Kinetics of hydrogen evolution reaction on a stainless steel electrode

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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 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 $10^{-4}-10^{-3}$ A cm$^{-2}$ and then shows a curvature with a rapid change of potential with current density in the region $10^{-3}-10^{-2}$ A cm$^{-2}$.

The galvanostatic transients obtained for 0.2 M manganese sulphate, 1.0 M ammonium sulphate and 0.1 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

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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

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**Fig. 1.** Polarization curves for hydrogen evolution at different pH values from 0.2 M manganese sulphate and 1.0 M ammonium sulphate electrolyte.

**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.