

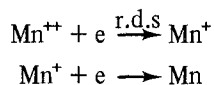
# The mechanism of manganese electrodeposition

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The mechanism of manganese electrodeposition from a sulphate bath on to a stainless-steel substrate has been studied by using current efficiency data to resolve the total  $i-E$  curves. A simple, two-step electron transfer mechanism:



is proposed to explain the following experimentally obtained parameters: cathodic and anodic transfer coefficients, reaction order and stoichiometric number. The mechanism also explains the effect of pH on  $i_{o,\text{Mn}}$  and on the corrosion currents.

## 1. Introduction

Electrolytic manganese is an important constituent of several types of steel and non-ferrous alloys. These applications often require manganese to be free of impurities. The electrolytic process for the production of metallic manganese is widely adopted because it results in a purity which is better than that attained in the aluminothermic and carbon reduction processes. The investigations carried out thus far on the electrolytic production of manganese have been directed essentially towards choosing optimum conditions for industrial practice. Such fundamental studies as have been made have been restricted mainly to the mechanism of action of the addition agent sulphur dioxide and to the equilibrium properties of the bath. The literature [1, 2] on the mechanistic aspects of manganese electrodeposition is therefore scanty. Since, however, such an understanding is of crucial importance, the present paper describes an attempt to elucidate the mechanism of manganese electrodeposition from a sulphate bath.

## 2. Experimental

A conventional three-compartment glass cell was used in the experiments. The cathode consisted of a stainless-steel rod designed to expose to the

electrolyte an area of  $1 \text{ cm}^2$  and achieve uniform current density distribution. An anode consisting of a lead alloy with 1% silver was used in the deposition experiments. A plate of electrolytic manganese served as the anode in the dissolution experiments. The electrolyte consisting of ammonium sulphate and manganese sulphate was prepared from Analar chemicals and was purified by about 20 h of pre-electrolysis at  $2 \text{ mA cm}^{-2}$  employing a mercury cathode and lead-silver alloy anode. The electrolyte was then filtered and its pH adjusted to the required value using sulphuric acid or ammonium hydroxide. Hydrogen gas was bubbled through the electrolyte to maintain a de-oxygenated atmosphere.

## 3. Results

Typical polarization curves obtained at different concentrations of manganese sulphate ( $0.2$ ,  $0.01$ ,  $0.05$  and  $1.0 \text{ mol dm}^{-3}$ ) with  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate at bulk pH 7 are shown in Fig. 1. The  $\log i-E$  plot, for  $0.2 \text{ mol dm}^{-3} \text{ MnSO}_4$  for example, shows two linear regions in the current density regions  $10^{-4}$  to  $10^{-3}$  and  $10^{-2}$  to  $10^{-1} \text{ A cm}^{-2}$  with a non-linear portion in the current density region  $10^{-3}$  to  $10^{-2} \text{ A cm}^{-2}$ . When the solution is stirred, this  $\log i-E$  curve is not affected in the high current density region ( $10^{-2}$

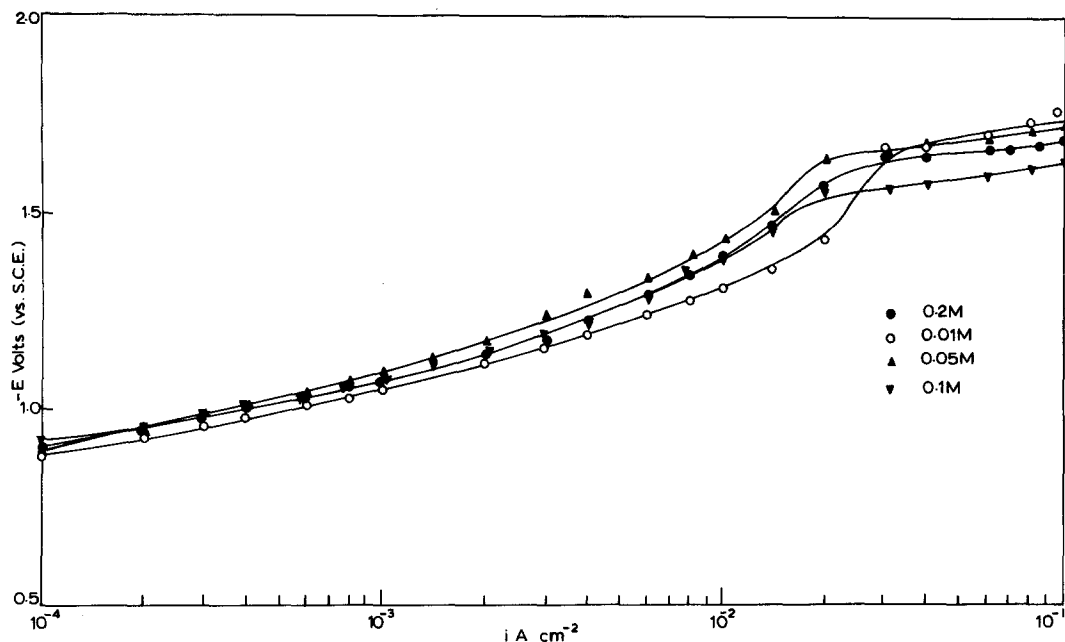


Fig. 1. Polarization curves for manganese deposition with  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate and varying concentrations of manganese sulphate at pH 7 ( $M = \text{mol dm}^{-3}$ )

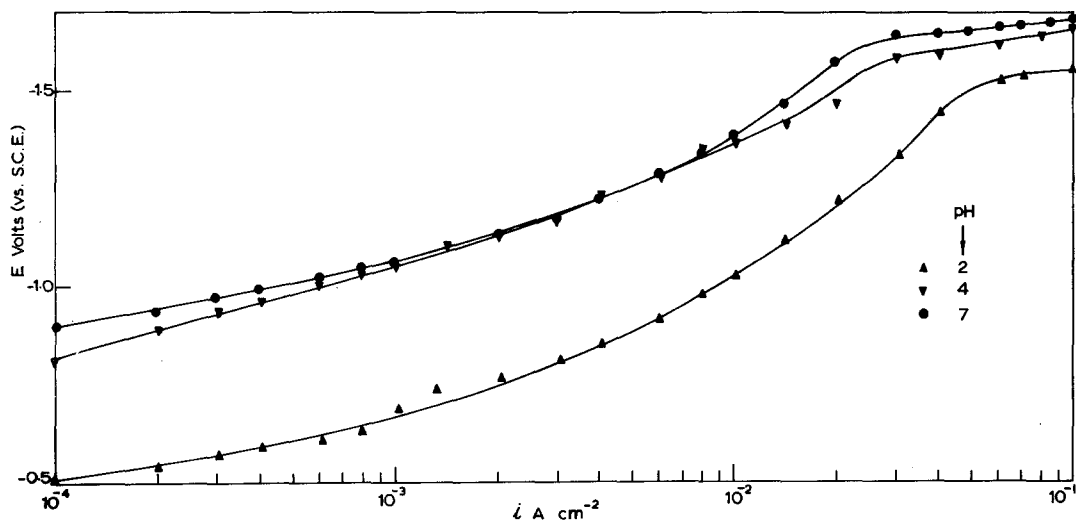


Fig. 2. Polarization curves for manganese deposition at different pH values from  $0.2 \text{ mol dm}^{-3}$  manganese sulphate and  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate electrolyte.

to  $10^{-1} \text{ A cm}^{-2}$ ), but shifts to slightly positive potentials ( $\sim 15 \text{ mV}$ ) in the low current density region ( $10^{-4}$  to  $10^{-2} \text{ A cm}^{-2}$ ).

Manganese sulphate – ammonium sulphate mixtures are known to have significant buffer

capacity in the pH ranges 2–3 [3] and 7–9 [4]. It is also known that manganese deposits corrode spontaneously in the manganese deposition bath even when the pH of the electrolyte is about 7. Hence, at lower pH values of the electrolyte, the

manganese would be expected to corrode at a rapid rate. At high pH values ( $\sim 9$ ), manganese hydroxide is precipitated. Hence, the effect of pH was studied in the pH range 2–9.

The polarization curves obtained at pH values 2, 4 and 7 of the  $0.2 \text{ mol dm}^{-3}$  manganese sulphate and  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate electrolyte are shown in Fig. 2. This figure shows no significant differences between the polarization curves for pH 4 and pH 7 whereas the curve for pH 2 shows a marked change. Firstly, the experimental  $\log i-E$  curve shifts to more positive values of potential at pH 2; secondly, the second linear portion which is observed at potentials more negative than  $-1.5 \text{ V}$  (versus SCE) starts at higher current densities than in the case of curves at higher pH values.

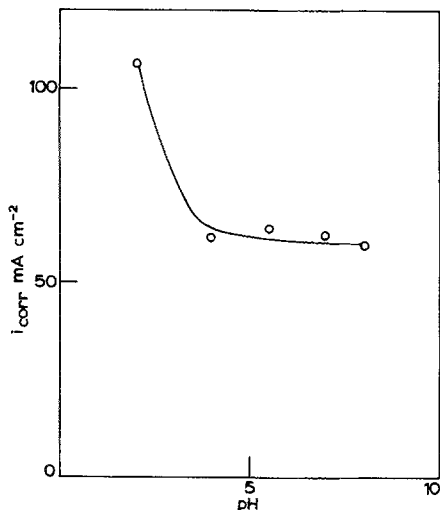


Fig. 3. Variation of corrosion current of manganese with pH.

The dependence of corrosion current on the pH of the solution is shown in Fig. 3. It can be seen that at low pH values, the corrosion current is high and changes with pH, but between pH 4 to 7 the corrosion current remains constant, i.e., it is independent of the pH of the solution.

#### 4. Discussion

The reversible potential for the  $\text{Mn}^{2+}|\text{Mn}$  half-cell in a solution containing  $0.2 \text{ mol dm}^{-3}$  manganese sulphate and  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate can be shown to be  $1.48 \text{ V}$  (versus SCE) taking the activity coefficients of manganese

sulphate and ammonium sulphate into consideration and using the  $E^{\circ}$  value of  $-1.18 \text{ V}$  (versus SCE) for the  $\text{Mn}^{2+}|\text{Mn}$  half cell. A reference to the steady-state cathodic polarization curves then shows that the  $\log i-E$  curve beyond  $1.15 \text{ V}$  (versus SCE) may be ascribed primarily to the manganese deposition reaction. This view is supported by the fact that the grey deposit on the stainless steel cathode obtained at potentials more negative than  $-1.5 \text{ V}$  was chemically analysed and found to be metallic manganese. However, the current efficiency for manganese deposition has been found to be about 50% only. The remaining 50% of the current is therefore utilized for another reaction, which is hydrogen evolution in the present case. It is therefore necessary to resolve the experimental  $\log i-E$  curves into  $\log i_{\text{Mn}}-E$  and  $\log i_{\text{H}}-E$  curves using the current efficiency data obtained at the values of current density at which the steady-state potentials were recorded. The  $\log i_{\text{Mn}}-E$  curves at different values of manganese concentration and different values of pH of the solution are shown in Figs. 4, 5 and 6.

From the linear dependence of  $E$  on  $\log i_{\text{Mn}}$ , the values of  $i_{0,\text{Mn}}$  and  $b_{c,\text{Mn}}$  at different pH values of the solution were obtained (Table 1). A unity order for the manganese deposition reaction was obtained from a plot of  $\log i_{\text{Mn}}$  versus  $\log C$  curve at an electrode potential of  $-1.6 \text{ V}$  (versus SCE).

Table 1. Table of exchange current densities  $i_{0,\text{Mn}}$  and the slopes of Tafel lines for manganese deposition from a solution containing  $0.2 \text{ mol dm}^{-3}$  manganese sulphate,  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate at different pH values of the solution

pH	$i_{0,\text{Mn}}$ ( $\text{A cm}^{-2}$ )	$b_{c,\text{Mn}}$
2	$1.2 \pm 0.7 \times 10^{-3}$	$120 \pm 10$
4	$1.5 \pm 0.05 \times 10^{-3}$	$120 \pm 10$
7	$1.1 \pm 0.3 \times 10^{-3}$	$120 \pm 10$

Table 1 shows that the variation of exchange current density,  $i_{0,\text{Mn}}$  in the pH range 2 to 7 is much less than an order of magnitude, and therefore, for the purpose of mechanism discussion, it will be taken that  $i_{0,\text{Mn}}$  is independent of pH in the range 2 to 7. Similarly, the cathodic transfer coefficient remains virtually the same in the

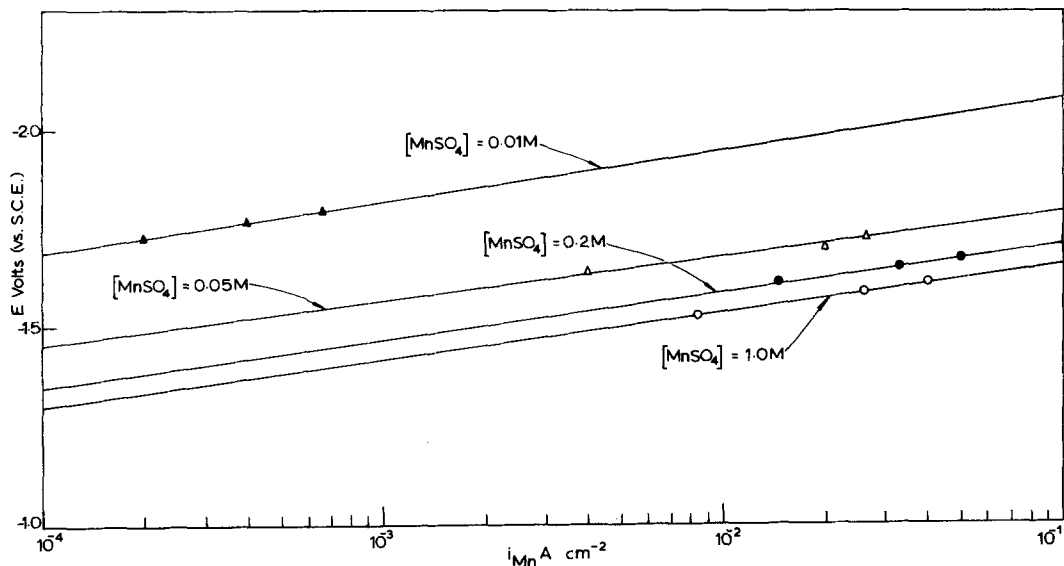


Fig. 4. Log  $i_{Mn} - E$  curves for manganese deposition from solutions at pH 7 containing  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate and varying concentrations of manganese sulphate ( $M = \text{mol dm}^{-3}$ ).

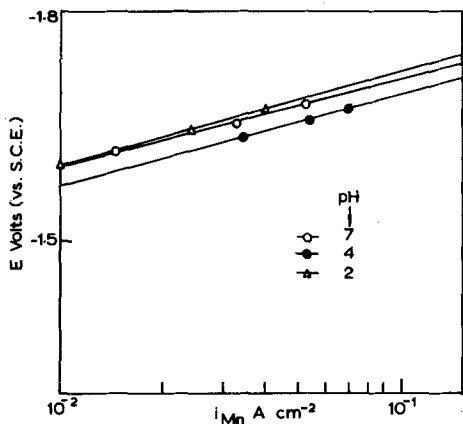


Fig. 5. Log  $i_{Mn} - E$  curves for manganese deposition from solutions containing  $0.2 \text{ mol dm}^{-3}$  manganese sulphate and  $1.0 \text{ mol dm}^{-3}$  ammonium sulphate.

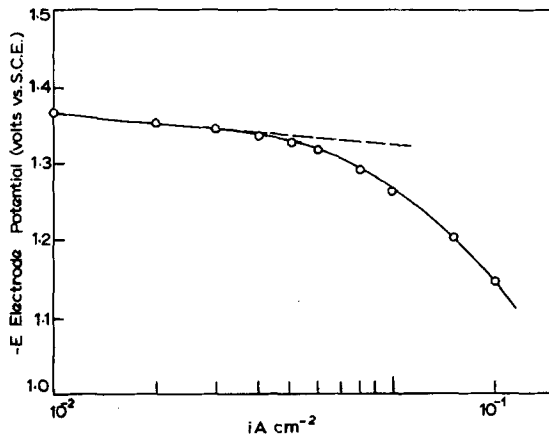
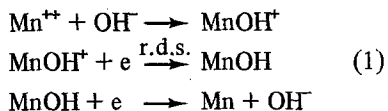


Fig. 6. Steady-state anodic polarization curve (—), Tafel plot (---) for manganese dissolution reaction.

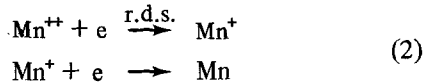
above pH range.

The following mechanism



which is similar to the mechanism for iron deposition and dissolution proposed by Bockris *et al.* [5], cannot be proposed because it does not explain the pH-independence of  $i_{0,Mn}$  and of the

corrosion current of manganese. Hence, the following two-step electron-transfer mechanism.



is proposed.

This mechanism (Equation 2) predicts 120 mV per decade for the cathodic Tafel slope, 40 mV per decade for the anodic Tafel slope, a value of unity for the order of the reaction and for the

stoichiometric number. In addition,  $i_{0,Mn}$  should be independent of pH as no  $H^+$  or  $OH^-$  ions are involved in the mechanism. Regarding the dependence of corrosion current on pH, this mechanism (Equation 2) predicts that the manganese dissolution reaction should be independent of pH, and therefore any pH dependence of the corrosion current should arise from the pH-dependence of the hydrogen evolution reaction. It has however been shown [6] that  $i_{0,H}$  is not significantly affected by pH in the pH range 4 to 7. The experimental results are in accordance with all these predictions. As regards the increased corrosion at pH 2, this may well be because, at pH 2, hydrogen evolution occurs from  $H_3O^+$  discharge (rather than  $H_2O$  discharge) and therefore proceeds more easily. Even this increase is only by a factor of about 2 in contrast to the

2.5 orders of magnitude increase of current for a decrease of 5 pH units (from 7 to 2) expected on the basis of the mechanism shown in Equation 1.

### References

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