Regularities of processes occurring on a MnO$_2$ electrode in the course of its electrochemical treatment in aprotic organic solutions of rare earth salts by cathodic intercalation

E.S. Guseva

Yuri Gagarin State Technical University of Saratov, Engels University of Technology (branch), ul. Politekhnicheskaya 77, Saratov, Saratov Region, 410054 Russian Federation
E-mail: kett-lada@mail.ru

Extensive fundamental studies of the kinetics of processes on solid metallic electrodes under cathodic treatment in solutions of alkali, alkali earth, and rare earth salts show the necessity of studying the factors determining the electrode history by removing undesirable effects on the course of the process in order to provide full control of the experiment [1, 2]. This is especially important at the initial stage of the electrochemical intercalation process due to interaction between the metal cation in the solution and the electrode surface being studied. Comprehensive studies of the effect of the potential, duration of cathodic polarization, temperature, and solution composition on the kinetics of electrolytic alloying by cathodic intercalation show that finding the regularities of electrochemical metal intercalation into electrodes is based on analysis of the results of the semigraphical processing of potentiostatic plots. The study is aimed at enhancement of the electrochemical characteristics of lithium-ion batteries with the LiLaAl/LaMnO$_2$ system by modification of a MnO$_2$ electrode with lanthanum. This favors the formation of additional vacancies for movement of lithium ions within the cathode material. This is aimed at solving the problem of enhancement of the electrode stability in the charge–discharge processes, a natural corrosion destruction process due to dissolution of a small amount of manganese ions from the spinel surface followed by their transportation to the anode, which, in its turn, results in anode surface deactivation. The presumable mechanism of dissolution of manganese ions includes disproportionation by the scheme: $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$. A critical problem is to choose an anode characterized by corrosion resistance to an electrolyte in the course of cycling. Inhibition of anodic processes on a lithium anode in the case of active interaction with the electrolyte leads to a decrease in the battery lifetime due to the electrode embrittlement and promotes short circuiting and battery failures later on. The chosen intermetallic compounds based on the LaLiAl anode favor corrosion inhibition in an aprotic electrolyte solution in the course of cycling and stability of the electrode morphology. The work also considers a proof of the fact that modification of the studied manganese dioxide electrode occurs as a result of electrochemical cathodic intercalation. It involves a shift in the electrode potential towards more negative values as a result of the process and points to significant changes in the electrode crystalline structure. Secondary ion mass spectrometry analysis shows a high electrochemical activity of rare earth adatoms and their intense propagation inside the manganese dioxide electrode. It is found that the percentage of the electrode material components changes due to chemical transitions in the studied electrode structure and changes in the stoichiometry of the phases that are formed.

Introduction

By its character and occupation of 4f orbitals, lanthanides are subdivided into the cerium Ce and terbium Tb subgroups. The first seven elements, from Ce to gadolinium Gd, belong to the cerium subgroup, while the rest of them, from terbium to lutecium, form the terbium subgroup. A change in the metallic radii, oxidation degree, melting and boiling points, and also magnetic moment and other properties determines the periodic character of occupation of 4f orbitals. The properties of lanthanides are mainly determined by $5d^1 6s^2$-electrons, so all lanthanides resemble d-elements of group III. Despite their similar properties, lanthanides still differ. Some properties change gradually in the series from cerium to lutecium, while other properties change periodically. The observed change in the properties is explained by lanthanide compression and a gradual decrease in the atomic and ionic radii in the above sequence of metals. Hence it follows that lanthanides with the +3 oxidation state are metals manifesting reducing properties [3, 7].

Lanthanum tends to form alloys; in most cases, they are not solid solutions (SS) but intermetallic compounds: $LaAl$, $LaAl_2$, $LaAl_4$, La_2Bi, La_2Sn_3, $LaSn_2$, $LaSn_3$, $LaCu$, $LaCu_2$, $LaCu_3$, $LaCu_4$, $LaAg_n$ ($n = 1, 2, 3$).

The aim of this work is to obtain a new cathodic material with the composition $La_y Mn_{1-y} O_2$ based on a manganese dioxide electrode by its electrochemical modification using cathodic intercalation in aprotic organic solutions of lanthanum salts.

Experimental

The studied objects were: 1) electrodes containing manganese dioxide (90% MnO_2), conducting technical furnace carbon P 267 E TU 38.11574-86 (5%), Fluoroplast F-4D suspension (5%) in the form of plates with a working surface area of 2.0 cm^2; 2) electrodes of the same composition modified by cathodic treatment in a dimethylformamide solution of lanthanum salicylate ($La(OH-C_6H_4-COO)_3$); 3) electrodes as in (2) additionally modified in 0.8 M $LiClO_4$ lithium perchlorate solution in a 1:1 mixture of propylenecarbonate (PC) with dimethoxyethane (DME) by cathodic treatment in potentiostatic mode. The potential range studied is from -2.0 to -2.9 V. The duration of MnO_2 treatment is 30 min in the lanthanum salicylate solution and 1 h in the lithium salt solution. The temperature range studied is $+40$ to $-20°C$. The electrodes synthesized in this temperature range were later subjected to cathodic treatment in 0.8 M $LiClO_4$ in a PC:DME (1:1) mixture at $E_c = -2.9$ V at a temperature of 20°C. The MnO_2 electrode surface was cleaned with alcohol prior to each experiment and dried in air for 5 min. A $La_y Mn_{1-y} O_2$ electrode was prepared by cathodic treatment of MnO_2 in a dimethylformamide solution of lanthanum salicylate (0.5 M) at $E_c = -2.9$ V, $t_{cath.treat.} = 0.5$ h.

The MnO_2 and, accordingly, $La_yMn_{1-y}O_2$ electrodes were rinsed before lithiation in 0.8 M $LiClO_4$ solution in a (1:1) PC+DME mixture. The cathodic treatment was continued for 1 h at $E=-2.9$ V. The auxiliary electrode material ($S=1$ cm^2) was aluminum foil, 99.99% (A99, GOST 11069-74), 100 μm thick, treated by cathodic intercalation in a lanthanum salt solution to provide the required chemical resistance of the LiAl anode material at a potential of $E=-2.9$ V for 0.5 h. The potentials of Li_xMnO_2 and $Ln_yMn_{1-y}O_2$ were controlled using nonaqueous SCE in 0.8 M $LiClO_4$ in a mixture of PC+DME (1:1 v/v) saturated with LiCl or $LnCl_3$, respectively. The potential of epy Li/Li^+ electrode *vs*. SCE is -2.85 V.

Results and discussion

As shown experimentally, electrochemical modification of a manganese dioxide electrode by rare earth (RE) cations from aprotic organic solvents of their salts is accompanied by the formation of new phases in the studied electrodes, with their composition, structure, and properties depending on the current density and time. This follows from the shape and appearance of $i–t$ curves. According to the cathodic intercalation process theory [4–6], the analysis data obtained point to the accumulation of intercalated lanthanide cations in the form of a solid solution in the manganese dioxide electrode matrix (Figure 1). Studies on the effect of the RE nature on the electrochemical behavior of a MnO_2 electrode show regions with different kinetic control of the process in potentiostatic $i–t$ curves (Figure 1) in potentiostatic mode. When the polarizing current is switched on at the initial stage, analysis of $i–t$ curves in $i–\sqrt{t}$ coordinates allows estimating the discharge current density $i(t=0)$ (Table 1) characterizing the rate of the intercalation stage, while the slope $\Delta i/\Delta(\sqrt{t})$ can be used to determine the diffusion process characteristics: intercalation constant k_i and the value of $C_{Ln}\sqrt{D_{Ln}}$ (Table 1).

The current density on the electrode tends to zero with an increase in the polarization duration under unvaried diffusion control. According to the kinetic theory of the intercalation process, this serves as conclusive evidence of establishment of a rare earth atom diffusion front and its propagation into the electrode.

The standard equilibrium potentials of the reactions $Ln \leftrightarrow Ln^{3+}+3e^-$ and $Li \leftrightarrow Li^++e^-$ are high (E_{eq} $La/La^{3+}=-2.52$ V; E_{eq} $Li/Li^+=-3.04$ V). The choice of the working potential ($E_c=-2.9$ V *vs*. E_{NSCE} (non-aqueous silver chloride electrode)) allows one to assume that energy-consuming reactions should occur without any particular hindrance. With account for the intercalating particle size and charge and the stability of the electron structures, one can expect a determining influence of the 4f electron distribution. Comparison of the data of potentiostatic MnO_2 cathodic intercalation curves (Figure 1) in dimethylformamide solutions of RE salicylates shows that the RE nature affects the time and the steady-state character ($t \geq 15$ min) and, accordingly, cathodic intercalation current density in the series of REs after gadolinium: europium Eu, dysprosium Dy, lutecium Lu, ytterbium Yb, terbium Tb. The values are close and do not exceed 20 ± 2 mA/cm^2. For REs preceding

gadolinium (Sm, Ho, Nd, La), the steady-state current density increases considerably but remains in the range from 23 to 28 mA/cm^2.
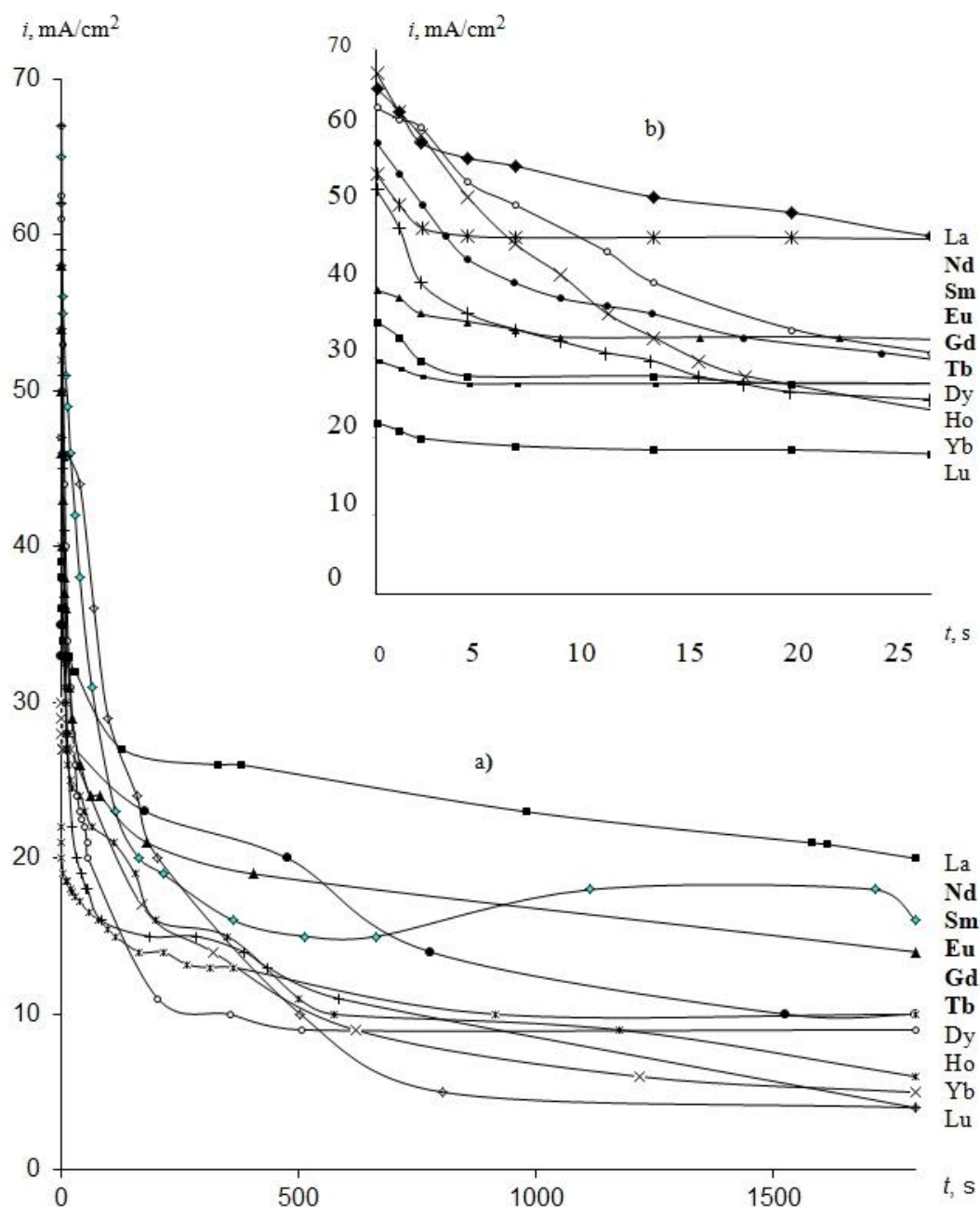
Figure 1. Potentiostatic i,t-curves of cathodic intercalation of lanthanides into a MnO$_2$ electrode from 0.5 M solutions of their salicylates in DMF at $E=-2.9$ V, polarization duration of 0.5 h, and temperature of 25°C: 1−lanthanum, 2−neodymium, 3−samarium, 4−europium, 5−gadolinium, 6−terbium, 7−dysprosium, 8−holmium, 9−ytterbium, 10−lutecium.

Comparison of $i(0)$, *i.e.*, the rate of the electrochemical intercalation act (Table 1) in the rare earth metal series La, Nd, Ho, Sm, Gd, Tb, Yb, Lu, Dy, Eu shows that in the series

from lanthanum to gadolinium, a consistent decrease in the following kinetic intercalation process parameters is observed: intercalation constant $k_i = \Delta i/\Delta(1/\sqrt{t})$, diffusion process component $C_{Ln}\sqrt{D_{Ln}}$, and discharge current density $i(0)$. From gadolinium (Gd) up to europium (Eu), the kinetic parameters of the process remain unchanged. This is due to the absence of valence electrons on the d-sublevel of europium in the cerium subgroup and ytterbium in the terbium subgroup. These REs cause the highest negative currentless potential ($E_{c/l}$) values in modified MnO_2 electrodes (Table 2). The currentless chronopotentiograms, similarly to the potentiostatic i–t curves (Figure 1), show potential and current density delay in time.

Table 1. Kinetic parameters of the cathodic process on a MnO_2 electrode at the potential of –2.9 V, polarization time of 0.5 h, and temperature of 25°C in 0.5 M rare earth salicylate solutions in DMF.

RE	Kinetic parameters of the process			Valence state
	$k_i = \Delta i/\Delta(\sqrt{t})$, $mA \cdot cm^{-2} \cdot s^{1/2}$	$C\sqrt{D}$, $mol \cdot cm^{-2} \cdot s^{-1/2} \cdot 10^{-5}$	$i(0)$, mA/cm^2	
La	5.20±0.1	3.18±0.01	67	III
Nd	4.60±0.1	2.81±0.01	65	III
Sm	4.40±0.1	2.69±0.01	63	III
Eu	4.30±0.1	2.63±0.01	54	(II)III
Gd	3.80±0.1	2.32±0.01	57	III
Tb	5.40±0.1	3.30±0.01	52	III(IV)
Dy	4.10±0.1	2.50±0.01	40	(II)III
Ho	6.60±0.1	4.03±0.01	35	III
Yb	4.90±0.1	2.99±0.01	30	III
Lu	1.00±0.1	0.611±0.01	23	(II)III

According to the basic concepts of the theory of the electrochemical intercalation process, this can be related to the multistage character of the process and possibility of formation of phases with different compositions owing to the possible change in the valence state of the intercalating rare earth cation in a modified $La_yMn_{1-y}O_2$ electrode. Another cause can be related to solid phase reactions in the bulk of the $Ln_yMn_{1-y}O_2$ electrode with recharging of Ln^{3+} ions: $Ln^{3+}+e^- \rightarrow Ln^{2+}$ (1) and subsequent intercalation of Ln^{2+} ions into the grains, $yLn^{2+}+2ye^-+MnO_2 \rightarrow Ln_yMn_{1-y}O_2$ (2), as confirmed by the scanning microscopy data (Table 3) and secondary ion mass spectrometry results (Figure 2) demonstrating the appearance of REE (for lanthanum as an example) in a MnO_2 electrode and redistribution of components (La, Mn, O) in the electrode material.

A proof of the fact that modification of the studied manganese dioxide electrode occurs as a result of electrochemical cathodic intercalation is based on a shift in the electrode

potential towards more negative values as a result of the process, which points to significant changes in the electrode crystalline structure (Table 2). Intercalation of Ln^{3+} cations into the MnO_2 cation sublattice is confirmed by the quantitative (at. %) redistribution of the elements in the modified $La_yMn_{1-y}O_2$ and, accordingly, $La_yMn_{1-y}O_2(C_{60})_n$ electrodes, as shown using the electron microscopy method (Table 3).

It is found that the percentage of the electrode material components changes due to chemical changes in the structure of the electrode studied and in the stoichiometry of the phases that are formed.

Secondary ion mass spectrometry studies of MnO_2 and La_yMnO_2 electrodes showed significant changes in the MnO_2 structure (Figure 2). This was confirmed by electron microscopy data (Table 3).

Table 2. Values of currentless potentials of a MnO_2 electrode at its cathodic polarization in 0.5 M rare earth salicylate solutions in DMF.

REs	$+E_{c/l}$, V, initial	$-E_{c/l}$, after cathodic treatment at $E_c = -2.9$ V, $t = 30$ min	
		$-E_{after\ switching\ off}$, V ($t = 1$ s)	$-E_{steady-state}$, V ($t = 300$ s)
La	0.40	0.83±0.01	0.72±0.01
Nd	0.31	0.82±0.01	0.68±0.01
Sm	0.45	0.82±0.02	0.65±0.02
Eu	0.35	0.70±0.01	0.58±0.01
Gd	0.45	0.69±0.03	0.49±0.03
Tb	0.34	0.68±0.01	0.32±0.01
Dy	0.45	0.5±0.01	0.28±0.02
Ho	0.47	0.48±0.02	0.25±0.01
Yb	0.90	0.45±0.01	0.23±0.03
Lu	0.55	0.4±0.01	0.23±0.02

Table 3. Elemental composition in the initial MnO_2 and in $La_yMn_{1-y}O_2$ electrodes after cathodic treatment in 0.5 M lanthanum salicylate solution in DMF at the potential of -2.9 V, polarization time of 0.5 h, and temperature of 25°C.

| Electrode material	C (at. %)	Mn (at. %)	O (at. %)	La (at. %)	F (at. %)
Initial MnO_2	3.44	79.28	17.28	–	–
$La_yMn_{1-y}O_2$	3.54	75.58	20.38	0.50	–

a)

b)
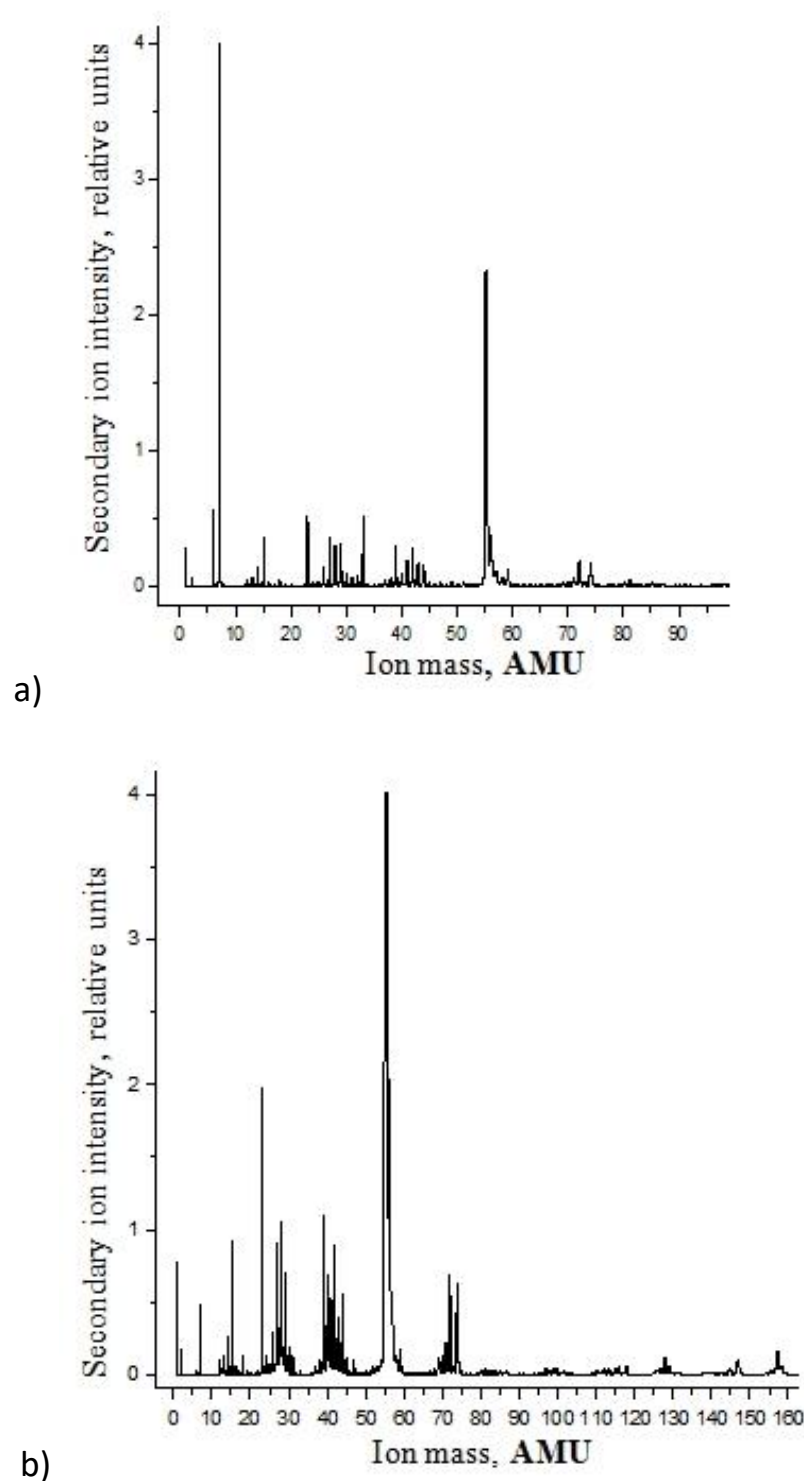
Figure 2. Secondary ion mass spectra for MnO_2 (a) and $La_yMn_{1-y}O_2$ (b).

Conclusions

In summary, the study on the effect of the rare earth cation nature on the kinetics of the cathodic lanthanide intercalation process into a MnO_2 electrode showed that cathodic intercalation resulted in a two-stage solid phase reaction in the $Ln_yMn_{1-y}O_2$ phase bulk:

1) recharging of Ln^{3+} ions on the surface with 2) the further intercalation of Ln^{2+} ions into the grain structure. Diffusion–kinetic parameters of the process of cathodic intercalation of adsorbed rare earth atoms decreased in the series of lanthanides:

$$Ln \rightarrow Nd \rightarrow Sm \rightarrow Eu \rightarrow Gd \rightarrow Tb \rightarrow Dy \rightarrow Ho \rightarrow Yb \rightarrow Lu$$
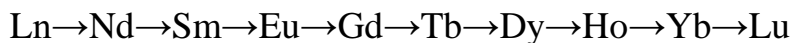
The most stable phases in the MnO_2 electrode structure were formed as a result of electrode treatment in a lanthanum salicylate solution, according to currentless chronopotentiometry data (Table 2). Mass spectrometry results proved the occurrence of chemical transitions in the studied $La_yMn_{1-y}O_2$ system accompanied by changes in the stoichiometric composition.

References

1. M. Bou, J.M. Martin, Th. Le Mogne and L. Vovelle, Chemistry of the interface between aluminium and polyethyleneterephthalate by XPS, *Appl. Surf. Sci.*, 1991, **47**, no. 2, 149–161.

2. A.N. Dey, Lithium anode film and organic and inorganic electrolyte batteries, *Thin Solid Films*, 1977, **43**, no. 1/2, 131–171.

3. B.N. Kabanov, I.I. Astakhov and I.G. Kiseleva, Electrochemical intercalation of alkali metals, *Usp. Khim.*, 1965, **34**, no. 10, 1813–1830 (in Russian).

4. N.N. Tomasheva, I.G. Kiseleva and B.N. Kabanov, Application of the chronopotentiometry technique for studying cathodic intercalation of alkali metals, *Elektrokhimiya*, 1972, **8**, no. 1, 112–116 (in Russian).

5. B.N. Kabanov, I.I. Astakhov and I.G. Kiseleva, Electrochemical intercalation of elements into electrodes, Elektrokhimia, 1972, no. 7, 955–971 (in Russian).

6. B.N. Kabanov, Intercalation is a new trend in studies of the kinetics of metal electrochemical deposition and dissolution/in: B.N. Kabanov, I.I. Astakhov and I.G. Kiseleva, *Kinetika slozhnykh elektrokhimicheskikh reaktsii* (*Kinetics of Complex Electrochemical Reactions*), Moscow, Nauka, 1981, 200–239 (in Russian).

7. J.-C.G. Bünzli, On the design of highly luminescent lanthanide complexes, *Coord. Chem. Rev.*, 2015, **293**–**294**, 19–47. doi: 10.1016/j.ccr.2014.10.013

8. S.S. Popova, B.N. Kabanov, L.A. Alekseeva *et al*., Effect of the solvent nature on the kinetics of lithium intercalation into an aluminum cathode, *Elektrokhimiya*, 1985, **11**, no. 1, 38–44 (in Russian).

♦ ♦ ♦