MEASUREMENT OF THE CHEMICAL REACTION RATE OF SOLID SOLUTIONS OF LITHIUM IN LEAD WITH ETHANOL IN NONAQUEOUS SOLUTION

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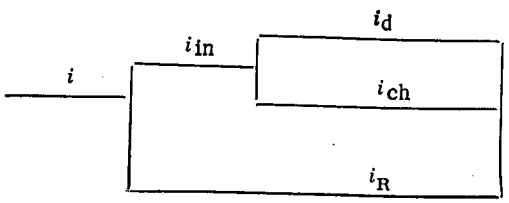
Extrapolation of the linear relationship i vs. $1/\sqrt{\tau}$ to infinite time has been used to measure the reduction rate of ethanol on lead in 2 N $LiClO_4$ in propylene carbonate under the conditions of formation of a solid solution of lithium in lead on the cathode. The character of the relationship between the ethanol reduction rate and the potential shows, that under the given conditions ethanol is reduced according to a chemical mechanism, i.e., by chemical reaction with the solid solution of lithium in lead.

The rate of the chemical decomposition of alloys of alkali metals has been measured in [1] for the case of the chemical reaction of liquid alkali metal amalgams with water and in [2] for the case of interaction with the components of the nonaqueous solution of intermetallides, obtained in the course of cathodic introduction of alkali metals in solid electrodes.

The procedure used in [2], based on the analysis of anodic chronopotentiograms is cumbersome, when applied to the case when cathodic introduction leads to the formation of a solid solution of the alkali metal, not to the intermetallic compound. The region of solid solutions corresponds on the anodic galvanostatic chronopotentiogram not to a horizontal plateau but to a slowly dropping curve which encompasses the whole region of potentials, thus introducing an inaccuracy into the calculation of the results.

In the present work the chemical reaction rate of the solid solution of the alkali metal with the components of the solution was measured at a cathodic potentiostatic polarization with extrapolation of the linear function of the cathodic current of $1/\sqrt{\tau}$ (where τ is the cathodic polarization time) to infinite time.

Let us consider the process of electrochemical cathodic introduction of the alkali metal A into the metal M at a constant potential E under conditions when the reducible substance Ox is present in the solution. The alloy A(M) formed is capable of entering a chemical reaction with Ox. Besides this, the alkali metal A diffuses into the depth of the cathode. The possibility of direct electrochemical reduction of the substance Ox must also be taken into consideration. Thus, in the general case the summary process (which dictates the current density i in the outer circuit) can be presented by the following scheme:



where i_{in} is the current density of the electrochemical stage of the process of introduction, i_R is the current density of the electrochemical reduction of Ox, i_d is the diffusion rate of the alkali metal into the depth of the cathode (in electrical units), and i_{ch} is the rate of chemical reaction of the alloy A(M) with Ox (in electrical units). The process shown in the scheme can in turn be presented as a series of consecutive stages. Thus, the chemical as well as the electrochemical reduction of the substance Ox consists of its diffusion to the electrode, the reduction of Ox, and removal of the reaction products. The following scheme shows that

$$i=i_R+i_{in}=i_R+i_{ch}+i_d. \quad (1)$$

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When i_d is small in comparison with i_{in}, we obtain when taking into account that the diffusion rate of the alkali metal in the electrode is inversely proportional to the square root of time

$$i=i_R+i_{ch}+\frac{A_1}{\sqrt{\tau}}, \tag{2}$$

where A is a proportionality coefficient. Since in the case of rapid diffusion of Ox in the solution the first two terms are practically independent of time, the relationship between i and time in the coordinates $(i, 1/\sqrt{\tau})$ will be a straight line. The $i_{\tau\to\infty}$ segment of this straight line on the ordinate must be equal to the sum

$$i_{\tau\to\infty}=i_R+i_{ch}. \tag{3}$$

In order to establish whether the reduction of the substance Ox follows a chemical or an electrochemical mechanism, or whether both processes take place, we must analyze $i_{\tau\to\infty}$ as function of the potential. In the case of a one-electron electrochemical reaction a Tafel relationship must exist between E and log i_R with a slope of 120 mV. The relationship between E and i_{ch} is more complicated. It is known that the rate of a heterogeneous chemical reaction is in many cases approximately proportional to the concentration of the active substance in the solid; in our case, we shall assume that

$$i_{ch}=kX, \tag{4}$$

where X is the mole fraction of the alkali metal in the alloy A(M) and k is the rate constant of the chemical reaction (expressed in electrical units). We shall assume that the conditions are close to equilibrium conditions and that the Nernst equation is applicable:

$$E=E_0+\frac{RT}{F}\ln\frac{a}{\gamma X}. \tag{5}$$

where a is the activity of the alkali metal ions in solutions, γ is the activity coefficient of the alkali metal in the alloy (it is assumed that $\gamma = 1$ when $X = 1$). Comparison of (4) and (5), and assuming a to be constant, gives

$$E=B-\frac{RT}{F}\ln\gamma-\frac{RT}{F}\ln i_{ch}, \tag{6}$$

where B is a constant. Since γ depends on the potential, the relationship between E and log i_{ch} is in the general case not linear. In the case of liquid amalgams of alkali metals (as follows from data presented in [3]) γ changes very little with the potential at small values of X, i.e., at relatively positive values of E. Thus, E must be a linear function of log i_{ch} with the slope of 60 mV. On the other hand, at more negative potentials γ depends strongly on E and as a result of this a practically linear relationship between E and i_{ch} can be obtained instead of the linear relationship between E and log i_{ch}. A similar "distortion" of E as function of log i_{ch} has been reported in [1, 4] for the evolution of hydrogen according to a chemical mechanism, where this "distortion" has not been explained.

In the case of some liquid alloys, for instance the alloy Li(Pb) at 800°K, the activity coefficient of the alkali metal also changes little with the potential in diluted alloys, but changes strongly in concentrated alloys [5]. For solid solutions of alkali metals the exact relationship between γ and concentration is not known in most cases. If we assume that this relationship possesses the same character as in the case of the liquid alloys, we can expect that a linear relationship exists for more positive potentials between E and log i_{ch} with a slope of 60 mV. At more negative values the potential must change more sharply as function of i_{ch}.

In the present work we have used a Li(Pb) alloy formed during the cathodic introduction of lithium into lead from a 2 N solution of $LiClO_4$ in propylene carbonate. The cathodic introduction was carried out at potentials from −1.5 to −2.3 V (all potentials are quoted against a silver chloride reference electrode). Under these conditions only a solid solution of lithium in lead is formed on the cathode during the initial period. Specially purified ethanol was added to the electrolyte solution to a concentration of 8.7 M. The procedure for the preparation of the solution has been described in [2]. The solution was

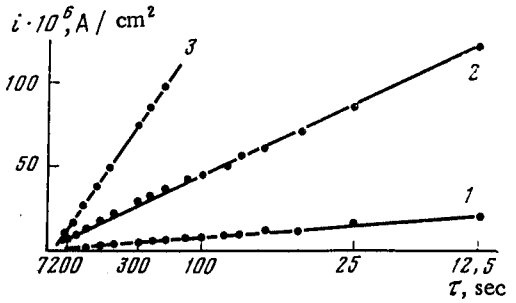

Fig. 1. Chronoamperometric curves on lead in a 2 N solution of $LiClO_4$ in propylene carbonate in the coordinates i, $1/\sqrt{\tau}$; −E; 1) 1.5; 2) 2.2; 3) 2.5 V.

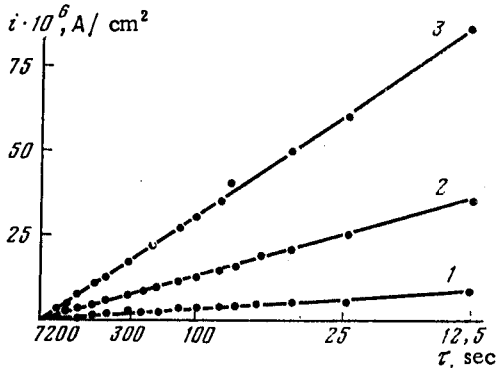

Fig. 2. Chronoamperometric curves on lead in the supporting electrolyte + 8.7 M C_2H_5OH in the coordinates i, $1/\sqrt{\tau}$; −E: 1) 1.5; 2) 1.8; 3) 2.0 V.

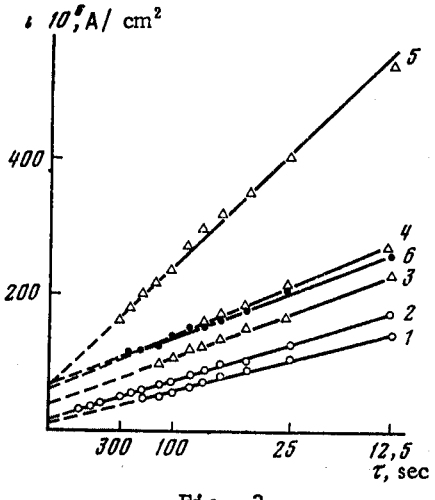

Fig. 3

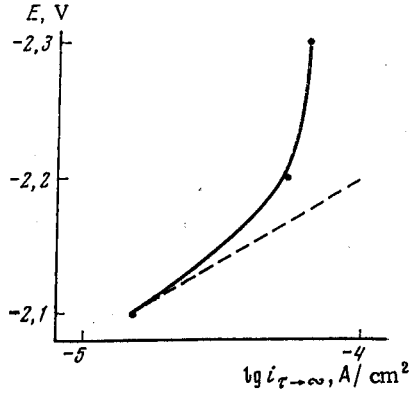

Fig. 4

Fig. 3. Chronoamperometric curves on lead in the supporting electrolyte + 8.7 M C_2H_5OH in the coordinates i, $1/\sqrt{\tau}$; − E: 1, 2) 2.1 V; 3, 4, 5) 2.2 V; 6) 2.3 V.

Fig. 4. Log $i_{\tau\to\infty}$ as function of the cathodic polarization potential. The broken line indicates the theoretical function for the electrochemical reduction of ethanol.

stirred with a magnetic stirrer. The ethanol enters into a chemical reaction with the alloy formed on the cathode:

$$Li(Pb)+C_2H_5OH\rightarrow C_2H_5OLi+{}^1/_2H_2. \quad (7)$$

S-000 lead in wire form was used as the cathode. Before the measurement the electrode was etched in nitric acid, washed with water and ethanol, and trimmed off with a scalpel. In order to provide as identical experimental conditions as possible the electrode was then subjected to cathodic polarization for two hours in the solution studied, using a potential of −1.4 V. The purpose was to form on the electrode a layer of the solid solution of sufficient thickness, with an alkali metal concentration near the surface corresponding to the given potential. During this time the potential dropped to a low value (of the order of 10^{-7} A/cm²). After this preparation, a given potential was applied to the electrode and the current density measured as function of time.

The current density as function of time in the coordinates i, $1/\sqrt{\tau}$ is shown in Fig. 1 at different cathodic polarization potentials for the "supporting electrolyte" solution, i.e., in the absence of ethanol. It can be seen that a linear relationship is obtained in these coordinates; consequently, the rate of the process is diffusion-controlled. The assessment of the diffusion coefficient by means of the Sand equation leads to the conclusion that diffusion is not the limiting stage in the electrolyte solution.

The decrease of the current with time starts practically instantly when the potential is applied. This is also observed after preliminary cathodic polarization, as well as in the cases where preliminary polarization was not applied. This indicates that already at the moment when our measurements started, the diffusion rate of the alkali metal into the depth of the electrode was lower than the rate of the electrochemical stage of the introduction process. This leads to the conclusion that the rate of the electrochemical introduction stage must be relatively high. For a potential of −2.2 V it was certainly not lower than 1.5 mA/cm². In the given case $i\rightarrow 0$ when $\tau\rightarrow\infty$. This indicates that no chemical interaction takes place under the given conditions.

In the presence of ethanol i is also a linear function of $1/\sqrt{\tau}$ at the potentials −1.5, −1.8, and −2.0 V (Fig. 2), and $i\rightarrow 0$ when $\tau\rightarrow\infty$. Evidently, at these potentials the solid solution of lithium in lead is too diluted and practically does not react with the ethanol.

On the curves obtained at more negative potentials (Fig. 3) the intial linear section is directed not towards the origin of the coordinates, but cuts off on the ordinate a certain segment $i_{\tau\rightarrow\infty}$. (Only the initial sections of the curves are shown in the figure, since after prolonged cathodic polarization the linear relationship between i and $1/\sqrt{\tau}$ is disturbed, due to structural changes in the electrode [6].) The values of $i_{\tau\rightarrow\infty}$ are in the range 15-65 μA/cm² for potentials from −2.1 to −2.3 V.

Figure 3 shows that the slopes of the curves obtained for the same potential differ significantly in some cases. The slope of these curves is governed by the coefficient of diffusion of alkali metal in the electrode. It is well known that fully identical conditions for the diffusion of the alkali metal in the cathode metal cannot be obtained, regardless of the uniform treatment of the electrodes [7]. Nevertheless, in spite of the different slopes, the points of intersection of the straight lines with the ordinate, which determine the ethanol reduction rate, are very close to each other for the same potential.

Mean values of $i_{\tau\rightarrow\infty}$ are given in Fig. 4. It can be seen that E as function of log $i_{\tau\rightarrow\infty}$ has not a Tafel character with a slope of 120 mV and is not at all logarithmic. This leads to the conclusion that the reduction of ethanol under these conditions follows a chemical, not an electrochemical mechanism.

Thus, the possibility has been demonstrated of determining the rate and mechanism of interaction of the components of a nonaqueous solution with the alkali metal introduced, when a solid solution is the product of introduction. An analysis of the data obtained has demonstrated that the reduction of ethanol with a solid solution of Li(Pb) follows a chemical mechanism.

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EFFECT OF PENETRATION OF METAL ELECTRONS INTO THE HELMHOLTZ LAYER AND CAPACITY OF THE DOUBLE LAYER AT THE METAL/SOLUTION INTERFACE

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The electron density distribution at the metal/vacuum and metal/homogeneous dielectric interface has been discussed in [1-6] and other sources. In our preliminary work on the theory of the electric double layer at the metal/electrolyte solution interface [7]* we have, together with this factor, also taken into account the dielectric inhomogeneity of the solvent near the interface [10].

The present communication discusses the inhomogeneous distribution of electron density in the metal and the effect of "extraction" of metal electrons by the dielectrically inhomogeneous liquid medium (solvent) in contact with the metal. The role of these factors in the formation of the electric double layer is analyzed and the theory of the dense part of the double layer discussed. The influence of the detailed distribution of electron density in the region between the phases on the formation of the potential of the zero charge point of the metal is also discussed. It must be pointed out that the penetration of metal electrons into the Helmholtz (dense) layer must also be taken into account when considering the adsorption processes and optical phenomena at the metal/solution interface.

In the theory of electron properties of the solid surface [4] one of the simplest models is the "gel" model in which the metal lattice is described by the uniform distribution of the positive charge of the ions of the supporting electrolyte. An extension beyond the frame of the "gel" model has been proposed in [3] (Ashcroft pseudopotential) which makes it possible to take into account in a given approximation the discrete structure of the metal lattice. In the further text we shall discuss the interface between the metal ($z < 0$) and a dielectrically inhomogeneous liquid medium ($z > 0$) (region of the dense layer $z < \delta$ and diffuse region of the electrical double layer in the solution $z > \delta$, where δ is the thickness of the layer density).

By using the electron density functional [11], this parameter can be presented in the framework of the "gel" model as a function which gives this extremum of the total energy of the metal $E_s = E_s[n]$:

*The double layer in the metal at its boundary with the electrolyte has been discussed for the first time in [8].

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