FUNDAMENTAL AND APPLIED NANOIONICS IN IMT RAS

Alexander DESPOTULI, Alexandra ANDREEVA

Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, Chernogolovka, Russian Federation, despot@ipmt-hpm.ac.ru

Abstract

Term and concept of a new branch of science and technology, namely, "nanoionics", were formulated in IMT RAS (1991-1992). It was the article "A step towards nanoionics". New area R&D devotes to nanoscale fundamentals of fast ionic transport (FIT) in solid-state materials, as well as to methods for design of FIT-nanomaterials, for description of local FIT-space-temporal processes, for creation of devices with FIT on a nanoscale ("nanoionic devices"), etc. Main achievements of IMT RAS in nanoionics are: (1) new optically-active nano-physical-chemical systems Ag(Cu)Hal -M, created in high vacuum (M are rare-earth/transition metals); (2) new classification of solid-state ionic conductors (it distinguishes for the first time a new class of solid state conductors - "advanced superionic conductors", i.e., materials whose crystal structures are closely to optimum for FIT); (3) new scientific direction "nanoionics of advanced superionic conductors"; (4) a crystal-engineering of heteroboundaries in FIT-materials and an invention of supercapacitors with coherent polarized heterojunction and record-high frequency-capacitance characteristics ("nanoionic supercapacitors"); (5) substantiation about possibility of using of nanoionic supercapacitors in deep-sub-voltage nanoelectronics; (6) definition of ways for heterointegration in supercapacitors of advanced superionic conductors and carbon nanostructures with a high quantum capacitance; (7) theory of a dynamic response of layered nanostructures with ionic hopping transport in a non-uniform potential landscape ("structure-dynamic approach of nanoionics"); (8) new fundamentals of electrostatics related to materials with FIT; (9) proposition of a non-linear non-local dynamics for FIT-materials. Future nanoionic researches are analyzed in terms of the dynamic theory of information.

Keywords: Nanoionics, nanoionic devices, advanced superionic conductors, structure-dynamic approach

1. INTRODUCTION

Term and concept "nanoionics" had been proposed in the Institute of Microelectronics Technology and High Purity Materials Russian Academy of Sciences (IMT RAS). It was the article "A step towards nanoionics" [1]) in which nano-objects with fast ionic transport (FIT) were characterized by the dimensionless parameter

$$P = \lambda/L \tag{1}$$

where L is an object size, λ is a characteristic length of localization of FIT-processes, for example, a localization of ionic space charge. Now, nanoionics is regarded as an interdisciplinary branch of science and technology, for example, as a division of solid state ionics [2], or, as a section of nanoelectronics [3].

According to the authors, nanoionics is defined by: 1) objects, i.e., nanostructures and nanosystems with FIT, for example, optically active nano-physical-chemical systems Ag(or Cu)Hal -M created in high vacuum (M is a metal in which the first ionization potential is smaller than one of Ag(or Cu) [4,5]; 2) properties, phenomena, effects and mechanisms of processes connected with FIT on nanoscale; 3) methods: design of nanomaterials and nano-objects with FIT [6-8], new theoretical system for description of dynamical response of layered nanostructures with 1D FIT in non-uniform on a nanoscale potential landscape (structure-dynamic approach of nanoionics, SDA) [9-12]; 4) dimensionless criterion of nanoionics $\lambda/L \sim 1$ [1]; 5) dimensional n-factor for solid state ionic systems [11]; and 6) perspective applications, e.g., nanoionic supercapacitors for deep-sub-voltage

nanoelectronics, nanoionic memristors (i.e., "memory resistors" - two-terminal functional nanostructures, where conjugate ionic/electronic processes and electrical resistance change significantly at a changing of the polarity of external electric influence), etc. [13].

In conditions of very limited available resources, our strategy for long-term R&D in IMT RAS was consisting in attempts of an expansion of borders of nanoionics in new directions. The main obtained results on nanoionics are listed in this report. A new theoretical system, i.e., structure-dynamic approach (SDA) of nanoionics, and a new optically-active nano-physical-chemical systems are considered in some details. The graph of R&D items (which were initiated in IMT RAS on nanoionics) is presented with some comments related to basics of dynamic theory of information.

2. METHODOLOGY

In this section, some challenges (in condensed matter/solid-state ionics) and methods of their solutions in nanoionics are discussed. A critical view on the interpretations of impedance spectroscopic data.

The method of impedance spectroscopy is used everywhere in solid state ionics, however authors of the report call into question the standard interpretations of frequency dependences of impedance $Z(\omega)$ by means of using of constant phase elements, as well as the interpretations of the universal dynamic response (UDR) by means of RC-grids.

UDR, i.e., the power law of conductivity, had been discovered by A.K. Jonscher in 1977 [14]:

$$\mathrm{Re}\,\sigma^*(\omega,T) \approx \omega^n \tag{2}$$

where $\sigma^*(\omega, T)$ is the real part of the complex (thermally activated) conductivity, and $n < \approx 1$. The law (2) holds in a wide frequency range. There has been no consensus until now on a standard theoretical explanation of the reasons and mechanisms of the physical averaging leading to the emergence of UDR in macroscopic solid ionic conductors. To date (the end of 2019), about 9,800 references had been made on two works by A. K. Jonscher devoted to UDR.

In the literature, there are many ideas (interpretations) related to the law (2). According to [15], "Structurally disordered solid electrolytes, both crystalline and glassy, as well as ionic melts, exhibit a set of spectroscopic peculiarities for ionic conductivity that is at variance with the predictions of simple random-hopping models". The negation of simple hopping models means that the macroscopic behavior is defined by an existence of unknown complex transient states of mobile ions. However, the remarkable 'universality' (1) refers to the independence of UDR from physical and chemical structures also as from details of ion-ion interactions.

According to [16] "The universal properties found suggest they originate from some fundamental physics governing the motion of the ions.". This statement can be understood as the existence of an unknown fundamentality in condensed matter physics. However, the proposition by [17] is more applicable for the analysis of UDR in ionic conductors: "both conductive and dielectric dispersions are simultaneously important in the frequency region of interest.". This proposition implies the existence of such well-known fundamentality as the Maxwell displacement currents in experimental samples. In our opinion, the law (1) is some result of a space-time averaging of interconnected currents, i.e., ionic hopping currents and Maxwell displacement currents on a nanoscale.

Mainstream for the realization of the idea of interconnected "conductive and dielectric dispersions" is the presentation of processes by the method of complex impedance (Z) of an appropriate equivalent electric circuit. In this approach, results are presented in a manner like "The Z′ and Z″ versus frequency plots are well fitted to an equivalent circuit model. The circuits consist of the parallel combination of resistance (R), constant phase element (CPE), and capacitance (C). Furthermore, the frequency-dependent AC conductivity obeys

Jonscher's universal power law" [18]. However, for a macroscopic sample, the physical sense of an equivalent-electric-circuit appears if each unit of the circuit means an elementary process. In this case, the whole circuit mimics the result of physical averaging for a set of elementary processes. Note, constant phase elements (CPEs), are phenomenological macroscopic objects without standard physical interpretation. CPE itself needs a definition through elementary physical processes and mechanisms just like for UDR.

Solid-state impedance spectroscopy gives roughly averaged experimental data, i.e., a large amount of information (which reflects interconnected local processes) gets lost. For clear interpretations of such data, we need theoretical approaches, which allow calculating the impedance Z through the state variables directly connected with local ionic hopping transport and local dielectric polarization.

2.1. Structure-dynamic approach of nanoionics

A new theoretical approach [9] addresses to the logic of elementary ion-transport processes on a nanoscale and emphasizes that solid-state ionic conductors are dynamical non-local non-linear systems. In such systems, key parameters (heights of barriers in potential landscape) depend on external influences. Dynamic behavior of an ionic space charge in parametric-dependent systems with long-range Coulomb interactions cannot be presented correctly by equivalent electric circuits where elements have constant parameters. These findings are obtained within the frame of SDA by computer experiments. Calculated data are in good concordance with results of impedance spectroscopy.

SDA takes into account the main nanoscale features of crystal structures of all solid-state ionic conductors, namely, a non-uniform potential landscape in which mobile ions hop. SDA does not use the derivatives on spatial coordinates in a set of differential equations, because the differentiation on space coordinates is a doubtful operation on a nanoscale. It provides more correct interpretations for a dynamic response in ionics.

In SDA, several theoretical innovations were proposed: method of effective uniform electrostatic field; new dimensional r_i-factor; new notion "Maxwell displacement current on a potential barrier"; laws of spatial averaging of potential differences in solid-state ionic conductors [9-12].

2.2. New optically-active nano-physical-chemical systems

Chemical reactions ways and final products can depend on conditions in which are located initial chemical components. Dimensional factors have to evince itself in solid-state chemistry. Therefore, the search for new solid-state optically-active physical-chemical nanosystems on the basis of haloids of Ag and Cu was carried out in [4,5]. Nanosystems of the Ag (Cu)I − M type (where M − La, Ce, Nd, Sm, Tb, Tm, Yb, Lu, Sc, Y, Al, etc.) were created (at 300 K) in high vacuum by method of deposition of M-films (5-10 nm thickness, the method of laser ablation) on the of β- Ag-(Cu)I with hexagonal structure of the wurzite and γ- Ag-(Cu)I with cubic structure of the blende (50-100 nm thickness). It was revealed, such nanosystems have state parameters, kinetics of ionic transport, unusual ways of synthesis and properties, which depend on dimensional factors. Works [4,5] show a possibility of synthesis in the Ag (Cu)I − M type physical-chemical nanosystems of a set new non-stoichiometric compounds (with variable composition and structure) and materials. New objects of nanoionics differ by high concentrations (~10^{21} cm^{-3}) of rare-earth (RE) and transition (TE) elements and, presumably, F-centers (an electron in a vacancy of Hal).

On the basis of generalization of the obtained experimental data, the criterion of insertion of a M-element in haloid was put forward: new compounds and materials are synthesized when

$$\varphi_{Ag}, \varphi_{Cu} > \varphi_{M} \tag{3}$$

where φ_{Ag}, φ_{Cu} and φ_{M} - first potentials of ionization for Ag, Cu and M, correspondingly. All RE elements, all 5f-actinoids (φ_{actin} ~ 500-600 kJ/mol <φ_{Ag}, φ_{Cu}), some 4d-elements: Zr (φ_{Zr} = 660 kJ/mol), Nb (φ_{Nb} = 664 kJ/mol),

Mo (φ_{Mo} = 685 kJ/mol), Al p-metal (φ_{Al} = 577 kJ/mol), Bi semi-metal (φ_{Bi} = 703 kJ/mol) and, for example, magnetic-active Mn correspond to the criterion (3). **In Figure 1** (A and B), the spectra of optical density D for two new optically-active physical-chemical nanosystems β-AgI - Nd and β-AgI - Mn are presented.
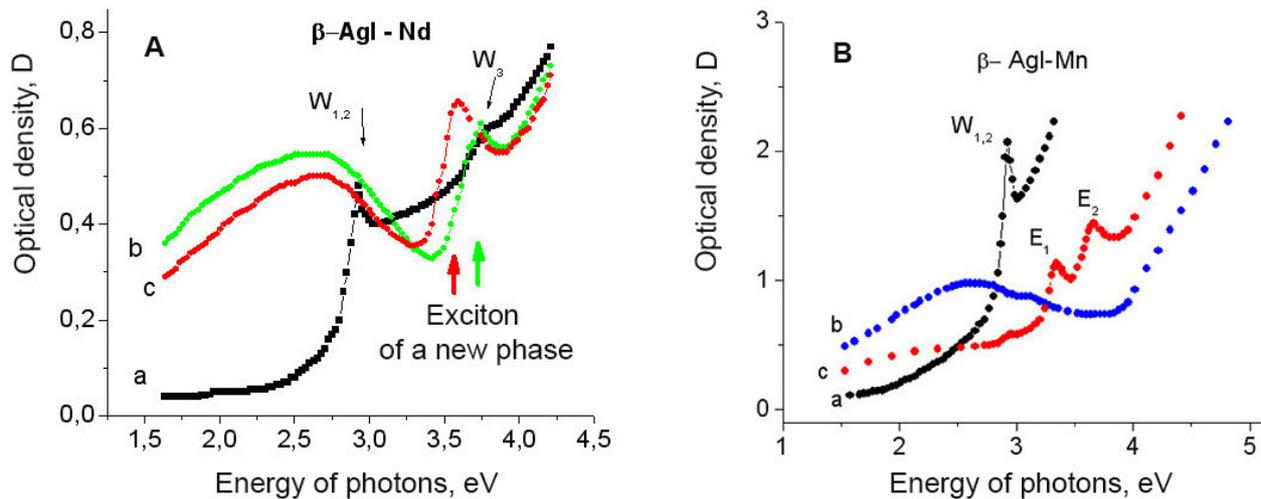
Figure 1 Spectra of the optical density D in two new physical-chemical nanosystems. (A) Nanosystem AgI-Nd: a - initial thin film sample β-AgI (50 nm thickness); b - the same sample after insertion of rare-earth Nd (7 nm film); c - the beginning of recovery of initial structure in the same sample in the ambient atmosphere (formation of Nd oxide). (B) Nanosystem AgI-Mn: a - initial thin film sample β-AgI (190 nm nm thickness); b - the same sample after insertion of Mn (19 nm film) at 300 K; c - the sample in new steady state (after 14 days of an exposition in the ambient atmosphere).

3.   SOME PROSPECTS

The beginning era of nanoionic devices demands a nonlocal non-linear theory of dynamic response of solid-state ionic conductors. Nanoionics tries to describe, for example, diffusion and reactions, in terms, which have sense only on a nanoscale, e.g., in terms of a non-uniform potential landscape. Therefore, search for fundamental properties (which can be included in a future theory of ionic transport on a nanoscale) are very important. The theoretical system, i.e., structure-dynamic approach (SDA) of nanoionics, is a step on this way.

The problem of high mobility of ions in ordered nanostructures is fundamental to various membranes and the hetero-systems of live organisms. Therefore, results of nanoionics have to be demanded in the new multidisciplinary BioElectronic Medicine/Semiconductor Synthetic Biology areas [19,20].

Information carriers with large masses (ions) are necessary for suppression of tunnel currents of leak in nanodevices of logic and memory of extremely small sizes. Therefore, research and development in the field of deep-sub-voltage nanoelectronics and design of nanostructures of AdSICs [13] can lead to creation of the hybrid highly functional electronic and ion devices combining quantum transport of electrons and the classical movement of ions.

By insertion of various chemical elements into simple Ag- and Cu-haloids and their numerous derivatives, for example, such as advanced superionic conductors of RbAg$_4$I$_5$ family, a set of new materials and chemical compounds with high concentrations of optically/magneto-active elements and F-centers can be synthesized. It is possible to expect a discovery of unusual combinations of properties: electronic conductivity, FIT, optical and magnetic activity, etc.
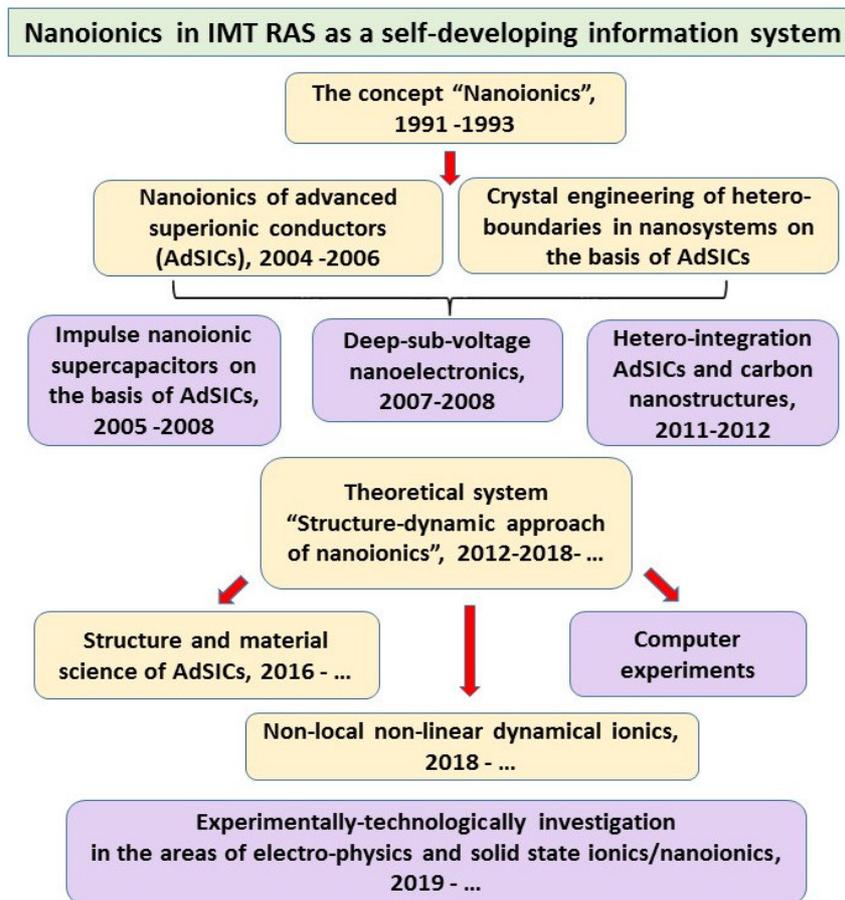
Figure 2 R&D on nanoionics in IMT RAS

Authors analyze results of development of a nanoionics in IMT RAS and prospects of further R&D in a foreshortening of fundamentals of "The dynamic theory of information" (the book of D.S. Chernavskii [21]) and from a point of view of influence of a strategic innovative management on achievements of applied science, see **Figure 2**. The analysis purpose - to establish compliance between methodological bases of scientific and technical searches and decisions on a choice of new directions of research in specific conditions.

In terms of the dynamic theory of information [21,22], the nanoionics can be defined as a developing information system. Main objectives of such systems (capable to perceive, remember and generate information) are the preservation and an increase of own valuable information, a forecasting of behavior of an environment and an own behavior.

4. CONCLUSION

The analysis shows that a nanoionics grows as a self-developing information system. Long-term stability of process of generation of information in this system is provided by interference of knots of "thesaurus-purpose-result" triad. For a further development of a FIT-theory on nanoscale and a deeper understanding of processes at a high-frequency response of nanostructures, the inclusion of local magnetic field in a FIT- theory is necessary. The obtained results, i.e., an expansion of ideas and approaches of a nonlinear dynamics (the section of modern theory of oscillations and waves) on the field of intersection of solid-state ionics and nanotechnologies, - can be considered as the initiation of new scientific direction "dynamical not-local non-linear ionics".

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