Development and investigation of a supercapacitor based on an aqueous electrolyte

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Abstract. The article is devoted to the development and research of a supercapacitor based on an aqueous electrolyte. The review of the current state in the field of energy storage is carried out. The processes occurring in the supercapacitor are considered. Sheets of paper with different carbon concentrations have been created. The design of the housing has been developed with the possibility of replacing the plates and electrolyte. This is an advantage in the process of conducting experiments. According to the results of the study, a prototype supercapacitor based on NaCl electrolyte with a capacity of 9F and a maximum output voltage of 1.2V is presented.

1. Introduction
A characteristic feature of scientific and technological progress is the introduction of electronics in all industries. Modern energy storage devices in the form of supercapacitors are widely used in electronic devices. Currently, several generations of capacitors with improving parameters have been created, which contributes to the further expansion of their scope of application. The first and second generation should include electrostatic and electrolytic capacitors. These capacitors have a small capacity from $10^{-12}$ to $10^{-6}$ F and are used in DC or AC circuits [1]. The rapid development of materials has led to the creation of the third generation of capacitors - supercapacitors.

At the initial stage of development, supercapacitors based on an aqueous electrolyte were widely used. As an example, we can cite the design of Howard Becker, who received the patent "Low-voltage electrolytic capacitor" [2]. The plates were two porous carbon electrodes. The capacitor had a capacity of 0.8 F and an output voltage of 0.5 V.

The first industrial sample of a supercapacitor called "Electrolytic capacitor with carbon paste electrodes" was created by Donald Boos in October 1970 [3]. The capacitor was made of two symmetrical tablet-shaped plates. Each plate consisted of a conductive carbon paste. The paste was obtained by drying the suspension. Next, 0.25 grams of paste was placed in a matrix and placed under the plunger. Since the plates did not have sufficient strength, a ring was used to hold them. Similar designs are found today in supercapacitors. We present the design of such a supercapacitor. Figure 1 shows the internal elements of an industrial design.

Figure 1. Internal elements of an industrial design of a supercapacitor
The plates have a round shape and are made of a suspension of carbon using a viscous binder material. A cellulose fiber membrane is installed between the plates. The sample shown has a capacity of 2F and a voltage of 1.25V.

In 1972, IBM employees Bert Hart and Richard Pikema received the patent "Electrochemical capacitor with a double layer" [4]. The device was a two-layer capacitor with low series resistance and high capacitance. The plates were made of activated carbon and separated by a highly porous 0.00127 cm thick gasket. The gasket was impregnated with highly concentrated electrolytes. The electrolytes were KOH or H₂SO₄.

The promising use of solid electrolytes makes it possible to obtain a wide range of operating temperatures, shock resistance, a long service life (25 years), as well as exceptionally high resistance to various other factors. Currently, quite a large number of works are devoted to the study of this direction. The paper [5] presents a recent review of achievements in the development of solid electrolytes.

It is worth noting that supercapacitors (ionistors) based on solid electrolyte RbAg₄I₅ were developed in the Soviet Union (Research Institute "Girikond") in 1975 [6-8]. The term "ionistor" was created in 1975 [9]. Later in the article, supercapacitors will be called by this term. The KI1-1 ionistors were produced at a voltage of 0.5 V and a capacity from 0.1 F to 50 F. The design was a cell of two electrodes with a solid electrolyte. The photo of the product is shown in Figure 2.

![Figure 2. Ionistor KI1-1](image_url)

The appearance of nanostructured materials made it possible to obtain a large surface area for charge accumulation. This has prompted the scientific community and industry to show interest in the development of ionistors for powering portable devices and electric vehicles. Scientists from the University of Florida have successfully developed a prototype ionistor, which is comparable in size to a lithium-ion battery [10]. Other studies are aimed at the use of graphene [11]. The use of graphene will make it possible to create lightweight and compact ionistors with the possibility of energy storage from 100 F to 600 F.

Ionistors are gradually changing a wide range of industries, including transportation, aerospace, and consumer electronics.

### 2. Problem statement

Renewable energy sources, electric vehicles, etc. use rechargeable batteries for energy storage and storage. Traditionally, lithium-ion batteries are used as energy storage devices. Therefore, it is worth considering the use of supercapacitors as a possible replacement or addition to lithium-ion batteries.

### 3. Theory

The ionistor consists of two electrodes, a membrane and an electrolyte. Filter paper, cellulose fiber paper, tissue paper, nylon mesh or porous plastics, polyamide, epoxy glass, fiberglass or any material with a high absorbent capacity can be used as a membrane. The structure of an ionistor is very similar to the structure of an electrochemical cell, but there is no charge transfer through an external circuit. Figure 3 shows a capacitor with two metal plates placed in an electrolyte.
If a voltage is applied between the plates, then positive charges will accumulate on the positive electrode, which attract an equal number of negative charges to the surface of the plates from the electrolyte due to Coulomb forces. The concentration of ions changes near the charged surface. Ions with the opposite charge are attracted to the electrolyte plates and ions having the same charge with the charge of the surface are repelled. As a result, a so-called double electric layer is formed in the plate/electrolyte system. At the same time, an equal amount of negative charges accumulates on the negative plate and forms another double electric layer.

Due to thermal fluctuations in the electrolyte solution, the ion layer "blurred" and spreads deep into the electrolyte. This blurred layer is called the diffusion layer. In the literature, this diffusion layer is described by the Gouy-Chapman theory [12].

The first ideas about a double electric layer were developed by Helmholtz [13]. He believed that a thin layer of ions is formed in the electrolyte, the charge of which is opposite to the charge of the surface of the solid and completely compensates for it.

A capacitor with two plates placed in an electrolyte has two double electrical layers. These two double layers are the basis of the capacitor and determine its efficiency.

Consider the formation of the electrode potential at the boundary of the plate/electrolyte. In electrochemistry, the electrode potential $\Delta \varphi_{p/e}$ is represented by the potential of the plate $\varphi_p$ and the potential of the diffusion layer of the electrolyte $\varphi_e$. The electrode potential arising between the surface of the plate and the adjacent layer of the electrolyte is determined by the expression

$$\Delta \varphi_{p/e} = \varphi_p - \varphi_e.$$  

Figure 4 shows the distribution of the electrode potential inside the diffusion layer.
To find the potential and concentration of ions in the diffuse part of the double layer, you can use the Poisson equation

$$\Delta \phi(x) = \frac{d^2 \phi}{dx^2} = -\frac{1}{\varepsilon \varepsilon_0} q(x),$$

(2)

where $\varepsilon$ is the dielectric constant of the electrolyte, $\varepsilon_0$ is an electrical constant, $q(x)$ is the charge density.

Using the Boltzmann distribution, we obtain the main equation of the diffuse part of the double layer – the Poisson-Boltzmann equation

$$\frac{d^2 \phi}{dx^2} = -\frac{1}{\varepsilon \varepsilon_0} \sum_i z_i e_0 c_i e^{-\frac{z_i e_0 q(x)}{kT}},$$

(3)

where $z_i$ is the charge of ions, $e_0$ is the charge of an electron, $c_i$ is the total concentration of the electrolyte solution, $k$ is the Boltzmann constant, $T$ is the temperature. We supplement the equation with the following boundary conditions

$$\phi(0) = \phi_0,$$
$$\phi|_{x\to\infty} = 0.$$

(4)

The exponential form of the potential distribution in the diffusion layer of the electrolyte is similar to the charge distribution inside semiconductors, near their interfaces. This distribution of carriers corresponds mathematically exactly to the shape of the distribution of ions in the diffuse layer on the side of the electrolyte.

The structure of the double electric layer is determined by the concentration of the electrolyte. With increasing concentration, the diffusion layer decreases, the double layer shrinks. The equivalent capacity of the double layer is formed by the sequentially connected Helmholtz capacity and the differential capacity of the diffuse layer

$$C_{equ} = \frac{1}{C_{H} + C_{diff}},$$

(5)

where $C_H$ is the Helmholtz capacity, $C_{diff}$ is the differential capacity of the diffusion layer. An equivalent electrical circuit is shown in Figure 5.

**Figure 5.** Representation of the equivalent capacity of the double layer

At a fixed electrolyte temperature and dielectric constant, the Helmholtz capacitance can be considered as a linear ideal capacitor with a constant capacitance when the voltage drops on it. The diffusion capacity is considered as a nonlinear quantity, since the capacity depends on the potential of the plates.

**Plates made of carbon materials**

The efficiency of an ionistor depends on the stored energy, so the capacity is one of the most important indicators for evaluating its effectiveness. The smooth surface of the electrode considered above is impractical for the design of an ionistor, since the value of the differential capacitance is less than 1F/m$^2$. With this capacity value, in order to obtain a capacity of 100 F, it is necessary to create a plate with an area of 100 m$^2$, so it is worth using carbon materials that allow increasing the surface area without significantly increasing the plates.
Let's consider carbon as a capacitor plate. Fine carbon powders are the most common material for creating ionistor plates. They can have a surface area of 1000 to 2000 m²/g. Note that the increase in the area of the plates is not limited to carbon. The material used must have a large porosity of the structure of at least 1 m²/cm³ and have good electrical conductivity. For example, as an alternative to carbon, nickel electrodes obtained by sintering or platinum black can be used. Figure 6 shows the plate of an ionistor with carbon filler.

![Diagram of the ionistor plate](image)

**Figure 6.** Device of an ionistor plate with a formed double electric layer

The pores and carbon channels must be permeable by the electrolyte ions to form a double layer of the plate/electrolyte to obtain the resulting capacity. The pores in the carbon and the porous channels in the layer determine the resulting capacity of the ionistor. The more pores the material has, the greater the permeable area for the electrolyte ions. However, the high porosity of the material increases the resistance of the carbon layer. In the industrial sample of the ionistor studied by the authors, shown in Figure 1, the resistance of the dry carbon layer was 452 Ω·cm². Therefore, at the design stage of the ionistor plates, it is necessary to conduct detailed studies and find the optimal ratio between the effective area and conductivity.

**Electrolytes**

The advantage of water electrolytes is a simple method of preparation, availability and low cost. In addition, water electrolytes are relatively safe and easily disposed of. Although water electrolytes have many advantages, they also have disadvantages. The main disadvantage is the small value of the output voltage of the ionistor, which is approximately 1.2 V. It is known that the energy of a charged capacitor can be calculated using the following expression

$$W = \frac{CV^2}{2},$$

where $C$ is the capacity, $V$ is the voltage between the capacitor plates.

Analyzing the above expression, it can be seen that when the voltage between the plates is doubled, the energy increases fourfold. Therefore, to increase the efficiency of the ionistor, it is necessary to increase the output voltage.

The next disadvantage is corrosion. Corrosion reactions reduce the internal conductivity of the element. One more disadvantage is the appearance of electrolysis with the release of oxygen and hydrogen when charging an ionistor based on an aqueous electrolyte.
Despite these disadvantages, water electrolytes should be used at the stage of research of new concepts and materials of ionistors. Electrolytes based on sulfuric acid, potassium hydroxide, potassium chloride, etc. can be used as ion sources. There are organic electrolytes [14]. Such electrolytes are most often used to create ionistors with a large output voltage range from 2.0 V to 2.7 V, compared to water electrolytes. Acetonitrile and propylene carbonate solvents are used in industrial samples. Electrolytes based on ionic liquids [15] are viscous melts of salts. This type of electrolytes has a high chemical stability, which allows you to get an output voltage of up to 5 V. The main disadvantage of ionic liquids is low conductivity at room temperature.

**Energy losses in the ionistor**

When charging a real ionistor, the current decreases over time not to zero, but to some finite value. This value is called the leakage current. The magnitude of this current is due to the presence of free ions. The leakage current causes the ionistor to self-discharge. Dividing the output voltage by the leakage current, the value of the resistance is found

\[ R_{LR} = \frac{V}{I_{LR}}. \]  \hspace{1cm} (7)

The leakage resistance corresponds to the active resistance connected in parallel between the plates. The amount of leakage resistance depends on the voltage on the plates. Figure 7 shows an equivalent ionistor circuit.

\[ Z = R_{ESR} - j \frac{1}{2\pi f C_i}, \]  \hspace{1cm} (8)

where \( f \) is the frequency of alternating current in Hz, \( C_i \) is the capacity of the ionistor.

The series resistance limits the output power and increases the charge and discharge time of the ionistor. In large-capacity industrial samples, the value of this resistance is 0.3 mOhm – 0.8 mOhm [16].

**DEVELOPMENT OF A CELL BASED ON AN AQUEOUS ELECTROLYTE**

As an experimental prototype, an ionistor cell was manufactured using a water-based electrolyte. Figure 8 shows the developed cell and a three-dimensional model.
The design of the case consists of two halves. A metal substrate with a carbon layer is placed in the case. Recesses for the output electrodes of the ionistor are made in each half.

At the initial stage of designing the plates, self-made sheets of paper with different concentrations of graphite were used. The paper served as a binding material, which made it possible to make almost any form of plates. Figure 9 shows graphite paper with different carbon concentrations.

The resistance of the carbon layer of the resulting paper was too large and ranged from 1 kΩ · cm² to 10 kΩ · cm². Experiments were conducted with different concentrations of carbon in paper, but no significant success was achieved. In further studies, a compressed graphite layer was used.

The plate of the developed sample is made as follows. A layer of carbon suspension with a size of 40x30x1.5 mm is applied to the metal substrate. The suspension is made by mixing 3 grams of graphite and 2.8 grams of 30% aqueous electrolyte based on NaCl. To provide the necessary viscosity during molding, a mixture of polypeptides obtained by partial hydrolysis of insoluble collagen protein was added to the suspension. The manufactured plates of the ionistor are shown in Figure 10.
The plates separated by a membrane made of regenerated cellulose were placed in the case and screwed around the perimeter. The membrane was previously impregnated with an electrolyte. The developed ionistor cell has a weight of 28 grams and dimensions of 60x50x6.4 mm.

4. Results experiments

The charge of the ionistor was produced by a constant voltage of 3V. Before charging, the ionistor had a zero voltage. During the charging process, the initial and final charging current was recorded, corresponding to the expression

$$I_{ch} = \frac{E}{R_{ESR} + R_{LR}} + \frac{E \cdot R_{LR}}{R_{ESR} (R_{LR} + R_{ESR})} \cdot e^{\frac{R_{ESR} + R_{LR}}{R_{ESR} R_{LR} C_i} \cdot t}, \quad \text{(9)}$$

where $R_{ESR}$ is an internal series resistance, $R_{LR}$ is the leakage resistance, $E$ is the voltage of the power supply, $C_i$ is the capacity, $t$ is the current time.

The value of the voltage on the ionistor is represented by the expression

$$V_f = \frac{R_{LR} \cdot E}{R_{ESR} + R_{LR}} \left(1 - e^{\frac{R_{ESR} + R_{LR}}{R_{ESR} R_{LR} C_i} \cdot t}\right). \quad \text{(10)}$$

During the experiments, 6 charge and discharge cycles of the ionistor were performed. The discharge was performed for an active resistance of 50 Ω. The time of each discharge cycle was 7 minutes. Figure 11 shows diagrams of the electrical values of voltage, current and power measured during the experiment.

![Figure 11. Voltage on the ionistor (a). Current and active power (b)](image)

The voltage diagram presented should be divided into three sections. The first section corresponds to the voltage value of the power supply. The second section shows self-discharge. The third section corresponds to a discharge for an active resistance of 50 ohms.

The capacity of the developed ionistor was determined by the expression

$$C_i = \frac{2 \cdot t_d \cdot (V_i - V_f)^2}{R_L \cdot (V_i^2 - V_f^2)}, \quad \text{(11)}$$

where $t_d$ is the discharge time, $V_i$ is the initial voltage, $V_f$ is the final voltage, $R_L$ is the load resistance.
Figure 12 shows a family of voltages obtained on an ionistor during discharge and a theoretical and experimental discharge curve for the calculated capacitance value is constructed.

![Figure 12](image-url)  
**Figure 12.** The family of discharge voltages (a) and comparison of the experimental voltage with the calculated value (b)

The theoretical curve of the ionistor discharge was found by the expression

\[ V_{C_i} = V_i \cdot e^{-\frac{t_i}{R_L C_i}} \]  
(12)

where \( t_i \) is the discharge time, \( V_i \) is the initial voltage, \( R_L \) is the load resistance, \( C_i \) is the capacity ionistor.

Figure 12 shows that the results of the calculation and the experiment are practically the same. The deviation is due to the fact that the expression does not take into account the internal series resistance and the internal parallel resistance of the ionistor. The results of calculating the ionistor capacitance and experiments for each cycle are presented in Table 1.

| Cycle | Initial charge current \( I_1 \), mA | Final charge current \( I_f \), mA | Initial voltage \( V_i \), V | Final voltage \( V_f \), V | Discharge time \( t_d \), s | Capacity \( C \), F |
|-------|-------------------------------------|---------------------------------|----------------|----------------|--------------------|------------------|
| 1     | 109                                 | 60                              | 0.588          | 0.203          | 440                | 8.57             |
| 2     | 89                                  | 48.5                            | 0.625          | 0.177          | 440                | 9.83             |
| 3     | 73.8                                | 42.7                            | 0.613          | 0.178          | 440                | 9.68             |
| 4     | 63.2                                | 37.1                            | 0.594          | 0.174          | 440                | 9.63             |
| 5     | 59.7                                | 34.2                            | 0.602          | 0.175          | 440                | 9.53             |
| 6*    | 76.5                                | 36.2                            | 0.659          | 0.157          | 440                | 10.83            |

* After partial renewal of the water electrolyte

5. Discussion of results

After analyzing the table data from the second cycle, it can be seen that the capacity of the ionistor, as well as the initial and final charging current, decreased with each cycle. This is due to the evaporation of the electrolyte during charging. Partial renewal of the electrolyte led to an increase in the charging current and the resulting capacity*. The highest charging current and the lowest capacitance value are obtained on the first cycle.

6. Conclusion

A prototype ionistor was developed and studies of water electrolytes based on \( C_6H_5O_7 \), \( H_2BO_3 \), \( NaHCO_3 \) and \( NaCl \) were carried out. During the tests, it was found that electrolytes based on \( C_6H_5O_7 \), \( H_2BO_3 \), \( NaHCO_3 \) are unsuitable for use. Ionistors using these electrolytes had a small capacity, a large
leakage current, a large internal resistance, and as a result, a rapid self-discharge. Of the above electrolytes, the best results were shown by an ionistor cell based on NaCl electrolyte, which has a capacity of 9F and a maximum output voltage of 1.2 V. In order to possibly increase the capacity, it is worth considering electrically conductive high-purity carbon black of the brands OMCARB C40, OMCARB C140, OMCARB CH85.

Ionistor plates made of carbon materials have a chaotic structure. Thus, the pores and channels of carbon plates can be represented as fractal surfaces and their influence on the formation of a double layer can be studied in order to improve the characteristics of the ionistor.

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