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***From the Editor's Desk***

# Anodes for Electrochemcial Processes (Part-II)

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**Lead dioxide Anode**

Their preparation and their applications are started in the year 1934. Although lead dioxide could be deposited anodically from different baths, lead nitrate bath has been preferred for getting a smooth and adherent deposit. Different substrate materials were tried for deposition of lead dioxide but graphite and/or titanium has been chosen as a best substrate due to adherent deposit. In order to get a deposit of 2 to 5 mm thick and free form pin holes, different techniques like rotation of the anode, fluidizing an inert material with flow of the electrolyte, ultrasonic and addition of surfactants have all been employed. These types of electrodes are used in the preparation of chlorates and perchlorates. Particularly it is used for the preparation of perchlorates from chlorides. Because of the nearness of the oxygen overpotential of lead dioxide and platinum, the former can be used as substitute for the latter in the preparation of chlorates, perchlorates and also for other applications. Where graphite anodes are employed, a coating of lead dioxide can prolong the life of the same by preventing wasteful disintegration. Processes like periodates, chromic acid and manganic sulphate yield higher efficiency with lead dioxide than with platinum anode.

## Lead dioxide with lead-platinum bi-electrode

The insertion of small size of platinum into the surface of lead prior to oxidation results in the formation of an adherent coating of lead dioxide and this can be used for prolonged periods at high current densities. These types of bi-electrodes are inexpensive, robust and easily fabricated and can be used successfully for the cathodic protections of marine structures, electroplating and other electrolytic processes.

## Manganese Dioxide Electrodes

They are used in electrolytic recovery for zinc, lead, copper and iron in an undivided cell. Also used in water electrolysis for hydrogen production. A thin coating of manganese dioxide is deposited on titanium electrolytically from an aqueous solution containing sulfuric acid and manganese sulfate. These types of electrodes are also prepared by thermal decomposition using titanium as substrate. But the electrode prepared by thermal decomposition was less porous than the one prepared by electrochemical deposition.

## Perovskite Electrodes

They are called as Perovskite oxide electrodes. These oxides are family of oxides having a crystal structure similar to that of the mineral Perovskite ($CaTiO_3$). As many of them have been found to possess either metallic or semiconducting properties of relatively low resistivity and some of the oxides like $Na_xWO_3$, $SrTiO_3$, $SrFeO_3$, $CaFeO_3$, $LaNiO_3$, $LaTiO_3$ and $La_{1-x}Sr_xCoO_3$ have been studied extensively for their electrocatallytic and physicochemical properties. Perovskite oxides are usually prepared by thermal decomposition of an appropriate mixture of metal salts or by the solid state reaction of metallic oxides. Some of these oxide electrodes have been tried as anode in water electrolysis.

## Other Anodes

**Chilex anode:** In electrowinning of copper, lead anodes cannot be used if chloride is present in the electrolyte. At Chuquicamata, Chile, where it is necessary to remove cupric chloride dissolved from the ore, an anode of copper-silicon alloy, called the chilex anode, has been developed. It has been claimed that it had a longer life, but the power consumption is high because of greater resistance.

**Silicon carbide anode:** Not much work has been carried out in the development of this anode. But it was reported that the same could be used in the preparation of perchlorates.

**Non-noble metal insoluble anodes**: Certain non-metallic compounds (carbides, nitrides, borides) of group IV to VI transition metals have been reported to possess corrosion resistance and good electrical conductivity. General preparation of these electrodes involve i. by direct reaction of elements, ii. by direct reaction of metal oxide and carbon in a reducing atmosphere, iii. By vapor phase deposition. The following table gives bird's eye view of electrode preparation and their application.

**Table-1**
**Different type of electrodes with their preparation methods and applications**

| No | Anode | Method of preparation | Application |
|---|---|---|---|
| | | **I. Conventional anodes** | |
| 1 | Graphite | | For preparation of hypochlorite, chlorates, bromates, iodates, chlor alkali, etc., |
| 2 | Platimum | | For preparation of perchlorate, persulfate, perborate etc., |
| 3 | Magnetite | Electrochemical | For preparation of chlorates |
| 4 | Silicon carbide | | For preparation of perchlorate |
| 5 | Lead, Lead-silicon, Lead-antimony | | For preparation of periodates |
| 6 | Chilex | | In electrowinning of metals |
| | | **II. Precious metal coated anodes** | |
| 1 | Platinum coated titanium | Cladding or rolling<br>Welding or electro-sparking<br>Chemical plating<br>Electroplating | For preparation of hypochlorite, chlorates, perchlorate, persulfate, perborate etc., |
| 2 | Platinum clad | Hot and cold rolling processes | For preparation of perchlorate, persulfate, perborate etc., |
| 3 | Platinum-Iridium | Electroplating<br>Thermal deposition | For preparation of chlorates |
| | | **III. Metal oxide anodes** | |
| 1 | Cobalt oxide | Anodic oxidation<br>Thermal decomposition | For chlor alkali and water electrolysis |
| 2 | Palladium oxide | Anodic oxidation<br>Thermal decomposition | For chlor alkali |
| 3 | Dimensionally Stable Anode | Thermal decomposition | Chloralkali, hypochlorite, halates, electrodialysis, organic synthesis, cathodic protection, electrowinning of metals from chloride bath. |
| 4 | Lead dioxide | Electrodeposition from $Pb(NO_3)_2$ & $Cu(NO_3)_2$ bath | Hypochlorite, halates, perhalates, electrodialysis, ozone, quinines, Redox mediated processes from sulphat, sulphate bath, Generataionl of Cr(VI), cathodic protection (V). |
| 5 | Manganese dioxide | Thermal decomposition<br>Electrodeposition | In water electrolysis |
| 6 | Spinel (eg. $CO_3$ $O_4$, $NiCO_2$ $O_4$) | Thermal decomposition or anodic decomposition from soluble salts of cobalt & nickel | Water electrolysis, electrowinning of metals |
| 7 | Perovskite | Thermal decomposition, solid state reaction in metallic oxides | Water electrolysis |
| | | **IV. Non-noble metal insoluble anodes** | |
| 1 | Titanium nitride, Titanium carbide | Direct reaction of elements<br>Direct reaction of metal oxide in reducing atmosphere with corresponding gases<br>Vapor phase deposition | For sodium chloride electrolysis. |