JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 51–55

Kinetics of hydrogen evolution reaction on a stainless steel electrode

P. RADHAKRISHNAMURTHY,* S. SATHYANARAYANA, A. K. N. REDDY

Electrochemistry Group, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

Received 15 March 1976

The kinetic parameters for the hydrogen evolution reaction on a stainless steel substrate have been obtained from a study of the steady-state polarization curves as well as the galvanostatic transients. The high Tafel slope obtained in the steady-state polarization measurements was ascribed to the presence of an oxide film present on the surface of the stainless steel electrode.

1. Introduction

Stainless steel is used as the cathode in the industrial process of electrowinning of manganese. Since manganese has a high negative standard equilibrium potential, hydrogen gas invariably evolves at the cathode during the electro-deposition of manganese. Hence, an understanding of the kinetics of hydrogen evolution is important in understanding the mechanism of the manganese deposition reaction. The kinetics of hydrogen evolution has been extensively studied on many metal electrodes [1]. However the literature available on hydrogen evolution kinetics on stainless steel is scanty [2]. This paper describes a study of the hydrogen evolution reaction on stainless steel from a manganese sulphate (0·2 M) and ammonium sulphate (1·0 M) solution.

2. Experimental

Standard circuits have been used [3] for obtaining steady-state polarization curves and galvanostatic transients. The solutions were prepared using Analar grade chemicals and double-distilled water. The required amounts of manganese sulphate and ammonium sulphate were weighed and dissolved in water to obtain the required concentrations. The solutions were pre-electrolysed [3], filtered and stored under a reducing atmosphere. About 300 ml of the electrolyte were taken and the pH adjusted to the required value with sulphuric acid or ammonium hydroxide. When selenious acid was used, the required amount was added from a stock solution prior to pH adjustment. The galvanostatic transients were obtained using a Tektronix 564B oscilloscope with a type 3A6 plug-in. The procedure employed for obtaining the steady-state polarization curves and galvanostatic transients has been described elsewhere [3].

3. Results

The steady-state polarization curves obtained for solutions containing 0·2 M manganese sulphate and 1·0 M ammonium sulphate at different values of pH are shown in Fig. 1.

Fig. 2 shows the polarization curve for this electrolyte at pH 7 in the presence of 0·1 $\mathrm{g\,l^{-1}}$ selenious acid. It can be seen from these figures that the log *I–E* curve is linear in the current–density region 10^{-4}–10^{-3} $\mathrm{A\,cm^{-2}}$ and then shows a curvature with a rapid change of potential with current density in the region 10^{-3}–10^{-2} $\mathrm{A\,cm^{-2}}$.

The galvanostatic transients obtained for 0·2 M manganese sulphate, 1·0 M ammonium sulphate and 0·1 $\mathrm{g\,l^{-1}}$ selenious acid solution are shown in Fig. 3. In the low current density region, the selenium deposition, which is under diffusion control, exhibits a transition time and the potential of the electrode is essentially controlled by

---

* Electrowinning Section, Central Electrochemical Research Institute, Karaikudi-623006, India.

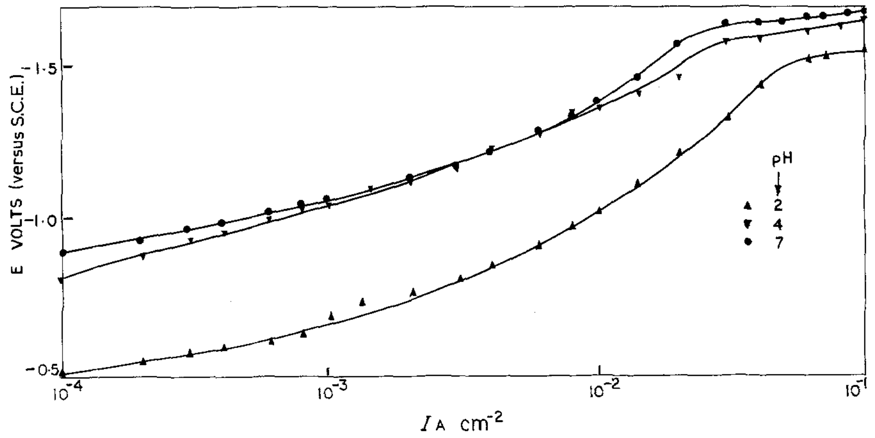

Fig. 1. Polarization curves for hydrogen evolution at different pH values from 0·2 M manganese sulphate and 1·0 M ammonium sulphate electrolyte.

this reaction. At high current densities, the linear portion DX on the transient (immediately after the transition time) corresponds to the hydrogen evolution reaction.

4. Discussion

Since the equilibrium potential for manganese deposition in the solutions employed is − 1·45 V (versus S.C.E.) the reaction occurring at all the potentials shown in Figs. 1, 2 & 4 corresponds to that of hydrogen evolution. This is supported by the fact that the equilibrium potential for the hydrogen evolution reaction is −0·65 V (versus S.C.E.) and the cathode potentials shown in Fig. 1 are negative (cathodic) to this equilibrium potential. In addition, gas evolution is seen at the cathode. In Fig. 2, also, the potential at the cathode is essentially determined by the hydrogen evolution reaction since the selenium deposition reaction becomes diffusion controlled at current densities much lower than those used in the present experiments [3].

In order to deduce the kinetic parameters for the hydrogen evolution reaction, it is necessary to know the respective degrees of mass transfer control and charge transfer control. The extent of mass transfer polarization is dependent on the ratio I/I_L where I_L is the limiting current density. Since H_2O is the reactant species for the hydrogen

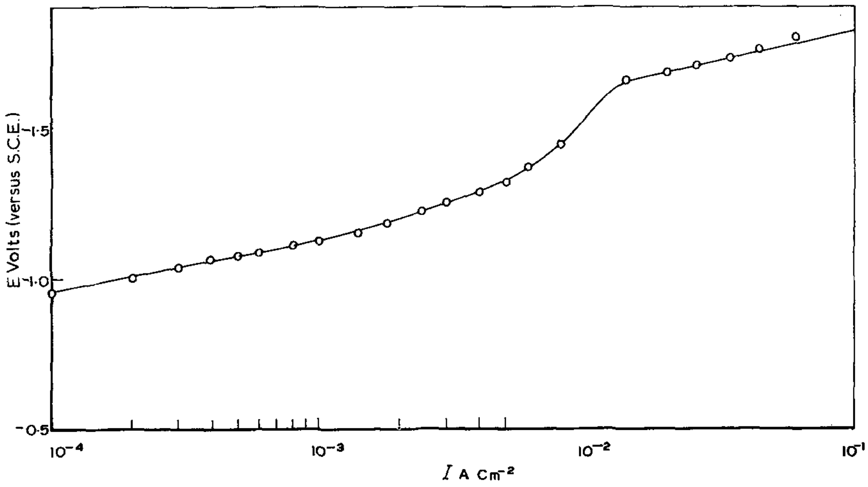

Fig. 2. Steady-state polarization curve for hydrogen evolution from a solution at pH 7 containing 0·2 M manganese sulphate, 1·0 M ammonium sulphate and 0·1 $g l^{-1}$ selenious acid.

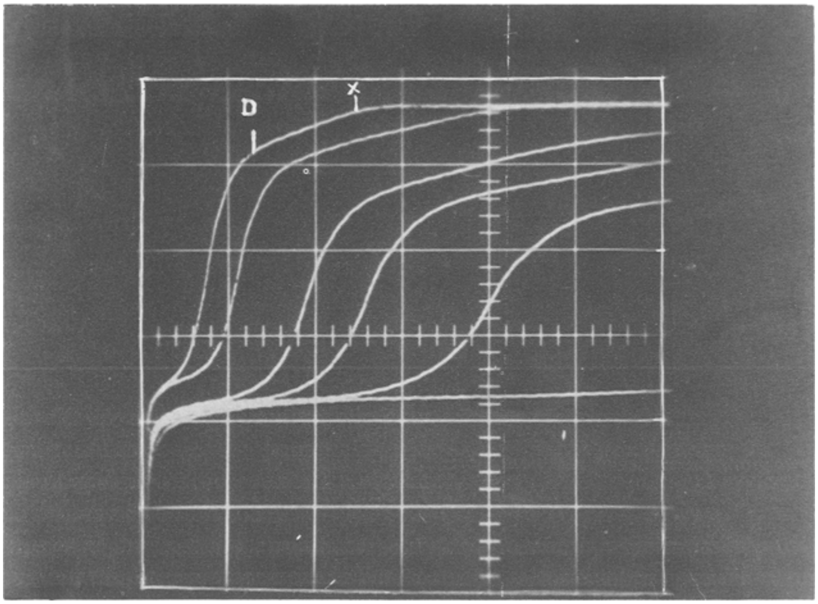

Fig. 3. X axis: time (0·1 s/div.); Y axis: potential (285·7 mV/div.) Galvanostatic transients obtained for a solution at pH 7 containing 0·2 M manganese sulphate, 1·0 M ammonium sulphate and 0·1 g l^{-1} selenious acid, at different current–densities from right to left: 10, 19, 30, 40, 69, 96 mA cm^{-2}. Rest potential from right to left: 0·02, 0·02, 0·01, 0·01, 0·00, 0·00 V.

evolution reaction at pH values $\geqslant 7$, it can be seen that

$$I_L = \frac{nFDC_{H_2O}}{\delta} = 11\ A\,cm^{-2}$$

assuming $D = 10^{-5}\ cm^2\,s^{-1}$ and $\delta = 10^{-2}$ cm (unstirred solution). As the current density employed in the experiments was always less than 0·1 A cm^{-2}, it is evident that mass transfer control can be ignored. This conclusion is confirmed by the fact that stirring had no marked effect on the current at these potentials.

Since at the lowest current density used

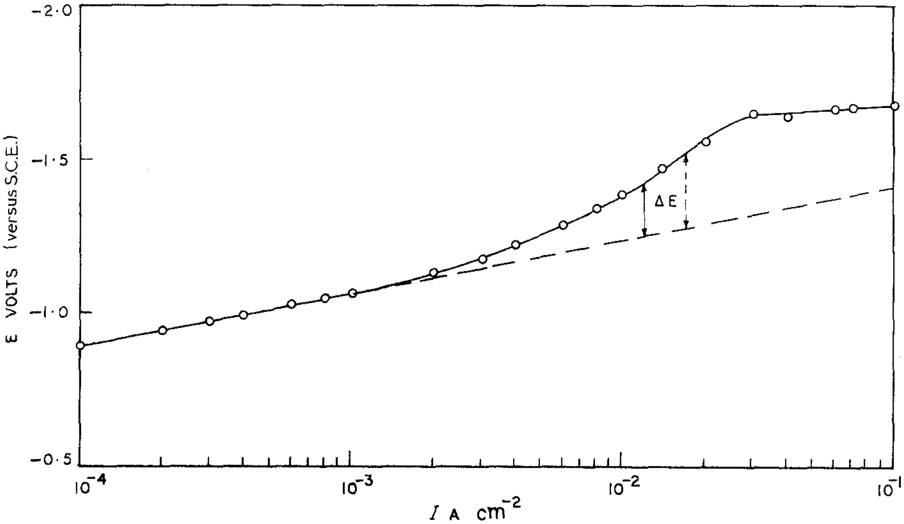

Fig. 4. Steady-state polarization curve (–) for hydrogen evolution from a solution at pH 7 containing 0·2 M manganese sulphate and 1·0 M ammonium sulphate and the Tafel line for hydrogen evolution reaction at high current–densities extrapolated from the low current–density region (- - -).

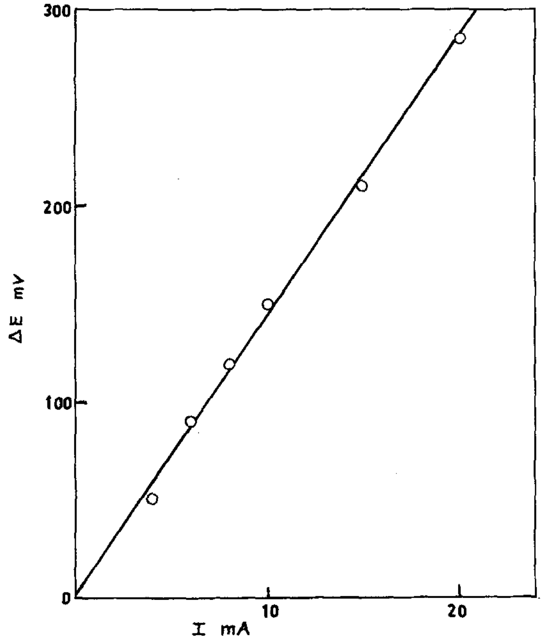

Fig. 5. Test for the presence of IR drop contribution in the measured potential.

(10^{-4} A cm^{-2}) at pH $\geqslant 7$, the cathode potential is about $-0{\cdot}9$ V (versus S.C.E.), the overpotential for hydrogen evolution reaction is greater than 0·2 V and therefore the rate of the backward reaction,

$$H_2 + 2OH^- \rightarrow 2H_2O + 4e$$

can be neglected under these conditions. Hence Tafel's law would be expected to be applicable for this reaction. It can be seen from Figs. 1 and 2 that while a good Tafel line is obtained over more than a decade of current density a significant deviation from linearity occurs at higher current densities ($> 3 \times 10^{-3}$ A cm^{-2}). Such a non-linear log *I–E* curve can be explained on the basis of an *IR* drop across the oxide film. If the non-linearity is due to an *IR* drop, ΔE, the deviation of the electrode potential from the value of potential obtained by extrapolation of the Tafel line (Fig. 4) at low current densities, should be proportional to the current. It can be seen in Fig. 5 that such a ΔE versus I plot is indeed linear. Therefore it may be concluded that the non-linearity of the log *I–E* curve in the region 10^{-3}–10^{-2} A cm^{-2} is due to an *IR* drop.

The slope of the ΔE versus I plot gives a resistance of about 14 Ω. If a 100 Å thick oxide film is assumed to be present, in order to give a resistance of 14 Ω, the specific resistance should be about $1{\cdot}5 \times 10^7$ Ω cm which is in the range of the values for semiconductors [4]. Hence, it can be concluded that the non-linearity in the log *I–E* curve is due to *IR* drop across the semiconducting oxide film present on the stainless steel electrode.

The exchange current-densities and transfer coefficients, obtained from the *IR*-corrected Tafel lines, are given in Table 1. It can be seen from this table that:

(1) the transfer coefficient is lower than the generally observed values of $\frac{1}{2}$, 1, $\frac{3}{4}$;

(2) in the presence of H_2SeO_3 the exchange current decreases and

(3) the exchange current density at pH 2 is large compared with the value at pH 4 and 7.

The high Tafel slope ($3RT/F$) is unusual for hydrogen evolution reaction on clean metals. However, such high Tafel slopes have been observed on film-covered surfaces and in these cases the high Tafel slopes observed have been attributed to the presence of an oxide film on the electrode surface. The presence of an oxide film on a stainless steel electrode was proved by O'Brien *et al.* [2].

Table 1. Variation of the exchange current–density and transfer coefficient with pH *for the hydrogen evolution reaction*

pH	I (A cm^{-2})	α
2	$(2 \pm 1{\cdot}0) \times 10^{-5}$	0·3
4	$(2{\cdot}7 \pm 1{\cdot}1) \times 10^{-6}$	0·3
7	$(7 \pm 1{\cdot}4) \times 10^{-6}$	0·3
7*	$(9 \pm 3{\cdot}0) \times 10^{-7}$	0·4

* 0·1 g l^{-1} selenious acid is present in the solution.

Meyer [5] put forward a theory based on two potential-dependent processes:

(1) a reaction consisting of charge transfer through the film and

(2) the usual charge transfer process across the double layer at the interface. However, his theory gives a value of

$$2{\cdot}303\,\frac{RT}{F}\left(\frac{\alpha_f + \alpha_s}{\alpha_f\alpha_s}\right),$$

where α_f and α_s are the transfer coefficients for the film reaction and the double layer reaction respectively. R, T and F have their usual meanings.

In order to explain the slope of $3RT/F$ a simpler theory is developed. One can write for the current density through the junction between the substrate metal and the oxide film semiconductor, the well-known expression [6]

$$I_j = k_j \exp(-fE_j) \qquad (1)$$

where k_j is a potential-independent constant for the junction current density, E_j is the potential difference across the junction and $f = F/RT$.

Using this expression along with the expression for the rate of the charge transfer reaction;

$$I_s = k_s \exp(-\alpha_s fE_s), \qquad (2)$$

(where k_s is a potential-independent constant and α_s and E_s are the transfer coefficient and the potential drop across the interface for the charge transfer reaction), the current continuity equation;

$$I = I_j = I_s, \qquad (3)$$

and the expression;

$$E = E_j + E_s, \qquad (4)$$

we obtain:

$$I = k_a \exp(-\alpha_a fE), \qquad (5)$$

where

$$k_a = k_j^{(\alpha_s/(\alpha_s+1))} \times k_s^{(1/(1+\alpha_s))} \qquad (6)$$

and

$$\alpha_a = \frac{\alpha_s}{1+\alpha_s}. \qquad (7)$$

Thus the Tafel slope is given by:

$$\frac{d(-E)}{d\,\ln I} = \frac{1}{\alpha_a f} = \frac{RT}{\alpha_a F} = \left(1+\frac{1}{\alpha_s}\right)\frac{RT}{F} \qquad (8)$$

and setting $\alpha_s = 0{\cdot}5$ we obtain the Tafel slope $3RT/F$. This is in good agreement with the experimentally obtained value of 190 mV dec^{-1}. This model may also be valid in the case of hydrogen evolution reaction on other metals, for instance, lead [7] and anodized Zr [5] which yield slopes of approximately $3RT/F$.

Comparing the potential scale of the galvanostatic transients (Fig. 3) with that of the steady-state polarization curves, the region D to X (Fig. 3), of the transient can be identified with the hydrogen evolution reaction; the slope of this portion of the transient arises from the highly irreversible character of the hydrogen evolution reaction. No approach to a transition time is expected because water is the reactant for the reaction at pH 7 and, therefore, there is virtually no mass transfer control. The exchange current-density for hydrogen evolution may be calculated in the following way from the transient. The galvano-static current is shared between two processes:

(1) double layer changing, I_{DL}, and

(2) the faradaic process of hydrogen evolution, I_F.

Therefore,

$$I = \text{constant} = I_{DL} + I_F$$

$$= \frac{-C\,d\eta}{dt} + I_0 \exp(-\alpha f\eta) \qquad (9)$$

where C is the double layer capacitance, η is the overpotential, I_0 is the exchange current density for the hydrogen evolution reaction and α is the transfer coefficient.

Since it is difficult to measure the slope, $d\eta/dt$, at different values of η on the restricted part of the transient, it is convenient to use the integrated form. The solution to the differential equation can be shown to be

$$-(\eta_2 - \eta_1) = \frac{I(t_2 - t_1)}{C} + \frac{1}{\alpha f} \times \ln\left[\frac{1-(I_0/I)\exp(-\alpha f\eta_2)}{1-(I_0/I)\exp(-\alpha f\eta_1)}\right]. \qquad (10)$$

Using the above expression over the region DX in Fig. 3 it was found that $I_0 \approx 1 \times 10^{-7}$ A cm^{-2} which is in reasonable agreement with the value $9 \pm 0{\cdot}3 \times 10^{-7}$ A cm^{-2} obtained from the steady-state polarization curves.

References

[1] S. Srinivasan, Dissertation in chemistry, University of Pennsylvania (1963).

[2] R. N. O'Brien and P. Seto, *J. Electrochem. Soc.* **117** (1970) 32.

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

[4] C. Kittel, 'Introduction to Solid State Physics,' 2nd Edn., John Wiley and Sons, Inc., New York, (1956) 347.

[5] R. E. Meyer, *J. Electrochem. Soc.* **107** (1960) 847.

[6] C. Kittel, 'Introduction to Solid State Physics,' 2nd Edn. John Wiley & Sons, Inc., New York, (1956) 389.

[7] S. Srinivasan, Dissertation in chemistry, University of Pennsylvania (1963) p. 180.