INVESTIGATION OF OXIDATION PROCESSES AT LEAD DIOXIDE ANODE

Mohammad Amjad

Chemistry Department, University of Engineering and Technology, Lahore

Abstract. The electrochemical behaviour of the lead dioxide anode for the oxidation of inorganic ions e.g., Cr^{+3} to Cr^{6+} and ClO^-_3 to ClO^-_4 and electrooxidations of organic compounds like simple alcohols and phenols in aqueous sulphuric acid has been investigated. Scanning electron micrographs of the surface of the anode were taken to establish surface changes. It is suggested that both chemical and electrochemical mechanisms occurred.

Introduction

The application of graphite and platinum anodes to electrochemical processes is well known. However, the recent researches on alternative inert anodes are mainly centred around the development of (i) platinum and other precious metals or their alloys coated over titanium; and (ii) coating of oxide or mixed oxides of certain metals on suitable substrates. The high cost of platinum has warranted several attempts to replace this metal by cheaper materials. A considerable amount of work has been carried out during the last two decades to obtain lead dioxide deposits in a suitable form to be used as anode in a wide variety of electrochemical oxidations, for example, the production of perchlorates [1] in addition to the electrooxidation of aromatic and unsaturated hydrocarbons, amines, phenols and amides. Applications that have reached large scale developments are the oxidations of quinoline [2], isobutanol [3] and phenol [4]. The potentiostatic growth of lead dioxide and the activity of deposits obtained from various Pb(II)-containing electrolytes has been reported already [5,7]. In this paper the application of thick deposits of lead dioxide electrodeposited on vitreous carbon from lead nitrate solution to electrochemical oxidations of inorganic ions e.g. Cr^{3+} to Cr^{6+} and ClO_3^- to ClO_4^- apart from the anodic oxidations of simple aliphatic alcohols and phenols has been discussed.

Results and Discussion

With the exception of phenols, the oxidation of all species studied occurred in a potential region where some oxygen is evolved and hence some current is observed in the absence of the substrate. Generally this current is not very significant and has been subtracted where appropriate prior to the presentation of current potential curves. It is of course possible that the presence of substrate affects the current due to oxygen but this was not investigated.

Oxidation of Inorganic Ions

Oxidation of Cr^{3+} to Cr^{6+}: The electrolytic oxidation of trivalent chromic cation to hexavalent dichromate anion which is used as a regenerable oxidant, in the manufacture of anthraquinone

and related compounds from polycyclic aromatic hydrocarbons is a reaction of utmost importance [6,8].

Log I–E curves for the oxidation of Cr^{3+} to Cr^{6+} on a lead dioxide electorde in 1M sulphuric acid are shown in Fig. 1. It can be seen that in the narrow concentration range 0.1–1.0M there appears to be a first order dependence of the current on concentration of Cr^{3+}. Linear regions above +1.62V with Tafel slopes values 120 ± 5mV were also observed. In these experiments the chromium was introduced as chromium(III) acetate and since acetate ion is knwon to oxidise on this electrode material a log I–E curve was recorded for 3M acetate ion in sulphuric acid; no significant current was observed in the potential region below +1.70V.

It was considered worthwhile to check this result employing chromic sulphate as the electroactive material. Insufficient variation of the concentration of chromic sulphate was possible to obtain a reliable concentration dependence. A scanning electron micrograph, taken at the end of the complete polarisation curve showed no appreciable change of the surface of the lead dioxide during the experiment.
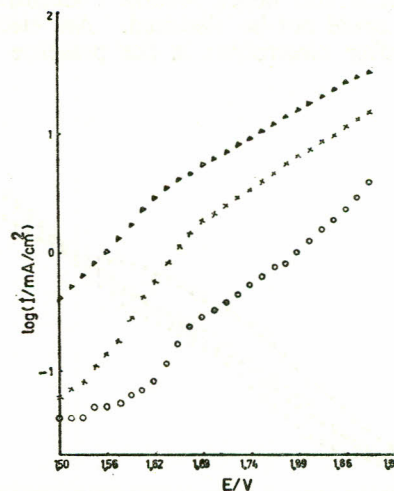
A preparative experiment was carried out with the

Fig. 1. Log I-E curves obtained after the subtraction of background current on lead dioxide in 1M sulphuric acid for (1) 0.1M (2) 0.5M and (3) 1.0 molar concentration of Cr^{3+} containing solutions.

former. A vitreous carbon rod, area 2.0 cm² was covered with a layer of lead dioxide by deposition in lead nitrate solution (charge100 C/cm²) and this lead dioxide electrode was employed as an anode in a divided cell. The cathode was platinum and the electrolysis was carried out at +1.85V vs. SCE. The solution was 1.0M chromic acetate +1M sulphuric acid. The electrolysis was terminated after the passage of 1186 coulombs and the current yield of dichromate was determined spectrophotometrically as 70% which could be improved. Earlier workers [9] have reported the optimum yield to be 75%.

Oxidation of ClO$_3^-$ to ClO$_4^-$: Steady state log I–E curves were recorded for a series of concentrations of chlorate ion in sulphuric acid, and perchlorate solutions also. Over the concentration range (1–5M at potentials after +2.0V there was a zero order dependence of the current on concentration as shown in Fig. 2. Furthermore, the current due to oxygen could not readily be subtracted since in some potential regions the current in the presence of chlorate was less than in its absence. Hence it appears that perchlorate formation must occur at potentials where in the absence of substrate oxygen is evolved and that adsorption of chlorate must occur as part of its oxidation mechanism. Similar results have been inferred by other workers [10,11].

A scanning electron micrograph recorded after these experiments indicated that the anode was badly corroded during the oxidation of chlorates in the presence of perchlorate media.

Oxidation of Simple Aliphatic Alcohols

Steady state log I–E curves were recorded for a series of simple aliphatic alcohols in 1M sulphuric acid. Typical are the curves for n-butanol shown in Fig. 3. Similar curves for isopropanol were obtained. The Tafel slopes were 130±5 mV. To obtain such curves very high concentrations of alcohols were essential and hence reliable concentration dependences could not be deduced. An electron micrograph after electrolysis in the presence of these alcohols indicated no change in the surface at the end of the polarisation of the electrode to potentials in the oxygen evolution region.

A preparative scale oxidation of n-butanol using a lead dioxide-covered vitreous carbon rod (100 coulomb/cm²) was carried out at +1.8V. Butyric acid (current yield 40%) was the only product observed.

Oxidation of Phenols

Steadystate log I–E curves for 0.5M phenol in 0.5 and 5M sulphuric acid at a lead dioxide-covered vitreous carbon anode were well-formed with Tafel slope values of 65±5 mV. At high potentials the surface was always blocked with a polymeric film which caused a large decrease in current, the film dissolved at high potentials and oxygen evolution was observed.

The dependence of the current on pH was studied further and a series of slow potential sweeps were carried out for 0.5M phenol in sulphuric acid of various concentrations. Two typical curves are shown in Fig. 4. The data was used to construct the Tafel plots as in Fig. 5 and it can be seen that I–E curves shift by approximately 250 mV per pH unit. This suggests that four protons are involved in the rate-determining step. Similar curves were obtained for p-aminophenol although severe deformations resulted from tarring of the electrode. It should be noted that the potential for oxidation of phenol and p-aminophenol is close to that for formation of lead dioxide in these solutions and hence it is possible that for these experiments the rate-determining step is a chemical reaction between lead dioxide and the phenol. The data for cresol is also compatible with such a mechanism [12]. Further evidence for such a proposal was sought by scanning electron micrograph after running the polarisation curves for p-aminophenol. There was clear evidence for the presence of lead sulphate on the surface and hence for this chemical mechanism.
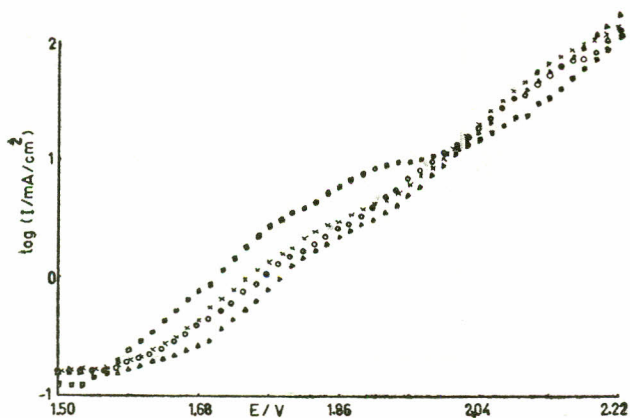

Fig. 2. Log I–E curves for lead dioxide anode in 1M NaClO$_4$ containing 1–5M NaClO$_3$, (□) 1M, (x) 3M, (o) 4M and (△) 5M.
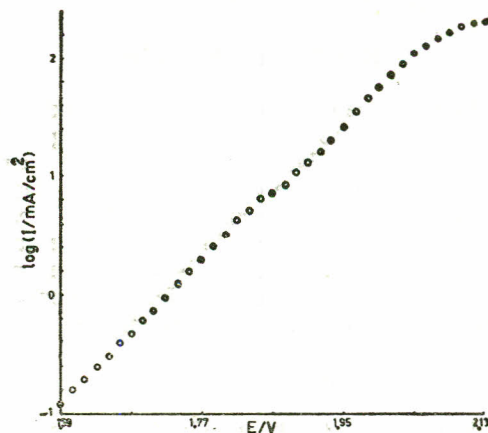

Fig. 3. Log I–E curves for 0.8M n-butanol after subtracting background current in 1M sulphuric acid on lead dioxide anode.

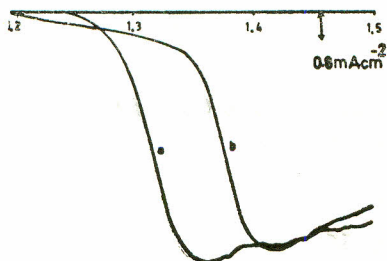Fig. 4. Linear potential sweep $0 \cdot 001$ V/sec at lead dioxide on carbon (a) in $0 \cdot 5$M phenol$+1 \cdot 5$M sulphuric acid and (b) in $0 \cdot 5$M phenol $+$ 2M sulphuric acid.
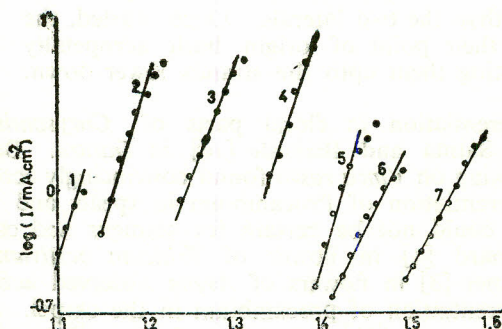
Fig. 5. Log I–E plots constructed from the curves obtained at $0 \cdot 001$ V/sec on lead dioxide in $0 \cdot 5$M phenol$+0 \cdot 05$M, 1M, $1 \cdot 5$M, 2, 3, 4 and 5M H_2SO_4 (from 1-7).

Experimental

Instruments used here have already been mentioned elsewhere [5,7]. Other experimental details have been given in the relevant portions. The electrolyses of butanol was undertaken in a two-compartment cell containing the working and secondary electrodes in the same compartment. The purity of the extracted product was checked by NMR.

Conclusion

It has been confirmed that oxidation of a range of substrates. e.g., Cr^{3+}, ClO_3^-, alcohols and phenols, does occur at a PbO_2 electrode. It is also clear that the electrode reactions are commonly slow and occur by a diversity of reaction mechanisms. The problems of obtaining reproducible electrodes, the concurrent oxygen evolution and the need to use very high concentrations of substrates limit the conclusions which may be drawn concerning the mechanisms of the individual reactions. Certainly the evidence available would suggest that both chemical and electrochemical mechanisms do occur.

References

1. A.T. Kuhn and P.M. Wright, *Industrial Electrochemical Processes* (Elsevier, Amsterdam 1971), p. 525.
2. V.G. Khomyakov, N.G. Bakhchisaraits'yan, M. Ya Fioshin, S.S. Kruglihov and L.I. Kazakova, Tr. Mosk. Khim-Technol. Inst., **32**, 249 (1961).
3. N.G. Bakhchisaraits'yan, M. Ya. Fioshin, E.A. Dzhafarov and M.A. Khrizolitova, Zr. Prikl. Khim., **35**, 1843 (1962).
4. A.I. Gladysheva and V.I. Lauronchuk., Uch. Zap. Tseut. Issled. Inst. Olovyan Prom., **1**, 68 (1966).
5. M. Amjad and D. Pletcher, Pakistan J. Sci. Res., **28**, (1976). (accepted for publication).
6. N.L. Weinberg, *Techniques of Chemistry* (Wiley-Interscience, 1974), Vol. V, p. 235.
7. M. Amjad, Pakistan J. Sci. Ind. Res., **21**, 43 (1978).
8. R. Clarke, A. Kuhn and E. Okoh, Chem. in Britain, **11**, 59 (1975).
9. E. Blasiak, L. Piszczek and W. Baranek, Prez. Chem. (Pol) **46**, (8), 447 (1967).
10. O. deNora, P. Gallone, C. Traini and G. Meneghini, J. Electrochem. Soc., **116**, 146. (1969)
11. M.P. Grotheer and E.H. Cook, Electrochem. Technol., **6**, 221 (1968).
12. A. Nilsson, A. Ronlan and V.D. Parker, J. Chem. Soc., Part I, 2337 (1973).