REDUCTION OF NO_3^- ON THE LEAD ELECTRODE

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UDC 541.13

The reduction of sodium nitrate on the lead cathode in alkaline solution was investigated. It was found that the reduction of NO_3^- takes place on the lead electrode following interstitial dissolution of the alkali metal and at potentials which are 0.7 V more positive than on mercury. The reduction of nitrate proceeds until the formation of ammonia.

The cathodic dissolution of metals in the electrode changes the chemical and energy state of its surface and thus affects significantly the rate of many processes, for example, of the electrolytic deposition of metals [1, 2], the reduction of organic compounds [3, 4] and the evolution of hydrogen [5-7]. A detailed description of the observed anomalies during measurement of the hydrogen overvoltage on silver and zinc in alkaline solution and an explanation of the causes are given in [8]. Several authors have studied these peculiarities and have given a quantitative theory on the dependence of the rate of the process of anion reduction on mercury and gallium on the structure of the double layer [9]. In the light of this theory, one would have expected that the dissolution of alkali metals in the electrode, which shifts the zero point considerably to the negative side [10], can greatly modify the rate of anion reduction. Hence it seemed of interest to investigate the reduction of anions in alkaline solutions on electrodes in which a dissolution of alkali metals takes place.

In the present work, we investigated the reduction of the anion NO_3^- on the lead electrode in NaOH solution. The measurements were carried out in solutions of sodium hydroxide and sodium hydroxide with addition of sodium nitrate. The alkaline solutions were thoroughly purified by electrolysis. The salt was twice recrystallized and ignited at about 300°C. An oxide-mercury electrode in alkaline solution of the same concentration was used as reference electrode. The potentials are given relative to the normal hydrogen electrode. The investigations were carried out by the methods of recording of polarization curves and oscillographic recording of the chronopotentiograms with superposition of a constant anodic current. All measurements were carried out in an atmosphere of pure hydrogen with constant stirring.

Figure 1 shows polarization curves obtained in 2 N sodium hydroxide and in solutions of sodium hydroxide with additions of sodium nitrate of different concentration at constant (2 N) total concentration of the sodium ions (the constant sodium ion concentration ensured the same composition of the surface layer of the intermetallic compound at different potentials). The curves φ, log i obtained in pure alkali on an electrode without pretreatment practically characterize only the process of hydrogen evolution since the rate of dissolution of the alkali metal in this case is considerably smaller than the rate of the hydrogen evolution [11]. The complex trend of the polarization curves of the hydrogen evolution depends on changes in the composition of the intermetallic compound on the electrode surface with changes in the potential [8].

The trend of the polarization curve in a solution containing sodium nitrate indicates the possibility that, in addition to the hydrogen evolution, another, faster process is taking place. One would expect that this process is either a reduction of the nitrate at the cathode or dissolution of alkali metal which takes place at a higher rate. However, it follows from the oscillographic chronopotentiograms that the trend of the polarization curves cannot be due to an acceleration of the dissolution of the alkali metal due to the presence of sodium nitrate in the solution. In fact, the quantity of alkali metal detected on the electrode

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 4, pp. 612-614, April, 1970. Original article submitted November 19, 1969.

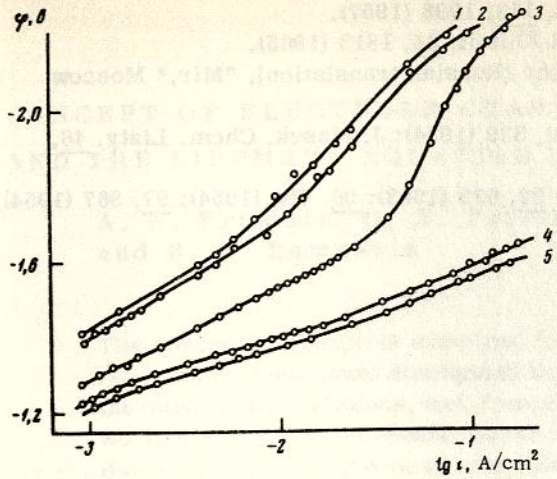

Fig. 1. Polarization curves obtained on the lead electrode in the following solutions: 1) 2 N NaOH; 2) 2 N NaOH + 0.001 N $NaNO_3$; 3) 2 N NaOH + 0.01 N $NaNO_3$; 4) 1.5 N NaOH + 0.5 N $NaNO_3$; 5) 1 N NaOH + 1 N $NaNO_3$.

surface during anodic decomposition of the intermetallic compound, obtained in alkaline solution, containing sodium nitrate, proved to be even slightly less than in the case of alkali solution without sodium nitrate (of the order of 10^{-9} g-equivalent/cm^2).

According to the literature data, the reduction of nitrate on mercury takes place with a large overvoltage and begins at more negative potentials than the potential of the reduction of alkali metal ions (−1.9 V normal hydrogen equivalent in presence of lithium ions) [12]. The reduction of nitrates is considerably facilitated only in presence of polyvalent cations in the solution (for example, ions of lanthanum, thorium, etc.): when a potential of about −1.0 V is attained, a sudden increase in the current is observed [13]. It is believed that this phenomenon is due to the autocatalytic effect of OH^- ions [13-15] formed in neutral solution during reduction of NO_3^- ions.

The accelerating effect of OH^- ions at potentials which are more negative than −1.9 V is observed on mercury only in the presence of polyvalent cations which are not present in our solution. One would have expected that the reduction of NO_3^- on the lead cathode in the potential range of −1.2 to −1.9 V should not take place. Nonetheless, the experiment (see figure) indicates that the process takes place, which, according to the analysis of the products, proved to be a reduction of NO_3^- to ammonia. The process, however, does not take place on a pure lead electrode but only on the sodium-lead intermetallic compound which is formed on the electrode surface during cathodic polarization. The approximately proportional dependence of the rate of the process on the concentration of the NO_3^- ions (figure) also indicates that a reduction of NO_3^- is taking place under these conditions.

The reduction of NO_3^- under these conditions becomes possible, evidently, owing to the large positive charge of the electrode surface in consequence of a shift of the zero charge point [10] which should take place as a result of the interstitial solution of the alkali metal. The large positive surface charge causes strong adsorption of NO_3^- anions, which is essential according to [14, 15] for the process of their reduction. Furthermore, the specific adsorption of the NO_3^- ions on the intermetallic compound is evidently more intense than on mercury. It is possible that in the case of the mercury electrode, the reduction of the NO_3^- ions in the absence of polyvalent cations is due to a shift of the zero point of the mercury by lithium atoms [12]. However, a sufficient shift of the zero point in the case of mercury can be achieved only at very high surface concentration of the alkali metal (a large volume concentration of the latter corresponds to it in a liquid metal), which is the case at a high negative potential of the electrode.

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