

# Intercalation of Sodium and Lithium into Graphite as a First Stage in an Electrochemical Method for Producing Carbon Nanotubes

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**Abstract**—A cyclic voltammetry method is used to show that the process of reduction of sodium (and, possibly, lithium) out of melts of corresponding chlorides on the molybdenum, glassy-carbon, and graphite electrodes is complicated by the process of dissolution of the corresponding alkali metal in the melt. A notion called “reversibility of material balance” is introduced. The notion reflects the ratio of the amount of substance that undergoes oxidation in the anodic half-cycle of a voltammetric curve to the amount of substance that is deposited in the cathodic half-cycle of the curve. The adsorption of sodium and lithium on glassy carbon and graphite plays an important role in the process of reduction, leading to an increase in the reversibility of the process. This is pronounced especially strongly at potential scan rates below  $1 \text{ V s}^{-1}$ . The sodium intercalation into graphite leads to a decrease in the reversibility of the process of reduction, the more so at potential scan rates below  $0.03 \text{ V s}^{-1}$ . However, the intercalation of lithium (probably because of its small atomic radius) does not exert practically any influence on the reversibility of process at the above potential scan rates.

**Key words:** sodium chloride, lithium chloride, sodium, lithium, deposition, intercalation, graphite, reversibility, carbon nanotubes

## INTRODUCTION

Since the instant when carbon nanotubes were discovered in 1991 [1], several methods designed for their production have been described in the relevant literature. These include the carbon evaporation in an electric-arc discharge, the destruction of carbon by means of a laser, the catalytic decomposition of gaseous hydrocarbons, the catalytic decomposition of fullerenes, and so on. In 1995, Hsu with co-workers (Sussex, Great Britain) produced carbon nanotubes by subjecting molten lithium chloride to electrolysis with the application of a carbon cathode of high purity [2, 3]. Starting since that time, the electrolytic method has been drawing attention of the researchers and, according to information at our disposal, three more groups in the world are busy investigating this method, specifically, Fray with co-workers (Cambridge, Great Britain) [4–8], Bai with co-workers in France [9], and a group in a city of Miskolc in Hungary [10–13]. It was established that the application of graphite as the cathode material instead of amorphous carbon also led to the formation of nanotubes [4]. Also found was that nanotubes can be manufactured by depositing on graphite not only metallic lithium, but other alkali and alkaline-earth metals as well, such as sodium, magnesium, and calcium [10]. Therefore, we deem it possible to claim

that the electrolytic method of production of carbon nanotubes holds some promise.

It is generally believed that, in the course of the electrolytic technique of production of carbon nanotubes, atoms of alkali and alkaline-earth metals (Li, Na, Mg, Ca), when deposited on the surface of a cathode, i.e. graphite, are intercalated in the space between layers of graphite, giving rise to a mechanical stress. At a certain time instant when the stress turns too high, graphite layers begin to spall and may appear in the melt, where they bend under the action of gravitational attraction between carbon atoms that have cleaved bonds, which leads to the formation of carbon nanotubes of different shapes and dimensions.

In our recent work [13] there was introduced the term “reversibility of material balance,” which was applied to a description of the process of electrochemical reduction of sodium out of its molten chloride. The aim of the present work is to compare the reversibility of processes of electrochemical reduction of sodium and lithium out of corresponding molten chlorides.

## EXPERIMENTAL

A description of the experimental setup, the procedures used for taking measurements, the procedure employed when preparing electrolyte, and the technique for processing voltammetric curves are given in [13].

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Experiments in molten sodium chloride were conducted at a temperature of 850°C, and those in molten lithium chloride were done at 700°C.

It is known that lithium chloride is hygroscopic and is capable of retaining moisture even at elevated temperatures. After keeping the cell at 300°C [13], the temperature was elevated to 500°C and the cell was kept at this temperature in a vacuum for one hour. At that time period there was realized a periodic blowing of the cell with purified and desiccated argon, in order to attain a maximum degree of the drying-up of the salt. A similar procedure was conducted also at a temperature of 600°C. Thereafter the salt was melted in an atmosphere of purified and desiccated argon.

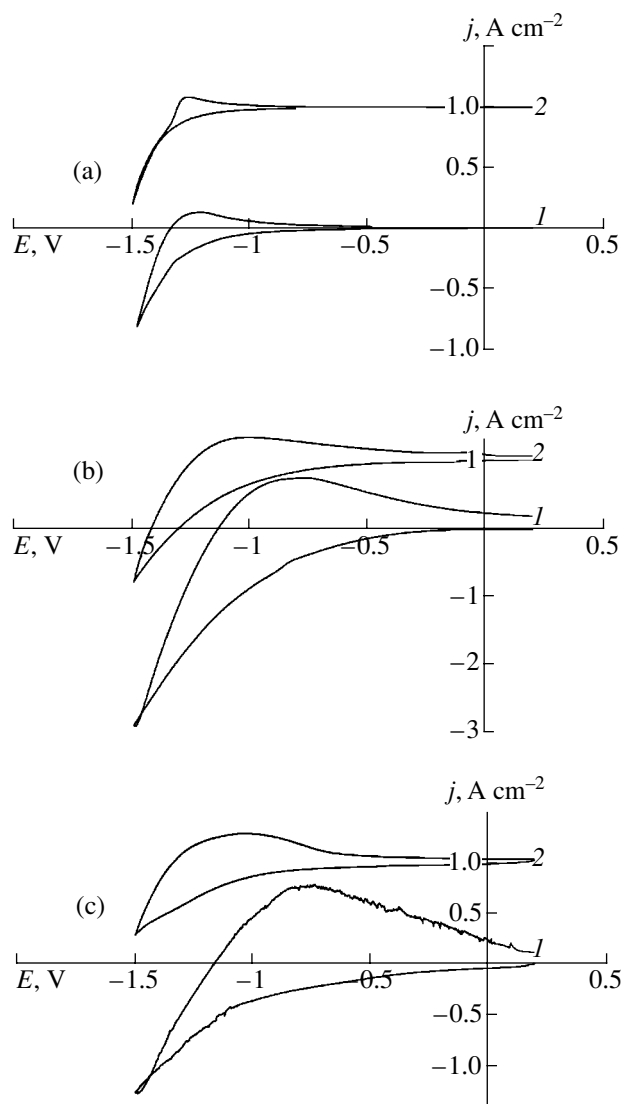
In order to obtain voltammetric curves in molten sodium chloride, we applied working electrodes that had been prepared from molybdenum (diameter 0.9 mm, surface area 0.29 cm<sup>2</sup>), glassy carbon (diameter 1.8 mm, surface area 0.2 cm<sup>2</sup>), and graphite (diameter 3 mm, surface area 0.47 cm<sup>2</sup>). In molten lithium chloride, voltammetric curves were obtained using the working electrodes of glassy carbon (diameter 1.7 mm, surface area 0.48 cm<sup>2</sup>) and graphite (diameter 3 mm, surface area 0.36 cm<sup>2</sup>). When working in a sodium chloride melt, a molybdenum wire 0.9 mm in diameter served as the reference electrode; and, when working in lithium chloride, a glassy-carbon rod 2.6 mm in diameter.

The recording of the voltammetric dependences was performed in the interval of potential scan rates  $\nu$  extending from 20 to 0.01 V s<sup>-1</sup>, starting with potential  $E_1 = 0.2$  V (NaCl) and  $-0.4$  V (LiCl) relative to the potentials of the carbon reference electrodes. The potential of reversal  $E_2$  was varied from 0 to  $-2.0$  V (NaCl) and from  $-0.5$  to  $-2.3$  V (LiCl).

## RESULTS AND DISCUSSION

Typical voltammograms, which were obtained in a melt of sodium chloride at potential scan rates of 3 and 0.3 V s<sup>-1</sup> and the potential of reversal  $-1.5$  V on the molybdenum, glassy-carbon, and graphite electrodes, are presented in Fig. 1. At first glance, the charge that corresponds to the anodic portion of the curve, is considerably smaller than that of the cathodic portion. In other words, a fraction of the metal that was deposited on the electrode surface undergoes no electrochemical oxidation in the anodic region. This may be connected with a decrease in the amount of metallic sodium at the electrode surface as a result of its diffusion into either the electrolyte bulk or the material of the electrode, i.e. graphite.

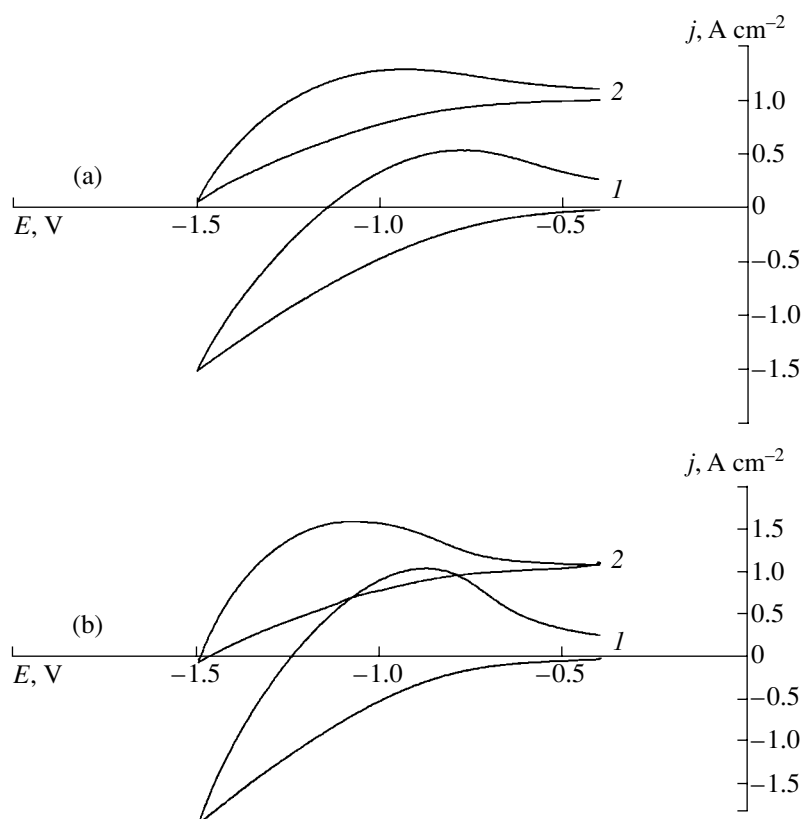
The appearance of the loops in curves 1 in Figs. 1b and 1c may be explained in the following manner. At high potential scan rates (1 V s<sup>-1</sup> and higher), the system has no sufficient time to follow the shift of the potential of the working electrode. This implies that sodium ions cannot instantaneously alter the direction of their motion at the time instant of the reversal of the



**Fig. 1.** Cyclic voltammograms, obtained in an NaCl melt at ( $I$ ) 3 and ( $2$ ) 0.3 V s<sup>-1</sup> in the potential region from +0.2 V to  $-1.5$  V on (a) molybdenum, (b) glassy-carbon, and (c) graphite electrodes. For identification convenience, curves 2 are “elevated” by 1 A cm<sup>-2</sup> along the axis of current densities relative to their true values.

potential scan. In other words, in the course of a certain time period after the change in the direction of the scan, we have a flux of sodium ions, which increases by its absolute value, which leads to the emergence of a loop in the curves. And the higher the potential scan rate and the more negative the potential of reversal, the more pronounced this effect.

The “wavy” character of curve 1 in Fig. 1c may be caused by some changes occurring in the state of the surface of the working electrode, because this particular curve was recorded in the middle of experiment and by that time considerable quantities of sodium could



**Fig. 2.** Cyclic voltammograms, obtained in an LiCl melt at (1) 3 and (2) 0.3 V s<sup>-1</sup> in the potential region from -0.4 V to -1.5 V on (a) glassy-carbon, and (b) graphite electrodes.

have undergone adsorption/desorption at the electrode surface or intercalation into the graphite lattice.

Typical voltammetric curves, which were obtained on the glassy-carbon and graphite electrodes in a melt of lithium chloride at potential scan rates equal to 3 and 0.3 V s<sup>-1</sup> and the potential of reversal equal to -1.5 V are presented in Fig. 2. One can notice that the ratio between areas enveloped by the cathodic and anodic branch of the voltammetric curves varies as a function of the potential scan rate. The area under the cathodic branches of the voltammetric dependences at a potential scan rate of 3 V s<sup>-1</sup> is larger than that under the anodic ones. However, this difference at 0.3 V s<sup>-1</sup> is not that significant, especially on the graphite electrode.

The ratio between the areas under cathodic and anodic branches of a voltammetric curve, which was called in [13] the degree of “reversibility of material balance,” may be expressed by the following expression:

$$\text{Rev} = 50 \left( 1 - \frac{A_{\text{anod}}}{A_{\text{cath}}} \right), \% \quad (1)$$

In this equation,  $A_{\text{anod}}$  and  $A_{\text{cath}}$  are the areas under the anodic and cathodic branches of a voltammogram, respectively. An area has a negative sign in the region of negative currents and a positive sign in the region of

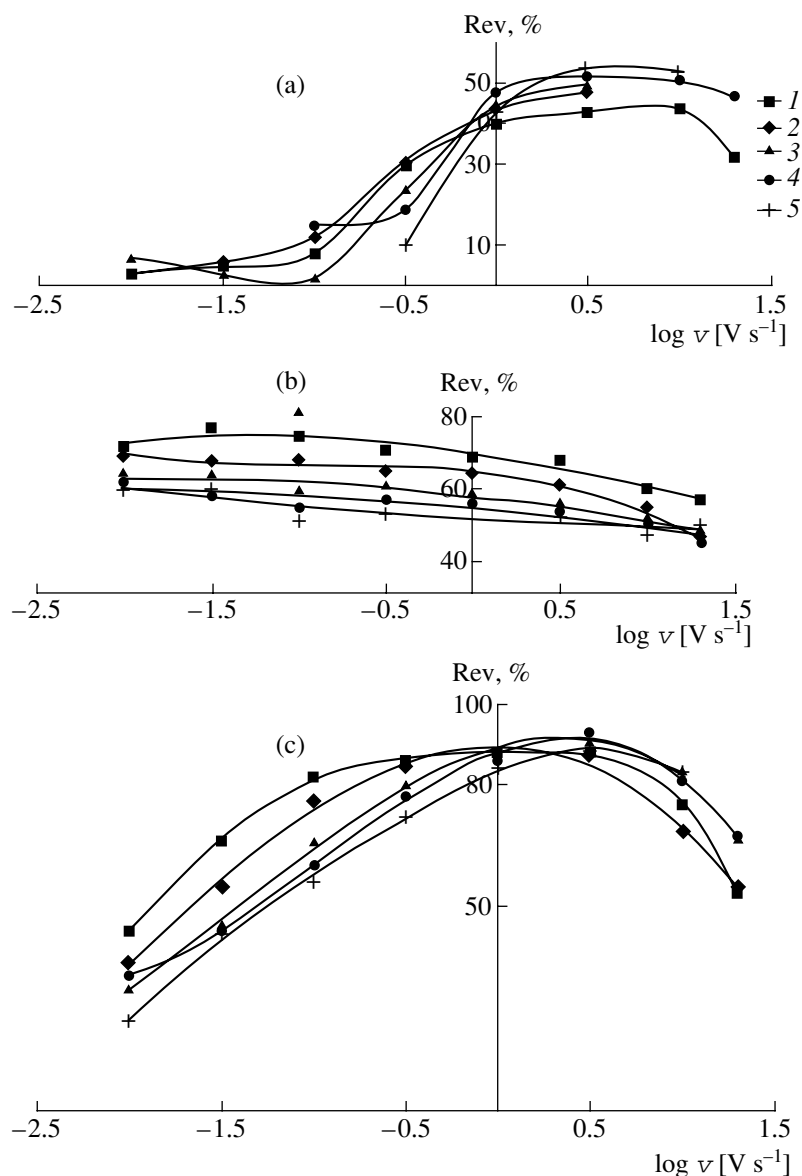
positive currents. The physical meaning of this equation may be demonstrated by analyzing the following simplest cases.

(a) When the cathodic branch coincide with the anodic one, i.e. when  $A_{\text{cath}} = A_{\text{anod}}$ , the entire metal deposited on the working electrode is kind of lost, i.e. the metal undergoes no electrochemical oxidation in the anodic half-cycle. Under these conditions Rev = 0%.

(b) In the case where the complete integral under the anodic branch is equal to zero (i.e. one half of the anodic branch is situated in the cathodic region of currents and the other half of this branch, in the anodic region), we have Rev = 50%, which implies that only half the deposited metal is lost.

(c) When the anodic branch completely counterbalances the cathodic one, i.e.  $A_{\text{cath}} = -A_{\text{anod}}$ , we have Rev = 100%. Under these conditions the process is completely reversible, which means that the entire metal deposited on the working electrode undergoes electrochemical oxidation and does not leave for the electrolyte.

The reversibility parameter Rev, which was calculated on the basis of a computer-aided treatment of voltammetric curves recorded in molten sodium chloride, is presented in Fig. 3 and Table 1. On the basis of the dependences we obtained, we deem it possible to draw the following conclusions.



**Fig. 3.** Dependences of the reversibility degree on the common logarithm of the potential scan rate for voltammetric curves obtained on (a) molybdenum, (b) glassy-carbon, and (c) graphite electrodes in an NaCl melt at (1)  $-1.0$ , (2)  $-1.25$ , (3)  $-1.5$ , (4)  $-1.6$ , and (5)  $-1.7$  V.

(1) For a molybdenum working electrode, the Rev vs.  $\log v$  dependence (Fig. 3a) has an S-shaped form. The value of the degree of reversibility for the majority of the curves recorded at  $v > 1 \text{ V s}^{-1}$  amounts to approximately 50% and tends to zero at  $v < 0.1 \text{ V s}^{-1}$ . Such a behavior may be explained by a fast diffusion of deposited sodium into the bulk melt [14]. At very low potential scan rates, practically the entire sodium leaves the electrode surface. This means that only an insignificant fraction of the deposited metal undergoes electrochemical oxidation in the anodic half-cycle. At high potential scan rates, however, only a fraction of sodium deposited in the cathodic half-cycle is lost and a fraction of sodium deposited at the beginning of the anodic half-

cycle undergoes electrochemical oxidation at the end of the anodic half-cycle.

(2) In the case of a glassy-carbon working electrode (Fig. 3b), values of the degree of reversibility amount to 50–60% at the maximum value of the potential scan rate ( $20 \text{ V s}^{-1}$ ). However, following a decrease in the potential scan rate, the amount of deposited sodium that undergoes electrochemical oxidation is steadily increasing, which means that the amount of sodium that passes into the bulk of molten sodium chloride by means of diffusion is steadily decreasing. This is caused probably by the capability of sodium to undergo adsorption at the surface of glassy carbon. In other words, there forms a certain stable compound of the

**Table 1.** Typical values of the degree of reversibility for the process of deposition/dissolution of sodium;  $E_1 = 0.2$  V,  $E_2 = -1.5$  V

Electrode	$v$ , V s <sup>-1</sup>	$-A_{\text{cath}}$ , mW cm <sup>-2</sup>	$A_{\text{anod}}$ , mW cm <sup>-2</sup>	Rev, %
Molybdenum	10	214.0	0.8	50
	3	137.2	0.3	50
	1	114.8	-11.1	45
	0.3	95.8	-49.8	24
	0.1	93.9	-89.2	3
Glassy carbon	10	1521.9	57.8	52
	3	1102.5	129.2	56
	1	787.8	134.6	59
	0.3	516.0	113.9	61
	0.1	356.3	69.7	60
Graphite	10	762.2	502.6	83
	3	521.3	425.5	91
	1	375.5	288.6	88
	0.3	229.1	137.1	80
	0.1	146.5	45.8	66

**Table 2.** Typical values of the degree of reversibility for the process of deposition/dissolution of lithium;  $E_1 = -0.4$  V,  $E_2 = -1.5$  V

Electrode	$v$ , V s <sup>-1</sup>	$-A_{\text{cath}}$ , mW cm <sup>-2</sup>	$A_{\text{anod}}$ , mW cm <sup>-2</sup>	Rev, %
Glassy carbon	10	799.2	11.9	51
	3	572.5	59.1	55
	1	408.8	72.3	59
	0.3	303.6	71.9	62
	0.1	230.7	73.7	66
Graphite	10	1034.2	468.1	73
	3	686.0	329.3	74
	1	450.6	233.3	76
	0.3	302.0	249.9	91
	0.1	287.1	220.4	88

formula  $\text{NaC}_x$ . However, the adsorption rate is lower than the rate of diffusion into the bulk of molten sodium chloride. As a consequence, stabilization of sodium deposited onto the electrode surface is pronounced better at small values of the potential scan rate.

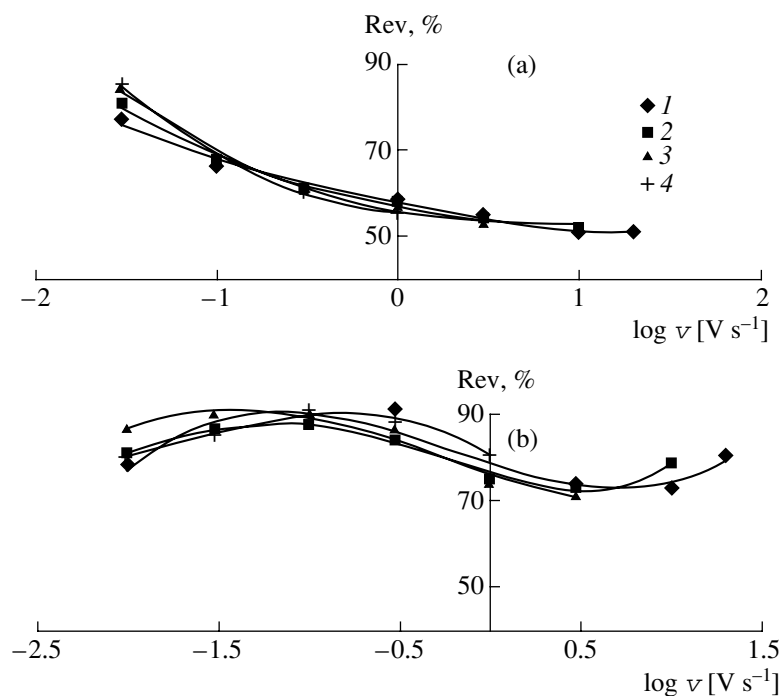
(3) At the maximum potential scan rate ( $20 \text{ V s}^{-1}$ ), values of the degree of reversibility for a graphite electrode are approximately the same or somewhat higher

as those for the glassy-carbon electrode. At a potential scan rate on the order of  $3 \text{ V s}^{-1}$ , the reversibility parameter passes through a maximum. At this point, values of the degree of reversibility for a graphite electrode are considerably larger than those for the glassy-carbon electrode. In other words, the number of sodium atoms present at the surface of graphite is larger than that present at the surface of glassy carbon. This is caused probably by a larger value of the specific surface area of graphite as compared with glassy carbon, which leads to an increase in the quantity of adsorbed sodium. Following a decrease in the potential scan rate, however, the degree of reversibility drastically drops to zero as opposed to what was observed in the case of a glassy-carbon working electrode. This is caused probably by the diffusion of sodium atoms into graphite and by the stabilization of sodium inside graphite at the expense of the formation of some stable intercalation compound.

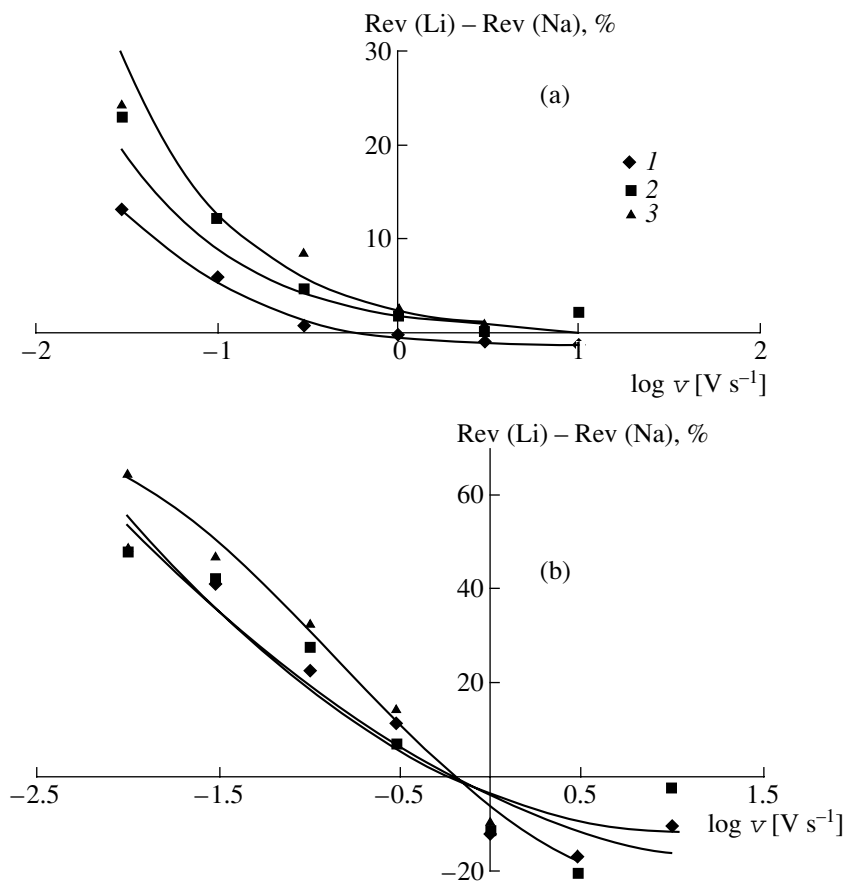
Our claims as to the adsorption and intercalation are confirmed by the shape and characteristics of the voltammograms we presented. In Fig. 1, upon going from a molybdenum electrode to a glassy-carbon electrode to a graphite electrode, we observe a tendency to a broadening of the anodic peak, as well as to a shift of its potential into the region of positive values. Usually, such a behavior takes place in the case where the process of reduction is complicated by either adsorption or formation of some compound. Thus, the shape and parameters of voltammetric curves we presented may serve as a testimony to that the adsorption, in the case of a glassy-carbon electrode, and the adsorption/intercalation, in the case of a graphite electrode, play an important role in the process of reduction of sodium.

The rates of the three competing processes we have described in the foregoing can be arranged in the following manner: (a) the fastest process is the diffusion of sodium into molten sodium chloride, probably by virtue of a specific mechanism of the diffusion (at the expense of an electron hop) [14]; (b) the rate of the sodium adsorption on carbon has intermediate values; and (c) the slowest process is the sodium intercalation into graphite leading to the formation of an intercalation compound.

The reversibility parameter, which was calculated for the voltammograms that were obtained in a lithium chloride melt on the glassy-carbon and graphite electrodes, is presented in Table 2 and Fig. 4 in the form of a dependence on the common logarithm of the potential scan rate. As follows from the dependence we presented in Fig. 4a, in the case of the glassy-carbon electrode, the value of the degree of reversibility amounts to approximately 50% at a potential scan rate of  $20 \text{ V s}^{-1}$ , whereas at  $0.03 \text{ V s}^{-1}$  it is equal to 75–85%. This could be explained by the adsorption of lithium atoms on the electrode surface with the formation of a surface compound of the formula  $\text{LiC}_x$ , i.e. similarly to what we observed in the case of sodium. A confirmation to this is the fact that the voltammetric curves presented in Fig. 2



**Fig. 4.** Dependences of the reversibility degree on the common logarithm of the potential scan rate for voltammetric curves obtained on (a) glassy-carbon and (b) graphite electrodes in an LiCl melt at (1) -1.5, (2) -1.6, (3) -1.7, and (4) -1.8 V.



**Fig. 5.** Dependences of the difference between reversibility degrees for electroreduction of sodium and lithium on the common logarithm of the potential scan rate for (a) glassy-carbon and (b) graphite electrodes at (1) -1.5, (2) -1.6, and (3) -1.7 V.

exhibit broad anodic peaks. It should be noted that lithium atoms display a more pronounced tendency to undergoing adsorption on carbon as compared with sodium atoms. The degree of reversibility in the case of lithium is higher than in the case of sodium at small values of the potential scan rate (Figs. 3b, 4a; Tables 1, 2). This conforms to the atomic radii of the alkali metals under investigation, specifically, 0.155 nm for lithium and 0.189 nm for sodium, respectively.

This effect is easier to notice in Fig. 5a, where we presented the difference between values of degrees of reversibility for processes of electrochemical reduction of sodium and lithium as a function of the common logarithm of the potential scan rate. As follows from the figure, at potential scan rates in excess of  $1 \text{ V s}^{-1}$ , the difference between values of degrees of reversibility in question is close to zero. This implies that the processes of electrochemical reduction of sodium and lithium at given potential scan rates resemble one another with respect to the degree of reversibility. However, with decreasing potential scan rate, the degree of reversibility of the process of reduction of lithium increases faster than that of the process of reduction of sodium, which may be caused by a stronger adsorption of lithium to carbon as compared with sodium.

For the majority of curves, parameter Rev in the case of a graphite electrode lies within the limits of 75–90% (Fig. 4b), which value is marginally larger than that for a glassy-carbon electrode and which may be explained by a higher degree of stabilization of lithium on graphite as compared with glassy carbon, i.e. analogously to the explanation we used for sodium. For lithium, as opposed to sodium, we observed no drop in the reversibility at small values of the potential scan rate (below  $3 \text{ V s}^{-1}$ ). Our explanation to this observation is that lithium has a far smaller atomic radius than sodium does (see above). Lithium atoms, when intercalated in the space between layers of graphite (the distance between the layers is equal to 0.335 nm) may freely leave graphite and undergo electrochemical oxidation following a change in the direction of the potential scan. In other words, the process of intercalation of lithium into the graphite lattice is reversible, whereas the sodium intercalation is an irreversible process. Consequently, the fraction of metallic lithium, which is deposited on an electrode and which undergoes electrochemical oxidation, is larger than that in the case of sodium. In accordance with formula (1), this leads to an increase in the degree of reversibility at potential scan rates under  $3 \text{ V s}^{-1}$ .

From the dependence of the difference between the values of degrees of reversibility for the processes of electrochemical reduction of sodium and lithium on a graphite electrode, which is presented in Fig. 5b, we infer that, at potential scan rates above  $1 \text{ V s}^{-1}$ , the difference between the values of degrees of reversibility in question is close to zero. Following a decrease in the potential scan rate, the difference between the values of

degrees of reversibility for the two processes dramatically increases, reaching 45–60% at the smallest value of the potential scan rate ( $0.01 \text{ V s}^{-1}$ ).

Another point worthy of being mentioned is the possibility of chemical dissolution of lithium in molten lithium chloride, which could have exerted an effect on the obtained values of the degree of reversibility in the cases of the glassy-carbon and graphite working electrodes.

## CONCLUSIONS

(1) The process of electrochemical reduction of sodium and, possibly, lithium on the electrode materials that were used in this work is complicated by the dissolution of the alkali metal in the relevant melt throughout an entire interval of potential scan rates.

(2) The adsorption of sodium and lithium on glassy carbon and graphite plays an important role in the process of electrochemical reduction, the more so at potential scan rates below  $1 \text{ V s}^{-1}$ . It leads to an increase in the degree of reversibility of the process.

(3) The sodium intercalation into the graphite lattice at small values of the potential scan rate (under  $0.03 \text{ V s}^{-1}$ ) diminishes the overall reversibility of the process. The lithium intercalation, on the other hand, hardly effects the process reversibility following a decrease in the potential scan rate to  $0.03 \text{ V s}^{-1}$ .

In the future we will make an attempt to try and create a quantitative model for the processes we have described in the foregoing and in so doing obtain quantitative values of the rates of the diffusion and adsorption/desorption of sodium and lithium, as well as determine the rates of their intercalation into graphite.

## ACKNOWLEDGMENTS

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