Proceedings of "Applications of Physics in Mechanical and Material Engineering" (APMME 2024)

Accumulation of Electrical Energy in Supramolecular Clathrates Through Quantum Effects

P. Chabecki[a], D. Calus[a,*] and F. Ivashchyshyn[a,b]

[a] *Faculty of Electrical Engineering, Czestochowa University of Technology, Dąbrowskiego 69, 42-201 Częstochowa, Poland*
[b] *Institute of Applied Mathematics and Fundamental Sciences, Lviv Polytechnic National University, Bandera Str. 12, 79013 Lviv, Ukraine*

Doi: 10.12693/APhysPolA.147.218 *e-mail: dariusz.calus@pcz.pl

In this study, we discuss the possibility of using supramolecular clathrates as materials that exhibit quantum-dimensional properties capable of providing high-density electrical energy storage. For this purpose, nanoscale structures with supramolecular bonding based on the host-guest principle were formed. The hosts were an expanded GaSe single crystal and a nanoporous SiO_2 matrix, and the guest component was an ionic liquid of two different chemical compositions. As a result of studies conducted by the impedance spectroscopy method, manifestations of such effects as quantum tunneling and Coulomb blockade were detected, which made it possible to accumulate an electric charge. A direct proof of this is the measured volt–ampere characteristics, which demonstrate a pronounced hysteresis characteristic for electrochemical current batteries. The obtained result indicates the possibility of creating fundamentally new devices for the accumulation of electrical energy with the quantum nature of the corresponding effects and phenomena.

topics: supramolecular clathrates, GaSe, Santa Barbara Amorphous-15 (SBA-15), ionic liquid

1. Introduction

Currently, the scientific community is focusing its efforts on the study of nanostructured materials and methods for their creation [1, 2]. This interest is caused by the possibility of developing materials characterized by a wide functional hybridity of properties and unusual effects [3, 4]. Reducing the size to the nanoscale allows us to identify the resonant features of electrons, which, in turn, opens up the prospect of creating fundamentally new functional devices for use in micro- and nanoelectronics, as well as in non-electrochemical energy storage systems [5–8]. This approach can become an alternative to traditional chemical power sources, which will directly contribute to the development of autonomous energy, and indirectly to renewable energy sources [9, 10]. There are predictions that quantum mechanisms of electric energy storage can provide specific energies that can be compared to the energy released by the combustion of petroleum products [6, 7].

In this context, a promising direction is the integration of organic and inorganic compounds to form nanohybrid structures. This combination is most effectively realized through the formation of clathrates with supramolecular bonds [11–13]. This organization of material makes it possible to easily create hierarchical architectures of varying complexity, while maintaining the characteristic properties of each component.

Based on our accumulated experience in studing nanostructured materials [14–17], we can develop inorganic–organic clathrates with predefined properties. Among the effects of practical importance, it is worth noting a significant increase in dielectric constant [18, 19] and a pronounced enhancement of the sensory response to external physical fields, which is due to the quantum nature of the processes [16].

Therefore, further research on the development of materials capable of accumulating electric charge at the boundaries of phase transitions is extremely important. This research is the subject of this paper.

2. Materials and method

The main materials studied in this work are clathrates formed on two types of matrices and guest components.

In the first clathrate, a layered GaSe semiconductor was used as a 2D matrix between the layers, of which the ionic liquid (IL_1) 1-butyl-3-methylimidazole tetrafluoroborate was introduced. The single crystal of GaSe grown by the Bridgman–Stockbarger method had a pronounced layered structure and p-type electrical conductivity. The band gap of the single crystal (according to optical data) is 2.02 eV. Since it is not possible to directly introduce an ionic liquid between the layers of the single crystal, we used a three-stage intercalation crystal engineering scheme described in [15], which resulted in a 6-fold expansion of the initial matrix. As a result, we obtained GaSe$\langle IL_1 \rangle$ clathrate with a 2D cation–anion plasma between the quantum sheets of the semiconductor.

In the second clathrate, the dielectric SiO_2 matrix SBA-15 (Santa Barbara Amorphous-15) of the Sigma Aldrich trademark was used, into the cavities of which the ionic liquid (IL_2) 1-Allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was introduced. The introduction of IL_2 into the pores of the SBA-15 matrix was carried out by thermal vacuum impregnation of the powdered matrix material. This technique was effectively used to form clathrates in previous studies [14, 16]. As a result, the clathrate SBA-15$\langle IL_2 \rangle$ was obtained.

In order to establish the peculiarities of the electronic energy structure of impurity levels of the clathrates, the spectra of thermal stimulated discharge in the short-circuit contact mode were measured under linear heating at a rate of 5°C/min from −245 to +350 K.

To study the processes of electric charge accumulation by these clathrates, the volt–ampere characteristics were measured in the range from −3 to +3 V, with a potential change rate of 0.050 V/s.

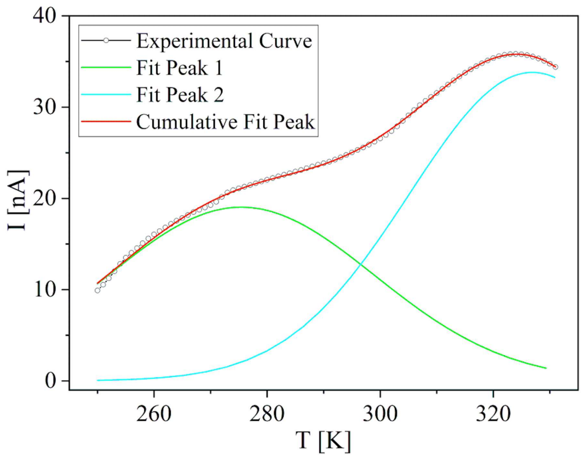

Fig. 1. Current spectrum of the thermally stimulated discharge for clathrate GaSe$\langle IL_1 \rangle$ and approximation by a superposition of Gaussian functions.

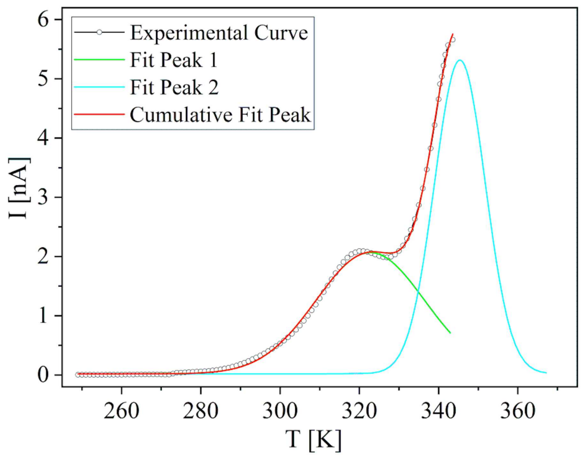

Fig. 2. Current spectrum of the thermally stimulated discharge for clathrate SBA-15$\langle IL_2 \rangle$ and approximation by a superposition of Gaussian functions.

3. Results and discussion

The study of the conductive and polarization properties of the GaSe$\langle IL_1 \rangle$ and SBA-15$\langle IL_2 \rangle$ clathrates was described in detail in our previously published works [18, 19]. From the analysis of the impedance spectra presented in these papers, we revealed the manifestations of such effects as quantum tunneling and Coulomb blockade, which, according to [6], provide conditions for accumulation of electric charge. To confirm this thesis, additional studies and data analysis were conducted, as discussed later in this paper.

For a detailed analysis of the processes involved in accumulation of electric charge in the studied clathrates, the spectra of thermally stimulated discharge currents were measured. As the spectrum of thermally stimulated discharge currents presented in Fig. 1 shows, the energy spectrum of GaSe$\langle IL_1 \rangle$ clathrate has a quasi-continuous distribution. For the purpose of a more detailed analysis, we approximated the $I(T)$ dependence by a superposition of Gaussian functions (Fig. 1). This dependence is approximated by two broad peaks corresponding to two different types of electric charge relaxation.

The first peak at lower temperatures is characterized by the Jonesher character of charge relaxation. This type of relaxation is caused by the formation of quasi-dipoles arising from the redistribution of charge carriers between nanoclusters in the strain field in such a way that neighboring pairs of different phases are charged with the opposite sign. The reason for this is the interaction of the anion–cation plasma with the semiconductor matrix.

The second peak at higher temperatures is responsible for the relaxation of spatial charge trapped by structural defects and impurity centers of the semiconductor matrix.

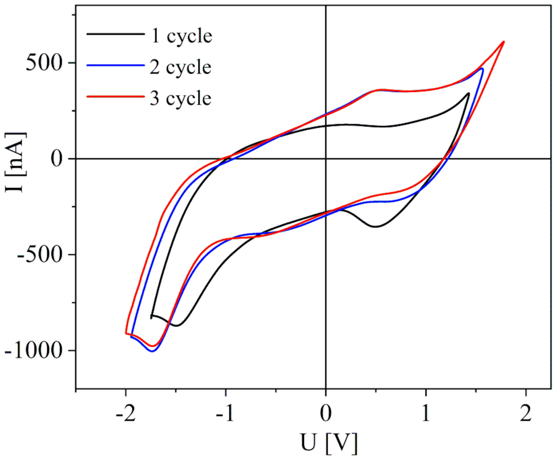

Fig. 3. The *V–A* characteristics for clathrate GaSe⟨IL_1⟩.

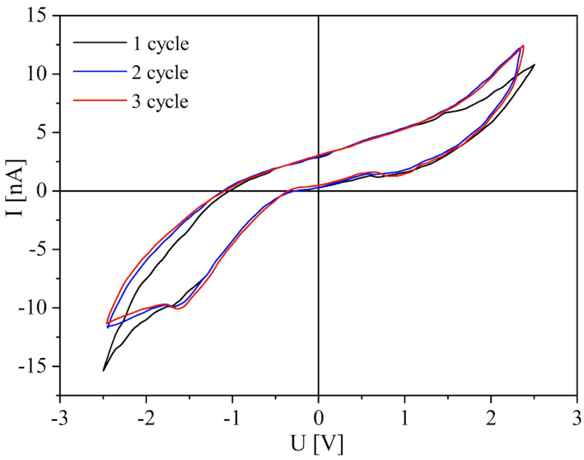

Fig. 4. The *V–A* characteristics for clathrate SBA-15⟨IL_2⟩.

The quasi-continuous impurity energy spectrum is also characteristic of the clathrate SBA-15⟨IL_2⟩, as shown in Fig. 2. The current intensity is an order of magnitude lower than that of the previous clathrate, which may be due to the dielectric matrix.

It should also be noted that the first peak at lower temperatures has shifted significantly towards the rise in temperature. This behavior may indicate the presence of immobilized spatial charges. They are stored unevenly, often being close to the electrodes. When heated, they are mobilized and neutralized either at the electrodes or in the sample by recombination with charges of opposite sign. The forces that move the charges are their drift in the local electric field and diffusion, which tends to eliminate concentration gradients. In general, field-controlled self-drift prevails. Considering the SBA-15⟨IL_2⟩ clathrate, the ionic liquid responsible for this type of relaxation is the one that provides intergranular movement of the grain.

The second peak for the SBA-15⟨IL_2⟩ clathrate at higher temperatures, as in the case of GaSe⟨IL_1⟩ clathrate, is responsible for the relaxation of the spatial charge trapped by the structural defects and impurity centers of the dielectric matrix.

The ability to accumulate electric charge by these clathrates was confirmed by measuring the voltammetric characteristics. Figure 3 shows the voltammetric characteristic for the GaSe⟨IL_1⟩ clathrate, which demonstrates a hysteresis character. The voltammetric characteristic demonstrates pseudo-capacitive accumulation of electric charge with cycle repeatability.

Figure 4 shows the voltammetric characteristic for the SBA-15⟨IL_2⟩ clathrate, which also demonstrates a hysteresis character. In this case, the working window of potentials is somewhat narrowed, but the current increases by almost two orders of magnitude. The voltammetric characteristic demonstrates a pseudo-capacitive accumulation of electric charge with repeatability of cycles.

4. Conclusions

This work presents a study of the possibility of using supramolecular clathrates GaSe⟨IL_1⟩ and SBA-15⟨IL_2⟩ as materials for the accumulation of electrical energy due to quantum-dimensional effects. By the method of thermal stimulated discharge, it was found that this type of clathrates is characterized by two main mechanisms of charge relaxation, i.e., (i) Johnsher relaxation and drift of electric charge along interfacial boundaries, (ii) relaxation of electric charge associated with carrier trapping on defects and impurity centers. The hysteresis character of the voltammetric characteristics indicates pseudo-capacitive accumulation of electric charge.

References

[1] A. Macagnano, J. Avossa, in: *Advances in Nanostructured Materials and Nanopatterning Technologies*, 2020, p. 297.

[2] I.D. Ibrahim, E.R. Sadiku, T. Jamiru, Y. Hamam, Y. Alayli, A.A. Eze, *J. King Saud Univ. Sci.* **32**, 758 (2020).

[3] G. Guan, M.Y. Han, *Adv. Sci.* **6**, 1901837 (2019).

[4] V. Maksymych, M. Klapchuk, A. Borysiuk, Y. Kulyk, V. Stadnyk, I. Bordun, Z. Kohut, F. Ivashchyshyn, *Mater. Res. Bull.* **163**, 112220 (2023).

[5] A.M. Ilyanok, US Patent no. US6570224B1, 2003.

[6] A.M. Ilyanok, European Patent no. EP1414078A1, 2003.

[7] A.W. Hübler, O. Osuagwu, *Complexity* **15**, 48 (2010).

[8] A. Hubler, S. Foreman, J. Liu, L. Wortsmann, *J. Appl. Phys.* **123**, 103302 (2018).

[9] S. Shapoval, N. Spodyniuk, V. Zhelykh, V. Shepitchak, P. Shapoval, *Pollack Periodica* **16**, 132 (2021).

[10] V. Zhelykh, P. Shapoval, S. Shapoval, M. Kasynets, in: *Int. Scientific Conf. Eco-Comfort and Current Issues of Civil Engineering*, Springer, Cham 2020, p. 499.

[11] R. Schlesinger, F. Bianchi, S. Blumstengel et al., *Nat. Commun.* **6**, 6754 (2015).

[12] W.-Q. Kan, J. Yang, Y.-Y. Liu, J.-F. Ma, *Inorg. Chem.* **51**, 11266 (2012).

[13] L. Dobrzycki, K. Woźniak, *J. Mol. Struct.* **921**, 18 (2009).

[14] P. Chabecki, D. Całus, F. Ivashchyshyn, A. Pidluzhna, O. Hryhorchak, I. Bordun, O. Makarchuk, A.V. Kityk, *Energies* **13**, 4321 (2020).

[15] F. Ivashchyshyn, A. Pidluzhna, D. Całus, O. Hryhorchak, P. Chabecki, O. Makarchuk, *Bull. Pol. Acad. Sci. Tech. Sci.* **69**, e136726 (2021).

[16] V. Maksymych, D. Calus, B. Seredyuk, G. Baryshnikov, R. Galagan, V. Litvin, S. Bujnowski, P. Domanowski, P. Chabecki, F. Ivashchyshyn, *Sensors* **23**, 4161 (2023).

[17] F.O. Ivashchyshyn, I.I. Grygorchak, M.I. Klapchuk, *Nanosist. Nanomat. Nanotehn.* **13**, 403 (2015).

[18] V. Maksymych, D. Całus, F. Ivashchyshyn, A. Pidluzhna, P. Chabecki, R. Shvets, *Appl. Nanosci.* **12**, 1147 (2022).

[19] P. Chabecki, *Energies* **15**, 6069 (2022).