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Corrosion and Adsorption Properties of Electrochemical Manganese Dioxide in the Acidic and Weakly Alkaline Sulfate Solutions

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Abstract—Corrosion and adsorption properties of manganese dioxide, which was anodically deposited on platinum, its powder, and compacted tablets of manganese dioxide in the solutions with various pH values are studied using various experimental methods.

It is shown that the corrosion rate of manganese dioxide decreases with increasing pH of solution, and the process proceeds by the electrochemical mechanism with conjugate chemical reactions of the formation and decomposition of the product of transition stage. The adsorption properties of manganese dioxide powder with respect to copper ions increase with increasing pH of solution, whereas the amount of manganese ions passing to the solution almost vanishes at pH 9.

Key words: anodic and cathodic polarization curves, corrosion potential, corrosion rate, manganese dioxide

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INTRODUCTION

The thermodynamic properties of MnO_2 were studied in several works [1–6]. The dependence of equilibrium potential on the concentration of Mn^{2+} and H^+ ions, on the oxidation state, and on other factors affecting the formation of potential was considered. In doing so, manganese dioxide is often considered as a mixture of MnO_2 and MnOOH.

Vetter [1] developed the theory of nonstochiometric electrodes with surface layers. He found that the chemical composition of γ-MnO_2, which was anodically deposited on platinum, is $MnO_{2x-2}(OH)_{4-2x}$. The oxidation state can vary from 2 to 1.5 within a single phase. The boundary values $x = 2$ and $x = 1.5$ correspond to MnO_2 and MnOOH, respectively. In this transition, a proton is incorporated into the structure, and the lattice parameters remain almost unchanged.

In some works [7–9], where the electrooxidation of manganese ions (Mn^{2+}) and the electroreduction of MnO_2 were studied, the chemical interaction between manganese dioxide and Mn^{2+} and H^+ ions was indicated. It was supposed that, in the first case, the interaction proceeds by the equation:

$$MnO_2 + Mn^{2+} + 2H_2O \rightleftharpoons 2MnOOH + 2H^+. \quad (1)$$

The equilibrium of reaction (1) is considerably shifted to the left (except for highly concentrated acidic solutions). Taking into account the hydrolysis, MnOOH forms on the dioxide surface in the concentrated and weakly acidic solutions. According to the x-ray diffraction analysis, MnOOH forms even at pH 1 [4]. In [10], the behavior of platinum disk electrode, at which manganese dioxide had been preliminarily deposited, was studied in the solutions containing both Mn^{2+} and H^+ ions. The authors concluded that, as a result of electrochemical conversions, a new phase of the products of subsequent chemical reaction and a layer of chemisorbed $(MnOH)^+$ ions form on the surface of manganese dioxide.

In [11], the activation energy of manganese dioxide dissolution was determined and it was concluded that the process rate is controlled by the diffusion of Mn(III) ions in the bulk solution.

Here, in order to obtain further information on the character of interaction of electrolytic manganese dioxide with solutions of various compositions, the corrosion behavior of MnO_2, which was anodically deposited on platinum electrode, MnO_2 powder and compacted tablets in the sulfate solutions in the pH range of 1 to 9 is studied.

EXPERIMENTAL PROCEDURE

To prepare the working solutions, twice-recrystallized manganese sulfate, sodium and copper sulfates, and sulfuric acid of reagent grade were used. The

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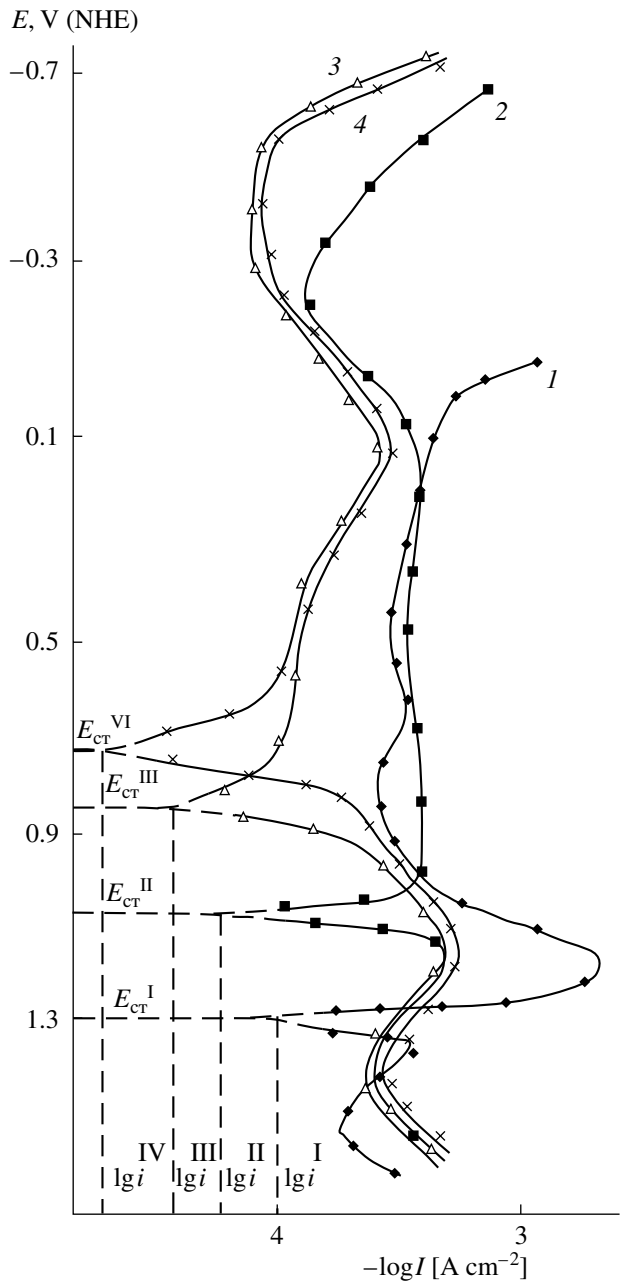

Fig. 1. Anodic and cathodic polarization curves of MnO_2, which was electrochemically deposited on platinum, at a temperature of 298 K, in 0.5 M Na_2SO_4 solution at pH values: (*1*) 1, (*2*) 3, (*3*) 5, and (*4*) 7.

source reagents were dissolved in the twice-distilled water. The polarization curves were measured in the thermostated cell with the cathodic and anodic compartments separated with a glass filter. A platinum grid was used as the auxiliary electrode. A saturated silver–chloride electrode served as the reference electrode; it was separated from the working electrode with an intermediate vessel to prevent the entry of chloride ions into the test solution. All potentials are referred to the standard hydrogen electrode. The deposition of manganese dioxide on platinum (S = 0.5 cm^2) was performed in 0.5 M $MnSO_4$ + 0.1 M H_2SO_4 solution, which was deaerated with argon, at a temperature of 298 K and an anodic current density of 0.01 A cm^{-2} for 40 min. The steady-state polarization curves on manganese dioxide, which had been plated on platinum, were measured using a PI-50-1.1 potentiostat with a PR-8 programmer.

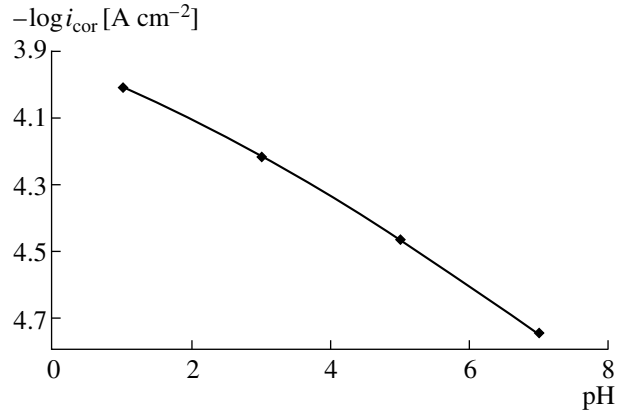

Fig. 2. The pH dependence of corrosion rate of MnO_2, which was electrochemically deposited on platinum, in 0.5 M Na_2SO_4 solution at a temperature of 298 K.

For the corrosion and adsorption measurements, γ-MnO_2 powder of reagent grade was thoroughly washed with distilled water up to the negative reaction towards Mn^{2+} ions and dried in a thermostat at 373 K for 10 h. The tablets 2 g in weight were fabricated of γ-MnO_2 powder in a press mold at a pressure of 50 mPa.

The concentration of Cu^{2+} ions in the solution was determined using the dithiocarbonate method with a KPK-2MP colorimeter. The analysis of solutions for the content of Mn^{2+} ions was performed using the potentiometric titration with potassium permanganate in the pyrophosphate medium.

EXPERIMENTAL RESULTS AND DISCUSSION

From the steady-state anodic and cathodic polarization curves (Fig. 1), it is seen that the steady-state potentials of MnO_2, which was deposited on Pt, shift in the negative direction with increasing pH of solution. A comparison between the corrosion rates, which were determined by the intersection of linear Tafel portions of anodic and cathodic polarization curves, near the steady-state potentials, and the corrosion rates, which were calculated by the amount of Mn^{2+} ions passing to the solution, showed that they are almost equal. As is seen from Fig. 2, logarithm of corrosion rate of γ-MnO_2 almost linearly decreases with increasing pH of solution.

Table 1 shows the dependence of corrosion rate of γ-MnO_2, which was electrochemically deposited on platinum, on the pH value of solution.

Table 1. The dependence of corrosion rate of γ-MnO_2 specimen on the pH of 0.5 M Na_2SO_4 + x M H_2SO_4

pH	The corrosion rate of γ-MnO_2, g cm^{-2} h	The corrosion rate, A cm^{-2}
1	1.78×10^{-4}	1.1×10^{-4}
3	1.02×10^{-4}	6.3×10^{-5}
5	6.33×10^{-5}	3.9×10^{-5}
7	3.08×10^{-5}	1.9×10^{-5}

Table 2. The dependence of corrosion rate of tableted γ-MnO_2 specimen on the pH value

pH	The corrosion rate of γ-MnO_2, g cm^{-2} h	The corrosion rate, A cm^{-2}
1	3.23×10^{-4}	1.98×10^{-4}
3	2.31×10^{-4}	1.42×10^{-4}
5	7.12×10^{-5}	4.38×10^{-5}
7	4.16×10^{-5}	2.56×10^{-5}

Table 2 lists the data on the corrosion of γ-MnO_2 specimens in the form of tablets.

Comparing the data presented in Tables 1 and 2, one can see that the corrosion rate is higher for the tableted γ-MnO_2 specimens; however, the tendency for a decrease in the corrosion rate with increasing pH value remains.

When 2 g of Na_2SO_4 powder are kept in 50 ml of 0.5 M Mn^{2+} solution with various pH values for 24 hours, a decrease in the amount of Mn^{2+} ions passed to the solution with increasing pH of solution is observed. The corrosion of γ-MnO_2 virtually ceases at pH 9 (Table 3).

Concurrently with the passing of Mn^{2+} ions to the solution, a decrease in the concentration of H^+ ions is observed. At the initial pH values of 7 and 9, a 24-hour exposure of specimen to the solution causes a decrease in the pH value. This can be explained by the passing of H^+ ions from the crystal lattice of specimen (where they, probably, are always present in the absorbed state) to the solution.

As is known, the potential of manganese dioxide electrode in the acidic solutions is determined by the reaction [1–6]

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O, \quad (2)$$

which is the sum of two successive stages:

$$2MnO_2 + 2H^+ + 2e \longrightarrow 2MnOOH, \quad (3)$$

$$2MnOOH + 2H^+ \rightleftharpoons MnO_2 + Mn^{2+} + 2H_2O. \quad (4)$$

According to equation (2), the number of H^+ ions, which enter into the reaction, and the number of formed Mn^{2+} ions are in the ratio 4 : 1. Actually, from Table 3, we obtain that at pH 1, 1 $v_{H^+} = 7.85 \times 10^{-3}$ mol, $v_{Mn^{2+}} = 1.87 \times 10^{-3}$ mol, the ratio is $\frac{v_{H^+}}{v_{Mn^{2+}}} = 4.2$, which satisfactorily agrees with the stoichiometry of equation (2). With an increase in the pH of solution, the rates of reactions (3) and (4) decrease, and reaction (1) becomes predominant. As a result, the number of Mn^{2+} ions passing to the solution decreases, and the pH value of solution decreases.

In works [2, 5, 6], it was experimentally found that the steady-state potential of γ-MnO_2, which was electrochemically deposited on platinum, depends on the pH value and the presence of Mn^{2+} in the solution. The authors experimentally studied the effect of pH value on the steady-state potential at the manganese dioxide/electrolyte interface in the absence and in the presence of Mn^{2+} ions. In the first case, $\frac{\Delta E_{ст}}{\Delta pH} = 0.060$ V; in the second case, the ratio increases with increasing concentration of manganese ions.

In our opinion, this division is, to some extent, formal, because the MnOOH phase is always present in the initial manganese dioxide and, in contact with an acidic solution, the dissolution reaction proceeds according to scheme (4) with the formation of Mn^{2+} ions.

For the overall reaction (2), the electrode potential is given by the equation:

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{H^+}^4}{a_{Mn^{2+}}} \quad (5)$$

Table 3. The data on the corrosion of γ-MnO_2 specimen (2 g of powder) in 50 ml of 0.5 M Na_2SO_4 solution at various pH values of solution

pH	The amount of Mn^{2+} ions passed to the solution, mol	The amount of H^+ ions absorbed by the specimen, mol	The specimen weight loss, %	The pH of solution at the end of experiment
1	1.87×10^{-3}	7.85×10^{-3}	5.00	1.8
3	2.24×10^{-4}	8.4×10^{-4}	0.60	5.0
5	3.64×10^{-5}	was not detected by the analytic titration	0.10	5.6
7	5.45×10^{-6}		0.15	6.2

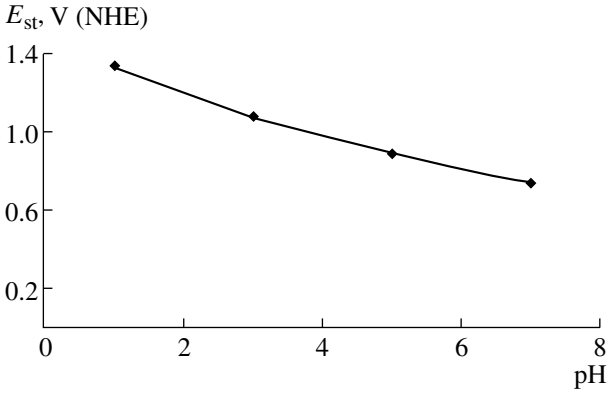

Fig. 3. The dependence of E_{st} on the pH value for MnO_2, which was electrochemically deposited on platinum, in 0.5 M Na_2SO_4 solution at a temperature of 298 K.

and, at a temperature of 298 K, $E = E^0 - 0.118$ pH – $0.029 \lg a_{Mn^{2+}}$.

Using this data, we can estimate the variation of γ-MnO_2 potential by the pH value of solution: at pH 1, 1 $c_{Mn^{2+}} = 0.0374$ M. Assuming that $a_{Mn^{2+}} \approx c_{Mn^{2+}}$, $E = E^0 - 0.118 \times 1 - 0.029 \lg 00374 = E^0 - 0.076$. With increasing pH of solution, the second term in the equation for the potential decreases and $\frac{\Delta E}{\Delta \mathrm{pH}} > 0.076$, which is observed experimentally (Fig. 3): $\frac{\Delta E}{\Delta \mathrm{pH}} \approx 0.090$.

ADSORPTION PROPERTIES

The adsorption properties of γ-MnO_2 with respect to the Cu^{2+} ions in the sulfate solutions, which were used as the model ones, were studied under the static conditions. The powder specimen (2 g) served as the adsorbent; it was placed in 50 ml of solutions with various acidities (pH 1–9). The experiments were performed for 24 h at a temperature of 298 K. At the end of experiment, the concentrations of adsorbate (Cu^{2+}) and adsorbent (Mn^{2+}) ions were determined by the photocolorimetric method and the potentiometric titration. Table 4 lists the results.

Comparing the data presented in Tables 3 and 4, we can see that the corrosion behavior of γ-MnO_2 in the copper sulfate solutions is similar to that in the sodium sulfate solutions, i.e. the amount of Mn^{2+} ions passing to the solution decreases with increasing pH of solution. However, the amount of adsorbed Cu^{2+} ions increases with increasing pH of solution. We can suppose that the adsorption of Cu^{2+} ions proceeds in the pores of γ-MnO_2 powder according to the molecular mechanism rather than the ion-exchange mechanism, because no desorption of equivalent amounts of Mn^{2+} ions or H^+ ions from γ-MnO_2 is observed with increasing adsorption of Cu^{2+} ions.

CONCLUSIONS

The corrosion and adsorption properties of γ-MnO_2, which was anodically deposited on platinum, and its powder in the sodium sulfate solutions with various pH values were studied using the methods of steady-state voltammetry, potentiometry, and photocolorimetry. It is shown that the corrosion of γ-MnO_2 in the test solutions proceeds by the electrochemical mechanism with conjugate reactions of the formation and decomposition of the product of the transition stage. Both the rate of γ-MnO_2 dissolution and the corrosion potential decrease with an increase in the pH of solution from 1 to 7.

With an increase in the pH of solution from 1 to 9, the adsorptivity of γ-MnO_2 powder with respect to the Cu^{2+} ions increases, whereas the amount of Mn^{2+} ions passing to the solution decays almost to zero. It is supposed that the adsorption of Cu^{2+} ions proceeds in the pores of γ-MnO_2 powder according to the molecular mechanism.

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Table 4. The effect of pH value of 0.01 M $CuSO_4$ solution on the adsorption properties of γ-MnO_2

The pH value of initial solution	Composition of solution	The amount of sorbed Cu^{2+} ions, g	The amount of Mn^{2+} ions passed to the solution, g	The pH value of final solution
1	0.01 M $CuSO_4 + H_2SO_4$	0.0064	0.096	1.5
3	0.01 M $CuSO_4 + H_2SO_4$	0.021	0.0093	4.1
5	0.01 M $CuSO_4 + H_2SO_4$	0.026	0.00155	5.3
9	0.01 M $CuSO_4 + NH_3$	0.030	traces	8.9

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