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Abstract

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FEATURES OF THE ELECTRODEPOSITION OF METALS FROM SOLUTIONS OF "UNUSUAL" PURITY

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As studies of the hydrogen-evolution reaction, which has been investigated most fully ([1–3]), have shown, the rate of the electrode process can change noticeably when the solution under study is contaminated by even a negligible amount of impurities. Traces of contaminants of organic or inorganic origin also exert a considerable influence on the electrodeposition of metals. However, this question still receives too little attention.

In studying the kinetics of metal electrodeposition processes, so-called "chemically pure" salts subjected to additional recrystallization are usually used. However, even then the necessary purity of the experiment is still not achieved: the purification of water from traces of organic contaminants, whose presence strongly affects the structure of cathodic deposits, is insufficiently well carried out; contact of the solutions under investigation with various "chemically resistant" plastics, which also affect the process of electrocrystallization, is often permitted.

In the joint discharge of metal and hydrogen ions (especially at low current densities, in the case of such electronegative metals as zinc and manganese), traces of impurities change the current efficiency of the metal, influence the magnitude of the cathodic polarization and the structure of the cathodic deposit. With even the slightest contamination of the solution by organic impurities, it is impossible to establish the influence of small amounts, the structure, and the individual properties of surface-active additives on the structure of the metal deposited on the cathode.

We present our experimental data on the electrodeposition of zinc and manganese from a solution of "unusual" purity.

Solutions of zinc sulfate were prepared by us from metallic zinc with a total impurity content of 10^{-5}% (obtained by the method of the Gipronikel Institute by sublimation in a nitrogen atmosphere), from distilled chemically pure sulfuric acid and water thoroughly purified from organic contaminants by prolonged boiling with potassium permanganate and triple distillation; the first portions of

Fig. 1. Microphotographs of the surface of cathodic zinc.

Figure 1: Fig. 1. Microphotographs of the surface of cathodic zinc.

the distillate (about 1/3) were not used. The resulting solution was additionally boiled and treated for a long time with current using platinum electrodes.

From a solution prepared in this way, at "standard" (^{4}) concentrations of zinc (60 g/l) and sulfuric acid (100 g/l), it was possible at 20° to deposit zinc with a fairly high current efficiency—about 60% at low current densities of 1 a/m^2, and up to 99% at 5 a/m^2, whereas in an electrolyte prepared from triply recrystallized chemically pure zinc sulfate, under the same conditions, intensive dissolution of zinc was already observed at a current density of 30 a/m^2.

The electrode potential of high-purity zinc in a pure zinc sulfate solution, both in the absence of current and under a small current, was shifted by 25–30 mV toward negative values in comparison with the potential of ordinary electrolytic zinc of grade TsO.

When working with solutions of high purity, attention must be paid to the material of the parts of the electrolytic cell that come into contact with the solution. Deposits of cathodic zinc consisting of large crystals of regular shape with mirror-smooth faces are obtained only in glass apparatus.

When parts made of ordinary plastics (viniplast, organic glass, polyethylene), and even of fluoroplastic, are used, a sharp change in the structure of the zinc deposit is observed: the crystals become irregular in shape and their size decreases.

Figure 1 shows microphotographs of the surface of cathodic zinc, demonstrating the pronounced influence of the material of the electrolyzer parts and of traces of organic impurities in the water on the structure of the deposits; the latter may serve as a peculiar and very sensitive "indicator" of the purity of the electrolyte used.

Fig. 1. Microphotographs of the surface of cathodic zinc. Electrolyte: 35 g/l Zn, 150 g/l H_2SO_4, $t = 50^\circ$, deposition time 1 h, $D_k = 6000$ A/m^2. 40×.
a —electrolytic cell and auxiliary fittings made of glass; **b** —device for fastening the cathode made of viniplast; **c** —the solution was prepared with bidistillate without additional purification from traces of organic impurities.

The use of high-purity solutions for the electrodeposition of zinc enabled us to develop a method for measuring the effective surface area of zinc, giving well reproducible results (^{5}). This method may be applied to the investigation of the surface of other pure metals as well.

No less interesting results were obtained in the electrolytic deposition of manganese from pure solutions. An electrolyte consisting of 50 g/l manganese as chloride and 110 g/l ammonium chloride was prepared by us from electrolytic

Fig. 2. Microphotographs of the surface of cathodic manganese.

Figure 2: Fig. 2. Microphotographs of the surface of cathodic manganese.

metal, distilled hydrochloric acid of chemically pure grade, and gaseous ammonia in water boiled with permanganate and twice distilled. For the experiments, only the middle third of the distillate was used, both for the acid and for the water. The manganese was dissolved at a low acid concentration (pH > 1). The solution was subjected to sulfide purification with manganese sulfide prepared from a previously purified solution of manganese chloride and ammonium sulfide, which was obtained by absorbing hydrogen sulfide in ammonia solution in twice-distilled water; the hydrogen sulfide was obtained from sodium sulfide of chemically pure grade and purified from arsenic.

After sulfide purification, the manganese electrolyte was treated by electrolysis at a low apparent current density of 20-50 A/m^2, in a glass vessel into which a glass anodic cell with a glass diaphragm, a platinum anode, and a cathode of pure aluminum had been placed. The catholyte was continuously stirred with a stirrer, and the anodic gases were drawn off. Manganese hydroxide precipitated in the catholyte; subsequently it was itself oxidized by atmospheric oxygen to dioxide and adsorbed possible organic and inorganic impurities from the electrolyte. After filtration, the solution was again treated by electrolysis; this operation

was repeated three times. After treatment of the solution by electrolysis, which was carried out for a total of 200-220 h, aluminum hydroxide was introduced into the solution; it had been obtained by anodic dissolution of A-00 grade aluminum in a neutral, pure solution of manganese chloride at a current density of 10 A/m^2, and, finally, the solution was filtered through a glass filter.

From a solution of the indicated purity at pH 7, it was possible at 20° to deposit manganese at a current density of only 10 A/m^2. At higher current densities, cathodic manganese could be obtained with current efficiencies hitherto unknown:

Current density, A/m^2	400	660	1000	2000
Duration of electrolysis, h, min	6ˆ52	4ˆ08	2ˆ45	1ˆ23
Current efficiency, %	84	93	91	90

All cathodic manganese deposits had a distinctly crystalline structure (see Fig. 2), even when suspended particles of manganese hydrates were introduced into the catholyte.

Fig. 2. Microphotographs of the surface of cathodic manganese. Electrolyte: 50 g/L Mn, 110 g/L NH_4Cl, $t = 20^\circ$, quantity of electricity 0.275 $A \cdot h/cm^2$. 40×. $a - D_k = 50$ A/m^2; $b - D_k = 400$ A/m^2.

The production of cathodic manganese deposits of the so-called indistinctly crystalline type (6) and the impossibility of depositing manganese at low current densities (7) are caused, in our opinion, by the presence of impurities in the electrolyte.

We have established that the process of formation and growth of crystals of the electronegative metals zinc and manganese in pure electrolytes does not differ in principle from the electrocrystallization of silver described by A. T. Vagramyan (8), and we believe that the kinetics of electrocrystallization and the action of additives should be studied in especially pure electrolytes.

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Note: Figure translations are in progress. See original paper for figures.

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