

Morphology of PbSO₄ formed on solid Pb in concentrated sulphuric acid: a note pertaining to a recent paper

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Received 2 June 1982

A scanning electron microscopy (SEM) study of the formation of PbSO₄ on Pb in H₂SO₄ at concentrations greater than 5 mol dm⁻³ is presented. The production of a tight and mechanically sound PbSO₄ film in concentrated H₂SO₄ postulated in an earlier communication is confirmed.

1. Introduction

Recently [1] we investigated the behaviour of PbO₂ in concentrations of H₂SO₄ in excess of 5 mol dm⁻³. This was approached by carrying out linear sweep voltammetry (LSV) on pure solid lead in different high concentrations of sulphuric acid at a series of sweep rates (10–100 mV s⁻¹). It was found that the maximum peak current values (i_p), and hence the charge values, decreased dramatically in passing from 5 mol dm⁻³ to 10 mol dm⁻³ H₂SO₄. This indicated that as the concentration of sulphuric acid was increased the form of the lead sulphate film became passivated at a smaller deposit thickness.

In this note we show photographic evidence in support of our electrochemical data.

2. Experimental procedure

The computer-controlled experimental set-up and electrode preparation have been described in previous publications [1, 2]. The linear sweep experiments were carried out at 23 ± 1° C with a Hg/Hg₂SO₄ reference electrode which was in the same H₂SO₄ electrolyte solution as the working electrode. The pure lead electrodes were cycled to a constant response between the limits 550 mV and 1550 mV, finally being held in the PbSO₄ region (550 mV). Again, the time needed for con-

stancy was approximately 1.5 h. The sweep-speed, ν was kept constant, that is, $\nu = 100 \text{ mV s}^{-1}$.

The experiments were performed in 5.0, 7.0 and 10.0 mol dm⁻³ sulphuric acid on pure lead rods (diameter = 0.3 cm) shrouded in Teflon in the form of stubs which screwed into the end of the rotating disc electrode [3]. After the electrochemistry had been carried out at the solid electrode, the electrodes were washed with tri-distilled water, rinsed with acetone and stored in a vacuum desiccator. For SEM observations the stubs were coated with a thin layer of gold by diode sputtering and examination was performed using a Jeol JSM 35 scanning electron microscope.

3. Results and discussion

Figure 1 shows the surface morphology of a pure lead electrode after redox cycling for 1.5 h in 5.0 mol dm⁻³ H₂SO₄. The final potential was 550 mV (PbSO₄ region). The prismatic PbSO₄ crystals are clearly visible and are dispersed on the surface of the electrode in an irregular fashion. Figure 2 displays the effect of increasing the concentration of the sulphuric acid electrolyte on the PbSO₄ crystals formed on the Pb electrode. Hence at 7 mol dm⁻³ H₂SO₄ the crystals become smaller, deformed and more compact, producing a tighter layer on the surface of the electrode. This is in accordance with what we published recently [1]

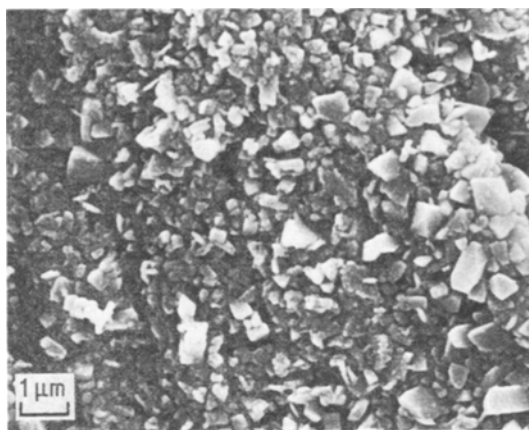


Fig. 1. 5 mol dm⁻³ H₂SO₄ electrolyte: Front of flat lead electrode after potentiodynamic cycling (550–1550 mV) for 1.5 h, ending at 550 mV.

suggesting that the PbSO₄ film becomes mechanically sound and tighter on the electrode.

At 10 mol dm⁻³ H₂SO₄ Fig. 3 shows that the PbSO₄ crystals become even smaller and are packed much closer together to give a very densely packed film of lead sulphate. Hence the

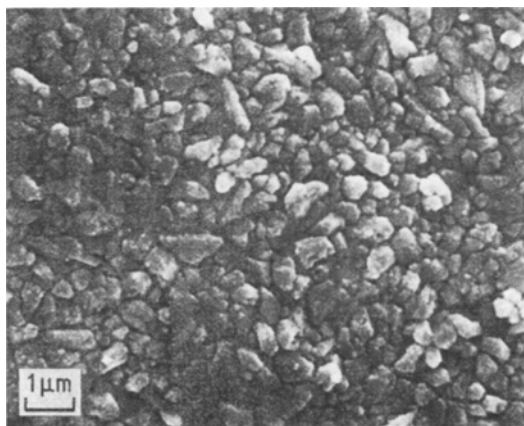


Fig. 2. As Fig. 1 but in 7 mol dm⁻³ H₂SO₄ electrolyte.

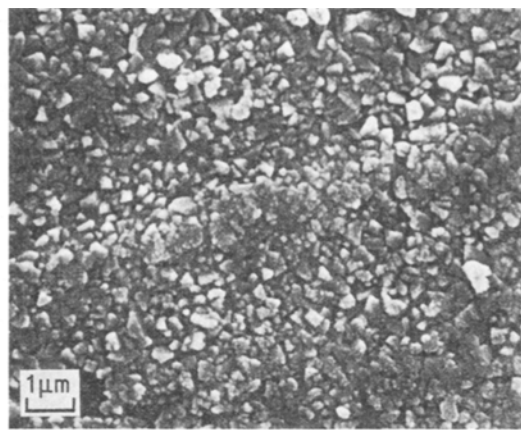


Fig. 3. As Fig. 1 but in 10 mol dm⁻³ H₂SO₄ electrolyte.

charge output of the PbO₂ electrode is drastically reduced in concentrated sulphuric acid because the mechanically sound film of PbSO₄ becomes very passivating and effectively resists oxidation to PbO₂ on cycling potentiodynamically between the PbO₂ and PbSO₄ regions.

The important conclusion of this note is that in H₂SO₄ concentrations > 5 mol dm⁻³ the PbSO₄ crystals become much smaller forming a tighter and passivating film.

Acknowledgement

We wish to thank the directors of Chloride Technical Ltd for financial support (J.A.B.).

References

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