

Cathodes for Electrochemical Processes Part-II

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For chlorate cells

In the conventional chlorate cells, the cathodes are copper, nickel, platinum, mild steel, low carbon steel or chromium plated steel. If mild steel or low carbon steel is used, dichromate is added to the electrolyte whose concentration can be in the range of 7-7 g/l, to overcome the cathodic reduction of hypochlorite and to a lesser extent chlorate. In recent years, titanium cathodes have been successfully tested and found not to exhibit a corrosion risk. Also attempts are being made by many researchers, to have mild steel coated with electrocatalysts exhibiting low hydrogen overpotential. The figure shows a typical magnesium chlorate production cell using Dimensionally Stable Anode (DSA) and stainless steel cathode. This technology was developed in CSIR-Central Electrochemical Research Institute, Karaikudi, Tamilnadu.



Figure-1

100A Magnesium Chlorate cell with Dimensionally Stable Anode (DSA) and stainless steel cathode

For perchlorate cells

The cathodes in most perchlorate cells are mild steel which is generally the material of construction of the cell when platinum is used as anode. The steel is protected by the chromates ion added to the electrolyte. The reduction of chlorate at the

cathode is prevented by the presence of the chlorate at the cathode is prevented by the presence of the chromates, which forms a protective film on the cathode. However, when lead dioxide is used as anode, the chromate addition has to be avoided and naturally mild steel cannot also be used as cathode. It has been found that stainless steel can be used as cathode, thereby avoiding the chromate addition.

Electro-organic synthesis

The cathode materials as already mentioned should have good electrochemical stability, high selectivity and electrocatalytic activity for the particular organic electrode reactions. The influence of hydrogen overpotential of a cathode on the electrocatalysis of any organic electrode reaction can be correlated in a simple way only when both the mechanism of hydrogen evolution and mechanism of the electroreduction process are same for all metals and at all values of electrode potential as the mechanism of hydrogen evolution. As the mechanism of hydrogen evolution is not the same for different metals, the nature of hydrogen overpotential has to be taken into account in addition to the value while selecting the cathode material for the electroreduction of the organic substances. The possible causes for overpotential of electroreduction reactions have to be understood for selecting the appropriate cathode material.

The adsorption of the organic at the electrode plays an important role though this has not been fully understood. There are not many general guidelines for production of its effect on organic electrode reactions. The electrocatalytic effect of the electrode material on the branching of an electrode reaction is more apparent at cathodes with low overvoltage, though it may also be observed at materials with high hydrogen overvoltage. The most commonly used cathode materials are lead, mercury, tin, copper, nickel, carbon, aluminium and platinum. In general lead or lead amalgam is preferred in many electroreduction reactions. However the problem of lead cathode is soft in nature and readily deformed during reaction. Lead has been used as cathode in the preparation of adiponitrile from acrylonitrile, reduction of i. glucose to sorbital, ii. acetone to pinacol and iii. phthalic acid to cyclohexadiene carboxylic acid. Tin electrodes have found application in the reduction of nitro compounds.

Steel and carbon cathodes have also found application in industrial electro-organic processes.

Cathodes for fuel cells

In all the four type of fuel cell systems viz., alkaline fuel cell, polymer electrolyte fuel cell, molten carbonate fuel cell and solid oxide fuel cell, the cathode is usually the oxygen/air cathode. In alkaline fuel cell and polymer electrolyte fuel cell system the desired oxygen reduction reaction is the one involving the four electrons, resulting OH^- or H_2O as the product. In molten carbonate fuel cell system the air (or oxygen) is usually mixed with some amount of CO_2 and fed to the cathode to have the regeneration of CO_3^{2-} as it is consumed in the anodic reaction. In the solid oxide fuel cell system the O^{2-} is regenerated, as the O^{2-} ions which are current carriers, take part in the anodic reaction with fuel viz., H_2 or CO .

The electrodes used in alkaline fuel are either Teflon bonded carbon electrodes with platinum or silver as electrocatalyst, sintered porous nickel electrodes with Raney silver as electrocatalyst or Teflon bonded silver doped with titanium, nickel and bismuth. Spinel such as NiCO_2O_4 and mixed oxide with Perovskite oxide structure have also been found to give satisfactory performance as electrocatalysts. In the case of polymer electrolyte fuel cell system Teflon bonded platinised carbon electrodes are used as oxygen/air cathode.

For molten carbonate fuel cell systems the oxygen electrode employs silver or lithiated nickel oxide. However, for solid oxide fuel cell systems the cathode materials are indium oxide doped SnO_2 . A few Perovskite oxides such as $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$, LaSrMnO_3 have been reported to promising cathode materials for solid oxide fuel cell systems.