present research, electrotechnical parameters and characteristics of a supercapacitor with electrodes made of a composite material consisting of graphene and nanoporous carbon were studied during charge/discharge processes using the voltmeter-ammeter method. The results obtained demonstrate that applying graphene as an electrode material for supercapacitors allows for charge/discharge mode implementation, provided that the time to charge the supercapacitor up to the capacitance value of 5.10 F is 5 s and the supercapacitor operating weight is 5.04 g.

Keywords

Graphene; supercapacitors; electrodes; voltmeter-ammeter method.

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Introduction

At present, supercapacitors (Fig. 1), also known as ultracapacitors or electric double-layer capacitors (EDLC), have become widely used in electronics and electrical engineering. They represent electrochemical devices able to store and release electrical energy through internal redeployment of electrolyte ions and are basically employed in power supplies briefly but often consuming a lot of power (e.g., cranking motors, pocket lamps, memory chips, etc.), as well as in filter and smoothing circuits. Supercapacitors occupy an intermediate position between electrolytic capacitors and storage batteries with regard to the electrical parameters, whereas they differ from them concerning operating principles (Table 1) [1–5].



Fig. 1. A supercapacitor

The main reason for the development of supercapacitors is the need for energy devices that would have significantly higher cyclability and power density compared to storage batteries [1].

Table 1

Comparative characteristics of the electrical energy storage devices

Parameter	Capacitors	Supercapacitors	Storage batteries
Discharging time	10^{-6} – 10^{-3} s	0.02–10 min	0.2–6 h
Charging time	10^{-6} – 10^{-3} s	1–10 s	0.2–6 h
Specific energy, W h/kg	<0.1	1–100	20–170
Power density, W/kg	>10.000	1.000–3.000	100–500
Watt-hour efficiency, %	~100	95–98	60–90
Life time (cycles)	∞	$>5 \cdot 10^5$	300–2.000

Supercapacitors have been studied for a long time. In the early 1950s, engineers from General Electric began experiments with components using porous carbon electrodes for fuel cells and batteries. Activated carbon is a “sponge-like” form of carbon; it is conductive, highly porous, and has a large specific surface area. In 1958, Becker developed a low-voltage electrolytic capacitor with porous carbon electrodes. He supposed that the energy could be stored in carbon pores, just like in a foil of the conventional electrolytic capacitor, because the electric double layer was not used at that time. In 1966, while working with fuel cells, researchers from Standard Oil (SOHIO) proposed a theory of power storage in carbon electrodes. In 1970, Donald L. Boos patented the electrochemical capacitor which represented itself as an electrolytic capacitor with electrodes made of activated carbon.

In 1975–1980, Brian E. Conway conducted extensive fundamental and technical studies using metal oxide-based electrodes. In 1991, he described the difference between the behavior of supercapacitors and storage batteries during electrochemical energy storage. In 1999, he introduced the term “supercapacitor” to explain the increased capacitance by surface redox reactions and the energy transfer between the electrodes and the electrolyte.

To date, electronic technology companies such as Panasonic, ELNA, Maxwell Technologies, NEC and some others have invested their money in projects aimed at improving the efficiency of electric batteries in electric vehicles to provide the necessary power to accelerate the car and allow for transformation of mechanical braking energy of the vehicle into electrical energy and its long-term accumulation [6].

Principle and Construction of the Electric Double Layer in Carbon Nanomaterials-Based Supercapacitors

The working principle of supercapacitors is based on the theory of the electric double layer (EDL) (or: Helmholtz layer) that exists at the electrode/electrolyte interface [7, 8]. Two polarizable porous electrodes commonly made of carbon-based materials are placed in an inert electrolyte (Fig. 2).

In 1879, G. Helmholtz discovered a previously unknown phenomenon: the occurrence of electric layers in materials with different types of conductivity after their mutual contact. This phenomenon is fundamental and contributes to obtaining equilibrium in a system which consists of materials having ionic and electronic conductivity by means of the charge transfer in the intermolecular space [6, 11, 17, 20].

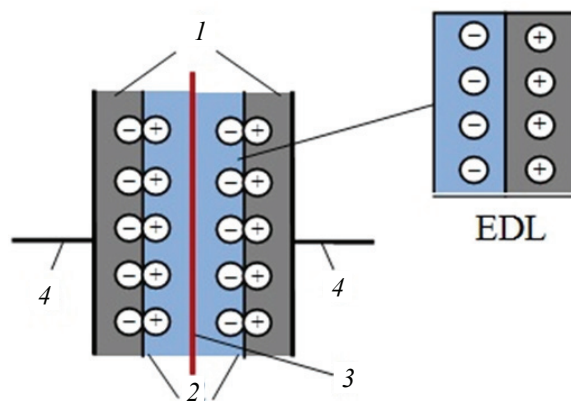


Fig. 2. A schematic representation of the electric double layer (EDL) operating principle:
1 – absorber carbon; 2 – electrolyte;
3 – porous membrane; and 4 – current tap

The electric Helmholtz layers present areas of charges located within a distance of 5 Å from each other and allowing for a loading of external charging sources. However, the charge voltage applied to the electrolyte (ionic-conductivity materials) is limited depending on the electrolyte type.

Since the Helmholtz layers are formed as a result of a contact between the solid and the electrolyte, it is obvious that finely dispersed materials (activated carbon such as activated carbon and carbon nanomaterials) can be used as solids. In this case, it is possible to obtain very large contact surface areas and, consequently, very large surface areas of the electrical double layer, the limiting theoretical value of which is $SED_L = 2600 \text{ m}^2$ per gram of highly porous material [8, 20].

The layer is formed according to the following mechanism: positively and negatively charged ions present in the electrolyte after passing an electric current are distributed over the active surface of the electrodes – the larger their surface area, the greater the capacitance of the supercapacitor. After increasing the electrode resistance, the ions gradually move into the bulk of the electrolyte, thereby releasing electrical energy. The more intensive the ion exchange between the electrode and the electrolyte, the faster the discharge rate of the supercapacitor; the same is true for its charging rate.

Supercapacitors may vary according to several criteria such as electrode material, electrolyte used or membrane layer. There are three types of electrode materials: carbon-based materials and derivatives thereof (graphene), polymeric materials and metal oxides. Carbon and its various modifications are commonly used as electrode layer for different reasons such as low cost, large membrane-material surface area, and the availability of accessible technologies for producing activated carbon and graphene.

Table 2

Comparative characteristics of electrolytes for supercapacitors

Parameter		Electrolyte		
		Aqueous (KOH, H ₂ SO ₄ , Na ₂ SO ₄)	Organic (C ₂ H ₅ N ⁺ BF ₄ ⁻)	Ionic liquids
Decomposition voltage	V	1.2	2.5	3.5
Specific capacitance	μF/sm ²	29.7	17.0	10
Specific energy	Wh/kg	12.3	29.3	33.7

Acetonitrile solutions of tetraethylene tetrafluoroborate ((C₂H₅)N⁺BF₄⁻) are generally used as commercially available electrolytes for supercapacitors. The limit value of the operating voltage in aqueous electrolytes must not exceed 1.23 V. However, when the voltage reaches 0.7–0.8 V, the potential of one of the electrodes can overcome the thermodynamic limit and cause decomposition of the electrolyte in the space around the electrode (Table 2). In this regard, organic electrolytes seem more attractive, although the electrode capacitance therein is lower than in aqueous electrolytes. The range of operating voltages in the organic electrolytes is substantially determined by the presence of impurities, mostly water. Thus, the decomposition potential of high-purity acetonitrile measured relative to a glassy carbon is 5.9 V, and it decreases to the values of 3.8 and 2.7 V [9].

In case of using activated carbon as electrode material, a more narrow range of operating potentials should be chosen to prevent decomposition of the organic electrolyte on the active surface of the electrode. When operating, the supercapacitor pores of the electrode material become filled with decomposition products of the electrolyte. The electrolyte degradation can be due to the presence of edge defects. Thus, to increase the life span of the supercapacitor and its functionality, surface treatment of the electrode material is usually performed. The electrode capacitance also affects the value of the energy density; therefore, numerous studies have been aimed at improving the capacitance of carbon materials [7, 8, 10].

The charge/discharge process takes place in the ion layer formed on the electrode surface. Under the influence of an applied voltage, both anions and cations move to the respective electrode and accumulate on its surface, thereby forming the EDL that balances its charge [3].

To determine the supercapacitor capacitance, it is required to calculate the amount of energy required to provide it with sufficient power during periods of peak consumption according to the following expression:

$$E = \frac{CU^2}{2}, \quad (1)$$

From this equation, it follows that the amount of energy stored in the supercapacitor E depends not only on its capacitance C , but also on its charge voltage U .

Another common way to estimate the capacitance of the device is presented by the following equation:

$$C = \frac{I}{(U_1 - U_2)} \tau, \quad (2)$$

where I is the discharge current, U_1 and U_2 are the supercapacitor voltages immediately before the period

of peak consumption and at the end of this period, respectively, and τ is the (discharging) time (Fig. 3).

However, commercially available supercapacitors have some significant disadvantages, including low operating voltage values and reduced specific energy indicators when increasing their weight and size [4]. Besides, it should be noted that commonly used carbon electrodes are rather expensive and cannot ensure the improvement of energetic characteristics during the transition from conventional electrolytes to ionic liquid-based ones. This is related to the ash content in the carbon electrodes, which makes up to 0.3 % of the carbon mass concentration. Moreover, the other drawback is that carbon has low conductivity due to which electroconductive soot (up to 20 %) should be introduced into the electrode material to reduce its surface area.

In this regard, the application of graphene-based electrodes for supercapacitors opens up new opportunities, primarily the range expansion of operating and design parameters to enable the realization of higher operating voltage levels and to ensure thermal stability and an increase in the number of charge/discharge cycles. Thus, a method to accurately determine parameters and operating conditions for such supercapacitors should be developed and implemented.

While implementing the idea of using graphene as electrode material, there is a very complicated problem of collecting the current from both electric layers

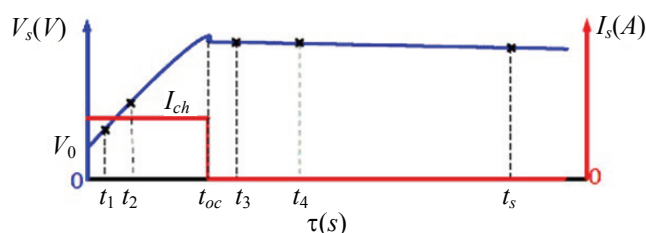


Fig. 3. The voltage (V) and current (I) dependence on the charging/discharging time

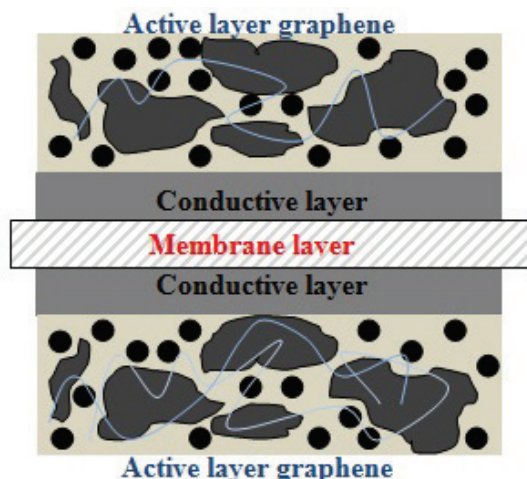


Fig. 4. The structure of graphene electrodes

(Fig. 4). If the collection of the current from one of the contacting materials (*e.g.*, activated carbon) is relatively easily performed by simply using metal current collectors that have conductivity close to that of coal, the collection of a graphene-based electric layer is rather problematic, since it is almost impossible to choose the material of the current collector. Otherwise, one more EDL will be formed at the electrolyte-electrode interface, and its specific characteristics would negate the benefits of the supercapacitor.

In this case, a system of two pairs of contact materials divided by an ion-conducting separator can be used (see Fig. 2) wherein two capacitors connected in series are generated. Each plate of these capacitors corresponds to the electric layer formed in the electrolyte, whereas the current collection is carried out from the layers formed in the porous electrode. The plate heteropolarity in the two-capacitor system takes place due to the ion-conducting separator.

It should be noted that porous septa (membranes) must be made of ion-exchange materials having a low electrical resistance and a relatively high selectivity for transferring ionized substances only with the same charge (positive or negative).

Such membranes present two unique properties [9, 10, 24]: high conductivity and selectivity. The latter is due to the effect of equilibrium between ionic groups fixed on the membrane and ions present in the electrolyte solution.

The nature of these properties is determined by the composition and concentration of the solution in contact with the membrane.

Materials and Methods

Recent studies from the world's leading laboratories in the field of high-capacitance chemical current sources have demonstrated the feasibility of

using carbon nanomaterials as electrode materials [3, 11–25]. New approaches for obtaining graphene make it possible to develop supercapacitors able to accumulate and release energy for short periods of time, thereby allowing them to be employed in various technical applications (*e.g.*, electric transport, autonomous current sources, electronics, *etc.*).

The technology of fabricating new types of supercapacitors is based on highly porous carbon (graphite) impregnated by a liquid electrolyte, with subsequent synthesis of multi-layered graphene.

The average energy density of supercapacitors is about 5–8 W h/kg, which makes graphene-based products commercially attractive against the background of rapid charging.

According to the latest research results, the specific energy storage density of supercapacitors increases due to large specific surface area (1500 m²/g) and higher conductivity when using graphene as electrode material [6, 10].

There is a variety of methods for measuring the capacitance of supercapacitors. In measurement technologies, ballistic, voltmeter-ammeter, resonant and bridge circuit methods have been mostly used. Among them, the voltmeter-ammeter method seems to be the most appropriate one for studying the properties of supercapacitors, since it is relatively simple and allows for measuring a large amount of charge.

In the circuit for measuring the capacitance presented in Fig. 5, the milliammeter (mA) detects the current flowing through the capacitor of capacitance C and the load resistor of resistance R , so that the capacitance determination according to Equation (2) and without any noticeable error becomes possible in the case where the current passing through the supercapacitor is much greater than the current flowing through the voltmeter. This will take place only for small capacitive reactance values, *i.e.* when measuring high capacitance values. In the case of measuring small capacitance value, more accurate results could be

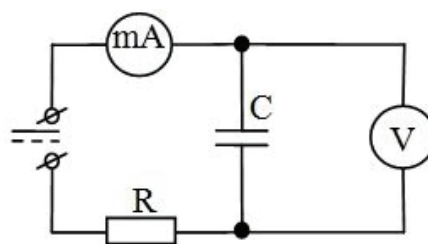


Fig. 5. A circuit for determining the capacitance by means of the voltmeter-ammeter method:

mA – milliammeter; R – load resistor; C – capacitance; and V – voltmeter

obtained by using other techniques. After applying a voltage to the circuit (voltmeter V), the charge current ($I(\tau)$) can be evaluated according to the following equation:

$$I(\tau) = I_0 \exp\left(-\frac{\tau}{CR}\right), \quad (3)$$

where I_0 is the initial current, and τ is the (charging) time.

The power, another important characteristic of supercapacitors, is given by:

$$P = \frac{U^2}{4r}, \quad (4)$$

where r is internal resistance or equivalent series resistance of the supercapacitor, which is composed of electrode materials, electrolyte, and an ion-exchange membrane.

To provide high power and energy characteristics of supercapacitors, it is very important to choose the optimal composition for the electrolyte and ensure a good electrical contact between the membrane and the active component of the electrode.

In the present work, a measuring cell was developed to run experiments related to graphene-based electrode materials (Fig. 6). It can be used with almost any material: electrodes, membranes, and electrolytes. The cell body was made of textolite which has a high resistance ($R = 10^{10} - 10^{12} \Omega$), thereby making it possible to virtually eliminate current leakages across the electrodes. Besides, textolite can be employed as insulating and structural material applicable for producing electronic and radio components.

Herein, studies on the capacitance of the supercapacitor carried out by the voltmeter-ammeter method allow for an evaluation of its performance and demonstrate its advantages and disadvantages.

The research was performed in acetonitrile and sulfuric acid (H_2SO_4) solutions of tetrafluoroborate at various concentrations. These electrolytes were chosen

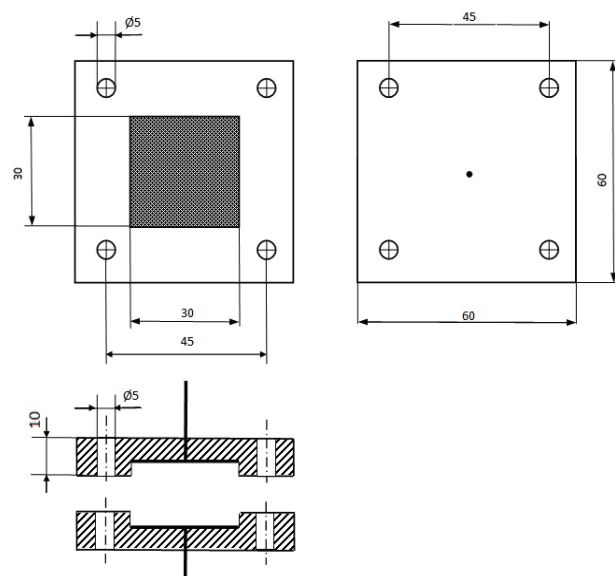


Fig. 6. A measuring cell

due to their stability, high conductivity and low cost, which in turn are important for industrial production.

Electrical measurements were performed in the above-described measuring cell. This cell is characterized by high integrity and resistance of its body, ease of assembly, and versatile thickness of electrochemical elements or groups (electrodes, membrane). The system represents a matrix structure, due to which it is possible to choose materials for the supercapacitor. In the electrochemical group, the electrolyte is located in pores of the graphene-based electrodes and the membrane. Given that the volume of the electrolyte present in the pores is extremely small, the removal of oxygen from the measuring cell is performed by keeping the electrodes at a potential close to the decomposition potential of the electrolyte for 5–10 min. The nominal loading parameter values of the supercapacitor under study are shown in Table 3.

To ensure the reliable separation of the electrodes, the membrane was clamped with rubber compactors. Moreover, during the measurements, the current value was limited, with subsequent records of the $U(t)$ dependence.

The method described herein was used to evaluate the capacitance and assess the sustainability of the electrode functioning (*i.e.*, cyclability) and identify other regularities.

Results and Discussion

Since graphene is the thinnest material existing in nature (Fig. 7), and besides, it possesses high conductivity and good chemical stability, supercapacitors with extra high capacitance can be produced thereof.

Table 3

Nominal loading parameters of the supercapacitor under study

Parameter	Value
Maximum discharge current, mA	70
Maximum discharge voltage, V	2.5
Discharging Time, s	240

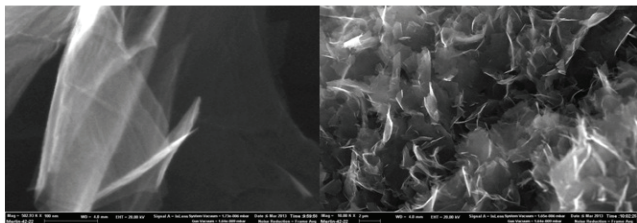


Fig. 7. Scanning electron microscopy (SEM) images of graphene (thickness 5 nm)

The latest research results show that the use of graphene as an electrode material for supercapacitors increases the specific energy storage density of those devices due to an increase in the specific surface area up to $1500 \text{ m}^2/\text{g}$ and very high conductivity [11].

The new production technology developed for supercapacitors is based on highly porous multi-layered or few-layered graphene nanoplatelets (GNPs) (Fig. 8) impregnated with a liquid electrolyte [7].

Nanoporous carbon (NPC) is the other electrode material for supercapacitors. Its deposition over GNPs increases the electric conductivity and alters the porous structure of the material. The surface area, porous and crystalline structure and electrical properties of the final nanocomposite can be varied over a wide range depending on the carbon precursor nature, GNP parameters, and synthesis and activation conditions [8, 10, 11].

The energy density of the supercapacitor with the GNP/NPC material-based electrodes was found to be about 5–8 W h/kg, which makes the nanoprodukt used commercially attractive against the background of rapid charging. Besides, it is worth noting that this nanoprodukt can withstand very high current densities exceeding 10^8 A/cm^2 [10, 11].

Considering the peculiarities of the voltmeter-ammeter method, a series of measurements was performed to determine characteristics and parameters

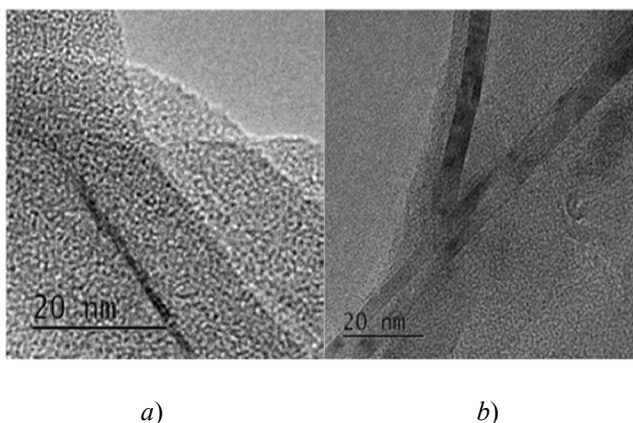


Fig. 8. Transmission electron microscopy (TEM) images of multi-layered (a) and few-layered (b) GNPs

of the developed EDL mechanism-based supercapacitor containing the graphene electrodes. During pilot studies, the main objective was to confirm its good performance ability. Cellulose paper (30 microns thick) was used as a separator, aluminum foil (0.2 mm thick) – as current collectors, acetonitrile-dissolved tetrabutylammonium tetrafluoroborate – as electrolyte, and a few-layered GNP/NPC nanocomposite – as electrode material. The latter was coated on the current collectors according to the paste-based technology.

Figure 9 demonstrates the supercapacitor performance measurement system, in which a B5-1820 power supply unit (ETALONPRIBOR, Mytishchi, Moscow Region, Russia) was employed as charger, and an AM-1097 multimeter (AKTAKOM, Moscow, Russia) was used for voltage and current measurements. During the capacitor charging up to the operating voltage, charge current I values were registered at a certain voltage U level, as well as at the time of changes in these parameters. To determine the performance, load resistors with different resistance R were connected to the supercapacitor by means of a R33 resistance box (ProfKIP, Mytishchi, Moscow Region, Russia). Over time, the discharge took place up to a certain voltage value, and discharge current values were registered within specific time interval $\Delta\tau$. Based on the $I(\tau)$ and $U(\tau)$ values obtained during the charging-discharging of the supercapacitor, current-voltage curves can be constructed in order to describe its behaviour (Fig. 10). As a result of the studies carried out, the operating parameters of the supercapacitor with the graphene-based electrodes were obtained (Table 4), provided that some assumptions were considered. Considering the results in Table 4, one can infer that using graphene-based electrodes Supercapacitors allows for charge/discharge mode implementation, provided that the time to charge

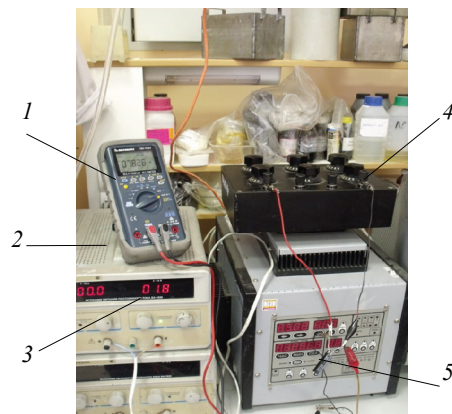


Fig. 9. A supercapacitor performance measurement system: 1 – multimeter, 2 – power supply unit, 3 – voltmeter, 4 – resistance box, and 5 – test specimen

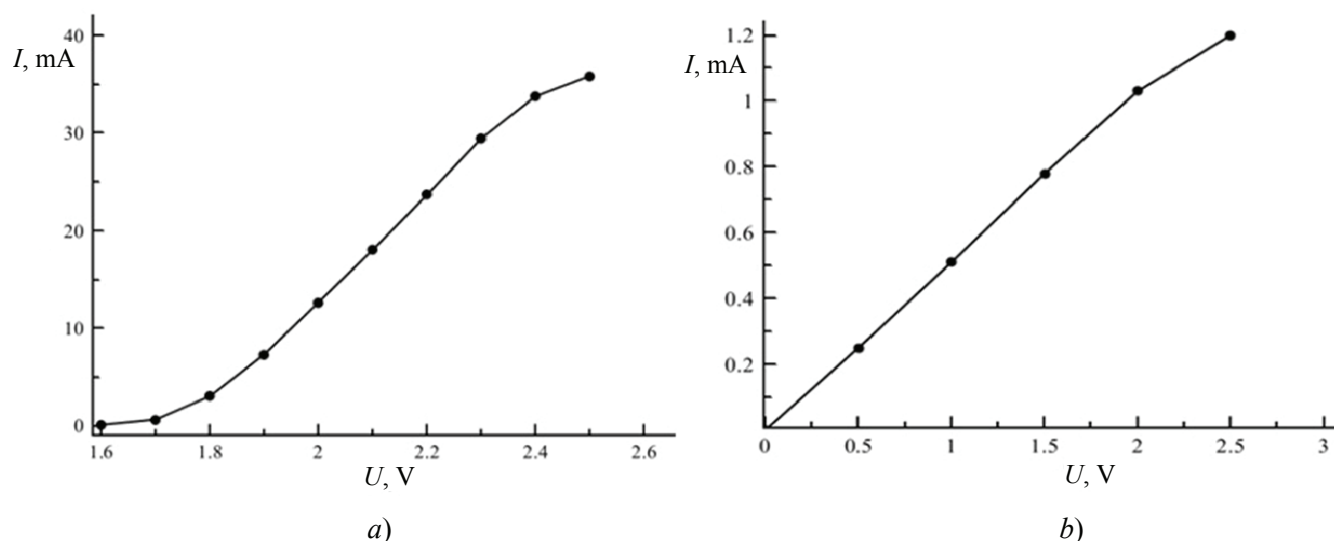


Fig. 10. Current (I)-voltage (U) curves obtained for the supercapacitor during the charge (a) and discharge (b) processes

Table 4

Characteristics of the supercapacitor

Parameter	Unit of measurement	Equation	Value
Capacitance	F	(2)	5.1
Discharging time	s	$\tau = -CR \ln \left(\frac{U_0}{U_1} \right)^*$	280
Charging time	s	–	5
Apparent energy	J	Equation (1)	15.9
Charge current	mA	Equation (3)	10–70
Charge voltage	V	$U(\tau) = U_0 \left(1 - \exp \left(-\frac{\tau}{CR} \right) \right)$	0.1–2.5
Self-discharge voltage	V	$U = U_0 \exp \left(-\frac{\tau}{Cr} \right)^*$	0.02–0.04
Operating weight	g	–	5.04

* U_0 and U_1 are the initial and final voltages, respectively;

** r is the internal resistance representing the sum of the electrode resistances.

the supercapacitor up to the capacitance value of 5.10 F is 5 s and the supercapacitor operating weight is 5.04 g. Further studies on the graphene-based electrode material for supercapacitors will be aimed at optimizing its morphological features for different types of electrolytes and operating conditions.

Conclusion

1. In the course of the present research, the operating parameters and performance characteristics of the supercapacitor with the graphene/NPC composite

material-based electrodes were determined, whereby it is possible to confirm its working efficiency.

2. It was found that a decrease in the charge current leads to an increase in the discharging time. Surely, under similar operating conditions, the capacitance depends on the current. If the discharge current is large, or if the supercapacitor is discharged for a long time, the resulting capacitance will be small.

3. Besides, it should be noted that the voltmeter-ammeter method employed herein makes it possible to study high-capacity supercapacitors and elucidate the external temperature effect on their operating conditions.

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