



Short communication

New electrochemical cells with membrane-electrode-assembly generating protonic heterojunctions “inorganic proton conductor–hydrogenated metal”

Yu.M. Baikov*

Ioffe Physical Technical Institute of Russian Academy of Science, 26 Politechnicheskaja, St-Petersburg 194021, Russian Federation

ARTICLE INFO

Article history:

Received 15 October 2008

Received in revised form 16 January 2009

Accepted 23 January 2009

Available online 6 February 2009

Keyword:

Proton conducting electrochemical cells

ABSTRACT

Electrochemical cells “hydrogenated metal–proton conductor–any second electrode” are of certain applied interest in connection with the development of the protonic heterojunction conception as an alternative to the three-phase-boundary conception. The first, but not single condition of the formation of protonic heterojunction is the heterogeneous contact of hydrogen-containing materials such as the hydrogenated metal and the proton conductor. The appropriate couples consisting of Pd or Ti in the role of electrodes and solid hydroxides in the role of proton conductors have been studied. The way of the preparation of such original electrochemical cells and their behavior in the temperature range 320–430 K are presented. A stable electromotive force (emf) of various electrochemical cells '(Pd)|NaOH, KOH|(Pd)', '(Pd)|CsHSO₄|(Pd)', '(Ti)|KOH·H₂O|(C)', '(Ti)|KOH·H₂O|(Ti)' has been observed. (Here (Pd), (Ti), (C) mean the main part of electrodes omitting the description of heteroboundaries.) The value of emf varies from 0.8 V to 1.4 V depending on physicochemical conditions. A certain part of this emf (0.8 V for Pd-cells and 0.2 V for Ti-cells) is due to heteroboundaries “hydrogenated metal–proton conductor”, which is found to be kinetically reversible to proton exchange. Isotopic effects of emf are the plain evidence in favor of potential determining role of protons. These data confirm the protonic heterojunction formation in electrochemical cells under study. It has given the impetus to working out the promising electrochemical devices with protonic heterojunctions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical cells are key component of different electrochemical devices such as primary and secondary batteries, fuel cells, electrolyzers etc. Factually all of electrochemical cells are heterogeneous assemblies, including electron-conducting electrodes (frequently metals) and ionic conducting electrolytes. As usual electrochemical processes are accompanied by a transport of a charge and a mass, i.e. ions and atoms, including their transfer through boundaries the formation of which in heterogeneous assemblies is inevitable. In many practically important electrochemical assemblies, the contact of the metallic and ionic components does not manifest the electrochemical activity without involving into process other substances, which are not the physical part of the assembly, e.g. gas or liquid as a fuel or an oxidant. This generates the well-known problem of a three-phase boundary (TPB), which is solved today by technological means.

An approach alternative to TPB supposes the creation of electrochemically active assemblies, which have specific heteroboundaries, which may be recognized as ‘ionic heterojunctions’. It means, by another word, that the ionic exchange between the electrode and electrolyte proceeds directly, i.e. without a participation of any other substances, being no physical part of an assembly. The most striking instance is a lithium ionic heterojunction, which is the key component of compact lithium batteries. The efficiency and wide application of these batteries stimulate the search of new promising electrochemical systems with ionic heterojunctions of different compositions.

The hydrogen-containing materials seem to be very attractive. However there is a serious obstacle in the way of development of protonic heterojunctions where protons are directly involved into a reversible exchange between the electrolyte and the electrode without any intermediate reagents. The matter is that in order to form a protonic heterojunction, one has to find an appropriate couple of hydrogen-containing materials. One of them has to work as an electrolyte and another as an electrode. Best candidates for this purpose are the protonics and the hydrogenated metal. (Hereafter “protonics” means inorganic proton conductors.)

* Tel.: +7 812 292 7937; fax: +7 812 297 1017.

E-mail address: baikov.solid@mail.ioffe.ru.

The basic possibility of proton heterojunction functioning in an electrochemical cell with inorganic proton conductor has been proved in 'high-temperature perovskite–protonics–hydrogenated metal' electrochemical cells [1–3]. The protonics SrCe_{0.95}Yb_{0.05}O₃ has been studied in a pair with V, Zr, Nb and LaNi₅ [1]. The protonics BaCe_{0.9}Nd_{0.1}O₃ has been studied in a pair with Pd [2,3]. There could hardly be any applied interest in these pairs, however. A technically acceptable high conductivity of perovskite protonics (0.1–1 mS cm⁻¹) can be reached only at temperatures above 600 K. However, the pressure considerably higher atmospheric level is required for the needed state of a hydrogen solution in metals (~0.1 H atom per metal atom) to be maintained at so high temperatures. This circumstance has prompted a search of other inorganic protonic conductors possessing enough high proton conductances below 500 K and capable of operating in electrochemical cell in a couple with metals amenable to hydrogenation, such as Pd and Ti. The choice of these metals has been based on the thermodynamic and kinetic properties of the Pd–H₂ and Ti–H₂ systems studied within a broad range of temperatures and pressures. Titanium has been chosen for comparison, because the behavior of the Ti–H₂ system differs markedly from that of Pd–H₂ system. It is important to note that the hydrogen solutions in Pd and Ti remain stable under H₂ pressure not higher than 100 kPa in the range of 300–500 K. The idea has been advanced to use mixtures of individual hydroxide compounds KOH, NaOH and H₂O in the role of electrolytes in pair with metal electrodes from Pd and Ti. The choice of such compounds has been underpinned by earlier studies which had revealed the noticeable proton diffusion ($D_H > 10^{-8}$ cm² s⁻¹) in these materials in solid state [4]. The presence of a proton heterojunction in cells 'PdH_x|KOH·nH₂O|M' has been demonstrated in [5,6] (here $x \leq 0.2$, $M = \text{PdO}_y$ or C; $n = 0.5$ or 1.0). The pioneering character of such electrochemical cell is that the electrolyte consists of the solid compounds based on hydroxides of alkaline metals. The investigation of the conductivity of these compounds has shown that solid monohydrate KOH·H₂O and solid eutectic mixture KOH+NaOH are pure proton conductors. The monohydrate has the conductivity $10^{-3} - 2 \times 10^{-2}$ S cm⁻¹ at 300–420 K. The eutectic has the conductivity 0.02–0.1 S cm⁻¹ at 360–460 K [7].

Individual solid alkali–metal hydroxides have been occasionally attracting people engaged in basic research as model objects for the study of the mechanism of protonic conduction [8–14]. Regrettably, the hydroxides NaOH, KOH, RbOH and CsOH exhibit a high protonic conductivity at temperatures noticeably above 500 K. Their compositions match the characteristic points in the phase diagrams of the systems KOH–H₂O [8,15] and NaOH–KOH [16], namely, the two eutectic compositions KOH\NaOH ($T_{\text{melt}} = 448$ K) and KOH\KOH·H₂O ($T_{\text{melt}} = 372.5$ K) and the monohydrate KOH·H₂O ($T_{\text{melt}} = 419$ K). (We are going to denote the KOH\NaOH and KOH\KOH·H₂O eutectics, using in chemical formulae not only the sign 'comma' (,), but also the back slash (\) to discriminate heterophase structures of eutectic electrolytes and of electrochemical cell as a whole.)

2. Experimental

2.1. The preparation of electrolytes

We used the analytically pure potassium and sodium hydroxides (Chemapol®) and doubly distilled water as starting materials for the ionic conductors. To study in detail the role of hydrogen in electrochemical processes the isotopic substituted compounds were used. The protium was replaced in the hydroxides with deuterium by isotopic exchange of anhydrous KOH with D₂ at 545 K and of the anhydrous NaOH\KOH eutectic with D₂ at 420 K by the

technique developed and refined at the Ioffe Institute [17]. The part of deuterium reached as high as 92–97.5 at.%. The KOD·D₂O monohydrate was obtained by mixing deuterated hydroxide with heavy water.

2.2. The preparation of hydroxide and hydrosulfate electrochemical cells

The preparation of electrochemical cells has been described in considerable detail in [6,12]. It makes use essentially of the relatively low melting points of the electrolytes chosen, a factor that simplifies considerably the technology of preparation of electrochemical cells of any size and configuration. The main procedure consists of inserting electrodes into the melt, or of the melt between the electrodes, at temperatures ~20 K above the melting point and subsequent cooling.

The palladium electrodes were made of foil with a Pd content of 99.999%. The titanium electrodes, both wire and ribbon, contained no less than 99.99% Ti. As carbon electrodes, we used spectral-grade graphite rods.

Four new electrochemical cells, '(Pd)|NaOH,KOH|(Pd)', '(Pd)|CsHSO₄|(Pd)', '(Ti)|KOH·H₂O|(C)', and '(Ti)|KOH·H₂O|(Ti)' have been synthesized. (Hereafter (Pd), (Ti), (C) and (M) mean the main part of electrodes omitting the description of heteroboundaries.) Unlike [3,5,6], not only palladium, but also titanium was used as a hydrogenated electrode. Two another protonics were used as electrolytes in addition to KOH·nH₂O studied in [5,6], namely NaOH\KOH eutectic equimolar mixture as a representative of bases and CsHSO₄ as a representative of acid salts. Baranov from the Shubnikov Institute of Crystallography (Russian Academy of Sciences) provided us with CsHSO₄, the synthesis and properties of which (including the superprotonic conductivity above 419 K) had been studied by him and his co-workers, e.g. [18]. This inorganic proton conductor possesses the high conductivity ~10⁻² S cm⁻¹ at 420–520 K. We are unaware, however, of any attempts to search protonic heterojunctions in electrochemical cells with acidic salts as electrolytes.

Since the CsHSO₄ decomposed above 480 K the technique of preparing the electrochemical cell was different from that for hydroxides. Pd electrodes and the hydrosulfate were pressed and sintered at 420–440 K until a mechanically strong assembly was obtained, which could suffice during studying a potential of the heteroboundaries '(Pd)|CsHSO₄'. Sintering without melting electrolyte was also applied to the anhydrous hydroxide eutectic for comparison and verification of both ways. Measurements of the potentials of the '(Pd)|NaOH, KOH|(Pd)' electrochemical cell with the sintered and melted electrolytes revealed no basic difference. Cells with the sintered electrolytes proved to be helpful in experiments on estimating the isotope shift of potential observed earlier in 'PdH_x|KOH·nH₂O|(M)' [5], when protium was replaced by deuterium. Isotopic substitution was carried out by bringing molecular deuterium in contact with the electrochemical cell in a tailored system allowing monitoring of the electrode potentials along with isotopic exchange.

The preliminary electrochemical activation of the synthesized cells similar to battery charging/discharging was needed to activate the metal–protonics interface and then to produce a hydrogen-containing electrode. For the cells with palladium electrodes, the activation stage was the same as that described in [5,6], irrespective of the type of protonics. In the case of titanium electrodes, emphasis was made on the pretreatment (for details, see [19]) aimed at eliminating the formation of a thick layer of TiO₂, which reacted with the melted alkali. A stable potential difference across the electrodes of activated cells and their possibility to operate as a rechargeable battery let us speak to the formation of electrochemical cells.

3. Results and discussion

3.1. Some general features of electromotive forces of cells

Electromotive forces (emf, E) of cells under present and earlier study at given temperatures are listed in Table 1 (items 1–4 from [5,6]). The whole temperature intervals are limited by the melting points of protonics from above and by the temperatures of phase transitions to the lower conductivity phase (see [7,15,16] and Section 1). The reproducibility of the emf for cells of the same compositions is within ± 15 mV. The isotope shift in the same cell is reproduced better than ± 10 mV. The particular attention has been given to the heteroboundary between the protonics and the hydrogen-containing electrode PdH_x or TiH_x . Table 1 lists potentials $U(M_1)$ of these boundaries that have been measured with respect to the third (pseudo-reference) electrode R (Pd or Ti).

3.2. Cells with Pd electrodes

After activation (charging), the electrochemical cells with Pd electrodes (Table 1, items 1–8) have an emf, most part of which is due to the potential difference at the protonics–negative electrode interface, as follows from comparison of the absolute values of $U(M_1)$ and E . The heterojunction potential $U(M_1)$ has been persisting for more than 100 h whatever temperature variation and storage conditions. Special measurements of the resistance of electrode in a form of a plate or a wire during charging provide a convincing proof that the PdH_x does form ($x < 0.2$) in most of the experiments. The same result has been obtained in [3,5,6].

The kinetic reversibility of proton transport through the 'PdH_x|NaOH, KOH' interface has been established in an experiment with a special cell with a Pd membrane, described in [5,6]. These experiments have brought the strong evidence in favor of a proton heterojunction. The same result has been obtained for the 'PdH_x|C₂H₅SO₄' interface.

The second electrode, which was presumably covered by a PdO film during the activation procedure, featured considerably unstable behavior. Its potential with respect to pseudo-reference Pd electrode was persisting for 3–5 h after charging and then slowly fell down from 150 mV to zero in the course of the next 5–6 h. To improve the reproducibility of potential measurements during a longer period that was needed, for isotopic effect investigations a graphite electrode was chosen as the second electrode (items 3, 4 and 9, 10).

To perform the study of the isotopic shift of the potential of protonic heterojunction ($U(M_1)$ in Table 1) the special procedure of a substitution deuterium for protium and *vice versa* in the course of isotopic exchange with corresponding gaseous phase (H_2 or D_2) has been worked out. The introduction of 60 at% D into the NaOH\KOH cell has lead to increasing the potential modulo by 60 ± 10 mV (items 5 and 6). In the cell with $\text{C}_2\text{H}_5\text{SO}_4$, isotopic exchange of the

gas with the electrolyte at 440–450 K has not been observed. However, potential $U(M_1)$ modulo increases by 25 ± 10 mV (items 7 and 8), which is due, in our opinion, to $\text{D}_2 \rightleftharpoons \text{PdH}_x$ isotopic exchange, i.e. the exchange between the "ambient" gas and the electrode only.

Observed isotopic shifts of potentials of protonic heterojunctions count in favor of the potential-determining role of protons in protonic heterojunctions (the detailed consideration is in [6]).

3.3. Cells with Ti electrodes

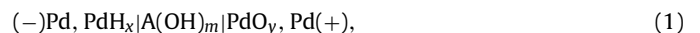
The behavior and properties of the activated cells with titanium electrodes have turned out to be qualitatively different compared to the cells with palladium electrodes. Specifically, it is seen from Table 1 that the potentials $U(M_1)$ of the protonic heterojunction on Pd electrodes and of protonic heterojunctions on Ti electrodes are remarkably different. It is natural to assume that this difference is associated with different electronic properties of metals and the chemical properties of their hydrides. It should be noted that the titanium electrode experiencing anodic oxidation at charging that makes it difficult to achieve the stable state of the cell potential. Therefore, this electrode has been replaced by a graphite electrode (items 9, 10 in Table 1).

The emf of the Ti-cell differs from that of the Pd-cell sooner quantitatively so that $E((\text{Pd})|\text{KOH}\cdot\text{H}_2\text{O}|(\text{C})) < E((\text{Ti})|\text{KOH}\cdot\text{H}_2\text{O}|(\text{C}))$. However, the isotopic shift of potentials of protonic heterojunctions by absolute value is higher for Pd-cell so that the modulo $\{U(\text{TiD}_x|\text{KOD}\cdot\text{D}_2\text{O}) - U(\text{TiH}_x|\text{KOH}\cdot\text{H}_2\text{O})\}$ is less than $\{U(\text{PdD}_x|\text{KOD}\cdot\text{D}_2\text{O}) - U(\text{PdH}_x|\text{KOH}\cdot\text{H}_2\text{O})\}$. These data require careful thermodynamic analysis. The observed noticeable isotopic shift appears to be a qualitative indication on protons contribution to the potential of heterojunction in cells with titanium, like it occurs in cells with palladium.

3.4. Electrode processes in studied cells

This paper presents the results of the pioneering study of original electrochemical cells, which can be synthesized by enough simple way from simple substances. However, the comprehensive picture of physicochemical processes in these cells is absent. Particularly there are no clear understanding processes on positive electrode. Nevertheless, the obtained experimental data can be interesting for planning future investigations of applied character.

The cell with Pd-electrodes working as rechargeable battery can be described as following [6]:



where $\text{A}(\text{OH})_m$ is the conditional formula of hydroxide proton conductor. It is very important to note that all of components in (1) are solids. The reaction of the cell with monohydrate ($\text{KOH}\cdot\text{H}_2\text{O}$) can be

Table 1

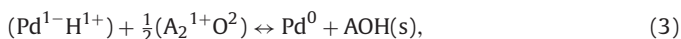
Electromotive forces E of electrochemical cells " $(-)\text{M}_1|\text{electrolyte}|\text{M}_2(+)$ ", potentials $U(M_1)$ at the " $\text{M}_1|\text{electrolyte}$ " interfaces with respect to pseudo-reference electrode R.

	Electrode R/ M_1	Electrolyte	Electrode M_2 /R	$-U(M_1)$ (mV)	E (mV)	T (K)
1	Pd/PdH _x	KOH\KOH·H ₂ O	PdO/Pd	700	1200	368
2	Pd/PdH _x	KOH·H ₂ O	PdO/Pd	800	1200	368
3	Pd/PdH _x	KOH·H ₂ O	C	800	1100	368
4	Pd/PdD _x	KOD·D ₂ O(95%D)	C	920	1220	368
5	Pd/PdH _x	NaOH\KOH	PdO/Pd	900	1050	408
6	Pd/PdD _x	NaOD\KOD(60%D)	PdO/Pd	960	1100	408
7	Pd/PdH _x	C ₂ H ₅ SO ₄	Pd	760	800	438
8	Pd/PdD _x	C ₂ H ₅ SO ₄	Pd	785	820	438
9	Ti/TiH _x	KOH·H ₂ O	C	~130	1365	363
10	Ti/TiD _x	KOD·D ₂ O(60%D)	C	~170	1390	363

written as



The reaction of the cell with anhydrous eutectic (KOH + NaOH) can be written as



where A means Na or K. Both reactions have been written taking into account proton as charge carrier from left to right at discharging and *visa versa* at charging.

Fig. 1 presents polarization curves and the power output (W) versus current for the cell ' $\text{PdH}_x|\text{NaOH, KOH}|\text{PdO}_y$ ' working as rechargeable battery at 390 K. More stable regime at this temperature has been received at initial parameters corresponding to $W \approx 0.75 W_{\text{max}}$. In this case it is possible to get back $\sim 40\%$ of a charge passed through a cell at charging. The PdH_x electrode (dashed curve 2) has kept the potential closed to that at no-current state. The "weak point" here is the right electrode (short dashed line 3) because of PdO_y film flaking.

Fig. 2 presents the impedance spectra of the ' $(\text{Ti})|\text{KOH}\cdot\text{H}_2\text{O}|\text{C}$ ' cell. It has been charged up to $E = 1.35 \text{ V}$ and then can be discharged through an external load. This cell stably operates with the following parameters: 0.77 V, 0.35 mA, 385 K, 120 h. The current density on the Ti electrode is of $\sim 1 \text{ mA cm}^{-2}$, and a current density on the graphite electrode is five times smaller. These parameters are much better than for the $(\text{Pd})|\text{KOH}\cdot\text{H}_2\text{O}|\text{C}$ cell, especially with regard to the operation duration and stability. While the number of charging/discharging cycles without of any destruction of both kinds of cells under study (Pd or Ti) has occurred to be the same (at least 20 cycles).

The impedance spectra in the range 10^{-2} – 10^5 Hz show that Ti electrode works kinetically reversibly and independent of the load. The maximum of $|Z''|$ for Ti electrode has been observed at ~ 10 – 15 Hz . Most probably that it is the frequency of a rotation of OH^- ions taking part in electrochemical reaction on protonic heterojunction. The more low-frequency part of impedance corresponds to the processes on a graphite electrode. But they are out of scope of this work.

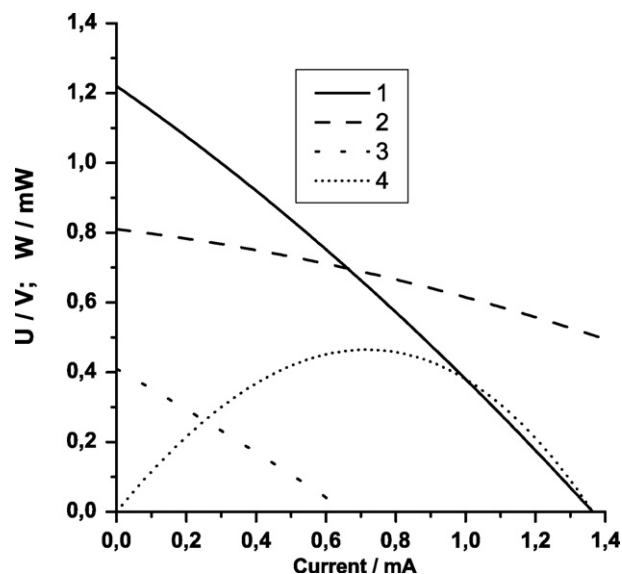


Fig. 1. The electrochemical cell ' $(-)(\text{Pd}),\text{PdH}_x|\text{KOH,NaOH}|\text{PdO}_y,(\text{Pd})(+)$ ' at 368 K. Polarization curves and power output—1: the cell potential (U , mV)—the current through the cell (mA); 2: the $\text{PdH}_x|\text{KOH,NaOH}$ potential vs (Pd)—the current; 3: the $\text{KOH, NaOH}|\text{PdO}_y$ potential vs (Pd)—the current; 4: the power output (W , mW)—the current. The size of electrodes is $5 \text{ mm} \times 10 \text{ mm}$. (Pd) is pseudo-reference electrode.

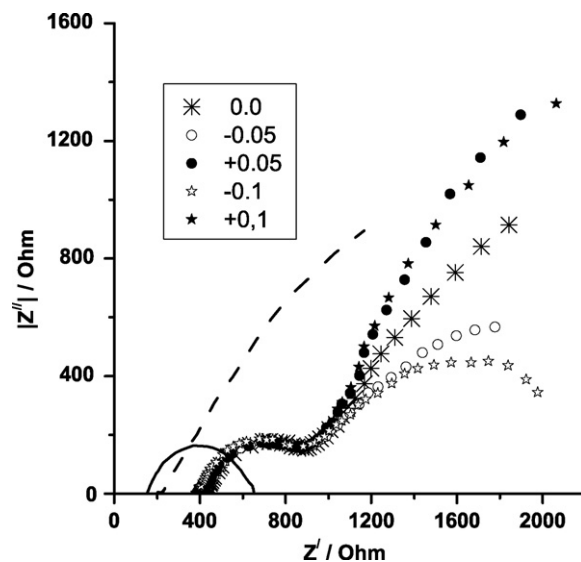


Fig. 2. Impedance spectra of ' $(-)(\text{Ti}),\text{TiH}_x|\text{KOH}\cdot\text{H}_2\text{O}|\text{C}(+)$ ' at 368 K. The figure at sign means the cell overpotential in the course of the impedance measurement. Solid and dashed lines are impedance spectra of interfaces ' $\text{TiH}_x|\text{KOH}\cdot\text{H}_2\text{O}$ ' and ' $\text{KOH}\cdot\text{H}_2\text{O}|\text{C}$ ' correspondingly measured vs Pd pseudo-reference electrode placed in the middle of the electrolyte. The frequency is decreased from left (10^5 Hz) to right ($5 \times 10^{-3} \text{ Hz}$). The maximum of $|Z''|$ on Ti-curve is at $12 \pm 1 \text{ Hz}$.

4. Conclusion

Original electrochemical cells synthesized from a hydrogenated metal (Pd, Ti), protonics ($\text{KOH}\cdot n\text{H}_2\text{O}$, $\text{KOH}|\text{NaOH}$, or CsHSO_4) and the second electrode (graphite, any metals) can be used for further investigations as key parts of different electrochemical devices. The possibility to form the proton heterojunctions with intriguing properties is of undoubted interest for basic research. It should be useful to find electrode materials enough cheaper than Pd to create the rechargeable battery for intermediate temperature interval 370–470 K. The impetus to such activity gives the cell ' $(-)\text{TiH}_x|\text{KOH}\cdot\text{H}_2\text{O}|\text{C}(+)$ ' synthesized for the first time. It acquires a stable emf ($E = 1.35 \text{ V}$, 363 K) and can operate as a rechargeable battery in the temperature interval 360–400 K.

Acknowledgements

The author thanks E.I. Nikulin, V.M. Egorov, A.I. Baranov, V.G. Ponomareva, G.V. Lavrova and T.A. Perevalova for valuable discussion and assistance. This work was supported by the Program "Influence of Atomic Crystalline and Electronic Structures on the Properties of Condensed Phases" (Russian Academy of Sciences), project No. P-03-02.

References

- [1] S. Horiike, A. Kunimatsu, K. Takahiro, S. Nagato, S. Yamaguchi, J. Alloys Compd. 293–295 (1999) 838–843.
- [2] Yu.M. Baikov, Tech. Phys. Lett. 25 (2000) 533–534.
- [3] Yu.M. Baikov, in: S. Linderoth, A. Smith, N. Bonanos, A. Hagen, et al. (Eds.), Proceedings of the 26th Risø International Symposium on Materials Science, Solid State Electrochemistry, Roskilde, 2005, pp. 115–121.
- [4] Yu.M. Baikov, E.K. Shalkova, Kinet. Catal. 21 (6) (1980) 1426–1430.
- [5] Yu.M. Baikov, E.I. Nikulin, V.M. Egorov, Tech. Phys. Lett. 32 (2006) 220–222.
- [6] Yu.M. Baikov, Solid State Ionics 178 (2007) 487–492.
- [7] Yu.M. Baikov, V.M. Egorov, Phys. Solid State 51 (1) (2009) 33–43.
- [8] P.M.S. Stephen, A.T. Howe, Solid State Ionics 1 (1980) 461–471.
- [9] K.-H. Haas, U. Schindewolf, J. Solid State Chem. 54 (1984) 342–345.
- [10] Yu.M. Baikov, Rus. J. Electrochem. 18 (1982) 1256–1261.
- [11] B.Sh. Elkin, E.K. Shalkova, Yu.M. Baikov, Inorg. Mater. 23 (1) (1987) 81–84.
- [12] B.Sh. El'kin, Solid State Ionics 37 (1990) 139–148.

- [13] M. Spaeth, K.D. Kreuer, Th. Dippel, J. Maier, *Solid State Ionics* 97 (1997) 291–297.
- [14] Yu.M. Baikov, *Tech. Phys. Lett.* 32 (10) (2006) 850–853.
- [15] W.M. Vogel, K.J. Routsis, V.J. Kehrer, D.A. Landsman, J.J. Tschinkel, *J. Chem. Eng. Data* 12 (4) (1967) 465–470.
- [16] H.W. Otto, R.P. Seward, *J. Chem. Eng. Data* 9 (4) (1964) 507–508.
- [17] Yu.M. Baikov, *J. Exp. Theor. Phys.* 51 (6) (1980) 1136–1141.
- [18] E.D. Yakushkin, A.I. Baranov, V.V. Grebnev, *Phys. Solid State* 49 (2007) 1353–1356.
- [19] A.M. Magdy, D. Pongkao, M. Yoshimura, *J. Solid State Electrochem.* 6 (2002) 341–350.