The Anodic Electrodeposition of PbO$_2$

C. J. Bushrod * and N. A. Hampson

Department of Chemistry, Loughborough University of Technology

SUMMARY—Lead dioxide may be deposited on suitable bases from aqueous solutions of lead salts. For commercial production only two electrolytes are suitable: nitrate and perchlorate. Of these the lead perchlorate bath is the simpler to operate.

INTRODUCTION

ELECTRODES formed by the electrodeposition of PbO$_2$ onto an inert basis[1] (Pt, Ag, Ni, Cu, stainless steel) have been used for primary power source applications[2] and are of interest in the field of electro-organic oxidation.

Electrolytic systems suitable for electrodeposition must utilize a soluble lead salt as electrolyte. This requirement limits the choice of a suitable anion to a small group of which the most readily available are perchlorate, nitrate, fluoborate, silicofluoride and plumbite. Under carefully controlled conditions satisfactory deposits may be obtained using these electrolytes.[1,3-5]

For commercial applications to achieve satisfactory deposition at a reasonable rate (~ 30 mAcm^{-2}) plumbite, fluoborate and silicofluoride are unsuitable as electrolytes. At current densities above about 5 mAcm^{-2} electrolytes based on these anions result in highly stressed, poorly adherent deposits which readily flake.
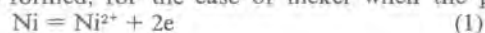
This note summarizes the results of experiments conducted with perchlorate and nitrate electrolytes.
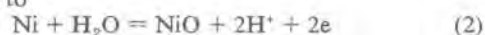
EXPERIMENTAL

Metal bases ($10 \times 5 \times 0.01$ cm) were annealed and etched. Washed (distilled water) bases were suspended symmetrically between cathodes (stainless steel—10 cm apart) in the electrolyte. Current was switched conventionally and charge equivalent to the required deposit (0.43 gm cm^{-2}) passed at the required rate.

RESULTS AND DISCUSSION

With the exception of platinum, if the current density is low, PbO$_2$ is not deposited, rather the basis dissolves. This tendency is more pronounced with metals such as copper and under conditions of high acidity. For PbO$_2$ to be deposited the basis must first be rendered passive for the basis metal dissolution process. The basis (anode) dissolves until the point of passivation is reached, when a passive layer is formed, for the case of nickel when the process

$$Ni = Ni^{2+} + 2e \qquad (1)$$

changes to

$$Ni + H_2O = NiO + 2H^+ + 2e \qquad (2)$$

* Electric Power Storage Ltd, Clifton Junction, Manchester.

the electrode passivates with the production of an insoluble layer of nickel oxide. The electrode potential then rises to that required for the formation of PbO$_2$.

$$Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e \qquad (3)$$
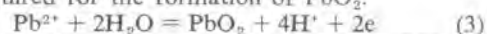
PbO$_2$ electrodeposits on metals other than platinum therefore incorporate a passive layer between the basis and the PbO$_2$.

It is necessary to control the pH of the electrolyte so that reaction (2) is favoured; if the pH is too low the passive layer may not be formed, so that the anode continues to dissolve. In the presence of high [H$^+$] it may be necessary to give a 'flashing' treatment, that is the current is increased momentarily to a very high value, favouring reaction (2).

LEAD PERCHLORATE ELECTROLYTES

We have obtained good adherent deposits of PbO$_2$ using electrolytes of ~ 2 mol l^{-1} lead perchlorate and 1 mol l^{-1} perchloric acid. Over fairly wide limits of [Pb^{2+}] current densities of up to 50 mAcm^{-2} have been employed without unduly high stresses being encountered, provided that [H$^+$] does not rise above 1 mol l^{-1}. Acidity was controlled by continuous circulation through a bed of PbO.

Dendritic growth of lead on the cathode was a complicating factor, so that it was desirable to keep the cathode current density as low as possible. This was done by using cathodes of large area (five times that of the anode).

Current efficiencies were $\sim 100\%$ based on the anodic oxidation.

LEAD NITRATE ELECTROLYTES

Optimum conditions for the production of PbO$_2$ electrodeposits at a rate of 36 mAcm^{-2} require 1.6 mol l^{-1} lead nitrate electrolyte. Successive depositions in electrolyte at controlled pH show a decreasing faradaic efficiency. Thus four successive depositions gave efficiencies of 93.5%, 69.2%, 42.2% and 25.4%. The effect is due to the presence of nitrite in the electrolyte (Fig 1), the nitrate ion is reversibly reduced to nitrite at the cathode and oxidized to nitrate at the anode.

$$NO_3^- + 2H^+ + 2e \rightleftharpoons NO_2^- + H_2O \qquad (4)$$
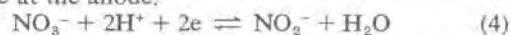
As might be expected, the amount of nitrite produced during the passage of a given quantity of electricity is found to depend on the cathodic current density. At low
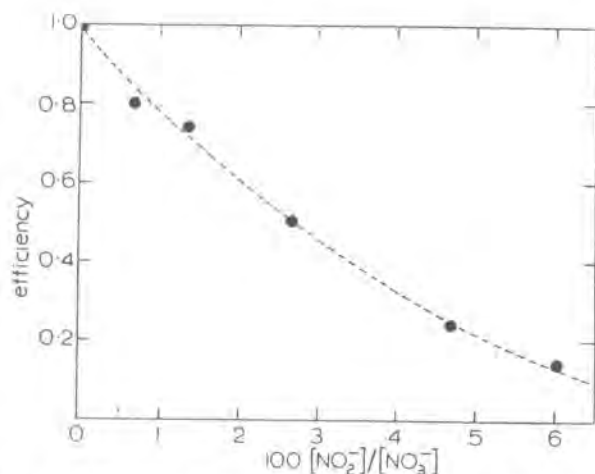
Fig 1. Effect of the nitrite ion on the faradaic efficiency for the anodic electrodeposition of PbO_2 from lead nitrate electrolyte.

current density (~ 1 mAcm^{-2}) the deposition process was 100%, at higher current density (~ 30 mAcm^{-2}) the efficiency fell markedly as nitrite was produced and at very high current densities (~ 100 mAcm^{-2}) ammonium ion is produced. Ammonium ion production 'takes over' from nitrite production as current density further increases. In the present experiments nitrite was removed from the system by oxidation with H_2O_2 or Pb_3O_4. This was coupled with pH control by pumping electrolyte through an external circuit containing a bed of PbO and additions of H_2O_2 (drip feed) or solid Pb_3O_4.

A certain residual stress in deposits obtained from nitrate electrolytes was corrected by the addition of buffers.[2]

THE EFFECT OF TEMPERATURE

With nitrate and perchlorate electrolytes investigated variation between 20° and 40°C does not materially affect the character of the deposit or anode efficiency.

ACKNOWLEDGMENT

REFERENCES

1 See e g J. C. White, W. H. Power, R. L. McMurtrie and R. T. Pierce, Jr, *Trans Electrochem Soc*, 1947, **91**, 73.
2 C. J. Bushrod and N. A. Hampson, in press.
3 P. Reutschi and B. D. Cahan, *J Electrochem Soc*, 1958, **105**, 369.
4 A. T. Zaslavsky, Y. A. Kondrashev and S. S. Tolkachev, *Dokl Akad Nauk SSSR*, 1950, **75**, 559.
5 W. H. Beck, R. Lind and W. F. K. Wynne-Jones, *Trans Faraday Soc*, 1954, **50**, 147.
6 W. H. Dodson, *J Electrochem Soc*, 1961, **108**, 401.
7 C. Dratschmann, *Batteries*, 1964, **17**, 569.
8 N. E. Bagshaw, R. L. Clarke and B. Halliwell, *J Appl Chem*, 1966, **16**, 180.