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STATE OF AGGREGATION OF THE CATHODE METAL, AND ELECTROCHEMICAL INCORPORATION

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The cathodic incorporation of lithium into liquid and solid gallium (24 to 60°C) and into liquid and solid Wood's alloy (60 to 90°C) was studied from 0.6 N $LiClO_4$ in propylene carbonate. It was established by chronopotentiometry, polarization curves, and chemical analysis that the rate of cathodic incorporation of the lithium from nonaqueous solution is independent of the state of aggregation of the cathode metal, while the anodic behavior of the intermetallic compounds may differ between solid and liquid electrodes, owing to side effects.

The electrochemical incorportation and the subsequent stage of diffusion of the incorporated atom in the cathode metal are structure-sensitive processes [1-3]. One could have expected, therefore, that the state of aggregation of the cathode metal would influence the rate of the process as a whole.

It is known, on the other hand, that incorporation can proceed via a mechanism where the rate of the process is limited by the rate of formation of the intermetallic compound as a chemical reaction [4, 5]. In this case the incorporation into solid and liquid cathodes should occur with the same rate.

In the present work we have studied the temperature dependence of the incorporation rate and the role of the state of aggregation of the cathode metal in the process of incorporation for the cases of alkali metals being incorporated into gallium (t_m = 29.5°C) and Wood's alloy (t_m = 71.5°C).

Both the liquid and solid electrodes were placed into a glass cup which had the platinum current lead fused into the glass. Platinum which either was placed into the same cell or was separated from the cathode compartment by a stopcock served as the anode. Lithium incorporation into gallium and Wood's alloy was conducted from 0.6 N $LiClO_4$ + 0.01 N LiCl in propylene carbonate. In addition, measurements were made for Wood's alloy in 1 N LiOH in water. Hydrogen atmosphere was used for the measurements in aqueous solution; a hermetically closed cell was used for nonaqueous solution. Reference electrode in the case of 1 N aqueous LiOH solution was a 1 N mercury—mercuric oxide electrode, and in the case of nonaqueous solution a silver—silver chloride electrode. The values of potentials for the aqueous solution are given relative to the nhe, those for propylene carbonate solutions relative to the normal lithium electrode (n.Li.e.) which had a potential against the silver—silver chloride electrode in propylene carbonate of −2.9 V.

The temperature dependence of lithium incorporation into gallium was studied over the temperature range of 24 to 60°C, that into Wood's alloy between 60 and 90°C.

The gallium cathode was polarized for 4 h at 0.85 V (n.Li.e.) in the nonaqueous solution, whereupon incorporated lithium was leached with water. The LiOH solution obtained was then titrated with 0.1 N H_2SO_4. The average rate of incorporation of lithium into gallium was calculated from the amount (Q_{chem}) of lithium thus found to have been incorporated in 4 h. The product formed during the incorporation of lithium into gallium was studied radiographically with an URS-50-I instrument.

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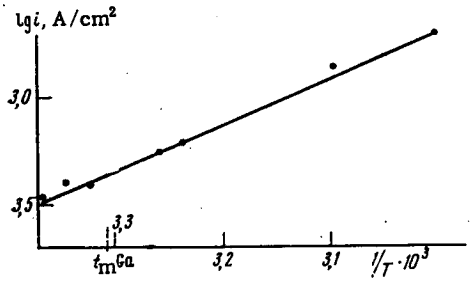

Fig. 1

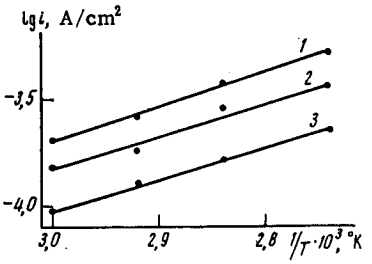

Fig. 2

Fig. 1. Temperature dependence of the rate of incorporation of lithium into gallium (temperature in °K). Nonaqueous solution, φ_c = 0.85 V.

Fig. 2. Temperature dependence of the rate of incorporation of lithium into Wood's alloy (temperature in °K). Nonaqueous solution, the φ_c values: 1) 0.4 V, 2) 0.6 V, and 3) 0.85 V.

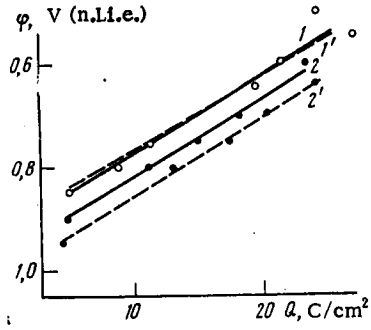

Fig. 3

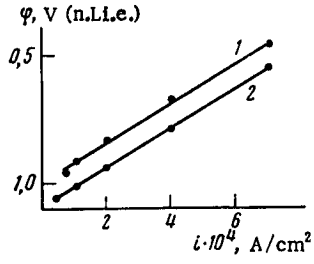

Fig. 4

Fig. 3. Potential dependence of the amount of lithium incorporated from nanaqueous solution at 26°C into solid (1, 1') and at 34°C into liquid (2, 2') gallium; the amount of lithium which had been incorporated in 4 h was determined by chemical analysis (1, 2) or calculated from the amount of charge passed (1', 2').

Fig. 4. Polarization curves of lithium incorporation at 70°C into solid (1) and at 80°C into liquid (2) Wood's alloy. Nonaqueous solution.

The rate of incorporation of lithium into Wood's alloy from nonaqueous solution was found by direct measurements of the cathodic current at potentials of 0.85, 0.6, and 0.4 V, assuming that the current yield is close to 100%. The temperature dependence of the rate of incorporation of lithium into gallium and Wood's alloy is shown in Figs. 1 and 2.

It can be seen from Figs. 1 and 2 that the rate of incorporation from the nonaqueous solutions increases with temperature. The activation energies calculated from the temperature dependence were found to be 46 kJ for gallium, and 34 kJ for Wood's alloy.

Formation of five intermetallic compounds, Li_3Ga_2, Li_2Ga, LiGa, $LiGa_2$, and $LiGa_3$, is possible in the lithium–gallium system [6]. Under our conditions the intermetallic compound LiGa is formed when lithium is incorporated into both liquid and solid gallium. This was established by radiographic examination of the incorporation product (Table 1) and comparison of the data obtained with literature data [7].

According to [5], the rate of incorporation of lithium into gallium is determined by the rate of formation of the intermetallic compound as a chemical reaction. This means that the energy of activation (46 kJ) found for lithium incorporation into gallium from propylene carbonate solution refers to the chemical reaction

TABLE 1. Comparison of the Radiographic Data for the Incorporation Product of Li into Ga with Literature Data for the Intermetallic Compound LiGa

Experimental			Literature data		Experimental			Literature data	
line No.	I*	d*, Å	I	d, Å	line No.	I*	d*, Å	I	d, Å
1	70	3,54	60	3,55	5	15	1,41	21	1,41
2	100	2,18	100	2,17	6	20	1.25	55	1,26
3	34	1,85	40	1,85	7	6	1.18	21	1.19
4	12	1,53	22	1,54	8	8	1,08	24	1,09

*I is intensity, d is the lattice spacing.

$$Li+Ga=LiGa. \quad (1)$$

It is difficult to say, in view of the complexity of the composition of Wood's alloy, precisely which reaction is characterized by the value found (34 kJ) for the activation energy of incorporation into Wood's alloy.

It is important to note that in the straight lines of Figs. 1 and 2 which show the temperature dependence of the rate of incorporation there are no breaks at the melting point of the cathode with gallium or Wood's alloy. This means that the mechanism of lithium incorporation into gallium and Wood's alloy does not change with the state of aggregation of the cathode metal.

Figure 3 shows the potential dependence of the amount of lithium incorporated into gallium from nonaqueous solution. The average rates of incorporation into liquid and solid gallium over 4 h are very similar. The small difference in the positions of curves 1 and 2 is mainly due to the temperature dependence of the rate (cf. Figs. 1 and 2). The potential dependence of lithium incorporation into Wood's alloy from nonaqueous solution is also linear (Fig. 4).

The linear potential dependence of the rate of incorporation, independence of the activation energy on the state of aggregation of the electrode metal, and absence of any jump in the rate at the point where the state of aggregation is changing mean that the rate-limiting step in the incorporation of lithium into gallium and Wood's alloy from nonaqueous solution is the formation of intermetallic compounds as a chemical reaction.

Thus, neither the mechanism nor the rate of incorporation into gallium and Wood's alloy depend substantially on the state of aggregation of the cathode metal. But the anodic behavior of the intermetallic compound may change with the state of aggregation of the cathode metal. We recall that the state of aggregation of the gallium intermetallic compound was the same with liquid and solid gallium. The intermetallic compound LiGa has a high melting point (740°C [6]), so that during cathodic incorporation from solutions it is always obtained in the solid state. The anodic chronopotentiograms for the liquid and solid electrode are shown in Fig. 5. The cathodic prepolarization of the electrodes was the same, so that the amounts of lithium in the liquid and solid gallium also were the same. But upon application of the anodic current, the electrode potential attains more rapidly the potential of pure gallium (i.e., a smaller quantity of lithium is extracted) in the case of the liquid electrode (Fig. 5). It is obvious that the anodic decomposition of the intermetallic compound follows a selective mechanism, i.e., occurs in such a way that only the alkali metal passes into the solution, while instead of the intermetallic compound, the cathode metal is left over at the cathode surface, which in the present case is gallium. If the decomposition occurs under conditions such that there are no gallium crystallization nuclei on the surface, then a layer of liquid gallium is formed there which, by uniformingly spreading over the electrode surface, will isolate the solid intermetallic compound from the solution; at this point the further decomposition of the intermetallic compound is practically suspended. But if the lithium had appreciable primary solubility in the gallium, then the formation of the liquid gallium layer on the electrode surface would not pose an obstacle to the complete anodic leaching of the lithium, since the lithium would pass from the cathode into the solution by diffusing across the liquid gallium layer. Since the solubility of lithium in liquid gallium at room temperature is very low, the decomposition of the intermetallic compound must cease with the formation of the liquid gallium layer between the intermetallic compound and the electrolyte (as the layer is liquid, it also will be continuous, provided the intermetallic compound is wetted by gallium).

Another possible explanation why at the liquid electrode one finds a smaller quantity of alkali metal than at the solid electrode is related to the interaction between the intermetallic compound and the water contained in the solution.

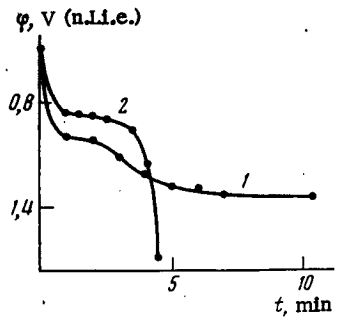

Fig. 5

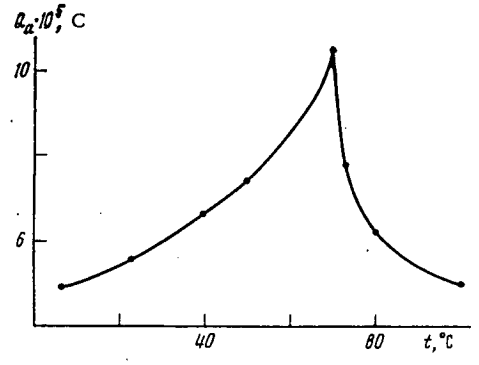

Fig. 6

Fig. 5. Anodic chronopotentiograms for solid (1) and liquid (2) gallium at 28°C; $Q_c = 3.5 \cdot 10^{-3}$ C/cm^2, $\varphi_c = 0.6$ V, $i_a = 2.5 \cdot 10^{-3}$ A/cm^2. Nonaqueous solution.

Fig. 6. Temperature dependence of the amount of lithium extracted from Wood's alloy, as found from the length of the arrest on the anodic chronopotentiograms in 1 N aqueous LiOH solution; $\varphi_c = -1.6$ V (nhe), $t_c = 25$ min, $i_a = 4 \cdot 10^{-5}$ A/cm^2.

The structural nonuniformity of the cathode surface is known to be very important in the incorporation of alkali metals from aqueous solutions. The rate of incorporation of the alkali metal atoms [8], their removal into the bulk of the cathode, and also their involvement in the chemical decomposition of water [9] depend on this structural nonuniformity. It may be that with the transition from solid to liquid metal more favorable conditions are set up for the chemical interaction between the intermetallic compound and water, as a competing process. As a result, the accumulation of alkali metal at the liquid electrode occurs more slowly than at the solid electrode, at equal rates of cathodic incorporation in aqueous solutions.

The increase in the importance of chemical interaction which occurs as one goes from solids to liquids ought to be particularly pronounced in the case of the gallium electrode, since during the melting of gallium one not only finds the usual smoothing of the surface but also a decrease in the interatomic distances, which also must lead to a lower efficiency of alkali metal ion discharge at the liquid cathode.

The situation is similar in the incorporation of lithium from aqueous solution into Wood's alloy.* The temperature dependence of the amount of lithium extracted from Wood's alloy which had been polarized cathodically in 1 N LiOH in water is shown in Fig. 6. The concentration of the lithium that had been incorporated was determined from the length of the arrest on the chronopotentiograms recorded by application of an anodic current of $i_a = 4 \cdot 10^{-5}$ A/cm^2. Cathodic polarization was conducted for 20 min at a potential of -1.6 V vs nhe. It was shown above that the rate of incorporation of the lithium into liquid and solid Wood's alloy steadily increases with temperature when incorporation is measured in nonaqueous solution (Fig. 2). It can be seen from Fig. 6 that the amount of lithium extracted from Wood's alloy after incorporation from aqueous solution also increases with temperature over the temperature range where the alloy is solid. But as the electrode is melted, the amount of alkali metal that can be extracted anodically from it decreases drastically with further increase in temperature.

Lithium incorporation from aqueous solutions into gallium was not studied, because this is difficult, owing to the high negative value of the equilibrium potential of the intermetallic compound LiGa. But the observation is worth mentioning that in the case of liquid gallium there is a difference between the amount of incorporated lithium calculated from the number of coulombs passed and that found by chemical analysis (Fig. 3, the dashed and solid curves). For the solid cathode the current yield is practically 100%, but for the liquid electrode it is less than 100%. In the case of liquid gallium, evidently, part of the lithium which is discharged is reacting chemically, either with traces of water in the nonaqueous solution or with oxidizing agents reaching the cathode

* The temperature dependences of the rates of incorporation of alkali metal from aqueous and nonaqueous solutions do not coincide quantitatively. According to Fig. 6, the activation energy for the incorporation of lithium from aqueous solution into Wood's alloy E = 11 kJ, which is close to the E value for the incorporation of sodium from aqueous solution into $NaPb_3$ alloy [10].

from the anode compartment. It is interesting to note that the amount of lithium found from the current differs from that found by chemical analysis by a quantity which is constant over the entire region of the linear i vs φ dependence. This is an argument in support of chemical oxidation of the incorporated lithium, because it means that the rate of the competing process which depresses the current yield does not depend on potential, and this process, therefore, is a chemical rather than an electrochemical one.

Thus, the above investigation has shown that the chief characteristics of the process – its rate and mechanism – are independent of the state of aggregation of the cathode metal in the systems examined in the present work. But the anodic behavior of the intermetallic compounds may differ between solid and liquid electrodes, owing to side effects.

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ADSORPTION OF IONS AND ELECTRIC DOUBLE-LAYER STRUCTURE ON TITANIUM – RUTHENIUM OXIDE ANODES

ADSORPTION OF SULFATE, CHLORIDE, AND PHOSPHATE IONS*

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The radiotracer technique was used to study the adsorption of sulfate, chloride, and phosphate ions on titanium–ruthenium oxide anodes as functions of potential and of anion concentration in the solution. Specific adsorption of the anions was shown to be present.

Titanium–ruthenium oxide anodes (TROA) presently are used in electrochemical chlorine production. Data on the adsorption properties and on electric double-layer structure on TROA are needed in order to elucidate the mechanism of this reaction. Such information is not available in the literature. In the present communication, experimental data are presented for the adsorption of sulfate, chloride, and phosphate ions on TROA as functions of potential and of anion concentration in the solution.

The TROA electrodes were titanium disks with an oxide layer consisting of 30% RuO_2 and 70% TiO_2 which had been applied to their lower surface by thermal decomposition of a mixture of titanium and ruthenium salts. The roughness factor of these electrodes was about 600.

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