

ELECTROCHEMICAL BEHAVIOUR OF CERIUM OXIDE INCORPORATED LEAD DIOXIDE ELECTRODES ELECTRODEPOSITED FROM Ce^{+3} CONTAINING Pb^{++} ELECTROLYTES

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ABSTRACT: A moderate layer of PbO_2 onto stainless steel from nitric acid solutions in the presence and absence of Ce^{+3} and Ce^{+4} ions has been electrodeposited. The properties like stability and the ability to support anodic oxidations of organic molecules have been investigated. The activity of these anodes depends on the preparation and pre-treatment of the electrode. The investigations suggest that the stability and activity of the lead dioxide anode is influenced by the presence of Ce^{+3} / Ce^{+4} ions in the lead dioxide electrodeposits.

Keywords: Lead dioxide-Cerium oxide anodes on stainless steel, electro-catalytic activity.

INTRODUCTION

Lead dioxide is favoured as an anode material for electrochemical oxidation processes. In addition to this interest in understanding the activity of the lead dioxide anodes remains the subject of recent research papers (Amjad and Joya, 2003; Amjad and Aziz, 2009). Several recipes for the electrochemical electro-deposition of stable PbO_2 coatings have also been reported (Mohd. and Pletcher, 2005).

Some current technological developments in electrochemical power sources are creating fresh interest in fundamental properties of solid oxide electrodes. Lead dioxide electrode is favoured as an anode material of choice for the electrochemical oxidation processes and industrial electro-synthesis and effluents degradations possessing properties like low electrical resistivity, chemical stability at high oxygen evolution potentials and being relatively cheaper than noble metals as competitors.

The activity of different lead alloy anodes for electrochemical oxidation processes has also been investigated. Pb-Sb (Monachov and Pavlov, 1994), Pb-As (Pavlov and Rogatehev, 1986), Pb-Sn (Pavlov *et al.*, 1989) and Pb-Ag (Pavlov and Monachov, 2000) alloy or electrodeposited lead dioxide from baths containing Pb^{++} ions in the presence of co-ions like Ag^+ , Cu^{++} , Bi^{+++} , As^{+++} (Amjad and Joya, 2003.) anodes show some enhanced activities for the electro-oxidation processes involving organic species.

The activity of lead dioxide electrode and its anodic behaviour in sulphuric acid aqueous electrolytes in the presence of alcohols has also been investigated and it has been suggested that a surface oxide species is involved in the oxidation at lead dioxide (Amjad and Tajammal, 2000).

The main objective of this research work is to investigate the electrochemical oxidation by incorporated

alloying elements in moderate to thick, stable PbO_2 anode electro-deposits on suitable base materials prepared in acidic media and to define the conditions leading to the satisfactory performance since the precise procedures employed for the manufacture of commercial anodes are mostly un-known. New methods to produce electrocatalytic Lead (IV) dioxide coatings on titanium and stainless steel have been pursued from time to time (Cifuentes *et al.*, 1998 and Song *et al.*, 2007). In one of the latest study electrochemical behaviour of electrodeposited lead dioxide-manganese dioxide composite anodes on mild stainless steel has been investigated (Amjad and Almas, 2008).

MATERIALS AND METHODS

Following chemicals were used for the research work:

Lead nitrate	A.R.	(Merck)
Cerium Nitrate	A.R.	(Merck)
Sulfuric acid	G.R.	(Merck)
<i>n</i> -butanol	A.R.	(Merck)

All the electrolyte solutions were prepared in double-distilled water.

All experimental work was conducted at laboratory temperature, $20^\circ\text{C} \pm 1^\circ\text{C}$.

The oxidation processes of *n*-butanol in H_2SO_4 were carried out in a single compartment Pyrex-glass beaker.

Working electrodes: A mild stainless steel exposed surface area 1.4 cm^2 was used as a base substrate for the electro-deposition of lead dioxide and cerium-oxide films anodically.

Counter electrodes: A lead strip exposed area $\sim 3\text{ cm}^2$ was used as counter electrodes. The counter electrode

was cleaned, as per need, by dipping in 50% nitric acid followed by thorough washing with distilled water.

Potentiostat: For required potential supply, a modified digital 2-electrode potentiostat was used.

Multimeter: The current-potential dependence responses were monitored by TES 2201 Multimeter (Taiwan) or DM 6011 Lutron digital Multimeter (China).

The steady state techniques were employed for current-potential dependences to investigate the process at the respective electrode.

The data was plotted in the form of $E - \ln I$ curves from which the relevant informative inferences about the behaviour and activities of relevant anodes were made.

RESULTS AND DISCUSSION

Electrodeposits of PbO_2 and $PbO_2 + Ce_2O_3$ on Stainless Steel: Potential – Current responses for the electrodeposition of Lead dioxide on stainless steel with and without incorporation of Cerium oxide from Lead nitrate 10 mM and Lead nitrate 10 mM containing Cerium nitrate 1 mM and 0.1 mM electrolytes are shown in Figure 1 and the corresponding E vs. $\ln I$ are plotted in Figure 2. indicating the nucleation and growth of lead dioxide and its composites with increasing potential of the working electrode. These plots are quite conventional for lead dioxide electrodeposits.

Effect of additives on redox processes: Electrochemical investigations on pure lead dioxide and cerium containing lead dioxide anodes in 1 Molar sulphuric acid electrolytes give the polarization curves as shown by Figures 3 and 4. These indicate distinctly the surface changes at the electrodes, the cerium ion addition effects with stability of the anode alongwith oxygen evolution in different regions. It has been observed from the E vs $\ln I$ curves under steady state conditions that the activity of pure lead dioxide and cerium containing lead dioxide anodes in sulphuric acid electrolytes is different. The activity of lead dioxide is increased with increasing the concentration of cerium ions in the PbO_2 deposits but due to enhanced passivity of the base electrode the activity of the deposit increases. The Standard Oxidation Potential E° for Ce^{+3}/Ce^{+4} taken as +1.4 to +1.6V, the composite electro-deposit on stainless steel base was polarized away from this potential to investigate the behaviour of the anode for the study of the redox processes on it in aqueous sulphuric acid and also for the oxygen evolution reactions.

Cerium oxide- Lead dioxide electrodes electrodeposited from $10^{-2}M Pb(NO_3)_2 + 10^{-2}M Ce(NO_3)_3$ and $10^{-1}M Pb(NO_3)_2 + 10^{-3}M Ce(NO_3)_3$ electrolytes, the electrodeposits appeared to be reasonably stable over the polarization limits investigated.

On the basis of above observation and result, it can be suggested that not only the activity, nucleation and the growth rate of PbO_2 on stainless steel is enhanced with the presence of cerium in the PbO_2 deposits but also the electrode has obtained good catalytic activity for the oxidation of simple alcohol molecules.

The electro-oxidation processes of 0.5M *n*-butanol was conducted in sulphuric acid electrolytes at Lead dioxide – Cerium oxide electrodes.

From steady-state $E - \ln i$ curve as shown in Figures 5 and 6, it has been observed that the electro-oxidation of alcohol starts in the same potential region where some oxygen evolution current is observed but variant trends in the rates with the concentration variations of alcohol with an ultimate zero order concentration dependence at potential -2.3V and beyond have been noticed.

However, by keeping the incorporated Cerium ion contents low in PbO_2 matrix, the concentration dependence of the alcohol for its oxidation becomes pronounced.

Electro-oxidation of *n*-butanol in sulphuric acid electrolytes at Lead dioxide – Cerium oxide electrodes: The anodic behaviour and activity of pure lead dioxide and cerium containing lead dioxide electrodes for the electro-oxidation of *n*-butanol in 1 M H_2SO_4 with different alcohol concentrations have been carried out.

The electrode was polarized anodically by increasing potential in steps, i.e. the usual $E - I$ curves and $E - \ln i$ curves were recorded. It is observed that the oxidation of alcohol starts at potential -1.6V, i.e. at a potential where discharge of water molecules is not possible and the electrode is free of adsorbed oxygen. From the polarization curve as in figure 1, it is also shown that the rate of oxidation of alcohol in sulphuric acid electrolytes at $PbO_2 - CeO_2$ electrode increases with increasing potential.

After this potential it was noted that some-times the current oscillated in potentials between -2.3V to -2.6V. This is apparently connected with a change in the surface of the anode and there is a simultaneous evolution of oxygen obviously indicating a change in the mechanism where in place of discharge of alcohol molecules being the slowest step, the oxygen evolution becomes the rate determining. After potential 2.6V, the curve suddenly starts rising again. At this potential the simultaneous evolution of oxygen bubbles can be seen though the oxidation of alcohol still goes on.

The shape of the polarization curve for the electro-oxidation of alcohol, *n*-butanol at $PbO_2 - CeO_2$ electrode in sulphuric acid electrolytes is governed by the state of the electrode surface. On active electrodes, however, the polarization curve for the oxidation of alcohols shows only one drop in the current due to the appearance of adsorbed oxygen.

The oxidation of alcohols occurred in a potential region where some oxygen is evolved and hence some current is observed in the absence of substrate. Generally this current is not very significant.

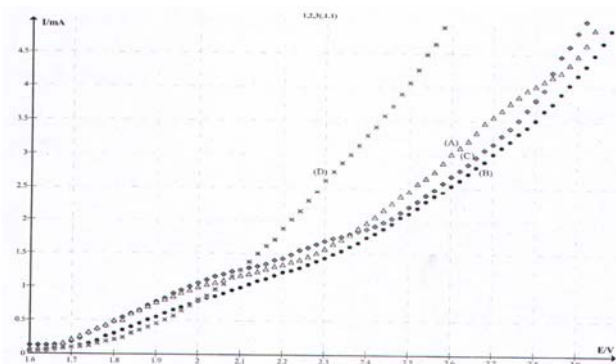


Figure: 1

- (A). S/ 10mM $\text{Pb}(\text{NO}_3)_2$
 (B). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
 (C). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
 (D). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$

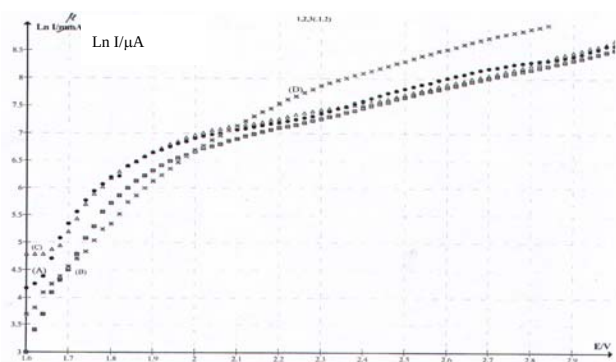


Figure: 2

- (A). S/ 10mM $\text{Pb}(\text{NO}_3)_2$
 (B). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
 (C). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
 (D). S/ 10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$

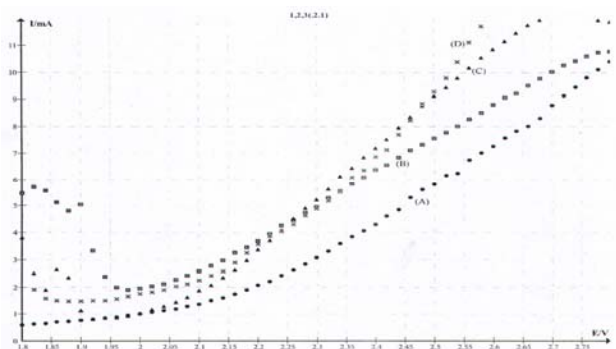


Figure: 3

- (A). S/10mM $\text{Pb}(\text{NO}_3)_2$ /1M H_2SO_4
 (B). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4
 (C). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4
 (D). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$ /1M H_2SO_4

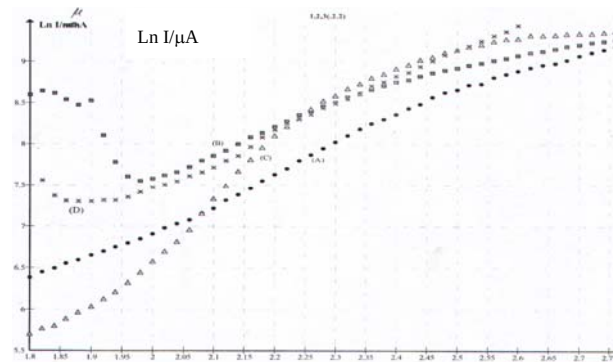


Figure: 4

- (A). S/10mM $\text{Pb}(\text{NO}_3)_2$ /1M H_2SO_4
 (B). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4
 (C). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4
 (D). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$ /1M H_2SO_4

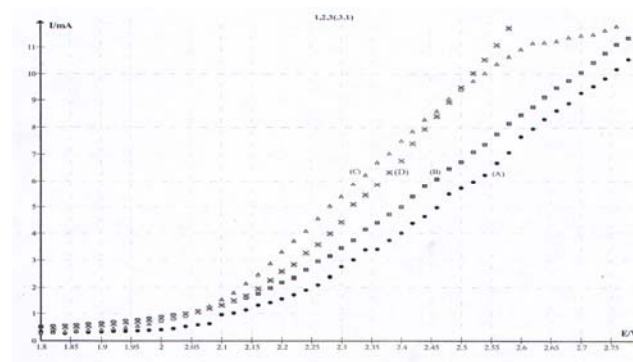


Figure: 5

- (A). S/10mM $\text{Pb}(\text{NO}_3)_2$ /1M H_2SO_4 + 0.5M n-Butanol
 (B). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4 + 0.5M n-Butanol
 (C). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4 + 0.5M n-Butanol
 (D). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$ /1M H_2SO_4 + 0.5M n-Butanol

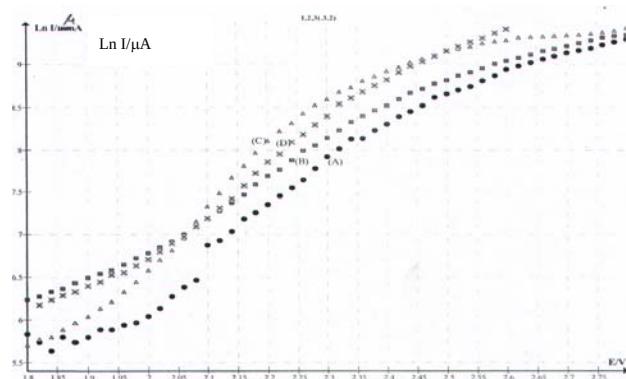


Figure: 6

- (A). S/10mM $\text{Pb}(\text{NO}_3)_2$ /1M H_2SO_4 + 0.5M n-Butanol
 (B). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4 + 0.5M n-Butanol
 (C). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 0.1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /1M H_2SO_4 + 0.5M n-Butanol
 (D). S/10mM $\text{Pb}(\text{NO}_3)_2$ + 1mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 1mM $\text{Al}(\text{NO}_3)_3$ /1M H_2SO_4 + 0.5M n-Butanol

Conclusion: The behaviour, stability and activity of pure lead dioxide and cerium containing lead dioxide electrodes in sulphuric acid electrolytes with and without the presence of simple alcohol, *n*-butanol, have been investigated. The electrode reactions are slower at PbO₂ than those on metal anodes and do occur by a diversity of mechanisms depending on the potential employed for the electro-oxidation. There is convincing evidence that the kinetic and the activity of the lead dioxide anodes are influenced by the cerium additives in PbO₂ matrix in the potential region before the oxygen evolution.

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