EFFECT OF THE NATURE OF THE ALKALI METAL ON THE KINETICS OF INCORPORATION INTO AN ALUMINUM CATHODE

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The mechanism and kinetics of the incorporation are shown to be substantially dependent on the nature of the alkali metal being incorporated. For the incorporation of lithium into an aluminum cathode, the rate of diffusion of lithium through the intermetallide layer is large and the process is limited by the chemical step of intermetallide formation at the cathode metal—intermetallide boundary. The large radius of sodium ions and the inability of aluminum to form intermetallic compounds with sodium lead to the incorporation being diffusion limited.

Under normal circumstances, aluminum is coated with a protective, air—oxide film and its stationary potential is shifted in the positive direction by more than 1 V relative to the equilibrium value. Activation of the aluminum can be brought about by introducing special substances, activators, into the solution [1]. The most effective of such substances to use is hydrochloric acid and its salts [2,3]. However, their activating effect lasts only so long as the metal is in contact with the solution. A more stable and prolonged activating effect is attainable by cathodically polarizing the aluminum in nonaqueous solutions of alkali metal salts at potentials more positive than the equilibrium potential of the alkali metal. Alkali metal atoms are thus introduced into the surface layer of the aluminum electrode [4, 5].

An investigation of the cathodic incorporation of an alkali metal into a solid electrode is also of great intrinsic interest for understanding the mechanism of formation of intermetallic compounds and solid solutions [6, 7].

In the present paper, we consider the results of an investigation of the cathodic incorporation of lithium and sodium from solutions of their perchlorates in dimethylformamide or propylene carbonate into an aluminum cathode.

Cathodic polarization was effected with a P-5848 potentiostat. With a KSP-4 potentiometer, we recorded curves of the change in the cathodic polarization current density and the potential of the aluminum cathode with time after the circuit was opened.

An aluminum (99.97%) wire 2 mm in diameter and 5 mm long served as the working electrode. Before each run, the electrode was mechanically polished to mirror brightness, washed with doubly distilled water, and dried. Potentials of the working electrode were measured relative to a silver chloride reference electrode in the working electrolyte solution saturated with KCl. A platinum wire was used as an auxiliary electrode.

All of the measurements were carried out in a glass cell with separate electrode compartments. The cell was carefully washed with chromic acid cleaning solution, then with a large quantity of flowing water, rinsed, and dried in a stream of warm air. Immediately before a run, the cell was rinsed with the working solutions.

We cathodically polarized the aluminum electrode in 0.5 M $NaClO_4$ in propylene carbonate and in 0.5 M $LiClO_4$ in dimethylformamide at room temperature and potentials of −2.4, −2.5, −2.6, −2.8, −3.0, and −3.2 V for 0.2, 0.5, 1, 2, 3, and 4 h.

The rate of incorporation increases as the potential of cathodic polarization shifts in the negative direction and with increasing duration of the preliminary cathodic polarization, as shown by the shift of the i—t curves in the region of larger i values (Figs. 1 and 2).

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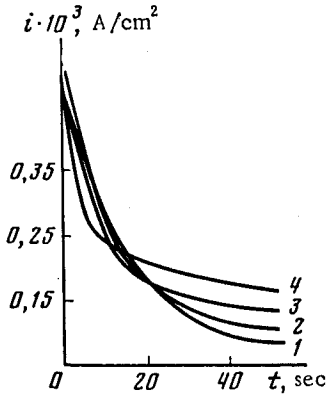

Fig. 1

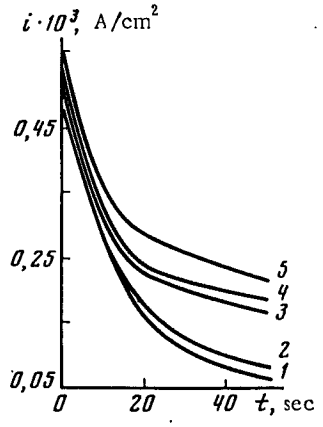

Fig. 2

Fig. 1. Rate curves of the cathodic incorporation of sodium into aluminum cathode from 0.5 M $NaClO_4$ in propylene carbonate at potentials of: 1) −2.4; 2) −2.5; 3) −2.6; 4) −2.7 V after prior cathodic polarization at the same potentials for 30 min.

Fig. 2. Rate curves of the cathodic incorporation of sodium into an aluminum cathode from 0.5 M $NaClO_4$ in propylene carbonate at a potential of −2.4 V after prior cathodic polarization under these same conditions for: 1) 10; 2) 30; 3) 60; 4) 90; 5) 120 min.

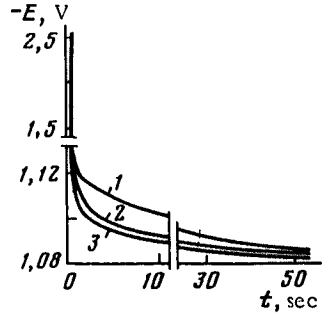

Fig. 3

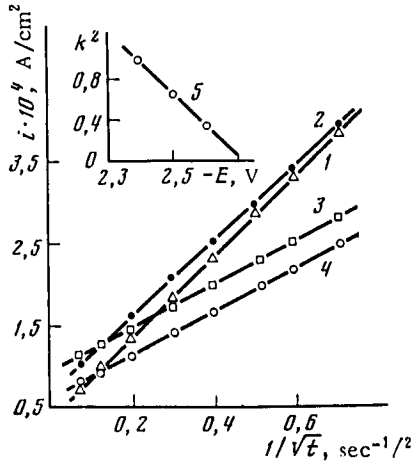

Fig. 4

Fig. 3. Drop in potential of an aluminum electrode after cathodic polarization in 0.5 M $NaClO_4$ in propylene carbonate for 30 min at potentials of: 1) −2.6; 2) −2.5; 3) −2.4 V.

Fig. 4. The $i-1/\sqrt{t}$ curves for the cathodic incorporation of sodium into an aluminum electrode from 0.5 M $NaClO_4$ in propylene carbonate at a cathodic polarization potential of: 1) −2.4; 2) −2.5; 3) −2.6; 4) −2.7 V; 5) the slope coefficient of the $i-1/\sqrt{t}$ curves as a function of the cathodic polarization potential.

When the circuit is opened, the electrode potential shifts to ∿ −1.12 V practically immediately (Fig. 3). In 5-10 sec, the shift of the potential slows down and the E—t curves enter on a plaeau of E values which are more negative the more negative the potential of the prior cathodic polarization was. The rapid shift of the cathode potential in the positive direction after the circuit is opened is evidence, according to [8], of the presence of an interaction between the solution and the products of the introduction of sodium into the aluminum.

Analysis of the rate curves for the cathodic incorporation of sodium into an aluminum cathode from 0.5 M $NaClO_4$ in propylene carbonate by plotting them in $i-1/\sqrt{t}$ coordinates (Fig. 4) showed that the process occurs via a diffusion mechanism and is described by the equation

$$i=k\frac{1}{\sqrt{t}}.$$

The constant k determined from the slope of the $i-1/\sqrt{t}$ curves gives a straight line in k^2-E plots (Fig. 4, curve 5). As shown in [9], the absence of a break in the k^2-E line serves to indicate that in the potential region studied there is only one phase formed on the cathodic incorporation of sodium into aluminum.

This conclusion agrees with the literature data, according to which no intermetallic compounds are formed in the sodium—aluminum system and the product of the cathodic incorporation must be only a solid solution [10]. After the cathodic polarization circuit is opened, the solid solution of sodium in aluminum rapidly decomposes under the action of solvent and the cathode potential is markedly shifted in the positive direction (Fig. 3).

The process of electrochemical incorporation includes the incorporation itself [11] and diffusion [12]. In order to study the nature of the limiting step in the incorporation of sodium into an aluminum cathode from solution of $NaClO_4$ in propylene carborate, we graphically integrated the i—t curves for various cathodic polarization potentials and incorporation times of 30 min and 2 h. Analysis of the dependence of the amount of sodium, Q_{Na}, being incorporated into the aluminum cathode showed that it is described by a linear equation (Fig. 5).

$$Q_{Na}{}^2=-k_1E+k_2.$$

Since the rate of cathodic incorporation is also linear with time in $i-1/\sqrt{t}$ plots, this fact shows how slowly sodium diffuses into the metal cathode compared with the rates of other steps in the process [12].

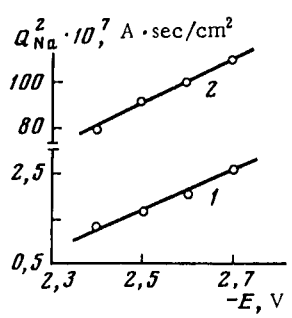

Fig. 5

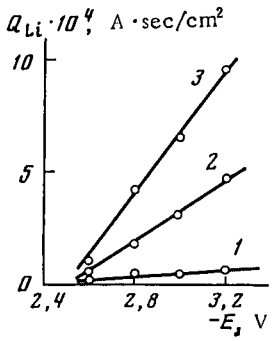

Fig. 6

Fig. 5. The dependence of the amount of sodium (Q_{Na}) being incorporated into an aluminum cathode from 0.5 M $NaClO_4$ in propylene carbonate on the potential with cathodic polarization times of: 1) 30; 2) 120 min.

Fig. 6. The dependence of the amount of lithium (Q_{Li}) being incorporated into an aluminum cathode from 0.5 M $LiClO_4$ in dimethylformamide on the potential with cathodic polarization times of: 1) 0.5; 2) 2; 3) 4 h.

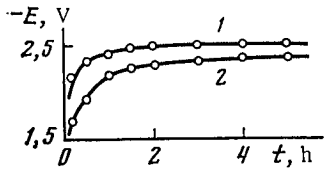

Fig. 7. Dependence of the stationary potential of an aluminum electrode on the duration of cathodic incorporation of alkali metal from 0.1 M $LiClO_4$ in propylene carbonate (1) and in dimethylformamide (2). Cathodic polarization potential, −2.7 V.

A similar study of the incorporation of lithium into aluminum from solutions of $LiClO_4$ in dimethylformamide allowed us to establish that in this case the process is limited by the crystallization of the intermetallide at the boundary with the metal electrode. The dependence of the amount of lithium being incorporated, Q_{Li}, on the cathodic polarization potential is described by a straight line in Q_{Li}—E coordinates (Fig. 6). A similar dependence was observed with the cathodic incorporation of lithium into aluminum from propylene carbonate solutions [4, 5] and with the cathodic incorporation of lithium into gallium [13].

The formation of intermetallic compounds, independent of the nature of the solvent, allows the alkali metal to accumulate on the electrode in greater or lesser amounts to which correspond the different electrode potentials after the cathodic polarization is turned off. The increased duration of the prior cathodic polarization also promotes the accumulation of alkali metal (Fig. 2).

Thus, from a comparison of the results of studying the cathodic incorporation of lithium and sodium into aluminum, it follows that the mechanism and kinetics of the incorporation process depend substantially on the nature of the alkali metal being incorporated. When lithium is incorporated, its rate of diffusion through the intermetallide layer is so great that the process begins to be limited by the chemical step of intermetallide formation at the cathode metal—intermetallide boundary. The greater radius of the sodium ions and the inability of aluminum to form intermetallic compounds with sodium lead to the incorporation process being diffusion limited in this case.

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INVESTIGATION OF THE $Cu/Cu_4RbCl_3I_2$ BOUNDARY BY THE POTENTIOSTATIC-PULSE METHOD

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A potentiostatic system, which provides for a rate of increase of the potential in the pulse front equal to $5 \cdot 10^5$ V/sec and a leakage current in the circuit of the reference electrode no greater than 10^{-11} A, has been developed. The time-dependent functions of the current for the $Cu/Cu_4RbCl_3I_2/Cu$ cell at potentials ranging from 1 to 200 mV and in the range of times from 2.5 μsec to 25 msec have been obtained. At short times (less than 10 μsec) the system is linear over the entire range of potentials, and at times up to 25 msec it is linear up to 10 mV. In the region of linearity the properties of the system are satisfactorily described by the model of diffusional relaxation of the double layer.

The solid electrolyte $Cu_4RbCl_3I_2$ was described in [1]. The conductivity of this electrode is determined by mobile Cu^+ ions and amounts to about 0.5 S/cm at 25°C [2]. Such a high conductivity allows us to treat the $Cu—Cu_4RbCl_3I_2$ system as a very convenient object for investigating electrode processes by relaxation methods.

The measuring cell was prepared by molding the electrolyte in a cylindrical Perspex mold under a pressure of about 500 MPa. The mold had an opening in a side wall, through which the reference electrode, i.e., a copper wire (diameter about 0.1 mm), was introduced into the electrolyte. Electrodes made in the form of disks from copper foil (99.9% Cu) were pressed against the end surfaces of the electrolyte. The cross section of the cell was $\sim$0.2 cm^2. The cell was placed in a tightening device with a pressure of about 200 MPa [3]. The assembly of the cell and the measurements were carried out in an argon atmosphere. The surfaces of the electrodes were polished with a diamond paste, washed with ethanol, and annealed for 2-3 h in a vacuum with a residual pressure of 0.02 to 0.1 Pa at a temperature of 800-900°C before assembly.

The existing potentiostats for electrochemical measurements (P-5827M or P-5848) are poorly suited to the investigation of solid-electrolyte cells, since they have too large a time constant ($\sim$0.1 msec) and are characterized by large currents at the moment of inclusion of the reference in the circuit. Nevertheless, the reference electrodes of the Cu/Cu^+ or Ag/Ag^+ type usually used in solid electrolytes have appreciable polarizability and have small surfaces. As a result, strong changes in the potential of the reference electrode, which make difficult the correct interpretation of the results of the measurements, are possible.

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