

LEAD DIOXIDE ELECTRODE FOR ANODIC OXIDATIONS

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Abstract. The lead dioxide covered vitreous carbon anode has been prepared by electro-deposition from various electrolytes. The performance characteristics of the thick deposits are described and the change of the surface with time before and after polarisation at different potentials has been elaborated with Scanning Electron Micrographs (SEM).

The interest in the development of dimensionally stable anodes as substitutes to precious metal anodes, e.g. platinum, gold and tantalum, has intensified in recent years [1-3]. The efforts are mainly centred on coating of oxides or mixed oxides of certain metals on suitable base substrates. Lead dioxide is one which satisfies the major requirements for the oxide anode. Therefore, the electrodeposition of the desirable active material onto cheap substrates such as graphite or carbon [4-6] from different Pb(II) containing electrolytes has been studied. Though nickel or mild steel substrates have been utilised in Japan [7-10] for depositing lead dioxide, it has lately been observed in Germany that titanium [11] is a suitable base for high quality deposits.

For electrochemical measurements it is found necessary to form dense deposits of lead dioxide onto a nonreacting base material. In this work the preparation of thick film lead dioxide anodes on vitreous carbon from various electrolytes is discussed. As in most studies (to be reported later) the electrolyte was aqueous sulphuric acid. Scanning electron micrographs (SEM) of the surface of the anode before and after polarisation in 1.0M sulphuric acid were taken to establish changes at various potentials and with time.

Results and Discussion

Lead dioxide has a tendency to form uneven and porous deposits and hence the electrode area of the lead oxide is difficult to define precisely. Furthermore, it is difficult to ensure that the surface is reproducible in each experiment. Despite these uncertainties potential sweep experiments combined with steady state measurements in quiet solutions have been employed to observe the electrochemical behaviour of the anode.

For preparing massive deposits electrochemically high concentrations of Pb^{2+} ions in solution are required. As the deposition process goes on the electrolytes are depleted of Pb^{2+} ions and the acidity of the solution increases with time. This is undesirable because low pH solutions give dendritic growth. Therefore, the plating baths enlisted in Table 1 were employed and the potentials of the electrode for electrodeposition were selected from linear sweeps recorded at slow scan rates in respective plating solutions.

Sodium ions (0.1M) were added to plating solutions 1 and 3 as $NaNO_3$ and $NaClO_4$ respectively to see the effect of these ions on the activity of the deposit. The activity of the deposits obtained from the different electrolytes having pH between 1 and 7 was determined and compared with each other from the polarisation characteristics of the anode in 1.0M chromium acetate in 1.0M sulphuric acid solution. The results are summarised in Table 2.

Consequently, it was decided that lead nitrate with pH 5 (maintained by the addition of lead monoxide) was suitable electrolyte for the preparation of massive lead dioxide anode. The lead nitrate bath is preferred since it may be readily controlled over long

TABLE 1. PLATING SOLUTIONS AND ELECTROLYSIS CONDITIONS FOR ELECTRODEPOSITION OF LEAD DIOXIDE ON VITREOUS CARBON AT 25°C AT CONSTANT POTENTIAL CORRESPONDING TO C.D. OF 4-5 mA/cm².

No. electrolyte (aqueous g/litre)	Cathode	pH controlled by addition of	Ref
1. 220 Pb(NO ₃) ₂	Platinum	PbO/HNO ₃	9
2. 350 Pb(NO ₃) ₂ 20 Cu(NO ₃) ₂	Copper	PbO/CuCO ₃	5
3. 100 HClO ₄ 55.5 PbO	Platinum	HClO ₄ /PbO	12

TABLE 2. PLATEAU CURRENTS IN mA/cm² FOR THE OXIDATION PROCESS Cr^{3+}/Cr^{6+} ON LEAD DIOXIDE DEPOSITED ON VITREOUS CARBON FROM PLATING SOLUTIONS.

pH of plating	Pb(NO ₃) ₂	Pb(NO ₃) ₂ + NaNO ₃	PbO+P HClO ₄	PbO+HClO ₄ + NaClO ₄	Pb(NO ₃) ₂ Cu(NO ₃) ₂
1	23.2	12.8	8.0	8.08	..
4	23.2	16.0	12.8	16.8	..
7	20	16.0	1.0	16.8	..
3.3	23.2

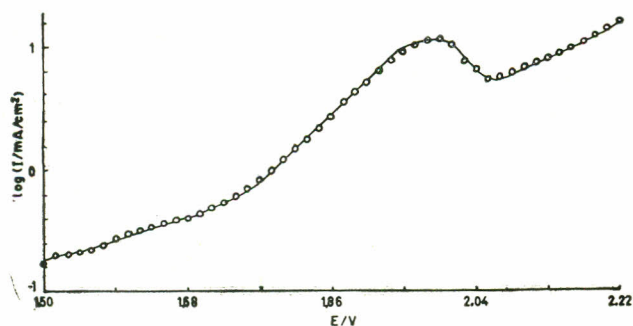


Fig. 1. Current potential curve in 1.0M sulphuric acid.



Fig. 2. SEM of freshly prepared PbO_2 on carbon, magnification, 3,000, 45° .

plating periods and also due to the quality of deposit obtained from the bath over a wide range of operating conditions. Moreover, the base substrate vitreous carbon was quite stable in the range of potential 1.32–1.35V vs. SCE corresponding to the current density 4 mA/cm² at which the deposition was carried out and under the conditions it was prepared from the nitrate bath.

Polarisation of Lead Dioxide in 1.0M Sulphuric Acid

The lead dioxide was deposited on vitreous carbon from lead nitrate 22% (with a starting pH of 5.0) until a charge of 40 coulomb/cm² had been passed. A current potential curve in 1.0M sulphuric acid was recorded and is given in Fig. 1. It has a linear region between 1.8 and 1.95V which was followed by an inflection around 2.01V. The slope of the linear portion of $d\log/i dE$ plot was 130 ± 5 mV as reported in earlier papers [13, 14].

Electron scanning micrographs were taken for the freshly prepared PbO_2 electrode and for the elec-

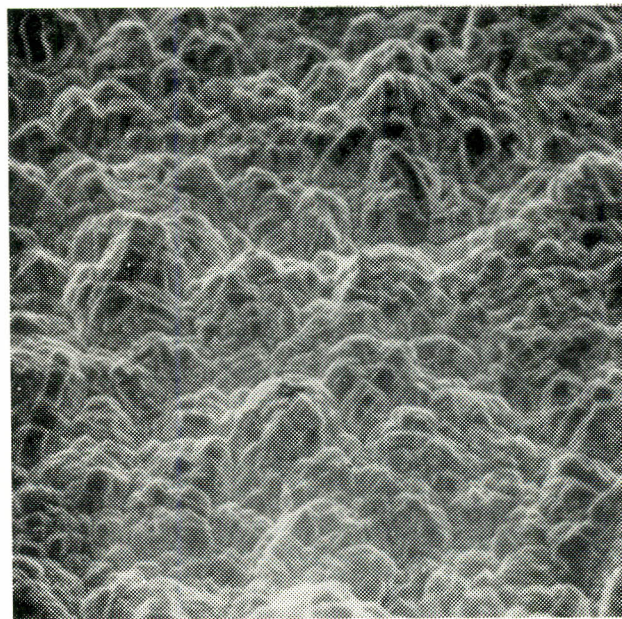


Fig. 3. SEM of lead dioxide electrode polarised to +2.2V in 1M H_2SO_4 , magnification 3,000, 45° .

trode following periods of polarisation at several potentials; typical micrographs are shown in Figs. 2 and 3. It can clearly be seen that when the PbO_2 is polarised at potentials beyond the inflection that a change in the form of the deposit does occur and a more regular beta-polymorph results. Lead dioxide obtained by any process whatsoever is always deficient in oxygen content in PbO_2 . It was evident from experiments with these electrodes that the prepolarisation results in a more stable, reproducible electrode. The current-potential curves thus obtained were without any inflection and could be retraced on the same electrode.

Experimental

The electronic equipment and cell assembly used has been mentioned elsewhere[15]. All the solutions were prepared in triple distilled water from chemicals of Analar Grade (B.D.H), but chromium(III) acetate (B.D.H.) laboratory reagent was used without further purification. In some electrodeposition experiments a copper gauze (2 cm²) in place of platinum gauze (1 cm²) was used as secondary electrode. The anolyte during deposition was constantly purged with oxygen-free nitrogen. The potentials quoted in the paper correspond to the saturated calomel electrode (SCE) as reference. The current responses at different potentials were measured by a Cambridge Unipivot Multimeter and the charges passed during the deposition were recorded by an electronic integrator (identical to Hi-Tek Instruments integrator) developed in the Laboratory. The scanning electron micrographs were taken with the help of S-2A Stereoscan scanning electron microscope (Cambridge) after detaching the deposits from the electrode base and mounting them on a small circular metal table.

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