

THE EFFECT OF SMALL QUANTITIES OF METALLIC IMPURITIES ON THE VALUE OF THE HYDROGEN OVER-POTENTIAL ON ZINC IN CONCENTRATED ALKALI SOLUTIONS

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The evolution of hydrogen at a zinc electrode in alkaline solutions exhibits a number of peculiarities which make it difficult to obtain satisfactorily reproducible curves for the hydrogen overpotential. The value of this overpotential at a zinc surface is appreciably affected by small quantities of metallic impurities present in the metal, the electrolyte or the walls of the vessels. The present work is devoted to a study of the effect of small quantities of metallic impurities on the hydrogen overpotential on zinc in the concentrated alkali solutions. The impurities used were iron, which diminishes the hydrogen overpotential, and thallium, which increases the value.

The electrodes used for obtaining the polarization curves consisted of zinc wires, mark TsO, of diameter 2 mm and total 2-3 cm², one of which was electrolytically coated by an alloy of zinc with iron and thallium. To obtain zinc alloys with a definite content of one or both of the metals indicated, special composition of electrolyte was used and suitable electrolysis conditions. An alloy of zinc containing 0.02-0.05% of iron was deposited from a solution containing 10N potassium hydroxide + 10% of the ion ZnO_2^{2-} + 0.001-0.002% ferrous iron, using a current density of 1-5 mA/cm².

Alloys of zinc containing 0.1-5% of thallium were deposited from acid solutions containing 10% of ZnO_2^{2-} and 0.0005-0.02% thallous thallium, using a current density of 1-2 mA/cm². The ternary alloy of zinc with 1-10% thallium and 0.01-0.03% iron was deposited from an alkaline solution containing 10% ZnO_2^{2-} , 0.02-0.05% ferrous iron and 0.002-0.02% thallous thallium. The thickness of the alloy coating amounted to a few tenths of a micron. The composition of the alloys was determined by analysis. This was done by inserting into the electrolysis vessel, together with the zinc wire intended for covering with the alloys, a weighed platinum sheet. At the end of electrolysis the platinum sheet, now electrolytically coated with an alloy of zinc and thallium, or of zinc and iron, was washed, dried and weighed; and the alloy was then dissolved in hydrochloric acid. The thallium and iron content in the solution was then determined. The solutions of alkali used for obtaining the cathode polarization curves were purified by polarization using a zinc cathode and a platinum anode for 2-3 days. The solutions containing the impurities were prepared by dissolving twice recrystallized salts in alkali solutions. The polarization measurements were carried out using ordinary thermostated glass apparatus with a zinc cathode and platinum anode. The temperature during the measurement was maintained at $20 \pm 0.1^\circ$. The potential of the zinc electrode investigated was measured by a compensation method against a mercury oxide electrode in alkali of the same concentration as that in the main cell. All the measurements were carried out in an atmosphere of hydrogen, the hydrogen being obtained by electrolysis. The cathode polarization curves were obtained during a period of 1-1.5 minutes, beginning with a high current density of the order of 10^{-1} A/cm², which was gradually reduced to $5 \cdot 10^{-5}$ A/cm².

EXPERIMENTAL RESULTS

To study the effect of iron impurities on the hydrogen overpotential on zinc, the iron was introduced on to the surface of the zinc electrode in various ways. These were: 1) direct precipitation of the iron from an alkaline solution containing iron impurity at the time of the experiment; 2) preliminary electrolytic deposition of iron from a solution on to the zinc electrode; 3) preliminary electrolytic co-precipitation on to the zinc electrode of an alloy layer of zinc containing 0.02-0.05% iron.

Figure 1 gives the cathodic polarization curves on zinc in 10 N potassium hydroxide, both in the absence of iron (curve 1) and in its presence in the electrolyte. In a solution containing ferrous ions (0.001%), the hydrogen

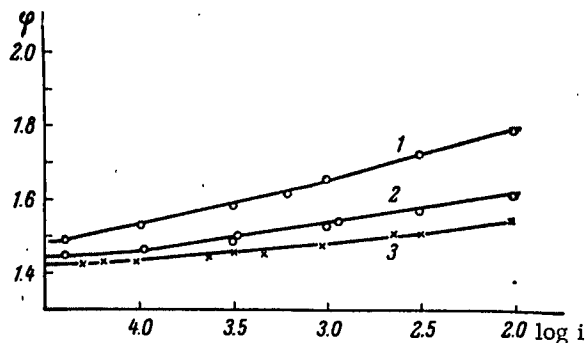


Fig. 1. Cathodic polarization curves. 1) on zinc in 1) 10 N potassium hydroxide; 2) on zinc after coating with iron to the extent of $3 \cdot 10^{-6} \text{ g/cm}^2$ in 10 N potassium hydroxide; 3) on zinc in 10 N potassium hydroxide containing 0.001% FeO_2^{2-} .

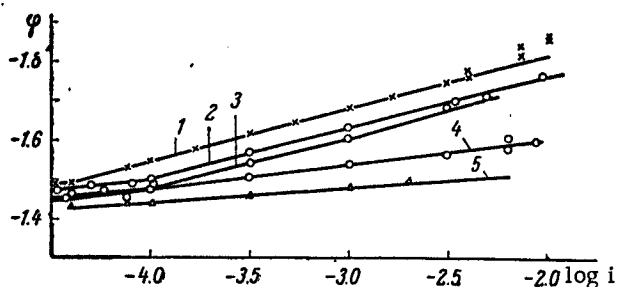


Fig. 2. Cathodic polarization curves in 10 N potassium hydroxide: 1) on zinc; 2) on a zinc-iron alloy containing 0.02% iron; 3) the same with 0.025% iron; 4) the same with 0.035% iron; 5) the same with 0.05% iron.

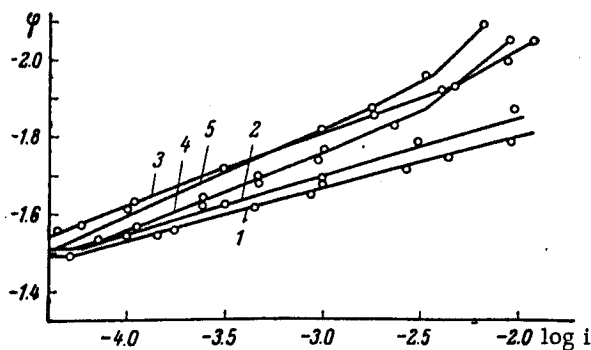


Fig. 3. Cathodic polarization curves obtained in 10 N potassium hydroxide: 1) on zinc; 2) on an alloy of zinc with thallium containing 0.1% thallium; 3) the same with 0.5% thallium; 4) the same with 5% thallium; 5) on zinc coated with thallium.

overpotential at the zinc electrode reaches a quite low value a short time (2-3 minutes) after the electrode is immersed in the solution; a shift of the stationary electrode potential of 60 mV in a positive direction is observed, together with a reduction in the slope of the curve up to 0.05 V (Fig. 1, curve 3). If the electrolyte containing the iron is rapidly changed for one consisting of pure 10 N potassium hydroxide solution, and the cathodic polarization of the electrode is continued at constant current density (10 mA/cm^2), then after 2-3 minutes a gradual increase in the hydrogen overpotential is observed up to 70 mV. The hydrogen over voltage curve taken under these conditions (curve 2) reaches a higher value than when the iron is directly precipitated on the zinc electrode from the electrolyte (Fig. 1, curve 3), though the value is lower than on pure zinc in pure 10 N potassium hydroxide solution.

It is seen from the curves in Fig. 2 that small iron content (up to 0.025%) in an alloy with zinc leads to an appreciable reduction of the hydrogen overpotential compared with that at pure zinc, and the shift of the stationary potential in the positive direction amounts to ca. 50 mV. The slope of these curves is very little different from that of the curves obtained on pure zinc ($b = 0.13 \text{ V}$). Curves obtained on an alloy containing 0.035% iron (curve 3) are in close agreement with those obtained on a zinc electrode after preliminary precipitation of $3 \cdot 10^{-6} \text{ g}$ of iron (Fig. 1, curve 2). Increase in the iron content in the alloy to 0.05% reduces the hydrogen overpotential to approximately the value obtained on direct precipitation of iron on zinc (Fig. 1, curve 3; Fig. 2, curve 5).

To study the effect of thallium impurities of the hydrogen overpotential on a zinc electrode, thallium was introduced in the same three ways. According to x-ray structure analysis carried out by Parks and Le Baron, zinc-thallium alloys obtained by simultaneous electrolytic deposition are the same in their properties as solid solutions obtained by high temperature fusion of the two metals.

Figure 3 gives the overpotential curves taken on zinc, on alloys of zinc containing 0.1-5% of thallium deposited on pure zinc, and also curves obtained on zinc coated with thallium. The curves show that for a thallium content of 0.5% in an alloy with zinc, the hydrogen overpotential is increased by 100-150 mV compared with that on pure zinc. Similar increase is found when the zinc is electrolytically coated with thallium. For current densities above $3 \cdot 10^{-3} \text{ A/cm}^2$ and anomalous increase in the hydrogen overpotential occurs. The curves show that the increase in thallium content above 0.5% leads to an increase in the slope of the overpotential curves up to 0.25 V. A large slope for overpotential curves on

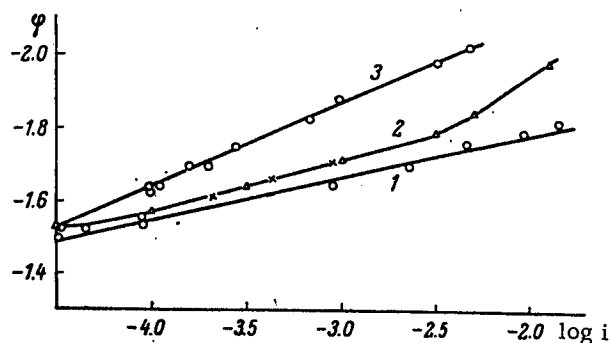


Fig. 4. Cathodic polarization curves on a zinc electrode in the following solutions: 1) 10 N potassium hydroxide; 2) 10 N potassium hydroxide containing 0.001% thallium; 3) 10 N potassium hydroxide containing 0.003% thallium.

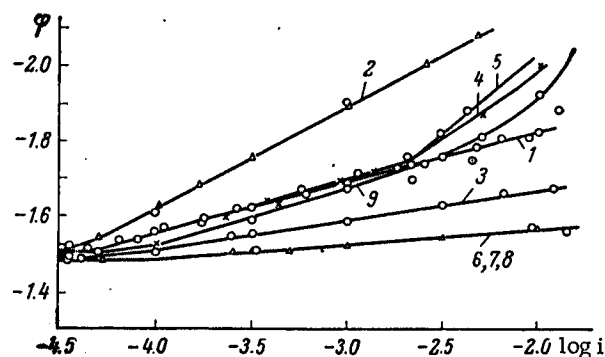


Fig. 5. Cathodic polarization curves taken on zinc and on zinc alloys in 10 N potassium hydroxide. 1) zinc; 2) zinc containing 1-2% thallium and 0.01% iron; 3) zinc containing 1-2% thallium and 0.04% iron; 4) zinc containing 5.0% thallium and 0.03-0.04% iron; 5) zinc containing 10% thallium and 0.04% iron, in 10 N potassium hydroxide containing 0.001% FeO_2^{2-} ; 6) zinc; 7) zinc covered with thallium in 10 N potassium hydroxide containing 0.001% thallous ion and 0.001% FeO_2^{2-} ; 8) zinc in 10 N potassium hydroxide containing 0.001% thallous thallium; 9) zinc containing 0.03% iron.

After the deposition of active iron on to the zinc has ceased, its effect on the hydrogen overpotential diminishes with time, and the hydrogen overpotential increases somewhat, reaching values characteristic for the alloy containing small iron quantities. This increase in the hydrogen overpotential on cessation of iron deposition from the electrolyte may be explained on the assumption that the iron diffuses from the surface into the surface layers of the zinc, forming solid solutions with the latter and intermetallic compounds of such formulas as FeZn_7 , FeZn_{13} and others [4].

The experimental data shows that alloys of zinc with small quantities of thallium (up to 0.5%) show high hydrogen overpotential, practically equal to the value on a pure thallium electrode. This is presumably to be explained by the effect of thallium in reducing corrosion of the zinc electrode, which has recently been described in a patent [5]. The mechanism of the effect of small quantities of thallium introduced into zinc on the evolution of hydrogen

metals is known to indicate the presence of adsorbed oxygen on the metal surface [2]. In the present case the presence of adsorbed oxygen may be explained by the strong oxidizability of zinc-thallium alloys [3]. This oxidizability, and also the slope of the curves, increases with increase in the thallium content in the alloy.

The hydrogen overpotential at a zinc electrode in 10 N potassium hydroxide is also increased by the presence in the solution of very small quantities of thallium (Fig. 4). Increase in the thallium concentration in the alkaline solution up to 0.003% leads to increased hydrogen overpotential at the zinc electrode. Compared with that obtained using an alloy containing 0.5% of thallium in zinc and also compared with a pure thallium deposit. Thallium in the form of an alloy with zinc, or in the form of an electrolytic deposit on the zinc surface, causes a shift in the stationary electrode potential in a negative direction of about 60 mV.

Figure 5 gives curves obtained on pure zinc and on a ternary alloy of zinc with various contents of iron and thallium. The presence of 0.01% of iron in an alloy containing 1% thallium has no effect on the hydrogen overpotential nor on the slope of the curve. Increase in the iron content, however, to 0.03-0.04% in the same alloy leads to a rapid reduction in the hydrogen overpotential to a value approximately the same as that in an alloy of zinc and iron containing 0.025-0.035% of the latter (Fig. 2, curves 3 and 4; and Fig. 5, curve 3). Increase of the thallium content in the ternary alloy to 5-10% increases the hydrogen overpotential at the alloy for low current densities to values corresponding to those of zinc containing only thallium. At a current density of $3 \cdot 10^{-3} \text{ A/cm}^2$ these curves also show a curvature, like the curves obtained on alloys with thallium. When the electrolyte contains simultaneously equal low concentrations of thallium and iron, the iron exerts the dominating effect on the value of the hydrogen overpotential.

DISCUSSION OF RESULTS

As can be seen from our experiments, the greatest effect on the hydrogen overpotential is that caused by iron directly precipitated from the electrolyte or at greater concentrations, amounting to 0.05%, in the alloy.

may be explained on the assumption that thallium is an adsorption-active metal, the surface concentration of which is higher than its concentration in the alloy layer. This specific adsorption of thallium atoms on the surface and the ready oxidizability of thallium may also explain the high value of the slope of the over-voltage curves on zinc alloys containing small quantities of thallium (0.1-0.5%). The specific adsorption of thallium ions on the surface of metallic mercury has been indicated by Frumkin and Titievskaya [6]. Arkharov, Klotsman and Timofeev [7] have shown that thallium (0.1%) in alloy with silver is adsorption-active. From published data [8] it appears that thallium forms stable compounds of mercury and potassium. It is probable that at sufficiently negative potential thallium forms similar compounds with zinc and potassium, which may possibly explain the sudden increase in the hydrogen overpotential with current density for large values of the latter.

In ternary alloys of zinc containing 0.01% iron and 1% thallium, the effect of the iron is not found, while with somewhat larger iron contents (0.04%) the effect of the thallium is prevented and the overpotential diminishes quickly. Within the assumptions made above on the mechanism of the effect of iron and thallium impurities (in particular) one of the possible explanations of this would be to assume that a compound of iron with zinc (for example, FeZn_7), having low overpotential [4], is dissolved to a limited degree in the thallium, the overpotential in this solid solution being of the same size as that on pure thallium because of the surface activity of the latter. Only when this compound reaches supersaturation concentrations in the thallium does the hydrogen overpotential rapidly diminish through the formation on the electrode surface of the free iron-zinc compound (FeZn_7), in which thallium is insoluble and upon which thallium is not adsorbed.

CONCLUSIONS

1. It has been shown that traces of iron in the electrolyte, electrolytically deposited on zinc, causes a greater reduction in hydrogen overpotential than iron present in the zinc itself. The gradual increase in the hydrogen overpotential with time after deposition of iron ceases, may be explained by diffusion of iron into the surface zinc layers.
2. The introduction of small quantities of thallium into alloys with zinc increases the hydrogen overpotential in the same way as electrolytic deposits of thallium on a zinc electrode, and also causes an increase in the slope of the overpotential curves and a shift of the stationary potential in a negative direction. The suggestion has been made of the part played by the surface activity of thallium on zinc in increasing the hydrogen overpotential.
3. In ternary alloys of zinc with thallium and iron, the hydrogen overpotential may be higher or lower than upon zinc itself, depending on the ratio of the concentrations of thallium and iron in the alloy.

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