



From the Editor's Desk

Cathodes for Electrochemical Processes Part-I

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Available online at: www.isca.in

In the large energy intensive electrolytic processes the cost of electric power is dominant factor in determining process economics. It is therefore, very important to reduce to a minimum the voltage drop for an electrolytic process. This leads to the use of electrodes having the lowest overpotential for the electrode materials.

In recent years increasing attention has been directed towards reducing the overpotential for the hydrogen evolution reaction, which is a common cathodic reaction in industrial electrolytic processes. Generally iron and steel possess lower hydrogen overpotential than many of the commonly studied metals. Hence efforts to decrease the hydrogen overpotential on steel have generally focused. In iron the increase in overpotential with time is due to the adsorption of impurities which may poison the electrode surface for the recombination of the hydrogen atoms. So efforts to decrease the hydrogen overpotential in steel have generally focused on improving the catalytic effect of the surface material or by alloy coating providing a larger effective surface area and alloying of metals.

The requirements of cathodes are low hydrogen overpotential, a good conductor, good electrocatalytic properties, high surface area, good corrosion resistant, minimum gas bubble formation, mechanically rigid, enhanced selectivity, availability at the low cost and health safety.

From the above requirements hydrogen overvoltage, conductivity and electrocatalytic properties are improved by alloy coating and alloying of two metals etc., but factors like electrodeposition of foreign metal contamination, oxidation and dissolution by current reversal shutdown, thickness of the coating, diffusion and adsorption of hydrogen determine the service life of the cathode.

Electrodeposition of foreign metal contaminants: The electrodeposition of foreign metal contamination may result in the reduction of catalytic activity and poisoning of cathode coatings. These things are effectively eliminated by using ultra pure electrolyte and by constructing the cathode chamber with corrosion resistance materials and also by the use of corrosion free pipelines for electrolyte pipe.

Oxidation and dissolution by current reversal shutdown: With the direction of current flow reversed from that of normal operation. This reversed current flow tend to result in the formation of hydroxides or oxides in the electrode which can render the electrodes inoperative and inactive.

Thickness of the coating: The coating must be physically strong and chemically stable in order to result erosion and damage.

Diffusion and adsorption of hydrogen: Cathodes of Fe, Ni, stainless steel and other metals will tend to absorb the evolved hydrogen in the electrocatalytic reaction and consequent decline in their catalytic activity. This will be eliminated by good cathode coatings which impede hydrogen adsorption and maintain high activity.

Cathodes for industrial applications

The cathodes employed in the various industrial electrochemical processes can be arranged in three groups. The first group will consists of electrodes whose hydrogen overpotential is very low (the exchange current density is very high). The second group will consist of electrodes which exhibit high hydrogen overpotential (the exchange current density is very low) and the third group of electrodes is those which have high exchange current density. The first group of electrodes is mostly used in chlor-alkali cells, water electrolysis, chlorate production and electro organic synthesis.

Chlor-alkali and alkaline water electrolysis cells

In chlor-alkali diaphragm cells and alkaline water electrolysis cells the main reaction is hydrogen evolution.

Initially, low carbon steel cathodes were used in chlor-alkali and alkaline water electrolysis due to its low cost, easy availability and low overpotential (about 300mV) at a current density of 200-300mA.cm⁻² at 80°C. Latter the Ni-Mo alloy coated cathode or Rany-Nickel alloy coated cathodes are used because of low hydrogen overpotential than former one. The cathodes with Rany-Nickel electro catalyst coatings have been

found to show increase in hydrogen overpotential with time, while Ni-Mo coated electrodes have been reported to be free from this disadvantage.

The electrocatalyst cobalt molybdate which is formed on a thin nickel sinter by a two stage process involving solid state reaction has been reported to be very stable in alkali (8N KOH) even at 90°C and low hydrogen overpotential in alkaline solution.

Porous nickel electrode with cobalt molybdate electrocatalyst coating has been suggested as a very efficient cathode for advanced alkaline water electrolyses cells.

For use in membrane cells for the production of chlorine-caustic soda, oxygen/air cathodes are being developed by various researchers in many advanced countries as the use of such cathodes can result in a substantial reduction of cell voltage leading to about 20-30% energy saving. The oxygen cathodes are based on the fuel cell cathodes.

Preparation of Nickel-Molybdenum alloy coated cathode

The substrate metals like mild steel, cast iron, nickel or stainless steel are galvanically coated with an alloy of nickel and molybdenum. The plating bath used is given bellow,

Nickel sulfate – 79.0 g/l

Nickel chloride – 24.0 g/l

Sodium molybdate – 4.0 g/l

Ammonium tartrate – 73.0 g/l

pH – 9.8

Current density – 4 S/dm²

Preparation of Raney-Nickel alloy coated cathode

These types of Raney-Nickel electrodes are producing by co-deposition of Raney nickel powder along with Ni plating bath. For the use in membrane cells for the production of chlorine-caustic soda, oxygen/air cathodes are used because of decrease in cell voltage and 20-30% energy saving.

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