Ion Conductors with the Conductivity over Lithium Ions and Solid Electrochemical Devices Based on Them

N. F. UVAROV[1,2,3], A. S. ULIKHIN[1] and YU. G. MATEISHINA[1,3]

[1]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

E-mail: uvarov@solid.nsc.ru

[2]*Novosibirsk State Technolgoical University, Pr. Marksa 20, Novosibrisk 630092 (Russia)*

[3]*Novosibirsk State University, Ul. Pirogova 2, Novosibirsk 630090 (Russia)*

Abstract

A review of works aimed at the development of solid electrochemical devices based on lithium systems is presented. The criteria for the choice of solid electrolyte are described, a brief review of the properties of known solid electrolytes under in solid lithium batteries and rechargeable batteries are described. Special attention is paid to the properties of composite solid electrolytes. Examples of known solid primary and secondary lithium current sources differing in design and type of solid electrolyte are presented. It is shown that the composite solid electrolytes (ceramic, polymer ceramic and glass ceramic) are most suitable for use in solid lithium rechargeable batteries. A brief review of the works aimed at the development of solid supercapacitors is given. The data on solid supercapacitors with solid electrolyte based on lithium perchlorate and carbon electrode materials are presented.

Key words: solid electrolytes, lithium ionic conductors, solid batteries and rechargeable batteries, solid supercapacitors

INTRODUCTION

Electrochemical devices allow one to perform or optimise the processes of accumulation, recuperation and transformation of electric energy. They are of substantial practical interest for the development of the systems of autonomous electric feed, stabilization of current and electric circuit control in various branches of industry, transport, domestic devices and computers. At present liquid solutions or melts of ionic salts are used as electrolytes in electrochemical systems; or polymeric ion-exchange membranes are employed. The transition from liquid and polymeric systems to solid electrolytes allows one to enhance the strength of the material, to broaden the range of working temperatures and to provide the unipolar character of conductance. Solid-state electrochemical systems are compatible with the basic elements of microprocessor technology and can be built into heterostructures, which substantially broadens the areas of practical application of electrolytes in the industry of nanosystems and nanomaterials. Electrochemical devices for accumulation, recuperation and transformation of energy include chemical current sources (batteries, rechargeable batteries and fuel elements), ionistors (capacitors with large specific capacitance) and chemotronic sensors that change the physicochemical characteristics of the electrode by means of the external signal. In the row of various electrochemical devices, lithium systems are characterized by the highest energy density and attract special attention.

Solid-state electrochemical devices possess high mechanical strength, are stable against the external pressure and temperature difference, possess unipolar conductivity and are promising for practical applications. Historically, solid-state lithium batteries were the first to appear; later the attention of researchers shifted to the development of solid lithium rechargeable batteries, while the works on the development of solid supercapacitors started to appear during the recent years. Studies aimed at the development of solid electrochromic electrochemical systems with lithium solid electrolytes are also to be marked. For the development of solid lithium systems, it is necessary to select the electrode material and electrolyte and to choose the type of cell design taking into account optimisation of all its elements for most efficient functioning.

The basic components of lithium solid devices are solid electrolytes with lithium ion conductivity. In order to develop efficient electrochemical devices with specific power $0.01-1$ W/cm^2 per unit electrode surface and thickness $0.1-1$ mm, it is necessary that the specific ionic conductance of the electrolyte is not less than $10^{-4}-10^{-1}$ S/cm. These values are achieved either in liquid electrolytes or in solid compounds of special type — superionic conductors.

and solid solutions on the basis of these compounds [7]. These compounds possess high ionic conductance at temperatures above $150-200$ °C; they are actively hydrolized in the air.

4. Solid solutions based on lanthanum-lithium titanate with perovskite structure $La_{2/3-x}Li_{3x}TiO_3$ [8]. Solid solutions can be obtained through lanthanum substitution by the cations of lanthanoids, alkaline or alkaline earth metals, and titanium by the ions of tantalum, niobium and other four- and six-charged cations. The highest lithium conductance ($1.5 \cdot 10^{-3}$ S/cm) at 25 °C was detected for compound $La_{0.55}Li_{0.36}TiO_3$ [8].

5. Compounds with the framework structure of LISICON type. Among them, the highest conductance at 25 °C ($4 \cdot 10^{-5}$ S/cm) is exhibited by the compound $Li_{3.6}Ge_{0.6}V_{0.4}O_4$ [9].

6. Substituted lithium titanophosphates [1?6] belonging to the structural type of NASICON with the three-dimensional framework. The highest conductance ($7 \cdot 10^{-4}$ S/cm) at 25 °C was discovered for compound $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ [10].

Temperature dependencies for known ceramic lithium solid conductors are presented in Fig. 1. In spite of the high ionic conductance, ceramic solid electrolytes still have not found application in solid electrochemical devices functioning at room temperature. This is connected
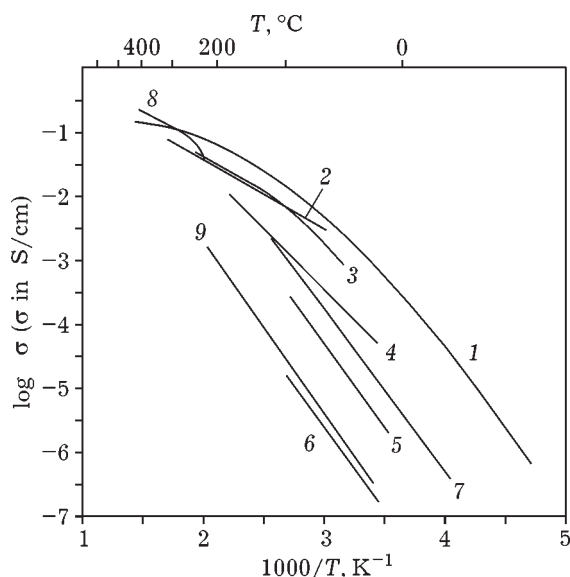
SOLID ELECTROLYTES WITH LITHIUM ION CONDUCTIVITY

Ceramic and amorphous solid electrolytes

On the basis of literature data $[1-6]$, it is possible to distinguish the following basic structures with superionic conductance with respect to lithium ions:

1. Solid solutions based on high-temperature phases of lithium sulphate and orthosilicate [5]. These compounds possess high lithium conductance at temperatures above 300 °C.

2. Lithium nitride $[1-5]$. This compound, as well as solid solutions based on it, are characterized by high lithium conductance $10^{-4}-10^{-1}$ S/cm at 25 °C. Unfortunately, they are unstable in the air, especially in the presence of moisture, and possess the low potential of electrochemical decomposition.

3. Double halides $LiX-MX_n$ (here M stands for doubly and triply charged ions; $X = Cl^-$, Br^-)

Fig. 1. Temperature dependencies of the conductivity of ceramic solid electrolytes with lithium ion conductance: $1 - Li_{0.34}La_{0.5}TiO_{2.94}$, $2 - Li_3N$, $3 - Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$, $4 - Li_{3.6}V_{0.4}Ge_{0.6}O_4$, $5 - 0.6LiI + 0.4Al_2O_3$, $6 - Li_9SiAlO_8$, $7 - Li_{29}PO_{33}N_{046}$ (LIPON), $8 - Li_{14}ZnGe_4O_{16}$ (LISICON), $9 - 0.57LiSiO_4 + 0.43Li_3PO_4$).
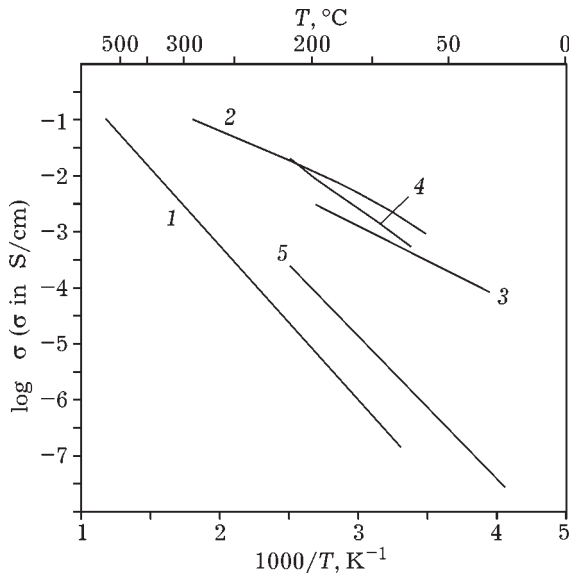
Fig. 2. Temperature dependencies of the conductance of amorphous solid electrolytes: 1 − $0.049LiI$−$0.341Li_2O$−$0.61B_2O_3$, 2 − $0.30Li_2S$−$0.26B_2S_3$−$0.44LiI$, 3 − $0.60Li_2S$−$0.40SiS_2$, 4 − $0.02Li_3PO_4$−$0.98(Li_2S$−$SiS_2)$, 5 − $Li_{2.9}PO_{3.3}N_{0.46}$ (LIPON).

with very high resistance of grain boundaries and hence with the necessity to agglomerate the material to high density. At the same time, the better is the sample agglomerated; the more difficult it is to provide reliable contact between the electrolyte and the electrode.

It is also possible to use amorphous systems based on glasses possessing high lithium conductance as solid electrolytes. Among amorphous electrolytes, it is necessary to stress those based on lithium metaphosphate [11], as well as glasses formed in the systems Li_2O−B_2O_3−P_2O_5 [12], Li_2O−P_2O_5−Ta_2O_5 [13] and Li_2O−P_2O_5−MoO_3 [14]. In the form of thin films, amorphous lithium conductors having the composition $LiPO_3$−Li_3N (LIPON) [15] and $LiNbO_3$ [16] with ionic conductance above 10^{-6} S/cm at 25 °C were obtained.

The highest lithium conductance at 25 °C is exhibited by sulphide glasses Li_2S−SiS_2 [17], Li_2S−LiI−SiS_2 [17] and Li_2S−LiI−SiS_2−P_2S_3 [18] obtained by quenching from the melt or with the help of mechanical activation of initial components. Temperature dependencies of the conductance of solid amorphous electrolytes are presented in Fig. 2. Amorphous systems possess a number of advantages: a complete absence of intergrain boundaries, high density and impermeability of the material for gas or liquid phases. Common disadvantages of amorphous

electrolytes are, first of all, their thermodynamic instability and the difficulties in achieving a reliable inter-phase contact at the boundary of the electrolyte with the electrode that changes the volume while charging-discharging processes take place.

Composite solid electrolytes

A reliable contact between the solid electrolyte and electrode is ensured in the case if composite solid electrolytes are used instead of ceramic electrolytes. It is known that in the majority of cases the conductance of ionic compounds increases as a result of their doping with a dispersed dielectric which is chemically inert with respect to the ionic salt. Composite solid electrolytes of the type ionic salt/oxide can be considered as a new class of ionic conductors possessing high ionic conductance [19−21]. A combination of high conductance with increased mechanical strength, broad possibilities of the purposeful control of electrolyte properties by varying the type and concentration of the additive determines the promising character of the use of composites in real electrochemical systems. An increase in the conductance as a result of doping with dispersed oxides is observed in almost all the composites based on classic (not superionic) ionic salts.

Passing to nanocomposites, along with further increase in conductivity we observe dimensional effects: salt amorphization and related disappearance of phase transitions. For the synthesis of these nanomaterials, it is possible to use the methods of solid-phase diffluence of an ionic salt over the surface of nanodispersed oxides and mechanical activation of the mixture under controllable conditions. Thermodynamic analysis and available experimental data show that the combination of these methods allows providing a good inter-phase contact and thermodynamically stable (for the given specific surface of the oxide) nanocomposites if the energy of adhesion between the components is sufficiently high. To decrease the energy of adhesion, the surface of the oxides can be functionalised with surface-active nucleophilic groups.

A special position in the sequence of lithium conductors is occupied by composite solid

electrolytes based on polymer systems. Usually this group includes the solutions of lithium salts in organic solvents thickened with polymers or other additives (gel electrolytes) [22], the solutions of lithium salts in polymers with heterogeneous additives − fine oxides (polymer composites) [23−27] and microheterogeneous mixtures of lithium salts with polymers [28]. Polymer composite electrolytes possess relatively high conductance but the number of lithium cation transfers in them is not large; in their mechanical characteristics they noticeably lag behind solid electrolytes based on inorganic systems.

Japanese scientists developed composite glass ceramic solid electrolytes on the basis of mixed sulphides of lithium, silicon and phosphorus, possessing the conductance at a level of 10^{-3} S/cm at room temperature [29−31]. They are formed during partial crystallization of glass and exceed all the presently known lithium ionic conductors (amorphous and crystalline) in the level of conductance. Being sulphide systems, electrolytes possess relatively narrow region of electrochemical stability and the ability to get rapidly hydrolysed in humid environment, which limits the range of their application. Recently, glass ceramic composite materials were developed on the basis of the $Li_2O-TiO_2-SiO_2-Al_2O_3$ systems with high lithium conductance (more than $1 \cdot 10^{-3}$ S/cm at 25 °C) [32]; they are already used by Ohara Inc. (Japan) to manufacture the plates of tight lithium-conducting membranes of the required thickness.

We developed composite solid electrolytes based on lithium perchlorate with high ionic conductance [33−35]. The highest conductance is exhibited by solid composite electrolytes having the composition $(1 - x)LiClO_4-xMgO$; their thermodynamic, electric and electrochemical properties were studied. It was discovered that the conductance of the composites passes through its maximum at $x = 0.8-0.9$ and reaches $1.8 \cdot 10^{-2}$ S/cm at 200 °C (Fig. 3). High (above 3.5−4 V) voltage of electrochemical decomposition of $LiClO_4$ in cells with aluminium electrodes provides evidence that the conductance in the composites is due to lithium ions.

The effect of the nature of oxide and the disperse state of the heterogeneous additive on the conductance of the composites based on lithium perchlorate was studied [36]. On the basis
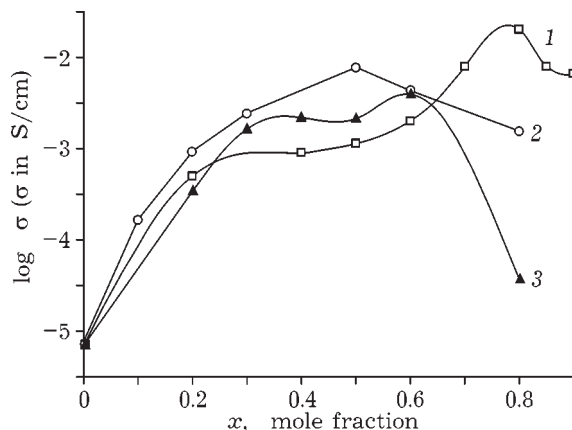

Fig. 3. Concentration dependencies of the conductance of composites $(1 - x)LiClO_4-xA$ containing different oxide additives: MgO (*1*), γ-Al_2O_3 (*2*), SiO_2 (*3*). $T = 200$ °C/

of the comparative investigation of $LiClO_4-A$ composites doped with oxide additives (A = α-, γ-Al_2O_3, α-, γ-$LiAlO_2$) with different specific surface, it was demonstrated that the composites with the addition of γ-phases of Al_2O_3 and $LiAlO_2$ in the case of the same specific surface of oxides possess higher conductance and lower activation energy than the composites containing α-phases of the same compounds (Fig. 4). This fact is explained by the similarity of the crystal structures of γ-phases and their increased surface activity in comparison with α-phases of the same compounds. The solid electrolytes thus obtained posses high unipolar conductance with respect to lithium ions, which opens the possibilities to use them in practical devices, in particular in medium-temperature lithium batteries and supercapacitors.

SOLID ELECTROCHEMICAL DEVICES BASED ON COMPOSITE SOLID ELECTROLYTES

Lithium batteries and rechargeable batteries

Composite solid electrolytes based on lithium iodide were used to make solid lithium primary current sources to feed cardiostimulators [37]. The batteries include lithium anode, composite solid electrolyte $LiI-Al_2O_3$ with different additives and the anode. Depending on anode material, battery voltage is 2−2.8 V; specific energy of the battery varies within the range 150−250 mW · h/g. The batteries are char-
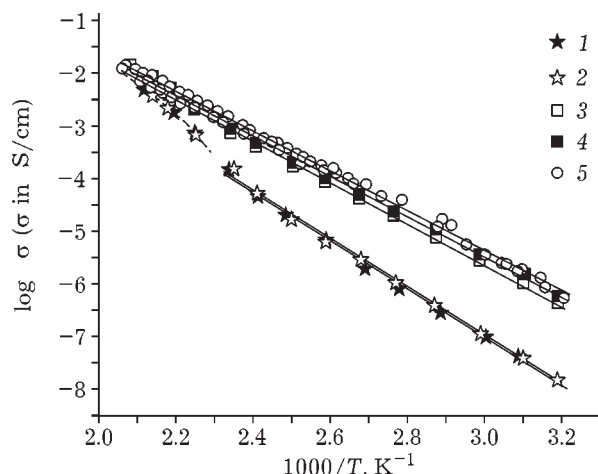
Fig. 4. Temperature dependencies of the conductance of composites $0.5LiClO_4-0.5A$ containing different oxide additives: α-Al_2O_3 (1), α-$LiAlO_2$ (2), γ-Al_2O_3 (3, 4), γ-$LiAlO_2$ (5).

acterized by long lifetime (storage time is 20 years without significant self-discharge) and high reliability [38]. For instance, since 1972 till 2000 Catalyst Research Corporation (the USA) manufactured 150 000 batteries for cardiostimulators, and no one of these batteries did not fail during those 17 years. The high reliability of solid batteries is due to the fact that the batteries do not contain liquid components, do not require additional separators, their total volume does not change during charging or discharging, the evolution or absorption of gases is absent, the cell is tight.

Attempts to make secondary lithium current sources (lithium rechargeable batteries) have been made since the 70s of the past century, but lithium rechargeable batteries still lag behind the rechargeable batteries with liquid electrolytes in such parameters as cycling and reliability. During the recent years, intense works are carried out in the world to develop solid secondary lithium current sources. One of the directions of these studies is the development of thin-filmed rechargeable batteries. In particular, American scientists made lithium rechargeable batteries several micrometers thick with the solid electrolyte of LIPON type [39, 40]. These rechargeable batteries are compatible with the elements of microelectronics but their manufacture is connected with the use of complicated technique of layer-by-layer deposition, which substantially increases the cost of

rechargeable batteries and limits the areas of their practical application. Review [41] presents the data on thin-film batteries obtained by the *in situ* electrolysis of solid electrolyte membranes.

A principal limitation for the practical application of thin-film rechargeable batteries is the low volume density of accumulated energy due to the small amount of electrode material per unit electrode surface area. To overcome this shortcoming, it is proposed to pass from two-dimensional to three-dimensional architecture of planar cells. One of the approaches may become the deposition of multiplayer coatings with serial switching of the electrodes. The authors of [41] discuss the possibilities to make three-dimensional electrochemical heterostructures on various substrates (carbon tubes, aerogel, microchannel plates, porous anode films) followed by the deposition of functional layers by means of physical, chemical deposition and electrochemistry. It was shown that the transition from two- to three-dimensional architecture leads to a substantial increase in the specific capacitance of the film lithium rechargeable battery [42].

The most successful results were obtained by Japanese scientists [29–31, 43]. To make solid lithium rechargeable batteries, they used composite glass ceramic materials composed of mixed sulphides of lithium, silicon and phosphorus possessing the conductance of the order of 10^{-3} S/cm at room temperature. On the basis of these electrolytes, they developed rechargeable batteries of tablet design that are able to survive more than 100 charge-discharge cycles [43] (Fig. 5). Electrochemical devices with composite solid electrolytes possess improved mechanical characteristics and operate within a broad temperature range, which allows one to increase the reliability of the devices. However, sulphide electrolytes possess insufficient electrochemical stability and are easily hydrolysed in humid environments. In this connection, the development of lithium rechargeable batteries on the basis of oxide or fluoride solid electrolytes does not lose its urgency.

Other solid electrochemical devices

Among other solid electrochemical devices, it is necessary to stress solid supercapacitors

with solid electrolytes. Supercapacitors (or ionistors) are electrochemical capacitors possessing high capacitance (about 1−10 000 F), they are ecologically safe, rapidly rechargeable current sources. Due to the high specific power, excellent cycling ability and the broad range of working temperatures, they substantially surpass conventional rechargeable batteries for some applications and can be used to feed various devices of small and medium power.

The remarkable properties of supercapacitors are connected with the fact that charge carriers (ions) are accumulated during charging on the electrode/electrolyte interface and form a double electric layer. Traditional electrode materials for ionistors are carbon materials based on activated carbon, carbon fibre and nanotubes, *etc.* However, a substantial increase in the specific surface of carbon materials (up to ~1000−2000 m^2/g) does not lead to a significant increase in specific capacitance (permittivity). It was established that the maximal achievable specific capacitance for various carbon materials does not reach 150−200 F/g [44]. This is explained by incomplete availability of the surface of carbon material, electric screening effects and insulation of small pores, relatively low electric conductance of highly porous carbon.

Additional increase in specific capacitance can be provided due to Faraday type processes (electrochemical reactions) that may proceed in

parallel to usual processes involving the formation of the double layer. In this case, the capacitance is called pseudo-capacitance; to achieve it, the developed surface of the carbon material is coated with a thin layer of electroactive substance capable of reversible electrochemical transformation. These agents may be, for example, the oxides of metals with variable valence able to undergo electrochemical intercalation which is accompanied by the change of the degree of cation oxidation. The appearance of "pseudocapacity" was discovered also in the electrodes with deposited oxides of transition metals, such as RuO_3, MnO_3, NiO, SnO_2; the highest specific capacitance (about 200−400 F/g) was observed when nanometer-sized particles were used [45]. Electrodes with deposited RuO_2 particles may be mentioned as an example; the specific capacitance of these particles reaches 850−1200 F/g [45, 46].

As a rule, liquid electrolytes are used to make supercapacitors. Nevertheless, works are carried out during in the recent years to make solid supercapacitors. These devices possess high mechanical strength, stability to external pressure, temperature difference, and are interesting for practical application. For example, the authors of [47, 48] described supercapacitors with solid polymer electrolytes based on Nafion membranes and polybenzimidazole, and electrodes based on RuO_2 with specific capacitance above 200 F/g; they survived 1000 to 10 000 charge-discharge cycles. Completely solid-state supercapacitors based on $H_3PW_{12}O_{40} \cdot nH_2O$ and $ZrO_2−Y_2O_3$ solid electrolytes were studied in [49] and [50], respectively. The major difference of lithium electrolytes from other ones is the broad range of electrochemical stability, due to which the electrochemical capacitor can be charged within a wider voltage range. The value of accumulated energy increases as a square with voltage increase, so the use of lithium electrolytes allows a substantial increase in the power intensity of the capacitor.

We developed model solid supercapacitors with composite solid electrolytes based on $LiClO_4$ and electrodes made of Taunit MD type carbon material with the addition of carbon black and solid electrolyte. The cells were made through layer-by-layer pressing; a net made
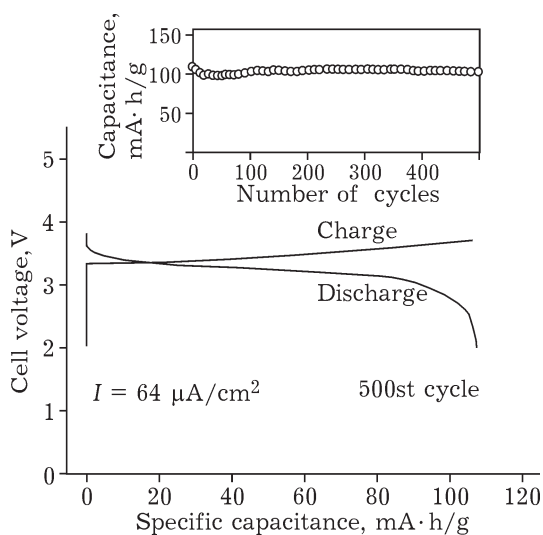

Fig. 5. Charge–discharge characteristics of solid rechargeable battery with solid glass ceramic electrolyte based on sulphides, indium anode and cathode made of $LiCoO_2$.
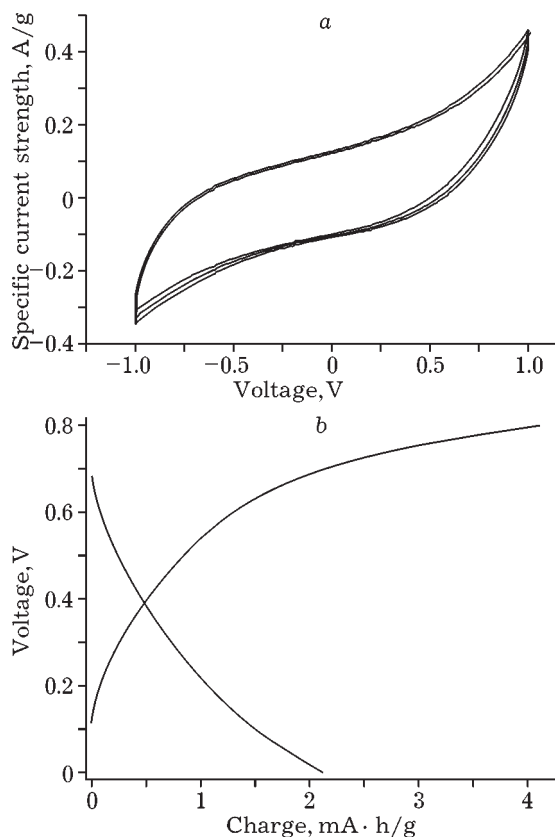
Fig. 6. Voltage-current curves for solid supercapacitor with carbon material Taunit MD (scan velocity: 10 mV/s) (*a*) and the curves of galvanostatic charge-discharge for the same cell (*b*).

of stainless steel was used as a current lead. The voltage-current characteristics and the curves of galvanostatic charge-discharge recorded at 200 °C in vacuum are shown in Fig. 6. During cycling (the cycling variation of the potential), the current strength values are well reproducible, which is the evidence of the high stability of inter-phase contacts in nanocomposite systems. Nevertheless, approximate values of the specific capacitance of the electrode material are 5 F/g, which is several times lower than the values obtained with the use of the liquid electrolyte. The indicated difference is due to the difficulty in preparing a high-quality electrode material. Mixing two or more solid components, it is very difficult to achieve the uniform distribution of the components over the volume of the material. In addition, it is almost impossible to ensure tight contact between the phases. To increase the capacitance, it is necessary to find the methods that would provide more uniform distribution of the com-

ponents over the electrode material, to optimise the chemical composition of the electrode, and to master the methods for treating the surface of carbon materials. Works in this direction are planned for future.

CONCLUSION

Significant advance was achieved as a result of investigations aimed at the development of solid-phase electrochemical devices based on lithium systems. Solid electrolytes with lithium ion conductivity that are suitable for use in solid lithium batteries and rechargeable batteries were selected. By present, the prototypes of thin-filmed lithium rechargeable batteries have been developed; studies aimed at the transition from two- to three-dimensional structures are carried out. It was shown that the composite solid electrolytes (ceramic, polymer-ceramic and glass-ceramic) are most suitable for use in solid lithium rechargeable batteries. The first works describing the development of solid supercapacitors appears, demonstrating that lithium electrolytes posses substantial advantages with respect to other types of electrolytes. Data on solid supercapacitors based on composite solid electrolytes and carbon electrode materials are presented.

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