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QUANTUM ACCUMULATION OF ELECTRICAL ENERGY AT INTERFACIAL BOUNDARIES IN HETEROPHASE INORGANIC / ORGANIC CLATHRATES

Vitalii Maksymych [1], Roman Shvets [1], Fedir Ivashchyshyn [1,2]

[1]Lviv Polytechnic National University, Lviv, Ukraine

[2]Politechnika Czestochowska, Czestochowa, Poland

vitalii.m.maksymych@lpnu.ua, fedir.o.ivashchyshyn@lpnu.ua

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Abstract. The work is devoted to the current problem of finding new ways and mechanisms of high-density electric energy accumulation. As a result of the conducted researches the system which allows to accumulate an electric charge at the expense of quantum effects and the phenomena without use of chemical reactions is offered. The basic idea was to form a material with a colossal area of the inner active surface with a sharply anisotropic chemical bonding character. Accordingly, the main goal was to create and study electrode materials based on intercalant heterophase structures with different types of hierarchy, capable of storing electrical energy at the quantum level. Based on the results of impedance spectroscopy, it was found that the obtained clathrate structures are promising for use as a cavitand electrode in a quantum battery, and, most importantly, can significantly increase its capacity.

Keywords: supramolecular ensembles, clathrates, nanohybrids, gallium selenide, impedance spectroscopy, quantum batteries.

1. Introduction

The current situation in autonomous power engineering rapidly encourages scientists to seek for new scientific and technical solutions to the problem of conversion and storage of electric energy. Today, there is no doubt that new systems should be created, in particular those being able to work at a quantum level. Due to the fact that quantum mechanisms of accumulation of electric charge are faster than others, a battery developed on this basis will have an important advantage over electrochemical systems, that is, its charging will be an order of magnitude faster. A promising area of research in this regard is the synthesis of heterostructured nanocomposite materials which would have a large interphase surface and provide anisotropy of electrical conductivity depending on the direction. For such structures there is a requirement to achieve large values of dielectric constant ($> 10^5$) in combination with the tangent of the angle of electrical losses less than 1, especially for frequencies less than 10^{-2} Hz. Under the above conditions, the possibility of accumulation of injected electrons at the interface of nanoheterophases was theoretically predicted [1, 2], and the corresponding heterostructures will operate as a quantum accumulator. For example, experts from Illinois University (USA) proposed a system of vacuum nanotubes and called it a "digital quantum battery". However, today it is presented only in the form of theoretical calculations [3]. Researchers from the USA proposed to use a thin dielectric layer with a large contact area which was implemented in nanocomposites of ceramics and glass. The value of their dielectric constant was $\varepsilon = 2 * 10^6$ [4].

The fact of the need to form new nanocomposite materials that would allow the implementation of quantum mechanisms of electric charge accumulation is obvious. A promising direction is the application of the clathrate principle of construction of substances, namely the synthesis of complex architectures such as "host-guest" at the atomic-molecular level. In such systems it is possible to achieve not only targeted change of the initial atomic-molecular structure and force fields of host materials, but also to form certain structures in the crystal field at the atomic-molecular level and, in the future, whole functional blocks. Created by the authors of this paper, the clathrates based on this principle testify the prospects of such an approach. For example, in the intercalation-formed clathrate $GaSe<CS(NH_2)_2<SmCl_3>>$ the principle possibility of accumulation of electric energy at the quantum level was realized and the effect of “spin-battery” was fixed [5]. The encapsulation method was used to create clathrate $MCM\text{-}41<SmCl_3>$ in which the occurrence of the effect of thermal EMF was recorded [6, 7].

Thus, the goal of this work is to develop the scientific basis for the formation of intercalate heterophase structures with different nano-limited geometry, composition and level of hierarchy of architecture, aimed at the conversion and accumulation of electrical energy at the quantum level.

2. Conceptual bases and methods of an experiment

A photosensitive gallium selenide (*GaSe*) single crystal was used as a semiconductor quasi two-dimensional crystal matrix (Fig. 1). Gallium selenide belongs to a broad class of A_3B_6 semiconductors with a layered structure. It should be noted that GaSe single crystals grown by the Bridgmen-Stockbarger method had p-type conductivity. The band gap (according to optical data) was 2.02 eV. The layered structure is caused by the presence of different types of chemical bonds along the layers (covalent bond) and between the layers (Van der Waals bond). Therefore, due to this structure, the anisotropy of properties, in particular electrical conductivity, occurs. Also, as it is well known [8], single crystals are characterized by the presence of "guest" positions which are oriented perpendicular to the crystallographic C axis of the regions of weak Van der Waals forces.

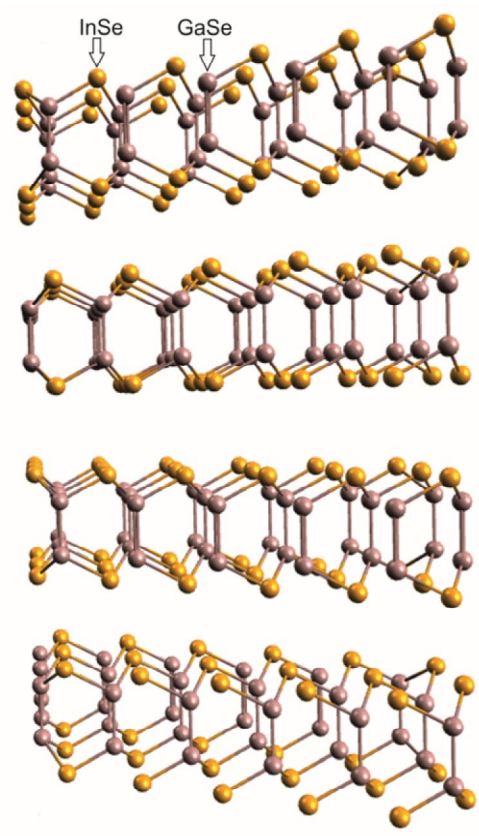

Fig. 1. Spatial representation of the GaSe structure

Samarium trivalent chloride was used as an inorganic guest component (Fig. 2) [9]. The choice of $SmCl_3$ as a guest component was based on its use in practice in the synthesis of organometallic compounds of samarium with paramagnetic properties using nanosized particles. This makes it possible to control the properties of encapsulates (for example, a combination of optical and magnetic properties), mainly to ensure their high sensitivity to external physical fields.

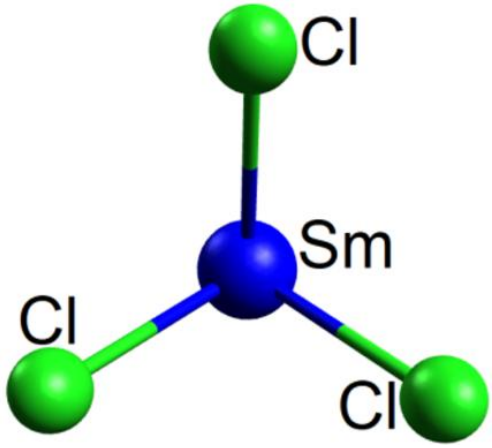

Fig. 2. Chemical formula of samarium chloride (III)

Thiourea ($CS(NH_2)_2$) being one of the simplest thioamides was chosen as the organic guest component and organic host for the inorganic guest $SmCl_3$ (Fig. 3).

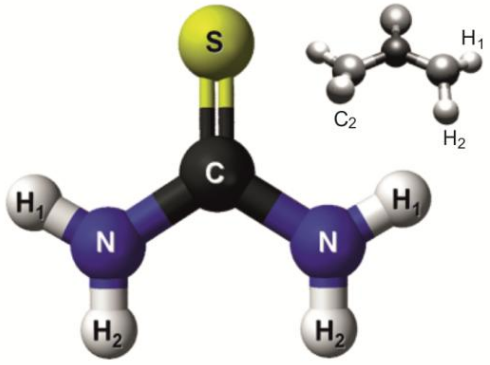

Fig. 3. Molecular structure of thiourea

Due to its nonlinear optical properties, thiourea is now widely used in the electronics industry, for example, as polarizing filters, electronic optical shutters, electronic modulators, and as a component in electro-optical and electro-acoustic devices. In addition, thiourea is widely used in various electrochemical processes [10]. For inclusion compounds, a thiourea molecule forms the crystal structure of the host, which has unidirectional channels that do not intersect. Guest molecules can be located inside these tunnels. For most guest molecules, the structure is rhombohedral (Fig. 4) and guest molecules are oriented randomly. In many cases, this rhombohedral structure is converted into a monoclinic structure at low temperatures. The inner surface of the thiourea tunnel is far from cylindrical, there is a contraction (diameter <5.8 Å) and extension (diameter <7.1 Å) along the tunnels. It is often advisable to

consider the structure of the host thiourea as a "cell" type rather than a "tunnel" type. Thiourea inclusion compounds are commensurate with guest molecules preferably located in the cells, which corresponds to two guest molecules per unit repetition of the distance of the thiourea structure along the tunnel and a guest / thiourea molar ratio of 1:3 [11]. The dipole moment of thiourea is $18.86 * 10^{-30}$ C *m and its relative dielectric constant is 2,224 [12].

In order to study structures with different degrees of hierarchy, clathrates $GaSe<CS(NH_2)_2>$ i $GaSe<CS(NH_2)_2<SmCl_3>>$ were formed by cavitation of guest content according to the "host-guest" type. The technology of synthesis and the properties of the obtained clathrates are studied in detail and described in [5].

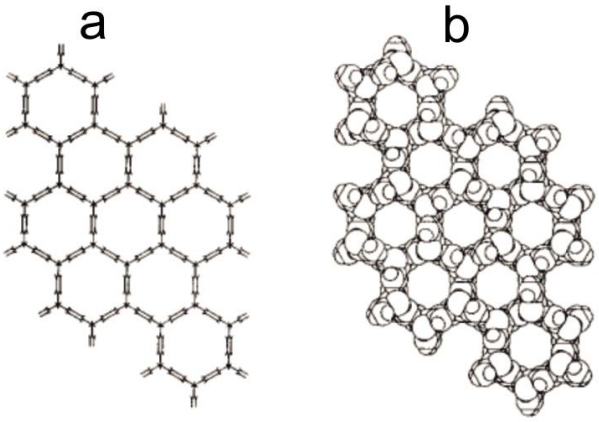

Fig. 4. Rhombohedral structure of the thiourea host without guest molecules: a) nine complete tunnels with atomic radii equal to zero; b) nine complete tunnels with van der Waals radii of atoms. The distance between the centers of adjacent tunnels is about 9.2 Å

However, in order to improve the technology of forming and storing electricity at the quantum level, a new approach to ensure a high value of capacitance density was developed being based on the idea of using a huge area of the inner active surface of materials with extremely anisotropic chemical bonds. It can be realized by non-exfoliative expansion of Van der Waals regions of materials with a layered crystalline structure.

Schematically, the device for quantum accumulation of electrical energy is shown in Fig. 5. The fourfold expanded single crystal of gallium selenide (2) was used as the active matrix for the capacitor. The electrolyte (3) was composed from gamma-butyrolactone, N-methylpyrrolidone (mixed solvent), maleic acid and trimethylamine in the ratio of 80 (70%: 30%)%: 10%: 10% (wt%) and acted as a current collector, washing the inner surface. l stands for an inverse electrode. The electrolyte and the inverse electrode are selected on the basis of the technology of aluminum capacitors, i.e., the shunting of the capacitance that occurs at the interface between the electrolyte and the aluminum inverse electrode is provided.

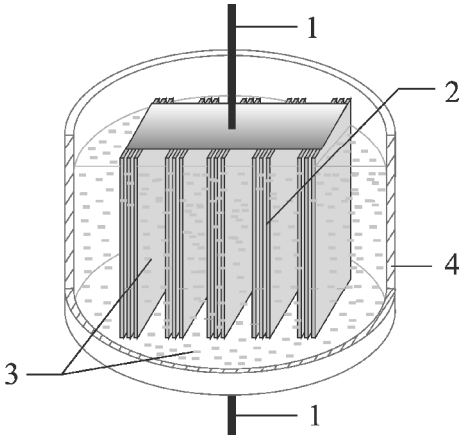

Fig. 5. Device for quantum accumulation of electrical energy

X-ray studies were performed in Cu-Kα (λ = 1.5419 Å) radiation monochromatized by reflection from the plane (111) of the Ge single crystal in the mode of the X-ray beam passage. The use of a perfect Ge single crystal and a collimating system of primary and scattered radiation made it possible to measure low-angle scattering spectra starting from the values of the wave vector s = 0.01 Å-1. A slit 0.1 mm wide corresponding to the spatial separation D(2θ) = 0.03 was installed in front of the detector. The registration of scattered radiation was performed in the scan mode in the angular range of 0.25–4.00 with a step of 0.05 and exposure time of 100 s.

The impedance measurements of the test cell were performed in the frequency range of $10^{-3} \div 10^{6}$ Hz using the measuring complex "AUTOLAB" of the ECO CHEMIE company (the Netherlands) equipped with computer programs FRA-2 and GPES. Removal of doubtful points was performed by the Dirichlet filter [13, 14]. The frequency dependences of the complex impedance Z were analyzed in the environment of the software package ZView 2.3 (Scribner Associates). Approximation errors did not exceed 4%. The adequacy of the constructed impedance models of the experimental data package was confirmed by the completely random nature of the frequency dependences of the residual differences of the first order [13, 14].

3. Results and discussion

In order to compare the properties and establish patterns, the electrochemical cell shown in Fig. 5 with electrodes based on the original *GaSe* single crystal, 4-fold expanded GaSe matrix, clathrate formed on the

basis of 4-fold expanded GaSe matrix - *GaSe<CS(NH$_2$)$_2$>* and clathrate of the hierarchical architecture of the guest component – *GaSe<CS(NH$_2$)$_2$<SmCl$_3$>>* was investigated.

To establish the mechanisms of accumulation of electric charge, impedance investigations of the cell being studied were performed (Fig. 5). Figure 6 presents Nyquist diagrams for the depicted device with unexpanded and 4-fold expanded *GaSe* single crystal. It is evident that for the original unexpanded *GaSe* single crystal the impedance hodograph takes the form typical of Faraday processes of electric energy accumulation. However, the use of a 4-fold expanded *GaSe* single crystal leads to a significant change in the behavior of the impedance hodograph, which takes the form typical of the capacitive accumulation of electrical energy inherent in supercapacitors.

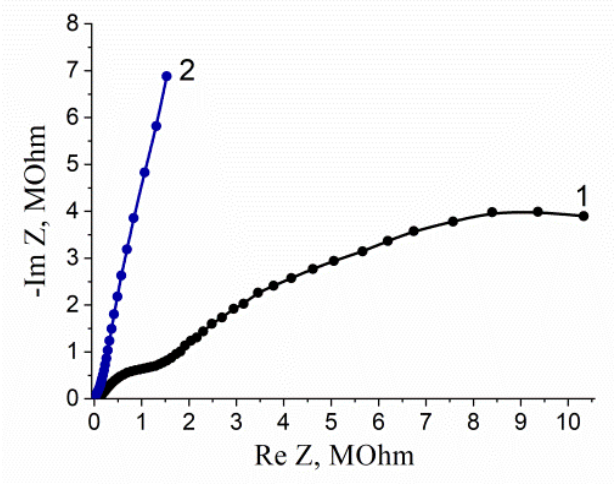

Fig. 6. Nyquist diagrams for the device of quantum accumulation of electric energy with an electrode of unexpanded (1) and expanded (2) gallium selenide.

From the point of view of practical application of the results obtained, it is important that a tangent of an angle of electric losses should possess the values less than unit (tgδ <1) in the infra-low frequency range. For this purpose, the frequency dependences of tgδ for the output *GaSe* single crystal and the 4-fold expanded one have been plotted and are presented in Fig.7.

As it can be concluded from the dependence of tgδ (ω), this condition is satisfied for the 4-fold expanded *GaSe* single crystal. With the use of the experimentally measured values of the complex resistance of monochrystal, the values of capacitance by the formula $C = \frac{1}{j\omega X_C}$ are calculated. A corresponding dependence C (ω) is presented in Fig. 8. For a 4-fold expanded *GaSe* single crystal, the specific capacitance reaches high values, namely, 10 F / g at a frequency of 10^{-3} Hz (Fig. 8).

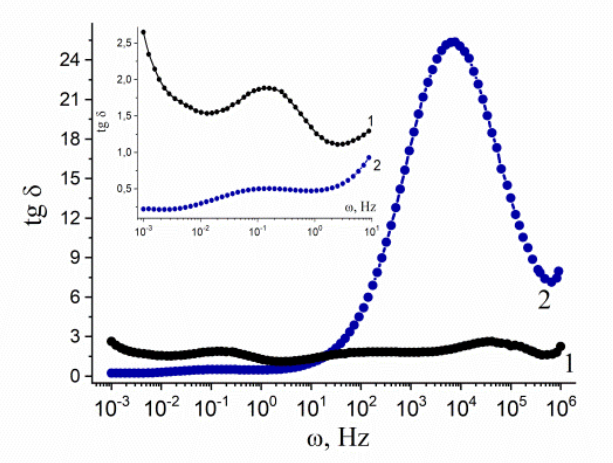

Fig. 7. Frequency dependences of the tangent of the angle of electric losses of the device of quantum accumulation of electric energy with an electrode of unexpanded (1) and 4-fold expanded (2) GaSe

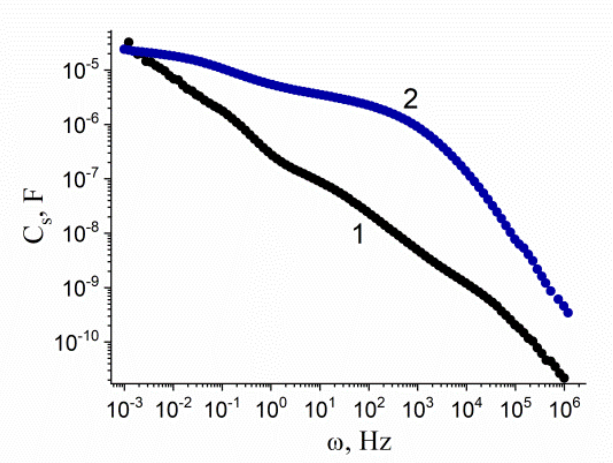

Fig. 8. Frequency dependences of the capacity of the quantum storage device of electric energy with an electrode of unexpanded (1) and expanded (2) gallium selenide

With the transition to DC, this value will obviously increase. Thus, the above results confirm the effectiveness of the proposed approach. Moreover, the possibility of forming dielectric nanofilms on intracrystalline surfaces will, in theory, significantly increase the specific capacitance by increasing the dielectric constant. It is also important that this allows combining large values of dielectric constant with high surface area. The accompanying important conclusion which follows from Fig. 8 shows a weak dependence of the capacitance on the frequency in a wide range of frequencies $10^{-3} \div 10^{3}$ Hz, which makes it possible to

create ultra-high capacitors for the radio frequency range which in turn makes it possible to combine large values of a dielectric constant with high surface area.

Next, an experimental cell with electrodes based on GaSe clathrate $GaSe<CS(NH_2)_2>$ and *GaSe* hierarchical architecture clathrate $GaSe<CS(NH_2)_2<SmCl_3>>$ was investigated. The corresponding Nyquist diagrams are presented in Fig. 9.

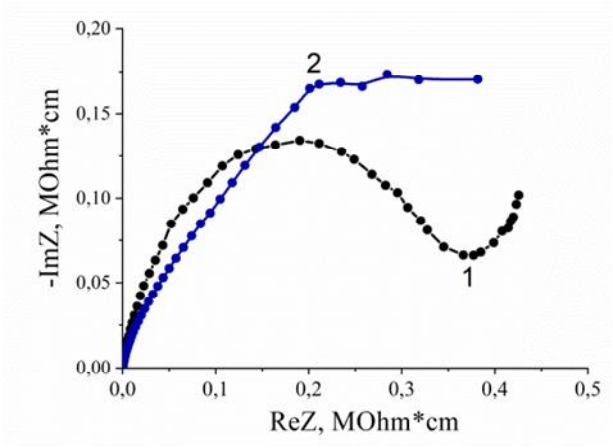

Fig. 9. Nyquist diagrams for the device of quantum accumulation of electric energywith cavitand electrode GaSe<CS $(NH_2)_2$> (1) and with cavitand electrode GaSe <$CS(NH_2)_2<SmCl_3>>$ (2)

Hodographs of impedance in both cases take the form typical of Faraday processes of the accumulation of electric energy. This behavior is most likely caused by the presence of a guest component in the extended *GaSe* layers.

The next step was to analyze the dependences of tgδ (ω) presented in Fig.10. As we can see, for GaSe clathrate $GaSe<CS(NH_2)_2>$ the experimental cell takes the value of tgδ <1 in the frequency range 0.2 ÷ 300 Hz. However, for clathrate of the hierarchical architecture $GaSe<CS(NH_2)_2<SmCl_3>>$ the experimental cell takes the value of tgδ <1 in the frequency range 0.02 ÷ 100 Hz. Fig. 11 shows the C(ω) dependences for the experimental cell with electrodes based on $GaSe<CS(NH_2)_2>$ clathrate and GaSe $GaSe<CS(NH_2)_2<SmCl_3>>$ hierarchical architecture clathrate. Comparing the obtained data with the results given above, we come to the important conclusion that the use of cavitation hierarchical architectures can significantly increase the capacity of quantum batteries due to the pseudo-capacitive component.

It is obvious that 4-fold expansion of the single crystal and subsequent placement of guest content in the formed gaps between the layers of the expanded matrix will lead to structural changes, as evidenced by the results of X-ray diffraction presented in Fig. 7. The presented X-ray diffraction patterns show that the diffraction maximum profile (004) is satisfactorily described by the superposition of the Gaussian peaks, which correspond to the scattering of X-rays from structural areas with different values of interplanar reflection distances. In other words, these results indicate the structural organization of the resulting supramolecular ensembles in the form of unexpanded packets of the original matrix, alternating with expanded areas of Van der Waals links with guest content (described by the authors in [15]) according to the mechanism of staged ordering in such matrices [16].

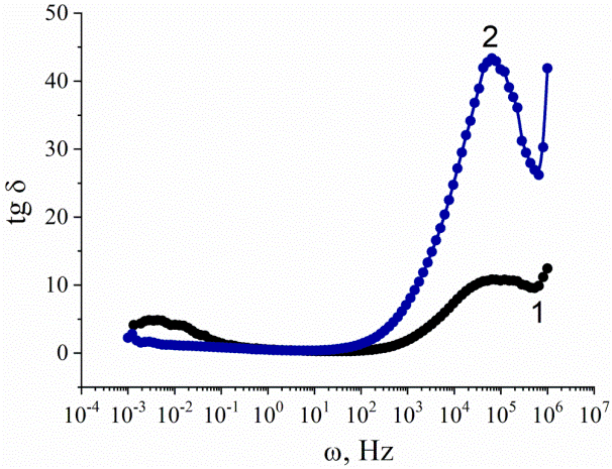

Fig. 10. Frequency dependences of the tangent of the angle of electric losses of the device of quantum accumulation of electric energy with cavitand electrode GaSe <$CS(NH_2)_2$> (1) and with cavitand electrode GaSe<$CS(NH_2)_2<SmCl_3>>$ (2)

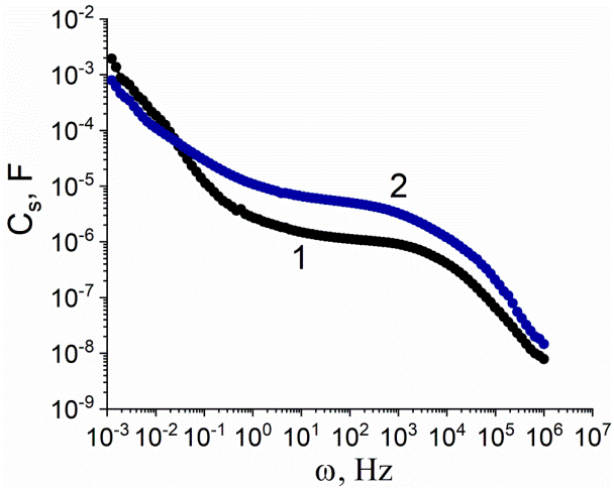

Fig. 11. Frequency dependences of the capacity of the quantum storage device of electric energy with cavitand electrode GaSe<$CS(NH_2)_2$> (1) and with cavitand electrode GaSe<$CS(NH_2)_2$ <$SmCl_3>>$ (2)

The diffraction reflection curve (004) of *GaSe* was recorded in the continuous scanning mode of the detector at a rate of 1/2 deg./min with automatic registration of

scattering intensity. The Bragg-Brentano focusing scheme J ¸ 2J was used.

The diffraction reflection curve of the GaSe sample *GaSe<CS(NH₂)₂>* shows an influx from smaller scattering angles caused by diffuse scattering. There is also a significant expansion of the maximum and a shift towards smaller scattering angles.

The diffraction reflection curve of the *GaSe* sample *GaSe<CS(NH₂)₂<SmCl₃>>* takes a complex profile. Thus, the main maximum shifts towards smaller scattering angles and an additional small angular maximum is clearly manifested. This result indicates the existence of crystal structures with a predominance of two interplanar distances. The intensity of background scattering is also increasing.

4. Conclusions

1 The accumulation of electrical energy at the quantum level in the constructed electrochemical cell is realized: a working electrode based on a material with a colossal area of the inner active surface with an extremely anisotropic nature of the chemical bond / electrolyte -gamma-butyrolactone: N-methylpyrrolidone (mixed solvent): maleic acid: trimethylamine = 80 (70%: 30%)%: 10%: 10% (wt%) / aluminum counter electrode.

2. The use of a quadruple-expanded *GaSe* matrix as a working electrode provides Faraday accumulation of electrical energy. The tangent of the angle of electrical losses in the infra-low frequency range assumes values ess than 1, and the specific capacity reaches high values - 10 F / g at a frequency of 10^{-3} Hz.

3. The device for quantum accumulation of electric energy based on cavitand and cavitate guest component *GaSe<CS(NH₂)₂>* and *GaSe<CS(NH₂)₂<SmCl₃>>* accordingly demonstrates the pseudocapacitive accumulation of electric charge. The use of cavitation hierarchical architectures can significantly increase the capacity of quantum batteries.

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КВАНТОВЕ НАКОПИЧЕННЯ ЕЛЕКТРИЧНОЇ ЕНЕРГІЇ НА МІЖФАЗНИХ МЕЖАХ У ГЕТЕРОФАЗНИХ НЕОРГАНІЧНО/ОРГАНІЧНИХ КЛАТРАТАХ

Федір Іващишин, Роман Швець, Віталій Максимич

Робота присвячена актуальній на сьогоднішній день проблемі пошуку нових способів та механізмів накопичення електричної енергії високої густини. В результаті проведених досліджень запропоновано систему, яка дозволяє накопичувати електричний заряд за рахунок квантових ефектів та явищ без використання хімічних реакцій. Основна ідея полягала на формуванні матеріалу з колосальною площею внутрішньої активної поверхні із різко анізотропним характером хімічного зв’язку. Відповідно, основною метою було створення та дослідження електродних матеріалів на основі інтеркалантних гетерофазних структур із різним типом ієрархії, здатних накопичувати електричну енергію на квантовому рівні. Методом інтеркаляційної наноінженерії були сформовані структури на основі монокристалів селеніду галію та впровадженими між його шари тіосечовини і хлориду самарію. На підставі отриманих результатів імпедансної спектроскопії встановлено, що одержані клатратні структури є перспективними для використання в якості кавітандного електрода у квантовому акумуляторі, а також, що найбільш важливо, дозволяють значно підвищити його ємність.

Fedir Ivashchyshyn, Doctor of Technical Sciences, Department of Applied Physics and Nanomaterials Science, Lviv Polytechnic National University. Alma mater: Vasyl Stefanyk Precarpathian National University. PhD (Solid State Physics) – 2012, Dr (Solid State Physics) – 2018. Scientific interests: Complex heterophase layered structures of hierarchical architecture.

Roman Shvets, Head of the laboratory Department of Applied Physics and Nanomaterials Sciense, Lviv Polytechnic National University. PhD. (Technology, Equipment and Production of Electronics) – 2015. Scientific interests: Technology of devices for generating and accumulating electrical energy.

Vitalii Maksymych, PhD. student, Department of Applied Physics and Nanomatirials Science, Lviv Polytechnic National University. MSc (Applied physics and nanomaterials) – 2018. Scientific interests: Low-dimensional clathrate structures for electronics and autonomous energy devices.