OXYGEN EVOLUTION ON LEAD DIOXIDE IN SULPHURIC ACID SOLUTIONS

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Introduction

Oxygen evolution in the lead/acid battery takes place as a side reaction during battery charge and as a partial anodic reaction during self-discharge of the positive plate. The successful development of a sealed battery requires detailed knowledge of the kinetics of the oxygen evolution and reduction reactions.

The evolution of oxygen on PbO_2 of different origin has been widely investigated by various methods [1 - 9]. A considerable part of the information gathered on the kinetics of the reaction has been obtained from studies of the current/potential characteristics. It is generally accepted that the Tafel law is obeyed. Unfortunately, however, values reported for the Tafel slope are scattered, being in the range 90 - 140 mV per decade. Similar controversy exists with regard to the dependence of the Tafel slope on temperature. For example, in an early paper [9], a normal proportionality was found to exist between the Tafel slope and the temperature, while other authors [1 - 3, 8] were unable to detect any influence of temperature. Data on the effect of electrolyte concentration (or pH) on the Tafel slope are also contradictory. For example, whereas one study found [6] the slope to be independent of the solution pH, Hyvarinen [2] observed the slope to decrease with increase in pH and attributed this result to a non-stationary phenomenon. A further investigation reported [7] an increase in the slope in more dilute acid.

The aim of the present work is to examine the oxygen evolution reaction on a lead anode in sulphuric acid, and is directed mainly towards evaluating the Tafel slope and its dependence on both temperature and electrolyte concentration.

Experimental

Test cell

A conventional three-electrode cell was employed. A platinum sheet with a large surface area was used as the counter electrode, and a mercurous

sulphate (Hg/Hg$_2$SO$_4$) electrode in the same solution or a saturated calomel electrode (SCE) were used as reference electrodes. All potentials are reported with regard to the SCE. The working electrode was a 99.9999% lead rod with an area of about 1 cm^2 pressed tightly into a Teflon holder. The temperature was controlled within ± 0.1 °C.

Electrode preparation

A solution of 1 N H$_2$SO$_4$ was used as an electrolyte for electrode preparation. The lead electrode was cathodically cleaned at -0.9 V for 3 h. Initial oxidation was carried out potentiostatically at 1.8 V for 24 h. The electrode was then subjected to galvanostatic cycling at 1 mA cm^{-2} down to 1.2 V and 100% overcharge for 60 h. Finally, a potentiostatic oxidation at 1.8 V for 24 h was performed. The electrode was washed with triply-distilled water, immersed in 0.01 N H$_2$SO$_4$, and subjected to further oxidation as described in the next section. The electrolyte was substituted with a more concentrated one under current without electrode removal from the cell.

Test procedure

The steady-state current/potential curves were obtained potentiostatically, with automatic *IR* correction, using a Solartron 1286 Electrochemical Interface. After changing the electrolyte, the electrode was kept at the highest potential used in the measurements until a steady-state current value was reached. The potential was varied, in 10 mV increments, in a negative direction and the stationary value of the current was recorded. The direction was reversed at $\sim$150 mV above the PbO$_2$/PbSO$_4$ potential. The average scan rate was $\sim$0.01 mV s^{-1}. A curve was accepted if the current values at the same potential from positive- and negative-going runs did not differ by more than 1%. This criterion was used for the data of 3 subsequent cycles. The slopes of the curves were evaluated by regression analysis.

Results and discussion

The steady-state current/potential curves for different electrolyte concentrations are plotted in Fig. 1. Only the linear parts of the curves are shown because these are pertinent to the study discussed here. Nevertheless, some comments on the upper potential limits of the linear regions are also necessary. In all solutions, there is a potential above which the current increases with time for a long period, together with the injection of PbO$_2$ colloidal particles into the electrolyte. This probably reflects a slow increase in the active surface caused by a surface reconstruction process. This is a well-known phenomenon [10 - 12], and is assumed to be dissolution–reprecipitation of the dioxide caused by a high local pH near the electrode [11], especially in high acid concentrations, or by material destruction under the attack of radical intermediates, such as OH$^{\cdot}$, O$^{\cdot}$, SO$_4^{\cdot-}$, by an unknown mechanism [12]. Whatever the nature of the surface reorganization, it is not
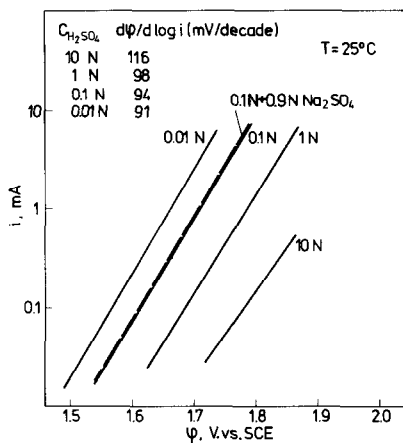
Fig. 1. Current/potential curves in different acid concentrations at 25 °C.

recommended for operation in conditions of dynamic instability of the surface. The upper potential limit has been chosen so as to avoid this region. In this way, hysteresis between the positive and negative runs is avoided and linearity is achieved.

It is seen that the slopes of the curves decrease when the concentration is reduced. The curves obtained in $0.1 \, N \, H_2SO_4$ and in $0.1 \, N \, H_2SO_4 +$ $0.9 \, N \, Na_2SO_4$ are practically identical; this suggests that the pH, but not the SO_4^{2-} concentration, is responsible for the variation in slope. The latter probably reflects some changes in the electrode properties, *e.g.*, number of active sites or interaction between surface intermediates. It can be easily accepted that parameters such as stoichiometry [13] and hydration [14] of the oxide can also change with pH under oxygen evolution, but it is not quite clear how these parameters will affect the kinetics of oxygen evolution.
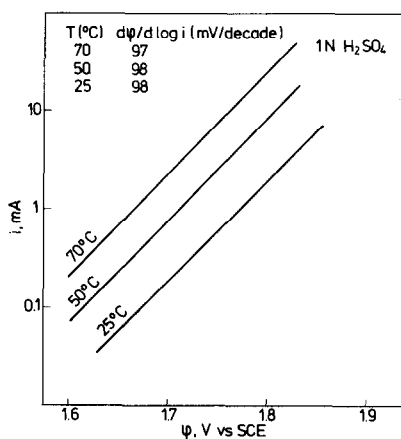

Fig. 2. Current/potential curves at different temperatures in $1 \, N \, H_2SO_4$.

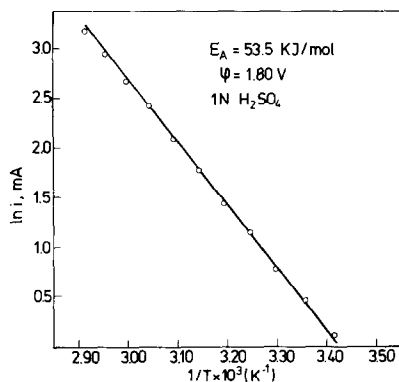Fig. 3. Arrhenius plot in 1 N H_2SO_4.

The current/potential curves in 1 N H_2SO_4 at different temperatures are shown in Fig. 2. The curves are parallel and this confirms that the Tafel slope is not dependent on temperature. Although this is unexpected from a theoretical point of view, it is not uncommon for the oxygen evolution reaction [15] as well as for other reactions [16]. The reason for such anomalous behaviour is not well understood [16 - 18] and obviously requires special investigation.

The activation energy obtained from the Arrhenius plot (Fig. 3) was found to be 53.5 kJ mol^{-1}. This is in agreement with data already published [2, 3].

Further work is in progress to extend studies on the kinetics of anodic oxygen evolution on lead dioxide.

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