

ACTIVATED LEAD ELECTRODE FOR ELECTROWINNING OF METALS

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Rising costs of power forecast for the future emphasis the need for the effective energy saving measures in the electrolytic extraction of metals. Introduction of newer anode materials in the electrolytic cells avoid problems like high energy consumption and anode corrosion associated with the conventional lead anodes. A new type of catalytic anode, known as activated lead electrode, has been investigated for its possible application in the electrolytic recovery of metals from their aqueous solutions. The anode consists of a lead substrate and an electrocatalyst like IrO_2 supported on the titanium sponge particles. Voltage saving anodic stability, ability to tolerate the chloride impurity in the electrolyte and catalyst poisoning, associated with the new anode system, have been examined.

Keywords: Catalytic anode, electrowinning and lower cell voltage

INTRODUCTION

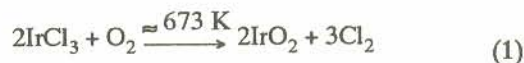
Lead and its alloys are customarily used as anodes in the electrowinning of metals like zinc, copper from the sulphate electrolytes. Oxygen evolution is the predominant anodic reaction which is having high overpotential on lead leading to higher cell voltage and increased rates of anode corrosion, contaminating the cathode metal.

The introduction of Dimensionally Stable Anodes (DSA) in chlor-alkali industries with significant energy saving led to attempts on the use of such anodes in other industrial electrolytic processes, especially in metal extraction processes. A marked reduction in oxygen overpotential is the primary advantage sought in the use of such catalytic anodes. Materials such as RuO_2 and IrO_2 are known to have good electrocatalytic properties for oxygen evolution [1]. Titanium substrate conventionally employed in dimensionally stable anode can conveniently be replaced by lead matrix [2,3].

A new type of catalytic anode, designated as Activated Lead Electrode (ALE) is investigated in this work. It consists of a lead substrate and titanium sponge particles activated with IrO_2 catalyst. Excellent corrosion resistance, lower working potential and ability to tolerate the chloride impurity present in the electrowinning circuit are its advantages.

Methods of preparation

Titanium sponge particles were etched in a boiling solution of hydrochloric acid and washed well with water. The activating solution was prepared by dissolving the chloride salt of iridium in iso-propylalcohol. The sponge particles were treated with the iridium chloride (IrCl_3) solution. The wet particles were dried and heated at 673K with a supply of air in an electrical muffle furnace. Iridium chloride was thermally decomposed to form iridium oxide, the required catalyst.



A minimum amount of catalyst was thus evenly distributed on a very large surface area, ensuring effective and economical use of the catalyst. Then the activated sponge particles were uniformly distributed over the surface of lead sheet and anchored using a hydraulic press. Table I lists the typical conditions of activation procedure

Energy saving

When metals like zinc, copper are electrowon from their acidic sulfate electrolytes, oxygen evolution occurs as the anode reaction



TABLE I: Typical conditions of activation

Thickness of lead substrate	1.5 mm
Size of titanium sponge particles	-30, +50 mesh
Amount of sponge particles	1 kg.m ⁻²
Activation temperature	673 K
Total duration of heat treatment	0.5 h
Catalyst loading as Ir	10 g.m ⁻²
Pressure applied during pressing	250 kg.cm ⁻²

This reaction on lead or its alloys is associated with higher polarisation leading to increase in cell voltage and hence higher energy consumption. Fig. 1 shows the anode potential-time curves for the lead and ALE. Oxygen evolution was found to occur relatively at less potential on ALE indicating the catalytic activity of the IrO₂ catalyst employed. Data on anode potential for lead and ALE used in zinc electrowinning are presented in Table II. Anode potential saving to the extent of 500 mV was achieved in the use of ALE. Anode potential is a major component of cell voltage and its saving would bring down the energy consumed in the electrowinning process.

Anodic stability

Corrosion of lead anodes under electrowinning conditions occur through the formation of Pb²⁺, PbSO₄ and PbO₂.

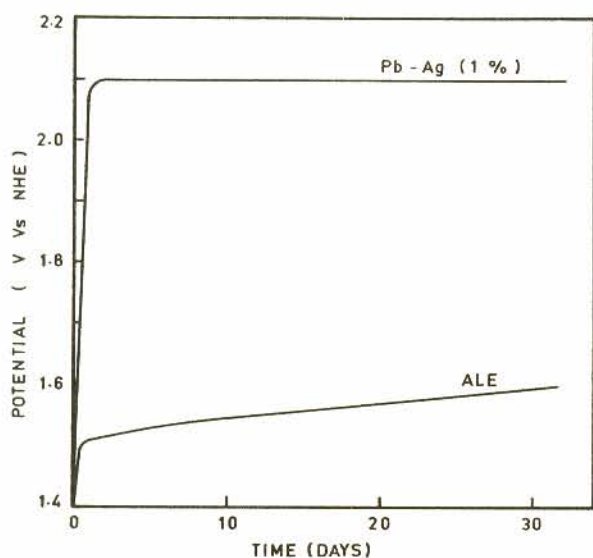
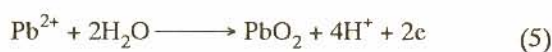
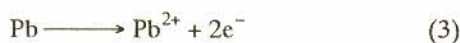
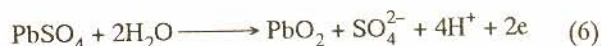
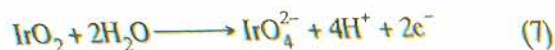


Fig. 1: Anode potential-time curve for lead and ALE.



These corrosion products are mainly responsible for the contamination of the cathode deposit by lead. This problem was largely overcome when ALE was employed as anodes. The IrO₂ catalyst is having better anodic stability and a very high anodic potential ($E_q = 2.057\text{V}$) is required for the dissolution of the active coating.



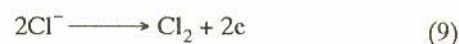
Stability, further, improves as the catalyst was spread over a very large surface area [4] provided by the titanium sponge particles, lowering the effective current density. Stability, in general, depends on the current density applied to the catalyst. Better stability of the catalyst employed would lead to increased service life of the anodes in the electrowinning of metals.

Influence of chloride

The impurities and additives present in the electrowinning electrolytes may impose further restrictions upon the selection of a suitable anode material. Plant scale operation in the electrowinning of metals like zinc prescribes a limit of about 50 mg l⁻¹ of chlorine in the electrolyte to keep the attack on lead anodes to the minimum. Higher levels of chloride aggravate the corrosion of lead anodes through the formation of PbCl₂.



This problem could be avoided by employing suitable catalytic anodes which promote the discharge of chloride ions to chlorine gas.



Catalysts like IrO₂ are known to have very good catalytic properties for chlorine evolution also [1]. Corrosion rates of the anodes due to chloride attack are shown in Table III. ALE was found to tolerate higher levels of chloride in the

TABLE II: Anode potential saving in zinc electrowinning

Current density A.m ⁻²	Anode potential (V vs NHE)		Saving in anode potential (V)
	Pb	ALE	
200	2.05	1.55	0.50
400	2.10	1.60	0.50
600	2.15	1.62	0.53

TABLE III: Anode corrosion in zinc electrolyte containing chloride

Chloride content g.l ⁻¹	Corrosion rate (g/Ah)		
	Pb	Pb-1% Ag	ALE
5	0.381	0.109	negligible
10	0.450	0.121	negligible
20	0.520	0.130	negligible

zinc electrolyte. These anodes, in this context, would be attractive for the extraction of metals, particularly from the secondary sources like ashes, drosses, scraps, etc., which are likely to contain higher amounts of chloride.

Problem area

Manganese, often present in the electrowinning electrolytes of zinc and cobalt, restricts the use of catalytic anodes like ALE. Table IV shows the rise in cell voltage for different amounts of manganese present in the electrolyte of zinc electrowinning for a period of 24 hours. Anodic deposition of MnO₂ on the anode surface blocked the active sites of the catalyst employed, leading to increased cell voltage.



Hence the advantage sought in terms of voltage-saving was partially lost in the poisoning of catalytic surface by manganese ions. However, measures like removal of the coated MnO₂, using suitable reducing agents, provide scope for the regeneration of the catalytic activity.

CONCLUSION

Activated Lead Electrode (ALE) comprising a lead substrate and titanium sponge particles activated with the IrO₂ catalyst, works at a reduced anode potential and permits a marked energy reduction and a longer anode life in the electrolytic extraction of metals. These anodes tolerate higher amount of chloride impurity in the electrolyte, avoiding anode corrosion and this tendency makes it more feasible to recover metals

TABLE IV: Influence of manganese concentration in the zinc electrolyte on cell voltage

Manganese concentration g.l ⁻¹	Cell voltage rise (mV)
0.5	50
1.0	70
5.0	300

electrolytically from the secondary sources which are often contaminated with chloride.

Presence of manganese in the electrolyte is a problem area identified, where the MnO₂ deposited, blocks the active sites, restricting the extent of energy saving. It necessitates the periodical cleaning of the anode surface to regenerate the catalytic activity.

Cost of the catalyst employed, its durability under oxygen evolution conditions and the extent of saving in the electrical power consumption are the major decisive factors in making this new anode system a commercial proposition.

Acknowledgements: The authors express their sincere thanks to the Director, Central Electrochemical Research Institute (CECRI), Karaikudi India, for his constant encouragement and keen interest in this work.

REFERENCES

1. S Trasatti and G Lodi, "Oxygen and Chloride Evolution at Conductive metallic Oxide Anodes", *Electrodes of Conductive Metallic Oxides, Part B*, Ed S Trasatti (Elsevier Scientific Publishing Company, Amsterdam (1981) 521
2. H B Beer, "Progress in Anodes for Metal Winning", *Extended Abstracts, Electrochemical Society Meeting*, 83(1) (1983) 874
3. H B Beer, "Anode with Lead Base and Method of Making Same", *U S Patent*, 4,425,217 (January 10, 1984)
4. J K Walker and J I Bishara, "Electrocatalytic Anode for Copper Electrowinning", *Anodes for Electrowinning*, Ed D J Robinson and S E James (Warrendale, PA:TMS, 1984) 79