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ELECTROCHEMICAL PROPERTIES OF THE ALUMINIUM FILMS WITH GRAPHENE-BENTONITE COVERING.

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The changes in the conductivity type, capacitance value, and equivalent circuit models of the composite materials, taking into account the impact of graphene-bentonite covers on the aluminum carrier, are discussed. The EIS spectra of the pure aluminum foil lay in the positive reactive resistance domain characterized by the impact of the inductance. The conductivity value is 3.9± 0.1 Sm/cm with decreasing electrostatic capacitance from 0.08 to 0.02 F/g in the frequency range 10-1÷104 Hz. Applying the graphene-bentonite coating changes types of conductivity, from electron type to ionic type. Conductivity has two orders smaller value, and rises with increasing the frequency from 0.014 to 0.02 Sm/cm. The electrochemical equivalent circuit in the case of covering by graphene-bentonite mixtures is the R-CPE parallel circuit has characteristic of the porous electrodes in a supercapacitor. Presence of a dielectric component (bentonite) on the foil surface limits the polarization of composite material and decreases the capacitance value.

Keywords: graphene, bentonite, aluminium foil, composite material, conductivity, capacity.

INTRODUCTION. Graphene shows many interesting optical, electronic, and mechanical properties because of its two-dimensional (2D) crystal structure. The high speed of charge moving in graphene with a 2D crystal lattice is the base of the high conductivity [1]. That is why, graphene has interesting electrical properties that can be use in modern energy conversion devices.

Nowadays, the main requirements for batteries and supercapacitors are long lifetime and fast charging rate during recharging. Supercapacitors incorporated inside the batteries are used to comply with high speed charging rates of the device. The properties of supercapacitors are low maintenance, low self-discharging, rising power capabilities, a charge-discharge process occurring in seconds, and long cyclic life [2]. Also, supercapacitors come out with a higher energy density compared to conventional capacitors. Electrodes of the supercapacitor are made of porous carbon, but not long ago, researchers started to investigate using graphene in elements of electrodes as covering on the aluminum conductive carrier [2].

On the other hand, aluminum is widely used in electrical power distribution systems, thanks to its advantages such as low density, high conductivity, and in expensive cost [3]. The rising of it selectrical capacitance and safety of start conductivity would generate greater economic benefits because of reduced line electrical losses in large power grids.

The active chemical property of aluminum makes it difficult to upgrade it selectrical conductivity by refinement and purification [4]. Furthermore, alloying is necessary for most of aluminum's practical applications to enhance its mechanical strength, but alloying is detrimental to high electrical conductivity because of more electron scattering centers [5, 6]. Thus, achieving electrical conductivity at a level of pure aluminum in practical applications is a major challenge. One of the main ways to solve this problem is the use of variouscovers, especially covers consisting of 2D structures and 3D structures such as graphene-bentonite mixtures [7, 8].

The target of this work is to detect the effect of a graphene-bentonite mixture on the electrical properties of the conductive aluminum foil carrier.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Natural bentonite from Dashukiv, Ukraine was used as the main 3D matrix of the composite for covering (Table 1).

Table 1.

The main physical and chemical properties of the bentonite.

Compound, mass %	Structure	Surface area, m^2/g
SiO_2 – 58.3; Al_2O_3 – 12.8; Fe_2O_3 – 6.8; CaO – 1.45; MgO – 1.6; Na_2O+K_2O – 0.5	Layered Grain size 50–110 nm	36±2

Graphene C-750 (Sigma–Aldrich) with a molecular weight of 12.01 a.u. was used as an electroconductive component of the composite. Such kind of graphene has a platelet shape and is composed of short stacks of graphene sheets with a size of 20–50 nm. For preliminary preparation, graphene was treated with 95% ethanol to remove absorbed water from the volume before mixturing.

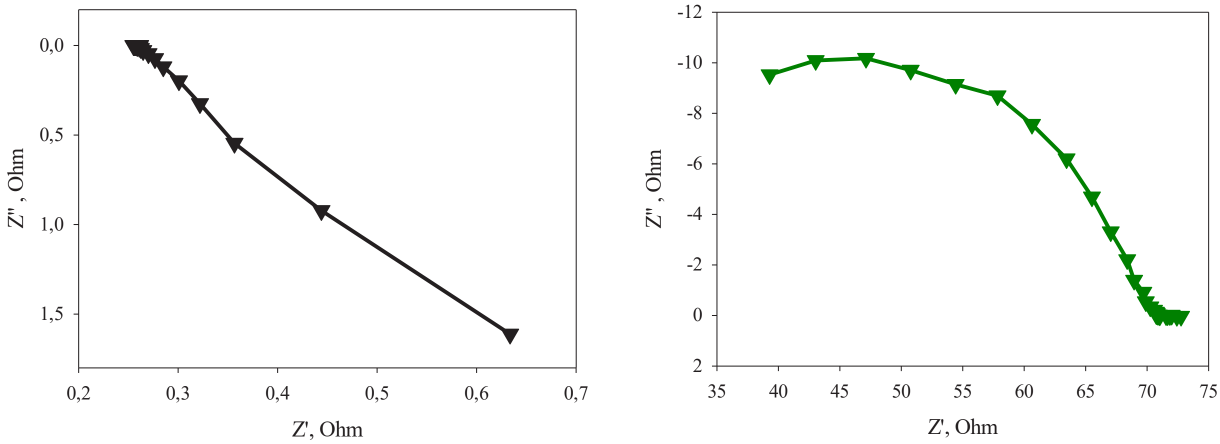
The covering mixture for the aluminum carrier consisted of 45% natural bentonite, 45% graphene as a conductive component, and 10% polyvinylidene fluoride (PVDF) binder Solef 6020 (Solvay, Belgium). Covers were prepared using slurry technology. For this the components of the mixture in the calculated quantities were added in portions to a previously prepared 7% solution of the binder in dimethylacetamide, and homogenized on a high-speed mixer at a stirring speed of 2500–3000 rpm for 40 minutes.

After that, the suspension was subjected to ultra sonic dispersion for a total duration of 5 min. Next, the finished suspension was applied using a Doctor Blade applicator to a 7–8 μkm thick aluminum foil tape (current collector). The coated foil was dried at a temperature of 60–70 °C for 1 hour, rolled on rollers, compacted by 25–30%, and cut into strips measuring 100 mm by 22 mm.

The impedance spectra of the samples were recorded in a two-electrode cell (Fig.1) on an Autolab 30 PGSTAT301N MetrohmAutolab electrochemical module in a two-electrode cell equipped with a FRA (Frequency Response Analyzer) module in the frequency range 10^{-2}–10^{6} Hz. The results were processed using Nova 2.1 and ZView2 software.

The impedance spectra of aluminum foil and foil with graphene-bentonite coating have significant differences in the form of impedance spectra and their electrochemical equivalent circuits (Fig. 2, 3, 6). The EIS spectra of the pure aluminum foil lay in the positive range of reactive resistance characterized by the impact of the inductance.

Fig. 1. The electrochemical analysis set-up.



a b

Fig. 2. Impedance spectra of Al foil (a), Al foil covered by graphene-bentonite mixture (b).

The electrochemical equivalent circuit of this sample is close to the equivalent circuit of the oscillatory circuit. The main difference in these circuits is changing the capacitance (C) element onto the constant phase element (CPE) element (Fig. 4, Table 2).

Fig. 3. Equivalent circuits of Al foil.

Table 2.

Calculations of equivalent circuits of Al foil

Element	Freedom	Value	Error	Error %
R3	Free(±)	0.2601	0.0009	0.35
CPE1-T	Free(+)	1.7 E5	62841	37.62
CPE1-P	Free(±)	-0.760	0.043	5.633
L1	Free(±)	2.11E-7	3.3E-8	15.764

Weighted Sum of Squares: 6.3843

Such elementcan be characterized by the element of supercapacitors with non-ideal, CPE behavior, and the capacitance of CPE circuits exhibits a power law dependence on potential sweep rate based on the CPE coefficient n.

$$Z_{CPE} = A^{-1}(j\varphi)^{-n}. \quad (1)$$

Reactive resistance X can include capacitive and inductive components that depend on the frequency of the alternating current supply circuit

$$X_L = \omega L, X_c = 1/\omega C. \quad (2)$$

The addition of reactive components is subject to complex rules. For the serial connection of L and C in the case of an oscillatory circuit, the expression will be valid:

$$Z = \sqrt{X^2 + R^2}; \quad (3)$$

$$X = \omega L - 1/\omega C. \quad (4)$$

According to eq. 4 for receiving a positive reactive resistance the capacitance should be high and give the possibility to ignore the value of the 1/ωC in eq. 4.

The calculations of the capacitance value from impedance spectra (Table 3) fully agree with this statement.The electrostatic capacitance decreases from 0.08 to 0.02 F/g in the frequency range $10^{-1}\div10^{4}$ Hz.

The conductivity value is 3.9± 0.1 Sm/cm with decreasing electrostatic capacitance from 0.08 to 0.02 F/g in the frequency range $10^{-1}\div10^{4}$ Hz. Such behavior is more special for materials with metallic (electron) types of conductivity (Fig. 4).

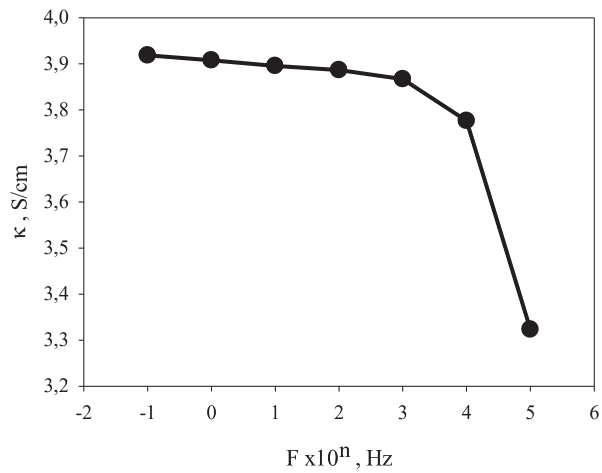


Fig.4. Dependence of electrical conductivity on frequency of the Al foil.

The appearance in the equivalent circuit of the CPE element is a formal description of a complex system, which gives only an external, qualitative appearance, without reflecting the physical essence of the phenomenon. In this case, CPE is the simplest model, which only formally approximates a more complex distribution of object parameters, and could be connected with the presence of aluminum oxides which take part in the formation of the porous system on the foil surface, and the mechanical deformation of the foil.

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Applying the graphene-bentonite coating changes the type of conductivity from electron type to ionic type.

Table 3

Capacitance data in the frequency range 10^2-10^4

F, Hz	C,F /g Al	C,F/gAl + Graphene with bentonite
1484,9710	0,0195	1,3978e-5
849,7515	0,0418	2,6147e-5
486,2609	0,0751	3,7145e-5
278,2561	0,0710	6,7204e-5
159,2297	0,0840	1,3327e-4
91,1166	0,0846	1,8769e-4

In case of the ionic type, the conductivity rises with increasing frequancy, butconductivity has two orders smaller value, and rises with increasing the frequency from 0.014 to 0.02 Sm/cm (Fig. 5).

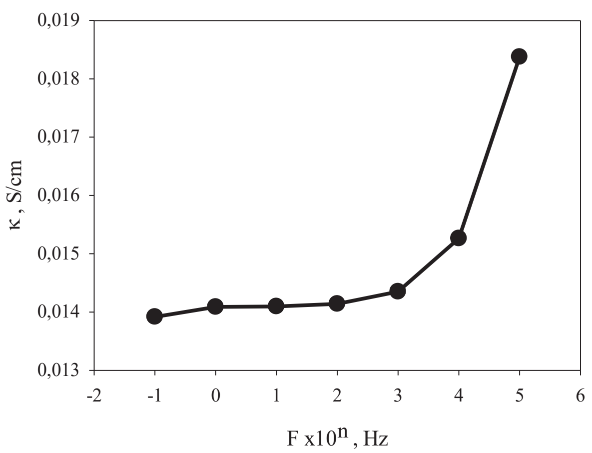

Fig. 5. Dependence of electrical conductivity on frequency of Al foil covered by graphene-bentonite mixtures.

The view of the impedance spectrum (Fig. 2 b) and the electrochemical equivalent circuit (Fig. 6, Table 4) also change in the case of covering by graphene-bentonite mixtures. It has a view that looks like the ZARC element (R-CPE parallel circuit) for porous electrodes of a supercapacitor [9, 10].

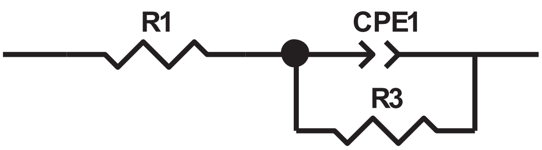

Fig. 6. Equivalent circuits of Al foil covered by covered by graphene-bentonite mixture.

Table 4.

Calculations of equivalent circuits of Al foil covered by covered by graphene-bentonite mixture.

Element	Freedom	Value	Error	Error %
R1	Free(±)	23.88	1.510	6.32
CPE1-T	Free(±)	1.378E-5	1.63 E-6	11.87
CPE1-P	Free(±)	0.5207	0.0124	2.40
R3	Free(±)	47.56	1.551	3.26

Weighted Sum of Squares: 6.3843

The presence of such a circuit exhibits the electrochemical double layer capacitors (supercapacitors) with non-ideal CPE element behaviour, and spectra fully lays in a negative value of the reactive resistance [9]. The presence of a dielectric component (bentonite) on the foil surface limits the polarization of composite material (Fig. 2. b) and decreases capacitance value (Table 3). Received equvalent model is very close to model of the porous electrode in the self-discharging conditions [10].

CONCLUSIONS. The experiment and calculations of conductivity and capacity of Al-graphene-bentonite composites established that the application of the graphene-bentonite coating forms an additional surface capacity that participates in the preservation of the electrical energy and protects the conductive carrier from electrical loss under the oxidation on the open air. Such an effect can be received due to the formation of the bentonite-graphene porous electrode with a self-discharging ability.

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ЕЛЕКТРОХІМІЧНІ ВЛАСТИВОСТІ АЛЮМІНІЄВИХ ПЛІВОК ІЗ ГРАФЕН-БЕНТОНІТОВИМ ПОКРИТТЯМ

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Обговорено зміни типу провідності, значення ємності та моделі еквівалентної схеми композиційних матеріалів з урахуванням впливу графен-бентонітових покриттів на алюмієвий носій. Спектри EIS чистої алюмінієвої фольги лежать в області позитивного реактивного опору, що характеризується впливом індуктивності. Величина електропровідності 3,9±0,1 См/см при спадній електростатичній ємності від 0,08 до 0,02 Ф/г в діапазоні частот 10-1÷104 Гц. Нанесення графен-бентонітового покриття змінює типи провідності, від електронного до іонного. Електропровідність має на два порядки менше значення і зростає зі збільшенням частоти від 0,014 до 0,02 См/см. Електрохімічна еквівалентна схема у випадку покриття графен-бентонітовими сумішами – паралельна схема R-CPE має характеристику пористих електродів у суперконденсаторі. Наявність на поверхні фольги діелектричної складової (бентоніту) обмежує поляризацію композиційного матеріалу та зменшує величину ємності.

Ключові слова: графен, бентоніт, алюмінієва фольга, композитний матеріал, електропровідність, ємність.

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