THE MECHANISM OF HYDROGEN EVOLUTION ON LIQUID GALLIUM FROM ALKALINE SOLUTIONS. II

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The mechanism of hydrogen evolution from alkaline solutions on liquid gallium of 99.996% purity has been studied previously [1]. In [1] it had been shown that at constant total electrolyte concentration the polarization curves in solutions containing Na^+ and K^+ as recorded with respect to a constant reference electrode (nce) coincide and do not depend on solution pH while the capacity as calculated from the current-time curves obtained when applying an anodic pulse to a previously cathodically polarized gallium drop in 0.33 N NaOH is close to the double-layer value. On the basis of the data obtained it had been concluded that on the gallium electrode, in contrast to the mercury electrode, there is no perceptible alkali metal deposition in the region of hydrogen overpotential, and hydrogen is evolved due to direct discharge of water molecules.

However, according to [2], the shape of the polarization curves on gallium in LiCl solutions depends on the Li^+ concentration in solution. In solutions containing LiCl in excess of 0.05 N there was a plateau on the i-φ curves where the elctrode potential changes little with current density through the electrode. As the LiCl concentration is increased, the plateau is extended, and the potential corresponding to the plateau shifts toward positive values. The distortion of the polarization curves was explained in [2] by discharge of lithium ions whose deposition kinetics is determined by Li atom diffusion from the surface to the interior of the elctrode. In 1.5 N Cs_2SO_4 solution at a current density of $5 \cdot 10^{-2}$ A/cm^2 the amount of hydrogen evolved as determined volumetrically corresponded to only one-half the current flowing through the electrode [3]. From this Porubaev et al. [3] have concluded that the remainder of the current ($\sim 50\%$) is used for Cs deposition. Additional analyses were not performed, however.

The phenomena described in [2, 3] caused us to return to the problem of hydrogen evolution mechanism from neutral and alkaline solutions on high-purity gallium of 99.9998%. Comparison of the electrocapillary curves obtained on gallium of 99.996 and 99.9998% purity [4] shows that a discrepancy of about 40 dyne/cm in the values of surface tension is observed at the potential of zero charge, which increases as the electrode potential is shifted toward negative values, reaching about 60 dyne/cm at -1.5 V. Consequently the electrochemical properties of the gallium brands mentioned may differ at potentials corresponding to the hydrogen overpotential region in alkaline solutions.

In the present work we have recorded polarization curves on the dropping gallium electrode in 0.5 N solutions of LiCl, LiOH, NaOH, KCl, and CsCl, as well as potential decay curves at decreasing cathodic polarization of a sessile gallium electrode in 4 N LiCl. The experiments were carried out at 32 °C. An nce served as reference electrode. The salts used were purified by twofold recystallization from twice-distilled water and by heating them red-hot, the alkali solutions were prepared by decomposing the amalgams of the corresponding metals in twice-distilled water. Prior to the measurements on the dropping electrode the solution was purified for 4-6 h by cathodic polarization at an auxiliary gallium electrode at -1.85 V.

Purification of the solution was extended to 15-20 h prior to taking the decay curves. It was noted that even when using the dropping electrode, insufficient purity of the solutions leads to elevated values of the slope of the polarization curves. The current density through the dropping electrode was calculated from the equation $i = (5/3)\,\bar{I}/S_{max}$ where $\bar{I}$ is the average current through the drop and S_{max} is the drop surface at the moment of detachment. The potential decay curves were recorded with an ÉNO-1 electron-beam oscillograph. The capacity was calculated from the initial portion of the curve using the equation $\Delta\eta_t = b \log [1 + 2.3\, i_0 t/(Cb)]$ where $\Delta\eta_t$ is the overpotential decay up to time t, i_0 is the polarizing current density, which was $4.8 \cdot 10^{-2}$ A/cm^2 in our measurements, C is the electrode capacity, and b is the coefficient in Tafel's equation. The value of b was found from the slope of the polarization curve taken on the test electrode.

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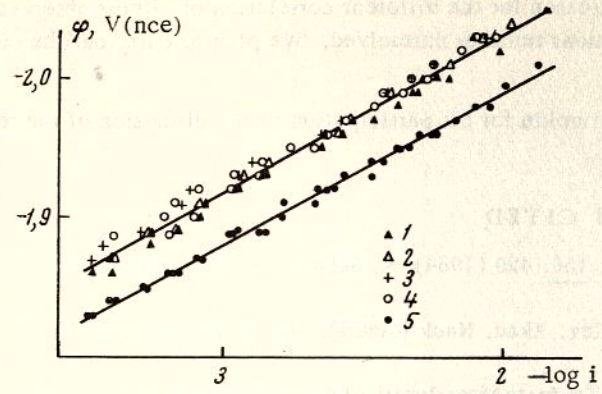


Fig. 1. Current density through the dropping gallium electrode as a function of potential in 0.5 N solutions: 1) LiOH; 2) LiCl; 3) NaOH; 4) KCl; 5) CsCl.

From the data given in Fig. 1. it is seen that in solutions containing Li^+, Na^+, and K^+, the polarization curves coincide and do not depend on solution pH. In CsCl solution the polarization curve is shifted toward positive potentials by 40-45 mV. The slope of the polarization curves is 110-115 mV and corresponds to an irreversible one-electron transition with $\alpha \sim 0.5$. The independence of the polarization curves shown from the nature of the cation precludes linking them to deposition of alkali metals on gallium since the potentials corresponding to the formation of alkali metal amalgams depend on the nature of the cation discharged. Thus, the half-wave potential of potassium deposition on mercury is 2.17 V vs nce; that of lithium is 2.34 V. It must also be noted that on mercury the slope of the polarization curves for alkali metal deposition is about 60 mV and is determined by the variation of the alkali metal concentration at the mercury electrode surface with current density.

The gallium electrode capacity calculated from the potential decay curve in 4 N LiCl was close to the double-layer value. ~ 14-18 $\mu F/cm^2$, and did not depend on the duration of prior cathodic polarization of gallium at high current desities.

We have, moreover, attempted to reproduce the experiments [3] where the amount of hydrogen evolved on a gallium electrode at cathodic polarization in 1.5 N Cs_2SO_4 was determined, under conditions as close as possible to those prevailing in the work quoted. The measurements were carried out on "technical grade" gallium, the solutions were prepared with distilled water, and the reagents were not subjected to further purification. It was found that the quantity of hydrogen evolved corresponded to within 5% to the current flowing through the electrode. The deviations seemed to be due to imperfections in the setup.

The independence of the polarization curves on the nature of the cation in solution as confirmed in the present work, and also the absence of perceptible accumulation of electrochemically active material on the surface of the gallium electrode during its cathodic polarization in LiCl solution allows us to conclude, in agreement with previous results, that even on high-purity gallium (99.9998%) alkali metals are not discharged in appreciable quantities in the potential range from -1.85 to -2.05 V vs nce, and that hydrogen evolution proceeds via direct discharge of water molecules: $H_2O + e \rightarrow 1/2\ H_2 + OH^-$.

Occlusion of alkali metals at cathodic polarization into a series of electrodes in alkaline solutions has been found in [5]. The effect of this process on the hydrogen evolution mechanism was considered by Kabanov et al. only from the viewpoint of a variation of the bond energy of adsorbed hydrogen with the metal. In [6] it was concluded that even on platinum in NaOH solution perceptible Na deposition occurs, and that hydrogen is evolved via its chemical interaction with water. However in [7] it was shown that introduction of indium into mercury leads to a lowering of the occlusion of alkali metals into mercury during cathodic polarization in alkaline solution of Li^+, K^+, and Cs^+, and that hydrogen evolution on concentrated indium amalgams proceeds over a wide range of potentials via the same mechanism as on gallium, viz., via direct water molecule discharge. Thus the role of occlusion of alkali metals during hydrogen evolution from alkaline solutions can only be resolved through studies of the reaction mechanism in every concrete case.

The effect of electric double-layer structure on the kinetics of water molecule discharge in solutions containing different cations is not fully understood. It is known that on mercury [8] and gallium [9] electrodes the differerential capacity on the negatively charged surface rises successively when going from Li^+ to Cs^+, owing to reduced hydration or increased polarizability of the ions in this order. It follows, for example, from the kinetics of electroreduction of anions as a function of the nature of the cation that the ψ' potential shifts at the same time towards the positive side, which indicates the appearance of specific adsorbability with increasing ionic radius. Therefore, hydrogen overpotential on mercury in acidified solutions of the salts of alkali metals increases successively when going from Li^+ to K^+ and finally to Cs^+ [10].* The ψ' effect, leading to an increase in hydrogen overpotential in acid solutions, must cause its lowering in alkaline solutions. However, the rate of water molecule discharge has been shown

* On gallium such measurements have not been carried out.

in the present work for the gallium electrode and in [6] for indium amalgam to be the same in Li^+, Na^+, and K^+ solutions, and to increase only in presence of Cs^+ ions. The reason for the different correlation of effects observed in the series Li^+, Na^+, K^+, and Cs^+ in acid and in alkaline solutions remains unresolved. We plan to carry out the corresponding measurements in the presence of Rb^+ ions.

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