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Effect of manganese (II) added to the electrolyte on the properties of lead anodes used in oxidation of ferrous sulphate to ferric sulphate

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The present paper deals with the possibilities of increasing the corrosion resistance of lead anodes during anodic oxidation of ferrous sulphate to ferric sulphate. This was achieved by preliminary passivation of lead anodes in a sulphuric acid and ferrous sulphate solution to which manganous sulphate was introduced. Owing to the passivation of lead anodes by the 20 mA cm^{-2} current a potential of 2.2 V vs SEH is established and on their surface, apart from PbO_2, MnO_2 is also formed. On the basis of voltametric measurements of lead anode oxidation, analysis of potential variations during their self-depassivation, X-ray microanalysis and scanning analysis of the passivated electrode surface the role of MnO_2 in increasing the corrosion resistance in sulphuric acid solutions containing ferrous sulphate was determined. Also a mechanism explaining the effect of MnO_2 formed on the lead anode surface on limitation of the destruction process of the passive oxide layer during oxidation of the ferrous to ferric ions was suggested.

1. Introduction

In spite of extensive studies carried out on the application of insoluble anodes in the electrolytic processes for copper production, electrodes made of lead and its alloys are still the most significant. Hence, studies are being performed to improve the suitability of such anodes for electrolysis by limiting their corrosion in sulphuric acid solutions [1–5]. The present paper deals with studies on electrochemical surface modification of lead anodes used in the diaphragm electrolytic process for copper presented in earlier papers [6, 7]. Diaphragm electrolysis is carried out to prepare pure copper in hydrometallurgical treatment of both copper concentrates and copper scrap using ferric sulphate as a leading agent. In diaphragm electrolysis the anode process is utilized for recovery of spent leaching agent, i.e. for oxidation of ferrous sulphate to ferric sulphate on lead electrodes. It was shown [6, 7] that during electrolysis carried out at a current density of 200 A m^{-2} the current efficiency of Fe (II) to Fe (III) oxidation drops gradually. After operation of a diaphragm electrolyser for 5 h the anode current efficiency of oxidation is 70%, whereas after 20 h of continuous operation it is only 30% (Fig. 1). The analysis of the working anode surfaces showed that they corrrode and become coated with $PbSO_4$. In order to decrease the rate of corrosion of lead anodes in oxidized ferrous sulphate solutions, the following procedure was suggested on the basis of certain literature data [8–10].

The lead anodes were electrochemically prepassivated at a current density of 200 A m^{-2} in acid iron (II) and manganese (II) sulphate solution of the following composition: 20 g dm^{-3} H_2SO_4 5 g dm^{-3} Fe (II), 25 g dm^{-3} Mn (II). The passivation time was 2 h. Then the electrodes were transferred to the appropriate diaphragm electrolysers and the solutions were continuously electrolysed and the anodic oxidation efficiency of Fe (II) to Fe (III) in a solution consisting of 50 g dm^{-3} H_2SO_4, 30 g dm^{-3} Fe (II), 10 g dm^{-2} Fe (III) was investigated. It was found that the decrease in the oxidation efficiency of Fe (II) to Fe (III) reached 70% after about 100 h. A comparison of the oxidation efficiency Fe (II) to

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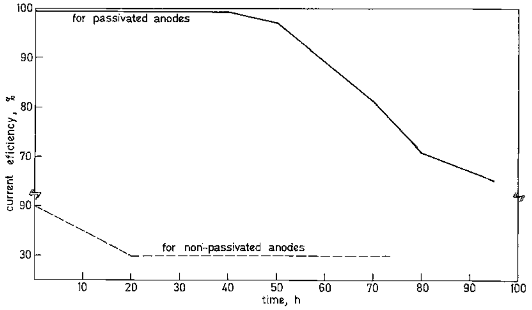

Fig. 1. A comparison of current efficiency in the oxidation Fe (II) to Fe (III) during continuous electrolysis for non-passivated (— — —) and passivated (——) anodes.

Fe (III) during continuous electrolysis for non-passivated and passivated anodes is shown in Fig. 1.

2. Aim of the work

In the present paper an attempt was made to explain the influence of manganese (II) on the increasing corrosion resistance of lead anodes during the anodic oxidation of Fe (II) to Fe (III). The results presented in this paper were obtained by:

voltammetric measurements of lead electrodes passivated in suitable solutions,

measurements of changes in electrode potentials during their depassivation,

X-ray microanalysis of passivated electrode surfaces together with their scanning analysis.

3. Experimental procedure

A pure lead rod (99.99% Pb) was embedded in a Perspex holder such that an area of 0.3 cm^2 was exposed. The electrode was placed in a typical electrochemical cell with a Pt counter electrode and Hg|Hg$_2$SO$_4$ electrode as reference. All experiments were carried out in solutions of suitable electrolytes at room temperature. The potential scan was programmed by means of a PS-20 potentiostat and GP-02 voltage scan generator. The potential current response was recorded by means of a Tacussel *XY* recorder. Prior to the experiment the electrode was polished and then anodically polarized in the same cell. Polarization was carried out at a current density of 20 mA cm^{-2} in electrolyte solutions of suitable compositions. The compositions of solutions are summarized in Table 1. Variations in the electode potentials with time during their depassivation were measured by means of an electrometer–voltmeter with recorder output. The input of the electrometer–voltmeter was higher than 10^{13} ohms. Photographs of the lead electrode surface after passivation in the suitable solutions were made by means of a Stereoscan 180 electron scanning microscope manufactured by the Cambridge Instruments Co. X-ray microanalysis of the electrode surface was performed by means of an attachment to a Link Systems microscope.

Table 1. Composition of electrolytes in which lead anodes were investigated

Solution	*Compositions of electrolytes, mol dm^{-3}*			
	H_2SO_4	*Mn(II)*	*Fe(II)*	*Fe(III)*
1	0.2	–	–	–
2	0.2	–	0.090	–
3	0.2	0.45	–	–
4	0.2	0.45	0.090	–
5	0.5	–	0.53	0.18

4. Results and discussion

4.1. *Passivation of lead anodes*

Lead anodes were placed alternately in solutions denoted by numbers from 1 to 4 in Table 1. These electrodes were anodically passivated with 68 mA current. The passivation time was 2 h. Under these circumstances the electrode potential measured with the respect to a Hg|Hg$_2$SO$_4$ electrode reached the value of about 2.2 V vs SHE, independently of the solution composition. According to the literature data [1] at 2.2 V the lead anode surface is coated with α-PbO$_2$ or β-PbO$_2$ and the passive PbSO$_4$ layer formed in consequence of lead being in contact with acid solution of the suitable sulphates (FeSO$_4$, MnSO$_4$) also becomes oxidized to PbO$_2$.

The anodes passivated under these conditions were transferred into a solution denoted No. 5 in Table 1. The composition of solution 5 corresponds to that in which Fe (II) was anodically oxidized to Fe (III) in the continuous electrolytic process. The electrodes placed in solution 5 were repassivated

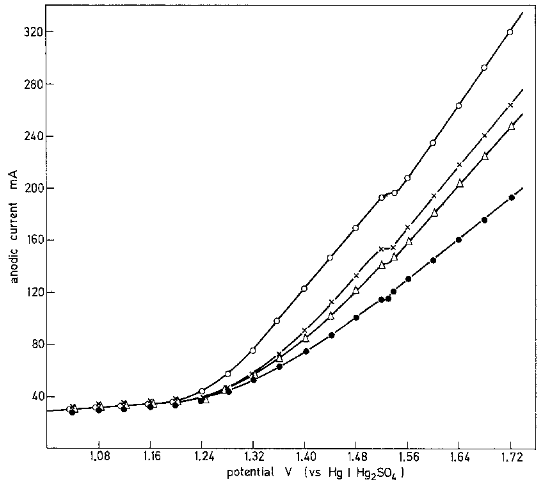

Fig. 2. A voltammetric curve for the lead anodes in a solution consisting of 0.5 M H_2SO_4, 0.53 M Fe (II), 0.18 M Fe (III) after passivation in different solutions (Table 1); —○— H_2SO_4 + $FeSO_4$, —×— H_2SO_4 + $FeSO_4$ + $MnSO_4$, —△— H_2SO_4, —●— H_2SO_4 + $MnSO_4$.

for 2 h with 68 mA and then the corresponding voltammetric curves were recorded for each electrode. The voltammetric curves were recorded over the potential range from 1.6 to 2.6 V at the potential increase rate 0.2 mV s^{-1}. The low potential limit was selected on purpose so that only PbO_2 would be formed on the anode surface. The voltammetric curves for electrodes passivated in different solutions are presented in Fig. 2. Each curve exhibits an inversion point at 2.1 V vs SHE. According to the literature data [11] this inversion should correspond to the oxidation reaction of $PbSO_4$ to PbO_2. Polarization of the electrodes taking place in solution 5 was found to depend on the type of solution in which they were previously passivated.

The weakest polarization in solution 5 is observed for the electrode passivated in sulphuric acid and ferrous sulphate solution (solution 2, Table 1). The strongest polarization is observed in the same solution for the electrode passivated in sulphuric acid and manganous sulphate (solution 3, Table 1).

Electrodes passivated in the solution of sulphuric acid (solution 1 Table 1) and in the solution containing sulphuric acid and ferrous and manganous sulphate (solution 4, Table 1) show very similar polarization. The results obtained above indicate that the manganese compounds left on the lead anode surface cause a decrease in depolarizing properties of the ferrous ions with respect to the lead electrodes operating in acid sulphate and ferrous sulphate solutions over the potential range corresponding to oxidation of Fe (II) to Fe (III) and to the oxygen evolution reaction.

4.2. *Depassivation of electrodes*

Depassivation of the lead electrodes passivated previously in various solutions is presented in Fig. 3. The potential drop of the lead electrode with time depends on the composition of the solutions in which it is depassivated and also on the composition of solutions in which this electrode was passivated previously. In each case the passivation current was such that the electrode potential being established corresponded to the $PbO_2|PbSO_4$ electrode potential. The electrode potential falls most rapidly in a solution containing sulphuric acid, ferrous sulphate and manganous sulphate (solution 4, Table 1). After about 2 h depassivation the potential of such an electrode becomes

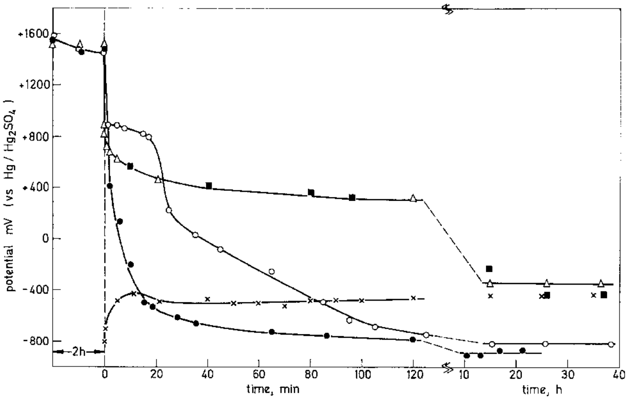

Fig. 3. Self depassivation of lead anodes after their passivation in different solutions (Table 1): —○— passivation and self-depassivation in the H_2SO_4 solution, —●— passivation and self-depassivation in the H_2SO_4 + $MnSO_4$ solution, —△— passivation in the H_2SO_4 + $FeSO_4$ solution and self-depassivation in the H_2SO_4 + $FeSO_4$ + $Fe_2(SO_4)_3$ solution, —■— passivation in the H_2SO_4 + $FeSO_4$ + $MnSO_4$ solution and self-depassivation in the H_2SO_4 + $FeSO_4$ + $Fe_2(SO_4)_3$, —×— potential of a lead electrode immersed directly in a solution consisting of: 0.5 M H_2SO_4, 0.18 M Fe (II), 0.53 Fe (III).

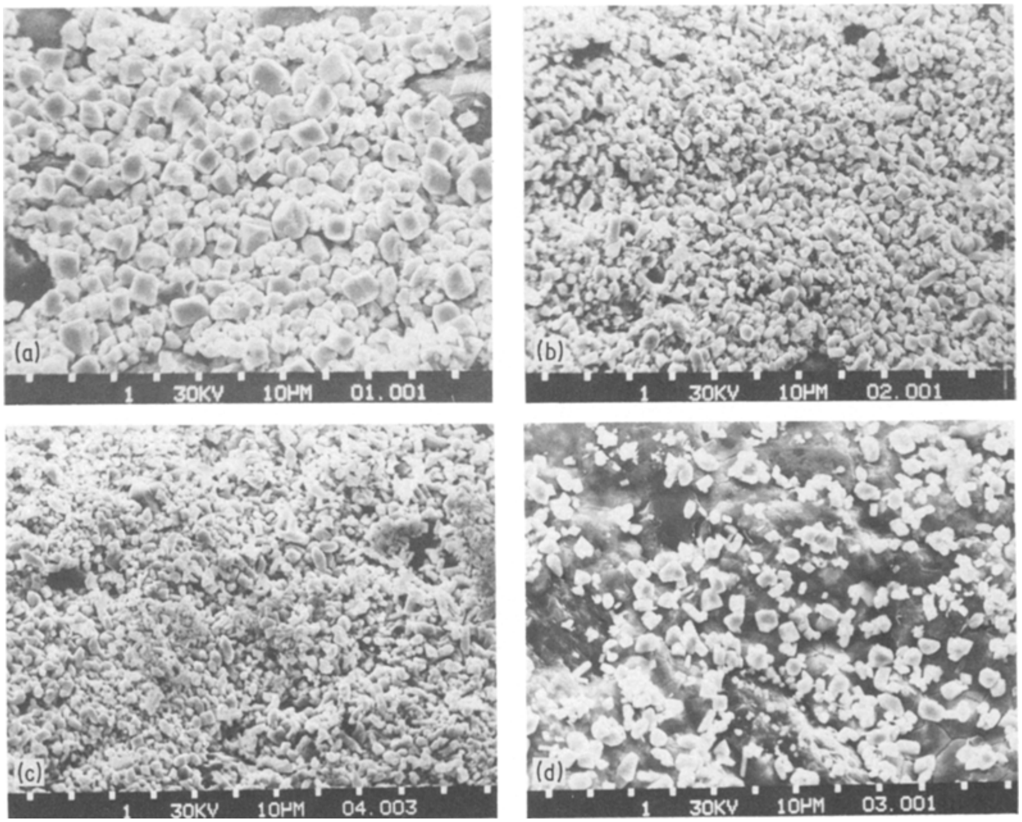

Fig. 4. Scanning electrode micrograph of the lead anode surface after passivation in solutions of the following compositions (magnified × 1020): (a) H_2SO_4, (b) $H_2SO_4 + FeSO_4$, (c) $H_2SO_4 + MnSO_4$, (d) $H_2SO_4 + FeSO_4 + MnSO_4$.

constant at – 0.82 V vs $Hg|Hg_2SO_4$, that is, – 0.20 V vs SHE. The same potential value is assumed by the lead electrode in 0.2 M H_2SO_4 solution after passivation in that solution. However, depassivation of the lead electrode in H_2SO_4 solution proceeds more slowly than in a solution containing the Fe (II) and Mn (II) ions in addition. According to the data provided by Ruetschi and Angstadt [12] the electrode potential being established in both cases corresponds roughly to that of the $Pb|PbSO_4$ electrode, according to the reaction:

$$PbSO_4 + H^+ + 2e = Pb + HSO_4^- \tag{1}$$
$$E = -0.302 - 0.0295\,\mathrm{pH} - 0.0295\,\log a_{HSO_4^-}$$

The lead electrodes passivated for two hours in a solution containing sulphuric acid and ferrous sulphate and in a solution containing sulphuric acid, ferrous sulphate and manganous sulphate and then placed in a solution of 0.5 M H_2SO_4, 0.53 M Fe (II) and 0.18 M Fe (III) (solution 5, Table 1) behave in a different manner during depassivation. After a sudden potential drop during initial depassivation, the potential becomes slowly stabilized up to about + 0.92 mV vs SHE. One can assume [12] that this potential corresponds to the reduction reaction of PbO_2 and formation of $5PbO{\cdot}2H_2O$

$$5PbO_2 + 10H^+ + 10e = 5PbO{\cdot}2H_2O + 3H_2O \tag{2}$$
$$E = 1.070 - 0.0591\,\mathrm{pH}$$

In the subsequent stage of depassivation the electrode potential decreases further with time and after about 20 h it assumes the value of + 0.22 V vs SHE. This potential value corresponds roughly to that of the $Pb|5PbO{\cdot}2H_2O$ system according to the reaction

$$5PbO{\cdot}2H_2O + 10H^+ + 10e = 5Pb + 7H_2O \tag{3}$$
$$E = 0.260 - 0.0591\,\mathrm{pH}$$

It is significant that the same potential value is assumed by the lead electrodes immersed directly in a solution where the ferric ions prevail over the ferrous ions of the following composition: 0.5 M H_2SO_4, 0.18 M Fe (II), 0.53 M Fe (III). The composition of the above electrolyte corresponds roughly to that of the solution after its anodic regeneration.

4.3. *Scanning analysis and X-ray analysis of the lead anode surface*

In order to compare the changes occuring on the lead anode surface after 2 h passivation at 20 mA cm^{-2} in solutions whose compositions are provided in Table 1, the surface of the anodes was subject to X-ray analysis and scanning analysis. The photographs of the lead anode surfaces are shown in Figs 4a to d. It was found that the lead anode surface depends on the composition of solution in which a passivation was carried out. When the passivation process was performed in the following solutions: H_2SO_4 (solution 1, Table 1), H_2SO_4 + Fe II (solution 2, Table 1) and H_2SO_4 + Mn II (solution 3, Table 1), after passivation the electrode surface was fully coated with lead sulphate crystals (Figs 4a–c). However, after passivation of lead in H_2SO_4 solution the $PbSO_4$ crystals were found to be much larger than those in the other two solutions (Fig. 4a). The anode surface passivated in a solution containing sulphuric acid, ferrous sulphate and manganous sulphate is shown to have an essential difference in appearance. On the surface of such an anode in Fig. 4d only single $PbSO_4$ crystals are observed, embedded in an amorphous layer of anode slime. X-ray microanalysis of that layer perfomed at the point indicated in Fig. 5 has shown that it contains both lead and manganese. The scanning analysis of the lead anode surface indicates that the presence of the manganous ions during passivation of electrodes in a sulphuric acid and ferrous sulphate solution prevents, to a large extent, the formation of lead sulphate on the surface of these electrodes in the subsequent depassivation process.

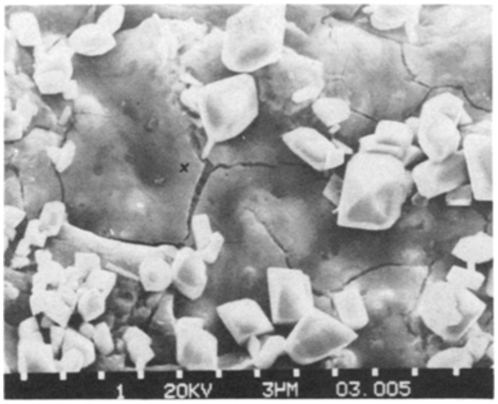

Fig. 5. Scanning electrode micrograph of the lead anode surface after passivation in a solution consisting of H_2SO_4 + $FeSO_4$ + $MnSO_4$ (magnified × 3200).

5. Conclusions

On the basis of the studies performed the following mechanism of passivation and depassivation of lead anodes in sulphuric acid, ferrous sulphate and manganous sulphate solutions was suggested to explain the favourable effect of the Mn (II) ions on the performance of lead anodes during oxidation of the ferrous ions to ferric ions. The following reactions take place on the passivated lead anode surface coated with PbO_2 and MnO_2 and placed in a solution containing sulphuric acid, ferrous sulphate and manganous sulphate:

$$5PbO_2 + 10Fe^{2+} + 10H^+ + 5H_2O = 5PbO\cdot 2H_2O + 10Fe^{3+} \quad \Delta G = -4008.2\,\text{kJ} \tag{4}$$

$$2PbO_2 + 4Fe^{2+} + SO_4^{2-} + 6H^+ = PbO\cdot PbSO_4 + 4Fe^{3+} + 3H_2O \quad \Delta G = -251.51\,\text{kJ} \tag{5}$$

$$2PbO_2 + 2Mn^{2+} + SO_4^{2-} + H_2O = PbO\cdot PbSO_4 + 2MnO_2 + 2H^+ \quad \Delta G = -74.18\,\text{kJ} \tag{6}$$

$$MnO_2 + Fe^{2+} + 4H^+ = Mn^{3+} + Fe^{3+} + 2H_2O \quad \Delta G = -17.18\,\text{kJ} \tag{7}$$

$$2Mn^{3+} + 2H_2O = Mn^{2+} + MnO_2 + 4H^+ \quad \Delta G = -53.92\,\text{kJ} \tag{8}$$

The values of changes in the thermodynamic potentials for the above reactions were calculated from the data collected in Table 2. Due to the presence of both the ferrous and manganous ions in solution, PbO_2 formed during passivation of electrodes reacts according to reactions 4–6.

Table 2. Standard free energies kJ mol^{-1}

Substances	G^0_{298}	*References*
H_2O	-236.96	13
PbO_2	-218.78	13
$5PbO \cdot 2H_2O$	$-1\,405.94$	12
$PbO \cdot PbSO_4$	$-1\,016.57$	12
MnO_2	-464.39	13
Mn^{2+}	-227.09	13
Mn^{3+}	-81.93	13
Fe^{2+}	-84.85	13
Fe^{3+}	-10.57	13
SO_4^{2-}	-741.28	13

These reactions yield lead compounds at lower oxidation states: $PbO \cdot PbSO_4$, $5PbO \cdot 2H_2O$ where the formation of $5PbO \cdot 2H_2O$ is most justified from the thermodynamic point of view. This was also confirmed by studies of electrode potential changes during their depassivation in a solution containing sulphuric acid, ferrous sulphate and manganous sulphate. A favourable influence of MnO_2 on the passivated anode surface is manifested by the fact that apart from PbO_2 it is an equally strong oxidizer of the ferrous ions present in solution. By oxidizing the ferrous ions to ferric ions manganese dioxide may be reduced itself to the manganic ion. Because of the instability of the manganese (III) compounds, the manganic ion undergoes disproportionation with reproduction of MnO_2. The reproduced manganese dioxide reacts again with the Fe (II) ions and the reaction cycle 7–8 is repeated. One can conclude, therefore, that MnO_2 acts as a 'continuous oxidizer' of the ferrous ions, preventing their penetration into the anode slime layer. The passive oxide layer present on the lead anode is, therefore, not so strongly destroyed. This conclusion is confirmed by the results of voltammetric measurements and by the scanning analysis of the lead anode surface passivated in the solution containing sulphuric acid, ferrous sulphate and manganous sulphate.

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