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HETEROGENEOUS CHEMICAL INTERACTION OF SOLUTES WITH FREE LITHIUM AND WITH LITHIUM INCORPORATED INTO THE CATHODE METAL

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The formation of intermetallic compounds of the alkali metals by electrochemical (cathodic) incorporation can be accompanied by chemical interaction of these intermetallic compounds with solution components [1, 2]. Using a procedure developed previously [3] one can determine the rate of this interaction by comparing the lengths of the corresponding arrests on anodic chronopotentiograms obtained under different conditions (without waiting, or with a waiting period after the end of cathodic polarization; during this waiting period, the electrode will practically be at the equilibrium potential of the intermetallic compound). Using this method one can determine the rate of the process taking place at open circuit. It has remained an open question whether the process is electrochemical (coupled reactions) or purely chemical, as in the decomposition of water by alkali-metal amalgams in solutions of alkalies [4].

The procedure described in [3] was used in the present work to examine the kinetics of the interaction of solid intermetallic compounds obtained by cathodic incorporation of lithium into lead and nickel, with water, ethyl alcohol, and D-ribono-γ-lactone (RL) as oxidizing agents. It had been found in [5] that the reduction of RL is intimately connected with electrochemical (cathodic) incorporation. For comparison we also studied the kinetics of reduction of these materials by free lithium that had been deposited electrochemically at the corresponding potential on substrates of lead or nickel.

The measurements were conducted at room temperature in 2 N lithium perchlorate in propylene carbonate. The cell was provided with a magnetic stirrer. The lithium perchlorate was twice recrystallized, the

TABLE 1. The Kinetic Reaction Parameters

Reactants	φ, V	Reaction order, n	Rate constant, $A \cdot cm^{3n-2} \cdot mole^{-n}$	Reactants	φ, V	Reaction order, n	Rate constant, $A \cdot cm^{3n-2} \cdot mole^{-n}$
Li-Ni, C_2H_5OH	2,0	1,0	0,001	Li-Ni, RL	2,0	0,8	0,01
Li, C_2H_5OH	3,0	1,2	0,03	Li-Pb, RL	2,4	0,5	0,004
Li-Pb, H_2O	2,4	1,1	0,08	Li, RL	3,0	1,5	2,2

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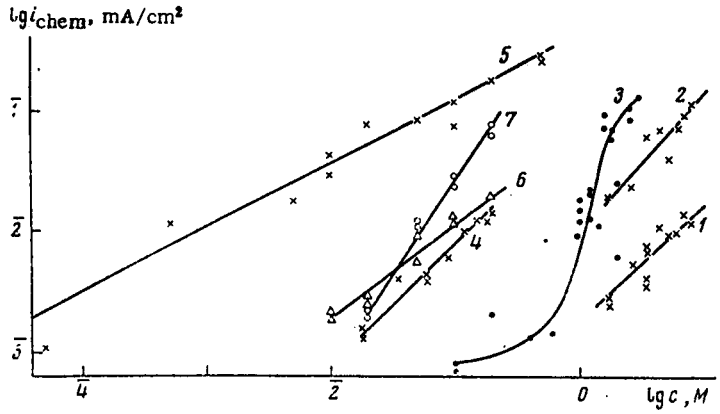

Fig. 1. Rate of interaction between the cathode material and the solute (c is the concentration of material in the solution): 1) (Li−Ni) with C_2H_5OH; 2) Li with C_2H_5OH; 3) Li with H_2O; 4) (Li−Pb) with H_2O; 5) (Li−Pb) with RL (from the data of [5]); 6) (Li−Ni) with RL; and 7) Li with RL.

propylene carbonate was distilled with a rectifying column (12-14 theoretical plates). Known concentrations of the test materials were added to the solution: water (twice distilled), absolute ethyl alcohol, or twice recrystallized RL. The electrodes used were in the form of rods made of S-000 lead or in the form of wire made of nickel (purity 99.99) and wound up into a spiral.

The kinetic reaction parameters (the rate constant and the reaction order) were determined graphically from log i_{chem} vs log c plots (Fig. 1), where i_{chem} is the rate of interaction expressed, for convenience, in electrical units.

One can see from the slope of the curves in Fig. 1 that the reaction between alcohol and Li−Ni intermetallic compound (curve 1), like that between alcohol and metallic lithium (curve 2), is a first-order reaction, corresponding to

$$\text{Li-Ni}+C_2H_5OH=C_2H_5OLi+\text{Ni}+{}^1/_2H_2$$

and

$$\text{Li}+C_2H_5OH=C_2H_5OLi+{}^1/_2H_2.$$

The equilibrium potentials of the systems Li, Li^+ and Li−Ni, Li^+ in $LiClO_4$ solution in propylene carbonate differ by 1 V (for Li, Li^+ one has $\varphi=-3.0$ V, for Li−Ni, Li^+ one has $\varphi=-2.0$ V; all potentials are stated relative to the silver−silver chloride electrode in the same solution), whereas the reaction rates of Li and Li−Ni with alcohol differ by less than an order of magnitude. This shows that the mechanism of alcohol reduction is not electrochemical. When the activity coefficient of the reactant in the activated complex is close to that of the reactant in the original solid phase, then one knows, according to absolute rate theory of heterogeneous chemical reactions, that the reaction rate ought to be approximately proportional to the reactant concentration in the solid phase. This seems to be true in our case. The activity coefficient of lithium in Li−Ni is many orders of magnitude lower than that in free lithium; however, the rates of alcohol reduction by the chemical mechanism found at Li and at Li−Ni are approximately proportional to the lithium concentration in the solid phase.

Curve 3 in Fig. 1 shows the results for the rate of chemical reaction of free lithium with water. Up to appreciable water concentrations (about 1 M), the rate of lithium dissolution remains low, but it rises sharply when the concentration is further increased. It appears that a film of lithium oxide or hydroxide is formed on the metal surface which is poorly soluble in propylene carbonate and blocks off part of the surface (the possibility that such a film would form has been pointed out in [6]), and thus it delays the chemical interaction; but with increasing water concentration in the propylene carbonate, this film begins to dissolve. The formation of an insoluble oxide film also causes difficulties in the determination of the true rate of chemical interaction between water and lithium intermetallic compounds. In [5], a correction for blocking of part of the electrode surface had been introduced in the case where water was interacting chemically with Li−Pb intermetallic compound, and in a plot of log i_{chem} against log c, a straight line had been obtained (curve 4) which corresponds to a first-order reaction, according to the equation

$$Li\text{-}Pb+H_2O=LiOH+Pb+{}^1/_2H_2.$$

The kinetics of RL reduction by Li–Pb intermetallic compound had been examined previously (curve 5) [5]. It had been found that this reaction is fast, and that the reaction order is close to 1/2. In the reduction of RL with Li–Ni intermetallic compound, the reaction order has been found to be close to 3/4 (curve 6). A fractional reaction order indicates that complications are present. In fact, it had been shown in [7] that different products can form during the reduction of RL. For RL reduction by free lithium, a reaction order close to 3/2 was obtained (curve 7). From these differences in the reaction orders one can conclude that the reduction mechanisms of RL are different for lithium and for its intermetallic compounds. It is confirmed by comparison of the reaction rates that RL reduction in both cases occurs via a chemical mechanism, since in the case of an electrochemical mechanism, the reaction rates should differ rather more strongly, because of the large difference between the potentials of lithium and its intermetallic compounds.

The rate constants and reaction orders calculated from the data of Fig. 1 by the method of least squares are reported in Table 1.

Thus, we have investigated the kinetics of chemical interaction of lithium and its intermetallic compounds as obtained during the cathodic incorporation of lithium, with alcohol, water, and D-ribono-γ-lactone. The data obtained indicate that diverse materials, each capable of interacting with alkali metal, are reduced not in a direct electrochemical way but via mechanisms including as a common feature the chemical interaction with the alkali metal or with its intermetallic compound, the latter having been produced electrochemically in advance.

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