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From the Editor's Desk

Anodes for Electrochemcial Processes (Part-I)

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Introduction

The anodes employed in electrochemical cells are made of metallic, non-metallic or semiconducting materials. The main properties which determine the suitability of an electrode for electrochemical industries are: i. Good electro-catalytic activity, ii. Good electrical conductivity, iii. Good mechanical and environmental stability.

In any electrolytic cell the total cell voltage is composed of the following components, i. Reversible anode and cathode potential, ii. Anode overvoltage, iii. Cathode overvoltage, iv. Ohmic drop between the anode and cathode and v. Ohmic drop in structural components.

As most of the electrochemical reactions occur at the electrode/electrolyte interfacial region, electro-catalytic activity of the electrode material for any particular reaction plays an important role in controlling the overpotential of the electrode. In recent years the evaluation has to take into account a number of variables involved such as, i. Electro-catalytic activity*, ii. Electrode life, iii. Operating conditions of the cell, iv. Initial and replacement costs and performance of the anode.

*Better electro-catalytic activity electrodes to bring down the energy consumption through low anode overpotential.

In recent years, the quest for the development of indestructible anodes either as a substitute for costlier anodes or to increase the life of the anodes in electrochemical industries, has grown very much and with the increasing interest in the scientific development of inert and insoluble anodes, a healthy competition is set up to carry out considerable amount of research both in the improvement of the existing anodes or in the development of new anodes. The complex nature of the evaluation problem stems from the number of variables involved such as electrode life, operating conditions or use cell and replacement costs.

Graphite and platinum are the best known anodes in electrochemical processes and less frequently anodes like magnetite, silicon carbide, lead and lead-silver or lead-antimony alloy are employed as insoluble anodes. But the recent researchers on the inert anode are largely centered round the development of lead dioxide anodes, platinum-coated titanium anodes. Possibilities of using platinum-clad electrodes and lead-platinum bi-electrodes are also drawing the attention of research workers. This editorial briefly presents the different type of anodes and their applications.

Types of Anodes

Platinum based electrodes: Platinum coated titanium anodes: J.B.Cotton was the first to report the important discovery that a thin layer of platinum applied to the surface of titanium would act as a non-consumable anodes. The protective surface film of titanium has peculiar properties. Even though the oxide layer of titanium is resistance to passage of current, it tends to have low resistance when a second metal makes contact with it. The titanium acts as a bulk carrier of current, while the platinum provides an escape path for the current to enter the solution. The platinum coating need not be impervious or continuous and the electrodes will carry high anodic current densities in many types of solutions. However due to the wear of platinum, this anode did not find extensive use in commercial cells. Platinum has been applied over titanium by the following methods, i. Cladding or alloying, ii. Welding or electro-sparking, iii. Vapour deposition, iv. Chemical or electrochemical deposition.

Coating of 10-20µ of platinum on titanium will be suitable for use as anode.

Platinum clad anodes: Possibilities of using platinum clad tantalum or titanium are also drawing attention of research workers. Platinum sheet may be bonded to tantalum or titanium by hot and cold rolling processes. This type of electrodes is used for producing perchlorates and persulphates.

Platinum-Iridium anodes: Platinum and iridium in the ratio (70:30) have been coated over titanium by thermal process and the same has been tried for the production of chlorates.

Metal Oxide Anodes

The advantages of these electrodes over other anodes are, i. Dimensional stability, ii. Longer life, iii. Ability to function effectively at higher current densities, iv. Purer products, v.

Lesser cell interruptions and vi. 10-15% power saving due to: Lower overvoltage, Lesser bubble effect resulting from higher free surface for the escape of gas, Higher electrical conductivity, Lower and constant cell voltage and Operation of lower inter electrode gap.

The main requirements for an oxide anode are: i. The possibility of forming ions of different valencies to ensure high conduction, ii. A low anodic potential at evolution of oxygen caused by holes being the principal current carriers and iii. The absence of retifying contacts at the boundary of oxide-metal current lead.

The discovery of Beer in later sixties that the performance of anodes made of thermally prepared noble metal oxides was better than those of noble metals provoked something of a technological revolution in the electrolytic industry. These oxides behave as catalysts and still a lot of work has to be done to understand the fundamentals of heterogeneous electro catalysts.

A lot of research work has been going on all over the world to develop an anode material that will be an economically and technically feasible substitute for conventional anode in electrochemical industries. Following are some of the anodes based on metal oxides, i. Cobalt oxide anode (Spinel type), ii. Palladium oxide anode, iii. Mixed oxides of precious metals like ruthenium, platinum, iridium, etc., coated over titanium, which is otherwise called Dimensionally Stable Anode (DSA), or Titanium Substrate Insoluble Anode (TSIA) or Permanent Metal Anode (PMA) or Oxide Coated Titanium Anode (OCTA).

The use of platinum as anode in the preparation of persalts is well known. The high cost of platinum has prompted several attempts to replace the same by a cheaper material. In the last three decades interest in the use of lead dioxide as anode in the place of platinum for the preparation of inorganic and organic chemicals has been very much in evidence as seen by the considerable amount of work that has been carried out to obtain lead dioxide deposits in a form suitable for use as anode.

Cobalt oxide anode, earlier it was prepared by coating of cobalt oxide over suitable substrate like platinum, graphite and titanium by anodic oxidation from a solution of soluble salts of cobalt. In recent years, the spinals (Co_3O_4, $NiCo_2O_4$ and $MnCo_2O_4$) are coated on carbon supports by evaporating the solutions of nitrates of the corresponding metals and then decomposing the mixture at 300-400°C. These type of electrodes are used in chlor-alkali and oxygen production by water electrolysis.

Palladium oxide coated anodes was prepared by coating the electrode surface with anodically produced palladium oxide. Such a coated electrodes can be prepared anodically on graphite, titanium, lead alloys, iron, nickel in a palladium salt solution. The coated electrodes are black in color and the electrode has very low chlorine over potential compared to platinum and lead dioxide. The electrodes are suitable in chlor-alkali industry.

Dimensionally stable anodes are basically a titanium skeleton covered with electrocatalytically active mixtures of oxides. These anodes consist of mainly ruthenium oxide deposited on titanium along with other metallic oxides like platinum, iridium, palladium, rodium and titanium. These types of electrodes are mainly used in chlor-alkali and for the production of chlorates.

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