

## ELECTRODEPOSITION OF LEAD DIOXIDE AND ITS APPLICATIONS

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After reviewing the earlier attempts to prepare lead dioxide electrodes, the successful development of suitable graphite substrate lead dioxide (GSLD) anode by electrodeposition of lead dioxide on graphite from lead nitrate-copper nitrate bath using rotation for cylindrical electrodes and to and fro motion for the plate electrodes, is described. Further developments in this field include the use of surfactant and ultrasonics during the electrodeposition of lead dioxide for obtaining smooth and adherent deposit free from pinholes.

The application of GSLD anode in the preparation of electro-inorganic chemicals like chlorates, perchlorates, bromates, iodates, periodates and certain other organic electrochemicals is also reported in this paper, with the emphasis on the successful working of a proto-type commercial cell (5000Amp) for the production of chlorates and perchlorates.

This paper briefly deals with the electrolytic preparation of lead dioxide powder from salts of lead as well as from lead monoxide.

A brief report on the studies on the preparation of lead-lead dioxide bielectrodes needed for cathodic protection in sea water is also included in this paper.

**Keywords :** Electrodeposition; Graphite Substrate Lead Dioxide (GSLD); Ultrasonics; Electro-Inorganic Chemicals; Bielectrodes

### INTRODUCTION

THE formation of oxides by the anodic oxidation of solutions of the salts of the metals is a group of reactions of considerable interest and the electrodeposition of lead dioxide by the anodic oxidation of plumbous salts is one of the examples of these reactions. The anodic deposition of lead dioxide is a familiar process and was known as early as 1829 when Fischer (1829) observed that crystalline scales of lead dioxide could be formed on the anode by electrolysis of a soluble lead salt.

The quest for the development of insoluble anodes either as a substitute for costlier anodes or to increase the life of anodes in electrochemical industries has grown very much in recent years. A survey of literature shows a continuous interest in the preparation of lead dioxide anodes beginning in 1934. In the last 25 years, interest in the use of lead dioxide as anode in the place of platinum for the preparation of certain inorganic and organic electrochemicals has been very much in evidence as seen by the considerable amount of work (Narasimham & Udupa, 1976) that has been carried out to obtain lead dioxide deposits in a form suitable for use as anode. The main requirements for an oxide anode are :

- i. The possibility of forming ions of different valencies to provide for high electrical conductivity.
- ii. A high anodic potential at evolution of oxygen.
- iii. Absence of rectifying contacts at the boundary of oxide-metal current lead.
- iv. Chemically inert.

#### PREPARATION OF GRAPHITE SUBSTRATE LEAD DIOXIDE (GSLD) ANODE

Lead dioxide satisfies the above major requirements. In the early works, the preparation of lead dioxide electrodes involved certain disadvantages. In the process developed by Japanese workers (Sugino, 1950; and Sugino & Shibasaki, 1948) massive lead dioxide electrodes were prepared and number of methods of making good electrical contact on lead dioxide had to be devised. Later developments (Griggery *et al.*, 1958; and Schumacher *et al.*, 1958) included in the use of costlier substrates like tantalum.

The successful electrodeposition of lead dioxide from lead nitrate-copper nitrate bath on graphite substrate carried out simultaneously by the authors (Udupa & Narasimham, 1958, 1961; and Narasimham *et al.*, 1961*a, b*) in India and Gibson (Gibson, 1960 & 1965) in U.S.A. obviates the difficulties experienced by earlier workers. While Gibson (1965) used a non-ionic surface active agent in the bath, Udupa and Narasimham (1958 & 1961) employed rotation for the cylindrical rods and oscillatory (to and fro) motion for the plates during deposition to inhibit gas bubbles from sticking to the surface, thereby avoiding pinholes and pitting in the coating. The electrodes thus developed have the following advantages :

- i. A thin coating of lead dioxide on graphite is adequate for use as anode.
- ii. The graphite provides mechanical strength for the brittle deposit.
- iii. Electrical contact to lead dioxide is conveniently made on graphite.
- iv. Preparation of such anodes for large scale operation does not present undue difficulty.

Cell assembly for lead dioxide deposition differed with the size and shape of the anodes required to be coated. The electrolyte contained 275–3000/litre lead nitrate and 25–30g/litre copper nitrate, with an initial *pH* between 3 and 4. The addition of copper nitrate is to prevent the deposition of dendritic growth of lead on the cathode as copper, being more electropositive than lead, deposits preferentially on the cathode. During electrolysis the *pH* became acidic due to the production of nitric acid and was maintained at 1 to 2 by adjusting the flow rate of the electrolyte. The acid produced was neutralised outside the cell by the addition of lead carbonate or lead monoxide and copper carbonate. Deposition was carried out at current densities of 3 to 5Amp/dm<sup>2</sup> and at a temperature of 60–65 °C. It is most important to have precleaning operations for the graphite anode prior to deposition, which consist in electrolyzing a 10 per cent (w/v) sodium hydroxide solution with the graphite as anode for 30min, dipping the anode in 10 per cent (w/v) nitric acid for

10min, and finally washing it thoroughly with distilled water. Table I gives some of the rods and plates of GSLD prepared.

TABLE I  
GSLD rods and plates

Rods			Plates			
Diameter (cm)	Length (cm)	No. of specimen	Length (cm)	Width (cm)	Thickness (cm)	No. of specimen
5	30	60	30	15	1.25	148
7.5	30	65	30	15	2.5	86
7.5	60	100	90	18	3.0	48
20	75	8				

These have been used in 200, 800 and 5000Amp cells for the production of chlorates and perchlorates and 500Amp cells for the production of bromates and periodates. Even if lead dioxide peels off without any attack on the graphite surface, it can be deposited again on the same graphite. Some of the GSLD anodes given in Table I include such once or twice redeposited electrodes. Calculations for optimizing the size of the anode with respect to weight and number of graphite rods needed for different diameters show that either 7.5 or 10cm diameter GSLD rods are preferable (Udupa *et al.* 1978). Fig. 1 shows GSLD plates and rods of different sizes.

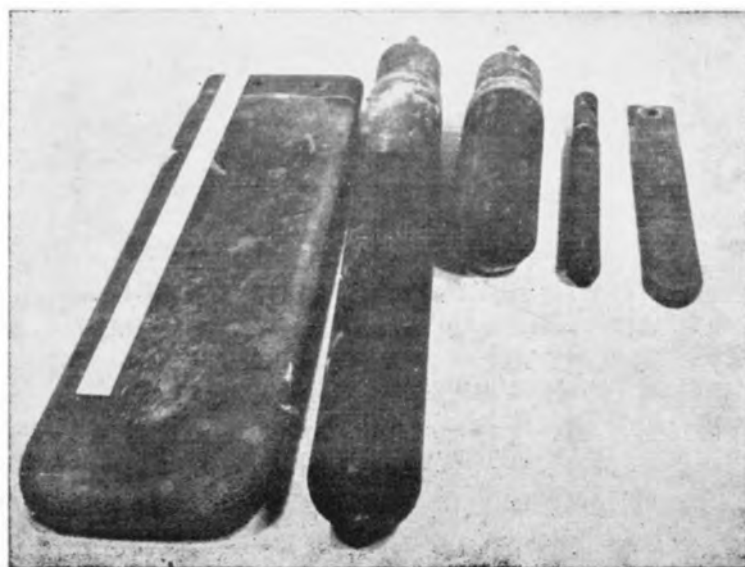


FIG. 1. Graphite substrate lead dioxide plates and rods of different sizes.

## INFLUENCE OF SURFACTANT AND ULTRASONICS DURING THE ELECTRODEPOSITION OF LEAD DIOXIDE

(a) *Effect of Quaternary Ammonium Surfactants*

In order to obtain deposits free from pinholes or pores, different techniques such as rotation of the anode for rods (Udupa & Narasimham, 1958 & 1961) the oscillation of the anode for the plates (loc. cit.) and fluidized bed technique (Sampath *et al.*, 1966; and Le Goff *et al.*, 1969) were employed and the operating conditions established. Several means of avoiding pinholes by the addition of both ionic and non-ionic surface active agents have been described (Gnanasekaran *et al.*, 1976).

In the course of measuring the stress in electrodeposited lead dioxide, the authors found the addition of cetyl trimethyl ammonium bromide (CTAB) not only lowered the stress but also facilitated in obtaining a pore free deposit on stationary graphite (Gnanasekharan *et al.*, 1970). The addition of 0.1g/litre of the surfactant decreases the surface tension of the electrolyte from about 75 dynes per cm to about 30 dynes per cm at  $60 \pm 2$  °C. This lowering of interfacial tension facilitates the easy release of the gas bubbles from the anode surface. It has been found (Gnanasekaran *et al.*, 1976) that the addition of quaternary ammonium surfactants (CTAB, tetradecyl and dodecyl trimethyl ammonium bromides) not only gives a smooth and adherent deposit free from pinholes under stationary condition but also permits the use of higher current densities during deposition. The beneficial effect of the cationic surface active agents like CTAB on the anodic deposition of lead dioxide may be due to the adsorption of the surfactant.

(b) *Influence of Ultrasonics*

For the first time, the influence of an ultrasonic field on the deposition of lead dioxide on to a graphite substrate from an aqueous solution of lead nitrate and copper nitrate has been investigated (Narasimham *et al.*, 1976) using an ultrasonic equipment (45kHz and 0-400W). In general, the deposits were smooth, adherent and free from pinholes at anode current densities up to 10Amp/dm<sup>2</sup>.

## APPLICATIONS OF GSLD ANODE

(a) *Chlorates*

Using GSLD anode (7.5dia × 60cm long) two numbers of 200Amp and 800Amp cells (Udupa *et al.*, 1971a, b, c) were set up and operated for 12 months to 24 months for the production of sodium and potassium chlorates. Based on the above results, one 5000Amp cell (Fig. 2) which is a prototype commercial cell for the production of chlorates has been operated (Narasimham *et al.*, 1976) using GSLD anode at an anode current density of 15-17Amp/dm<sup>2</sup> and a temperature of 50-60 °C.

An electrolytic process for the preparation of sodium chlorate liquor of high concentration (630-660g/l NaClO<sub>3</sub> with 5-10g/l NaCl) suitable for the *in situ* production of chlorine dioxide for textile or paper industries, was developed by employing the GSLD anode (Thiagarajan *et al.*, 1971).

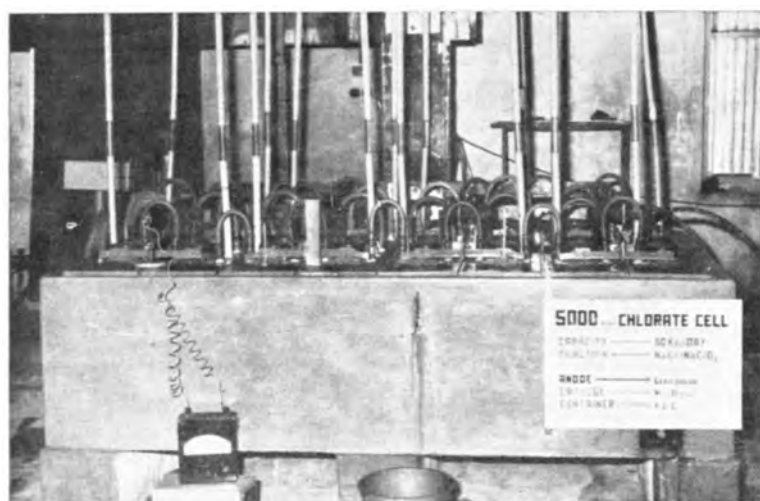


FIG. 2. Photograph of the 5000Amp chlorate cell.

Potassium chlorate, though normally produced by direct electrolytic oxidation of potassium chloride, was also produced by another process (Udupa *et al.*, 1968) which consisted of the oxidation of sodium chloride to sodium chlorate using a mixed electrolyte consisting of sodium chloride, sodium chlorate and potassium chlorate in the cell and by double decomposition of the converted sodium chlorate with solid potassium chloride at boiling temperature. The novelty of the process is in the working out of the suitable range of compositions of feed and effluent liquor. The operating conditions of the 5000Amp cell for the production of potassium chlorate by both the processes are given in Table II.

TABLE II  
*Operating conditions of the 5000Amp cell for the production of potassium chlorate*

	Indirect Process (Narasimham <i>et al.</i> , 1976; & 1968)	Direct Process (Narasimham <i>et al.</i> , 1976)
Cell	R. C. C.	R. C. C.
Volume of the cell(l)	810	810
Anode	GSLD	GSLD
Cathode	Mild Steel	Mild Steel
Cell feed g/l	220-240 NaCl 210-240 NaClO <sub>3</sub>	220-240 KCl 40-50 KClO <sub>3</sub>
Cell effluent g/l	110-120 NaCl 430-460 NaClO <sub>3</sub>	200-220 KCl 75-80 KClO <sub>3</sub>
Addition agent g/l	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -2	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -2
Anode current density (Amp/dm <sup>2</sup> )	15-17	15-17
Cathode current density (Amp/dm <sup>2</sup> )	8	8
Temperature (°C)	45-50	48-65
Current efficiency (per cent)	75-80	70-75
Energy consumption kWh/kg of KClO <sub>3</sub>	7.0-7.5	7.0-8.0

The advantages of GSLD anode in chlorate cells are as follows :

- i. longer life for graphite anode
- ii. clarity of effluent; and
- iii. employment of higher current density which in turn helps in using a smaller cell with less initial investment on graphite.

The processes for the production of sodium chlorate and potassium chlorate using GSLD anode have been released to one and four parties respectively.

(b) *Perchlorates*

Sodium perchlorate, which is conventionally produced from sodium chlorate using platinum anode, has been prepared using GSLD anode and thereby replacing the costly platinum anode. On the basis of results obtained on laboratory scale (Narasimham *et al.*, 1961), two cells of 75Amp and one cell of 400Amp were operated for the production of perchlorate using the GSLD anode (Narasimham & Udupa, 1976) at the anode current density of 15–25Amp/dm<sup>2</sup>, temperature of 40–45 °C and pH between 6 and 7. The current efficiency was 70–75 per cent with an energy consumption of 3–3.3 kWh (D. C)/kg of sodium perchlorate. It was found that the thickness of the deposit had a definite effect on the life of the anode and experiments showed that a thickness of 3 to 5mm would be needed in the preparation of perchlorates (Udupa *et al.*, 1969).

However, it has been found by Nagalingam *et al.* (1969) that GSLD anode could be used for preparing sodium perchlorate directly from sodium chloride in one cell without recourse to process in between to isolate chlorate. The results (Udupa *et al.*, 1971) obtained on 75Amp and 400Amp cells, indicated that the GSLD anode could be used for more than 450 days of continuous electrolysis in this process. A typical prototype commercial cell of 5000Amp (Fig. 3) was designed

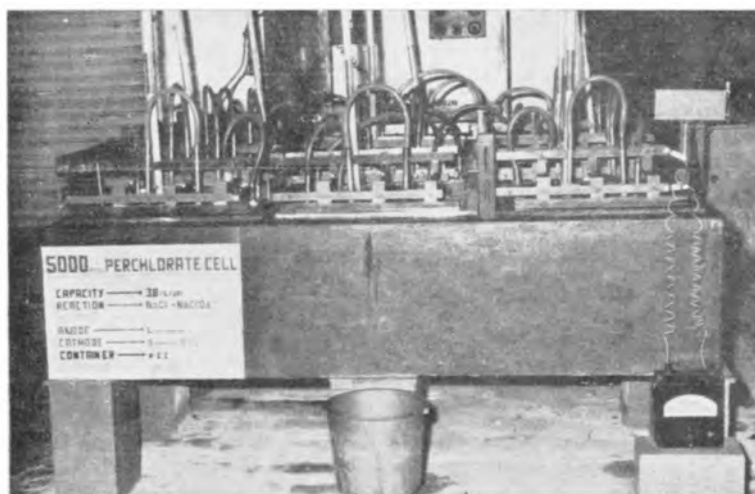


FIG. 3. Photograph of the 5000Amp perchlorate cell.

and operated (Udupa *et al.*, 1978) continuously for about 9 months at the optimum conditions, which are shown in Table III. Fig. 4 shows the variation in concentration of NaCl, NaClO<sub>3</sub> and NaClO<sub>4</sub> in the cell liquor with duration of electrolysis.

TABLE III

*Operating conditions of 5000 Amp cell for the production of NaClO<sub>4</sub> from NaCl*

Volume of electrolyte	:	700 l and 180 l for make-up
Concentration of NaCl (g/l)	:	285-300
Current (Amp)	:	5000
Anode current density (Amp/dm <sup>2</sup> )	:	18.5
Cathode current density (Amp/dm <sup>2</sup> )	:	15
Cell Voltage (V)	:	4.2-5.0
Temperature (°C)	:	45-50
pH	:	6.2-6.8
Final concentration of NaClO <sub>4</sub> (g/l)	:	650-700
Current efficiency (per cent)	:	55-62
Energy consumption (kWh/kg NaClO <sub>4</sub> )	:	12.8-14.5

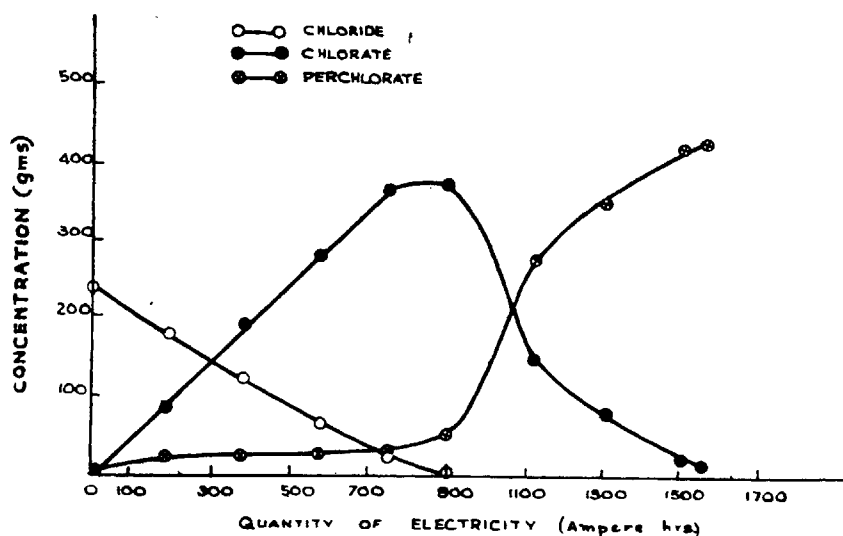


FIG. 4. Variation of the concentrations of chloride, chlorate and perchlorate of sodium with quantity of electricity.

The novelty of this process is the oxidation of chloride to perchlorate in the same cell without alteration of operating conditions or recourse to intermediate processing. In contemplating the direct oxidation of sodium chloride to sodium perchlorate, none of the commonly used anodes viz., graphite, magnetite, DSA or TSIA or platinum can be successfully employed as a single anode material and GSLD is the natural and economic choice at present.

Sodium perchlorate solution obtained by both the above methods and having less than 10g/l sodium chlorate was used for double decomposition with either potassium chloride or ammonium chloride to give potassium perchlorate or ammonium perchlorate respectively and the products conformed to the required specifications (Udupa *et al.*, 1978). These processes were released to three parties and all of them are in commercial production.

### (c) Bromates, Iodates and Periodates

Based on the resultant conditions of laboratory experiments, one 75Amp cell was run with a GSLD anode for the production of sodium and potassium bromates (Sundararajan *et al.*, 1962) employing anode current density of 16–20Amp/dm<sup>2</sup> and temperature of 55–60 °C. One 500Amp cell (Pushpavanam *et al.*, unpublished) was recently designed and operated under the same operating conditions. A current efficiency of 90–95 per cent was obtained with an energy consumption of 4–4.5 kWh/kg of bromate.

The electrochemical preparation of sodium iodate from iodine was studied using GSLD anode and a nylon cloth-wrapped stainless steel cathode (Venkatachalapathy *et al.*, 1967). Based on the laboratory scale experiments, one 500Amp cell was run and a current efficiency of 73–77 per cent was obtained corresponding to an energy consumption of 3.0–3.4 kWh/kg of sodium iodate.

In the oxidation of iodic acid to periodic acid (Ramaswamy *et al.*, 1963), a GSLD anode with rough surface or prepolarised surface of lead dioxide gave better efficiency.

All the above three processes have been released for commercial exploitation.

## LEAD DIOXIDE POWDER

Lead dioxide powder is used as an oxidising agent in dyestuffs, explosives etc and as a curing agent for liquid polysulphide polymers. While the preparation of lead dioxide powder involves both chemical and electrochemical methods, a systematic electrochemical study was lacking for the direct preparation of lead dioxide powder of desired size from the salts of lead. However, the electrolytic preparation of lead dioxide powder from lead monoxide suspended in sodium chloride was worked out by the authors earlier (Gnanasekaran *et al.*, 1970).

Later, in the work carried out by the authors (Narasimham *et al.*, 1972) for the electrolytic preparation of lead dioxide powder from salts of lead, analogy was taken from the cathodic reaction for metal powders. The most important advantage of the powder prepared by electrochemical method over most of the other kinds is its extraordinary purity. Variables permitting close control of chemical and physical properties of the oxide powder include :

- i. Composition of the electrolyte (concentration of metal ion and pH);
- ii. temperature of the electrolyte;
- iii. rate of circulation of electrolyte;



- iv. current density;
- v. size and type of anode and cathode and their distance from each other;
- vi. removal of deposit on the anode; and
- vii. addition agent.

In general, high current density, high acidity, and low metal ion concentration favour the formation of powder. Addition agent is added to get fine powder.

A low concentration of lead nitrate (75g/l) containing 0.5 to 1g/l sodium lauryl sulphate was electrolysed in a divided cell (porous pot as diaphragm) having GSLD anode and stainless steel cathode at an anode current density of 30Amp/dm<sup>2</sup> and temperature of 30-40 °C to obtain lead dioxide powder of >92 per cent lead dioxide content and practically passing through 100 mesh sieve (Narasimham *et al.*, 1972). X-ray analysis confirmed that the powder was  $\beta$ -lead dioxide.

On the basis of results obtained on the laboratory scale, one 100Amp cell was designed and operated (Lalitha *et al.*, unpublished) and the results confirmed the earlier data.

#### LEAD-LEAD DIOXIDE BIELECTRODES

Anodic polarization of lead and lead alloys at high current densities in chloride solution results in the formation of a thick, voluminous, porous deposit of lead chloride. When a platinum microelectrode was introduced into lead or lead alloys, Shreir (1961) found that lead dioxide was formed on the surface of lead in chloride medium during anodic polarisation at high current densities.

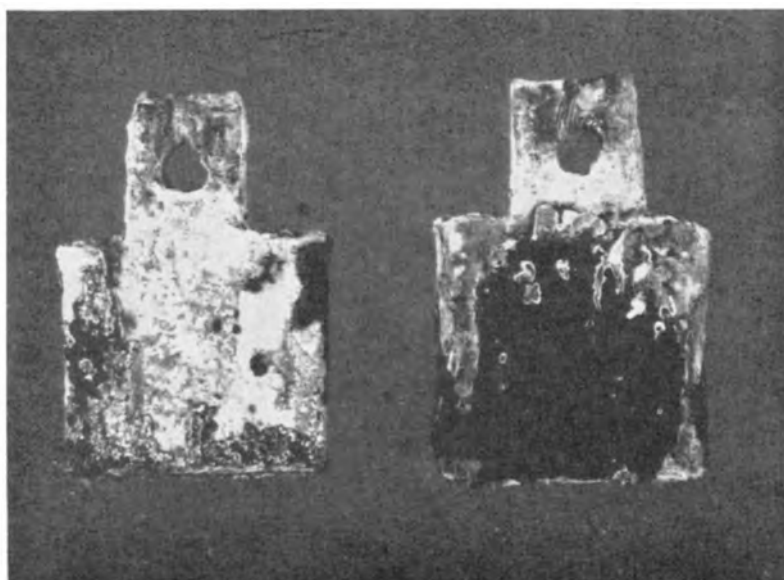


FIG. 5. Photograph of the surface of lead in 3 per cent sodium chloride solution : (a) without microelectrode; and (b) with lead dioxide microelectrode.

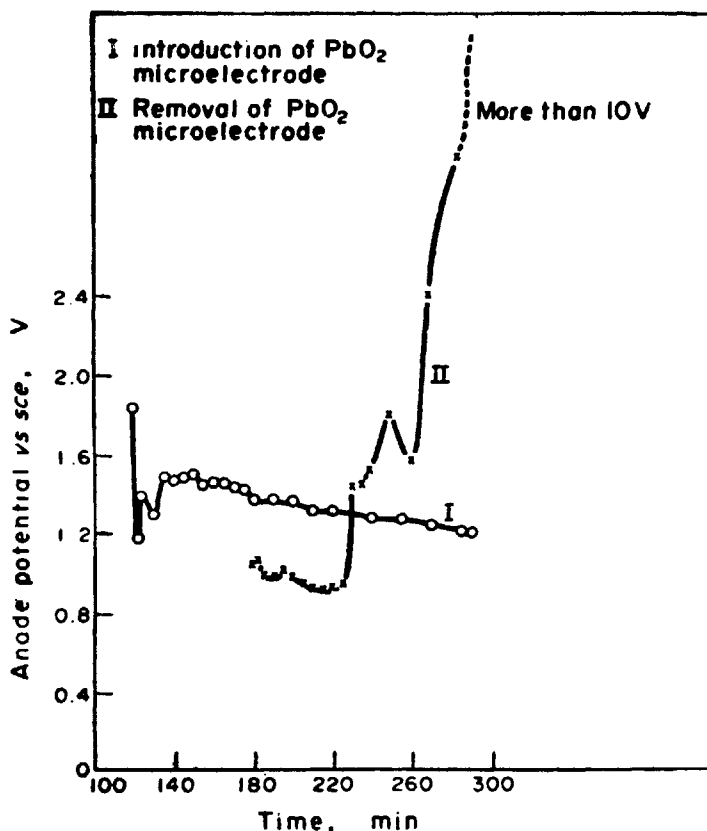


FIG. 6. Effect of insertion and removal of microelectrode on the potential-time behaviour of lead.

As a replacement for costly platinum, lead dioxide pieces which fell during the electrodeposition of lead dioxide were shaped into small cylindrical microelectrodes, inserted into the lead or lead alloys and anodically polarized in chloride solution (Narasimham & Udupa, 1977). In this case lead dioxide is also formed on the surface of the lead or lead alloy (Fig. 5). It has been found that the formation of lead dioxide on the lead-lead dioxide bielectrode is good in 3 per cent sodium chloride solution at an anode current density of  $3 \text{ Amp/dm}^2$  and at room temperature. The effect of withdrawal and insertion of lead dioxide microelectrode clearly indicated that the microelectrode was necessary to obtain the film of lead dioxide on lead surface in chloride medium (Fig. 6). Studies on the weight change during anodic polarization of lead and lead alloys embedded with lead dioxide microelectrode in chloride solution and in synthetic sea water showed that lead-silver (1 per cent) alloy was by far the best anode from the point of view of the formation of a compact and crackfree deposit of lead dioxide on the surface (Figs. 7 and 8). The lead-lead dioxide bielectrode is suitable as an anode for cathodic protection with impressed current in sea water.

(a)



FIG. 7.

(b)



FIG. 7.

(c)



FIG. 7. Photograph of Pb-PbO<sub>2</sub> bielectrode after anodic polarization in 3 per cent sodium chloride solution : (a) Lead (b) Lead-antimony (6 per cent) (c) Lead-silver (1 per cent).

(a)



FIG. 8.

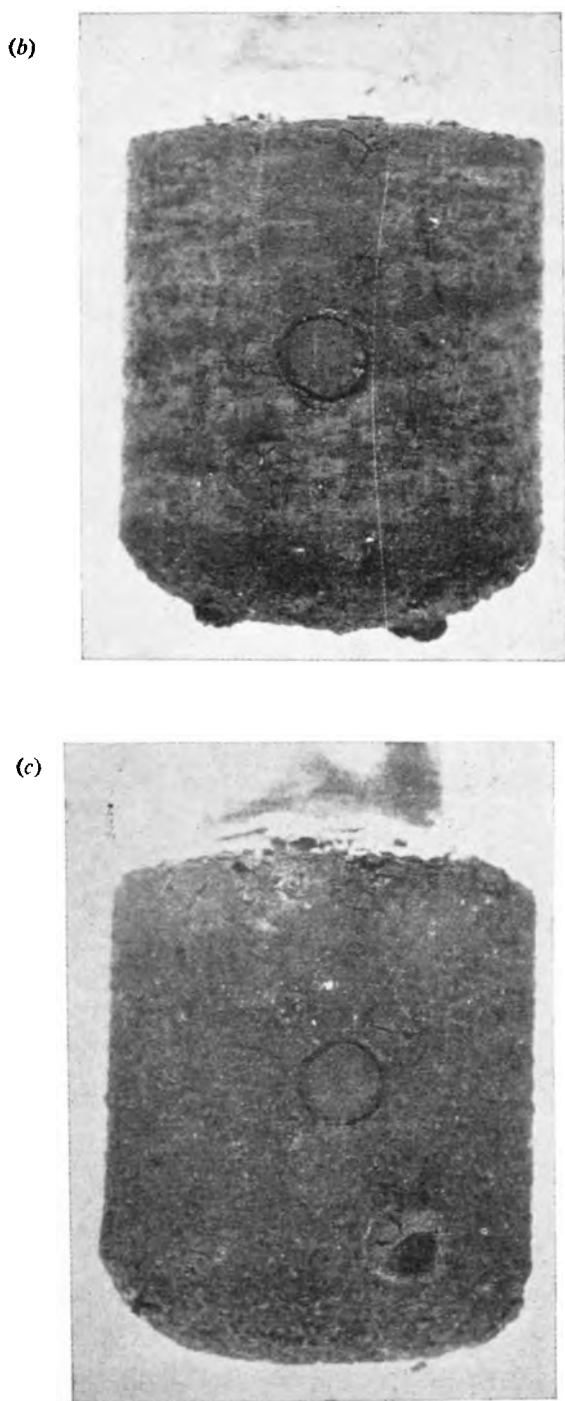


FIG. 8. Photograph of Pb-PbO<sub>2</sub> bielelectrode after anodic polarization in synthetic sea water :  
(a) Lead (b) Lead-antimony (6 per cent) (c) Lead-silver (1 per cent).

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### Discussion

R. NARAYAN (*Department of Chemistry, Indian Institute of Technology, Madras*): What associated fundamental research has been done in this connection—particularly on the role of CTAB and sodium lauryl sulphate, adsorption and their influence on the anode and cathodic processes?

K. C. NARASIMHAM: As regards fundamental research on electrodeposition of lead dioxide is concerned, kinetic studies on the electrodeposition of lead dioxide have been carried out using both galvanostatic and potentiodynamic techniques from lead nitrate bath. Coming to the role of CTAB and sodium lauryl sulphate, it is very interesting to note that sodium lauryl sulphate which is an anionic surfactant is preferred only in the case of the production of lead dioxide powder to obtain the required fineness, whereas the same is not suitable in the electrodeposition of lead dioxide. On the other hand CTAB and other quaternary ammonium type cationic surfactants are very well suited for getting a smooth deposit of lead dioxide even under stationary conditions. Though CTAB is a cationic surfactant it has influence not only on the electrodeposition of lead dioxide which is normally unexpected, but also on the electrodeposition of copper at the cathode which is as expected. However, it is again interesting to note that with CTAB addition, the metal that is deposited on the cathode is not pure copper but an alloy of copper and lead, whereas in a bath without CTAB pure copper alone is deposited on the cathode. Experiments were also carried out for estimating the amount of CTAB consumed both anodically and cathodically during each deposition and it has been found that the amount of consumption is greater at the cathode than at the anode. Some preliminary work had also been carried out on the electrodeposition of lead dioxide from a bath containing CTAB as addition agent using potentiodynamic technique. Some of these have already been published.

HIRA LAL (*Department of Chemistry, Indian Institute of Technology, Bombay*): I do not seem to have understood the role of copper nitrate in  $PbO_2$  deposition, and of sodium fluoride in perchlorate production. Would you please comment on these aspects?

K. C. NARASIMHAM: As already mentioned copper nitrate is added to lead nitrate solution to the extent of 25 to 30g/l to avoid deposition of lead on the cathode and which when allowed to deposit, would deposit in a dendritic form and thereby causing shorting during electrolysis. Copper being more electropositive will preferentially deposit in a smooth sheet form on the cathode instead of lead and incidentally the concentration in lead is conserved only for the lead dioxide deposition.

Sodium fluoride is added to the sodium chlorate solution for the production of perchlorate when lead dioxide is used as anode. This addition increases the current efficiency of the process. It has been reported that sodium fluoride adsorbs on the anode and increases the potential of lead dioxide anode almost to the value obtained with that of platinum anode.

S. GURUSWAMY (*Central Electrochemical Research Institute, Karaikudi*): I would like information on the role of additives like surfactants in modifying electrochemical reactions to the practical needs of industry?

K. C. NARASIMHAM: It may be very difficult to answer in a generalised way the role of surfactant in modifying electrochemical reactions. Depending on the reaction, a particular surfactant may be useful. The function of the surfactant may also be differing in different reactions.

G. A. TEDORADZE (*Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow*):

1. Is Current efficiency about 60 per cent enough to economic working of electrolyser ? 2. Have you cooled the electrolyser ? The lead dioxide has relatively high electrical resistance.

K. C. NARASIMHAM : 1. The current efficiency of 60 per cent is obtained only when chloride is directly oxidised to perchlorate in the same cell and this efficiency is economical enough. In the two stage electrolysis, namely the oxidation of chloride to chlorate and chlorate and perchlorate, the efficiencies are of the order of 70 to 80 per cent in each. 2. Yes. The electrolyser was cooled by passing cold water to maintain the temperature. As regards electrical resistance of lead dioxide, it has been reported that it is better than even graphite, except for the fact that it can also act as a semiconductor.

L. I. KRISHTALIK (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*):

Remarks: I am happy to note that lot of work has been done on the electrodeposition of lead dioxide and its applications for the production of chlorates, perchlorates and other inorganic electrochemicals. Similar type of work is also being carried out in Russia and we do hope that would be in a position to exchange more information between our two countries in future in this important work.