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Mechanism of action of selenious acid in the electrodeposition of manganese

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The effect of selenious acid as an addition agent in the electrodeposition of manganese was studied by analysing the current–potential curves for manganese deposition. The mechanism of action of this addition agent was found to be essentially similar to that proposed for sulphur dioxide, namely to affect the manganese deposition indirectly by influencing the hydrogen evolution reaction which is a parallel reaction at the electrode surface.

1. Introduction

Attempts have been made to increase the current efficiency and the quality and corrosion resistance of the deposit in the electrowinning of manganese by the use of addition agents. Of these, sulphur dioxide is regularly used in the industrial process, and its mechanism of action has been the subject of many studies [1–3]. On the other hand, the literature available on the addition agent, selenious acid is scanty. Even though some views have been put forward [4] based on the similarities in the properties of sulphur and selenium, a clear understanding of the mechanism of action of selenious acid is lacking. This study has, therefore, been directed towards unravelling the role of selenious acid in manganese electrowinning, by analysing the current–potential curves, decay transients and galvanostatic transients. The effect of selenious acid on the corrosion of manganese has also been studied.

2. Experimental

Double-distilled water was used for the preparation of the electrolyte. The required amounts of Analar manganese sulphate and ammonium sulphate were weighed and dissolved in water to get the required concentrations (0·2 M manganese sulphate and 1·0 M manganese sulphate). The solution was pre-electrolysed at a mercury cathode at 2 mA cm^{-2} current density for about 20 h and filtered. The required amount of selenious acid was added from a stock solution. The pH of the solution was then adjusted to 7. Cylinder hydrogen was further purified and used to maintain a deoxygenated atmosphere in the cell.

A three-compartment glass cell has been used for electrolysis along with a stainless steel cathode and a lead anode containing 1% silver.

A standard procedure [5] was used for tracing the current–potential curves, decay transients and galvanostatic transients. In the determination of current efficiency by weighing, errors due to corrosion were minimized by removing the cathode from the cell without breaking the electric circuit and by giving an immediate dip in 1% potassium chromate solution. A similar precaution was adopted for determining the corrosion current by weight-loss measurements.

3. Results

The steady-state polarization curves obtained for a solution containing 0·2 M manganese sulphate, 1·0 M ammonium sulphate at pH 7 containing selenious acid at concentrations 0·0, 0·025, 0·05 and 0·1 g l^{-1} are shown in Fig. 1. It can be seen

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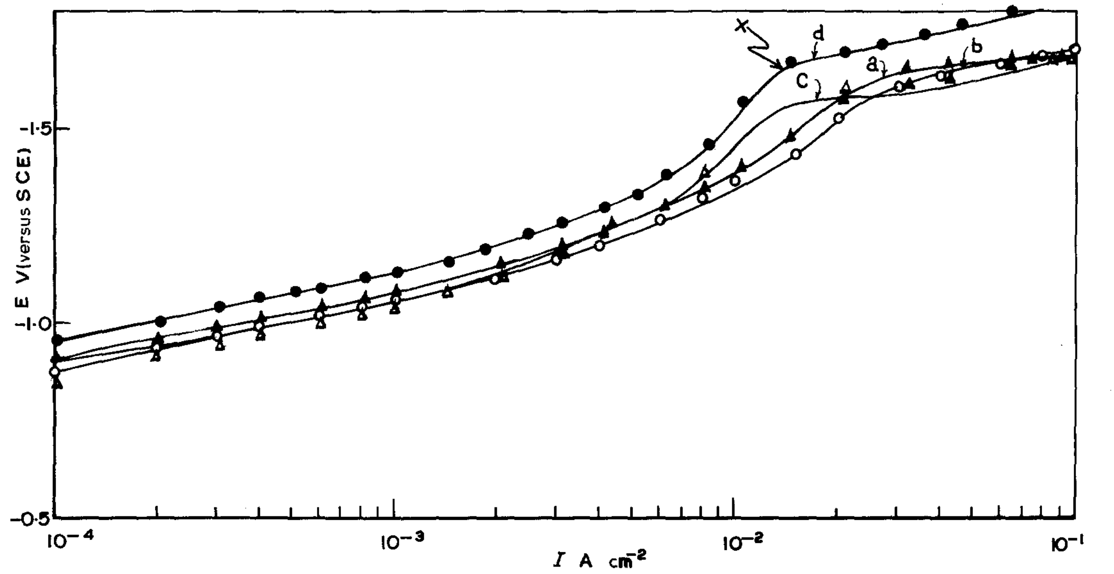

Fig. 1. Steady state polarization curves for manganese deposition from a solution at pH 7 containing 0·2 M manganese sulphate, 1·0 M ammonium sulphate and different selenious acid concentrations. (a) 0·00; (b) 0·025; (c) 0·05; (d) 0·10 g l^{-1}.

from this figure that the current–density corresponding to the point marked ‘x’ (which corresponds to the start of manganese deposition) decreased as the concentration of selenious acid was increased.

Table 1. Variation of corrosion current with selenious acid concentration

[H_2SeO_3] (g l^{-1})	I_{corr} (mA cm^{-2})
0	62·4
0·05	52·68
0·1	49·76
0·2	48·6

The well-defined transition times observed for selenium deposition are shown in Fig. 3 (p. 53).

The variation of corrosion current with selenious acid concentration is shown in Table 1.

4. Discussion

The reversible potential for the reaction:

$$SeO_3^{2-} + 3H_2O + 4e \rightarrow Se + 6\ OH^- \qquad (1)$$

is – 0·473 V versus SCE under the experimental conditions. Therefore, the reduction of selenite ion is thermodynamically possible at all potentials negative to –0·473 V versus SCE. A glance at Fig. 1. shows that even at the lowest current density used (10^{-4} A cm^{-2}) the cathode potential is about – 0·6 V indicating that reduction of selenite to selenium is possibly taking place on the cathode. This was confirmed by the fact that the deposit at these potentials has a red colour which is the same as that of selenium.

The effect of stirring was to make a portion of the current–potential curve become parallel to the potential axis at about 10^{-3} A cm^{-2}. That this value corresponds to a limiting current due to the transport of selenite ions, was indicated by the Nernst diffusion layer formula yielding a selenite limiting current of $1{\cdot}5 \times 10^{-3}$ A cm^{-2} with a Nernst layer thickness of 10^{-3} cm.

In unstirred solutions, this limiting current must be much less because of an increased diffusion layer thickness. It is probably because the lowest current density used in these experiments exceeded this limiting current that the latter was not observed in unstirred solutions.

At current densities higher than about 10^{-3} A cm^{-2}, selenium deposition is likely to occur under limiting diffusion control. This is confirmed by the well-defined transition times which were obtained, Fig. 3 (p. 000). The transition times obtained for selenium reduction at different current densities yield a $I\tau^{1/2}$ versus I plot (Fig. 2) which does not follow Sand's equation. The deviation from Sand's equation has been attributed [6] to

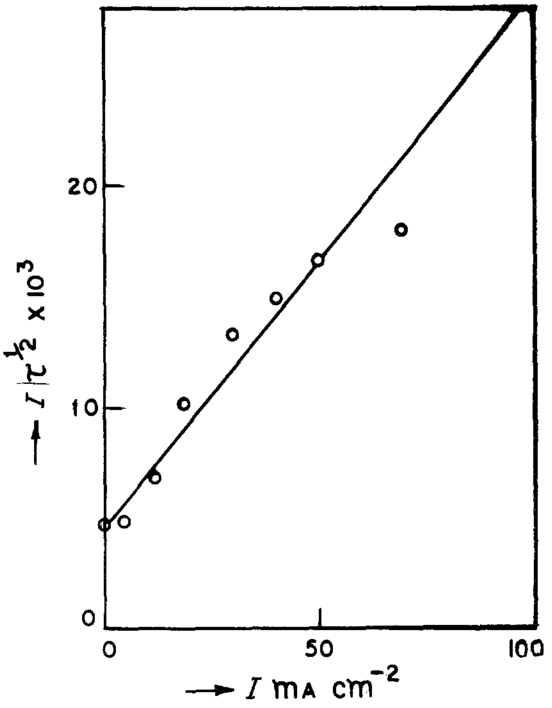

Fig. 2. Plot of $I\tau^{1/2}$ versus I.

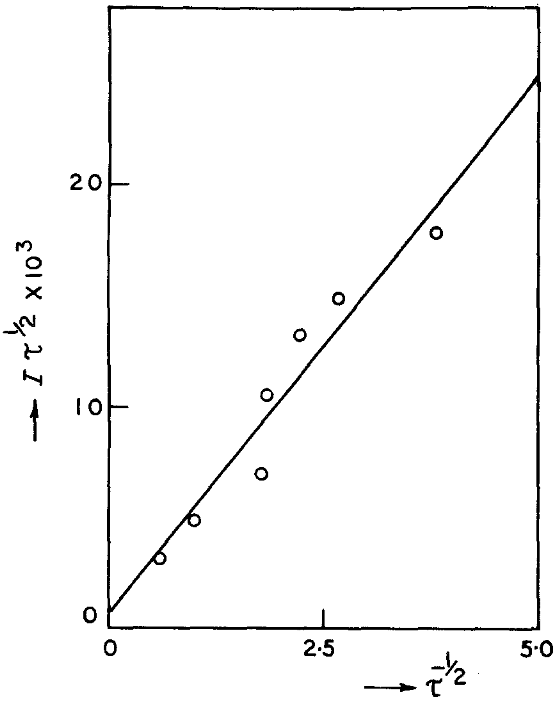

Fig. 3. Plot of $I\tau^{1/2}$ versus $\tau^{-1/2}$.

complications such as the charging up of the electrical double-layer, reduction or growth of oxide layers, and absorption at the electrode surface. The transition times, however, are too long for double-layer charging, and it is suggested here that the complicating process in the present experiments is the reduction of the oxide layer on the stainless steel surface. Evidence for this oxide reduction has been found in a study of the kinetics of hydrogen evolution on stainless steel [7]. According to Bard [6] the criterion for the existence of such a complication is that a straight line should be obtained if $I\tau^{1/2}$ is plotted versus $\tau^{-1/2}$. Fig. 3 shows that this is indeed the case.

It can therefore be concluded that hydrogen evolution and manganese deposition occur on a partially or completely selenium-covered stainless steel surface in solutions containing selenious acid as addition agent.

In unstirred solutions containing selenious acid, the cathodic current at all potentials positive to that of manganese deposition (Fig. 1) can be taken as being essentially due to hydrogen evolution since the limiting current for selenium deposition has already been exceeded at the lowest current density used. Hence, the region on the log *I-E* plots in the range 10^{-4} to 10^{-3} A cm^{-2} can be taken as the Tafel plot for the hydrogen evolution reaction. The exchange current densities for hydrogen evolution reaction at various concentrations of selenious acid are given in Table 2. It is evident from this table that the hydrogen evolution reaction is hindered in the presence of selenious acid at concentrations greater than 0·05 g l^{-1}. This result constitutes the experimental proof for the hypothesis proposed frequently [8, 9] in the literature to the effect that selenium increases the hydrogen over-voltage.

From the decay transients obtained at various current densities (Fig. 4) it is seen that, when a constant current is switched on, the potential rises

Table 2. Variation of exchange current for the hydrogen evolution reaction with selenious acid concentration

$[H_2SeO_3]$ (g l^{-1})	I (A cm^{-2})
0	$7 \pm 1{\cdot}4 \times 10^{-6}$
0·025	7×10^{-6}
0·05	$7 \pm 1 \times 10^{-6}$
0·1	$9 \pm 3 \times 10^{-7}$

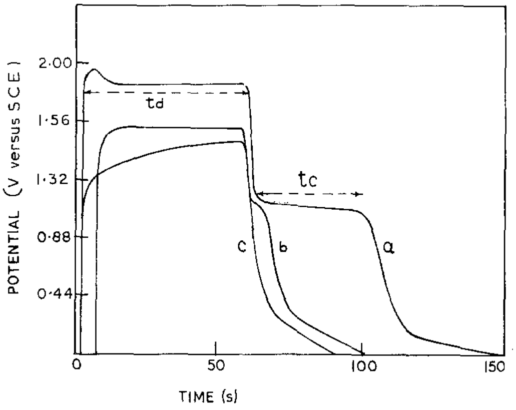

Fig. 4. Open circuit potential decay transients for manganese deposition at different current densities. (a) 100 mA cm^{-2}; (b) 25 mA cm^{-2}; (c) 20 mA cm^{-2}.

to a value corresponding to that current density and remains constant as long as the deposition current is on. When the current is switched off, the potential falls, at first rapidly and then slowly, to the initial value when the deposition current density is low (< 20 mA cm^{-2}) (Fig. 4a). When the deposition current density is greater than a critical current density, the potential falls suddenly to the corrosion potential of manganese and remains constant until all the deposited manganese is dissolved, and then falls off to the initial value (Fig. 4c). Hence, one can identify the minimum value of current density required for manganese deposition (Fig. 4b).

The values of minimum current density thus obtained in the absence and presence of selenious acid are given in Table 3. Two points emerge from Table 3. Firstly, the minimum current density required for manganese deposition decreases in the presence of selenious acid, a fact observed in the steady-state experiments and secondly, the minimum current density required for manganese deposition is high on a fresh stainless steel cathode and less on a stainless steel electrode on which a layer of manganese deposit is formed and dissolved.

Since both hydrogen evolution and manganese deposition reactions occur simultaneously at the cathode, any decrease in exchange current density for the hydrogen evolution reaction must decrease the rate of hydrogen evolution and consequently

Table 3. Minimum current density (c.d.) required to obtain manganese deposition

c.d (mA cm^{-2})	*Time of corrosion, t_c*	
	$[H_2SeO_3] = 0$ (gl^{-1})	$[H_2SeO_3] = 0·1$ (gl^{-1})
10	–	–
20	–	–
30*†	–	0·15
25	–	0·6
20	–	0·58
10	–	0·05
8	–	–
9**†	–	0·06
8·4	–	0·001
40	–	
50*	0·26	
45	0·31	
42	0·30	
35	0·15	
30	0·11	
25	–	
26**	0·08	
24	Kink seen	

*† Minimum c.d. required in the presence of H_2SeO_3 on a fresh stainless steel electrode.

**† Minimum c.d. required in the presence of H_2SeO_3 on a stainless steel electrode from which manganese is dissolved off once.

* & ** Refer to the minimum c.d.'s required in the absence of H_2SeO_3.

Table 4. Current efficiency for manganese deposition in the absence and presence of selenious acid at different current densities

c.d. ($mA\ cm^{-2}$)	% c.e.	
	$[H_2SeO_3] = 0\ (g\,l^{-1})$	$[H_2SeO_3] = 0{\cdot}1\ (g\,l^{-1})$
10	0	0
30	25·54	60·43
50	37·08	66·68
70	53·11	71·03
90	52·05	64·33

increase the rate of manganese deposition. The increase in efficiency of manganese deposition observed (Table 4) on addition of selenious acid to the solution is thus understandable as arising from the decrease in the exchange current density for hydrogen evolution.

The exchange current densities obtained for manganese deposition are found to be independent of selenious acid concentration (Table 5). Thus, it appears as though the effect of selenium in manganese deposition is indirect in the sense that selenious acid decreases the rate of the hydrogen evolution reaction and thus helps in increasing the rate of the manganese deposition reaction.

Table 5. Variation of exchange current density for the manganese deposition reaction with selenious acid concentration

H_2SeO_3 ($g\,l^{-1}$)	$I_{0,\,Mn}$ ($A\ cm^{-2}$)
0	$1 \pm 0{\cdot}02 \times 10^{-3}$
0·025	1.1×10^{-3}
0·05	$5 \pm 1 \times 10^{-3}$
0·1	$4 \pm 1{\cdot}2 \times 10^{-3}$

A similar mechanism has been proposed for the action of sulphur dioxide [2] in the electrodeposition of manganese, where it was shown that sulphur dioxide decreases the rate of the hydrogen evolution reaction and thus increases the current efficiency for manganese deposition.

The decrease in the corrosion current of manganese in the presence of selenious acid, shown in Table 1, can be explained as follows in the light of above conclusions. Since it was shown that selenious acid has no direct effect on the manganese deposition reaction, it can be assumed, on the basis of the microscopic reversibility principle, that the dissolution reaction is also unaffected by selenious acid. Further it has been shown that selenious acid decreases the rate of hydrogen evolution. Hence the decrease in corrosion current can be explained on the basis of the Evans diagram where the curve corresponding to the hydrogen evolution reaction shifts towards lower current densities in the presence of H_2SeO_3 and the curve corresponding to manganese dissolution remains unaffected.

References

[1] J. H. Jacobs and P. E. Churchward, *J. Electrochem. Soc.* 94 (1948) 108.

[2] B. V. K. S. R. A. Tillak, S. R. Rajagopalan and A. K. N. Reddy, *Roczniki. Chem.* 38 (4) (1964) 673.

[3] A. T. Sanzharovskii, *Dokl. Moskov. Selskakhoz. Acad.im.K.A. Timiryazeva, Nauch. Kont.* 32. *Chem. Abs.* 54 4201g.

[4] N. Dhananjayan, M.Sc. Thesis, Madras University, Madras (1962) p. 62.

[5] P. Radhakrishnamurthy, Ph.D. Thesis, I.I.Sc., Bangalore (1972).

[6] A. J. Bard, *Analyt Chem.* 35 (1963) 340.

[7] P. Radhakrishnamurthy, S. Sathyanarayana and A. K. N. Reddy, *J. Appl. Electrochem.* 6 (1976).

[8] N. P. Shul'gina and M. N. Polukarov, *Uch.Zap.*, Perm. Gos. Univ. 159 (1966) 112. *Chem. Abs.* 83645e.

[9] J. Yanickis, B. Stulpinas, B. Girciene and A. A. Suliakas, *Vopr. Uscrverch. Gal'uanopokrytii Inst. Khim. Technol, Akad. Nauk Lit. SSR* (1961) 40. *Chem. Abs.* 57 3187b.