



SUPERIOR ANODES

Precious metal containing mixed metal oxide (MMO) electrodes have revolutionized the electrochemical industries, especially electroplating and chlorine generation. MMO electrodes have also enabled the development of other electrochemical processes by improving production efficiency.

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Chlorine and sodium hydroxide are produced by the electrolysis of brine, one of the largest industrial electrolytic processes in the world. The importance of chlorine and sodium hydroxide to the processing industries cannot be overstated. Chlorine is used in the manufacture of polyvinyl chloride (PVC), now widely used in the construction industry, as well as a wide variety of other chlorinated polymers, solvents and specialty chemicals. Sodium hydroxide is used extensively in the pulp and paper industry, in the extraction of aluminum from bauxite, in the clean-in-place systems in the food, beverage and dairy industries and in the manufacture of specialty chemicals. Due to the price sensitivity in these industries, commercial viability is driven by the ability to purchase these chemicals at the lowest possible price. The major contributor to the production costs is the power consumption for the process, which is directly dependent upon the voltage of the operating cells. MMO electrodes (i) significantly reduced the anode overpotential and therefore the cell voltage, (ii) allowed improved cell designs to be introduced, reducing the inter-electrode gap to further lower the cell voltage and (iii) provided higher efficiencies for chlorine production. Hence, the replacement of graphite anodes by MMO electrodes resulted in a dramatic reduction in energy costs, leading to the economic manufacture of chlorine and caustic soda.

Development of these catalytic electrodes also led to experimentation in other important industrial processes, with particular focus upon replacing lead anodes in electroplating and electrowinning cells. In addition to the obvious environmental issues, lead electrodes, like graphite, continuously corrode. This results in the formation of sludge in the cells and higher cell voltages. The original MMO electrodes used in these oxygen evolving processes were based on ruthenium oxide and rapidly failed due to the instability of RuO₂ under these conditions. Stable coatings were developed by replacing RuO₂ with iridium oxide and today coatings based on iridium oxide are the dominant catalytic coatings used in electrolyses to form oxygen.

Ultimately many formulations of catalytic coatings have been developed to improve performance and lifetime of the electrodes. This has led to an ever increasing use of MMO electrodes in electrochemical processes.

This paper briefly explores the development of MMO electrodes and discusses how the electrodes work. The selection of a MMO electrode for particular applications is considered, including a comparison to the use of platinum and platinum/titanium electrodes. Brief accounts of the preparation and limitations of MMO electrodes are also provided.

The History of MMO Electrodes.

By the mid 1950s the commercial production of titanium was well advanced in the USSR, UK and USA, the principal market for the metal being the aerospace industry. The results of studies by J.B.Cotton (Central Research and Development, Metals Division, ICI, UK) indicated that titanium exhibited excellent corrosion and erosion resistance in sea water. The use of the metal as an inert electrode material was considered, particularly since titanium could be fabricated into a wide variety of shapes and sizes. However, when polarized anodically in aqueous electrolytes, the metal rapidly formed a passive film of titanium oxide. To effectively use the metal as an electrode it was necessary to develop a stable, conductive coating. To this end C.H.Angell, a coworker at the ICI laboratory, successfully electroplated an adherent coating of platinum on a titanium substrate and this electrode was quickly commercialized for cathodic protection systems.

The platinized titanium electrode appeared to offer an alternative anode structure to graphite for use in the commercial production of chlorine and sodium hydroxide. The Pt/Ti anode represented a dimensionally stable anode that would provide a fixed inter-electrode gap as well as eliminate the carbon sludge formed in the cells during operation. However, little enthusiasm for the anode was shown by the chlorine industry, which argued that both platinum and titanium were expensive and the latter metal was relatively scarce. In addition unexpectedly high rates of platinum corrosion in dilute brine solutions further limited acceptance of the Pt/Ti anode. It was also shown that the presence of organic compounds in the electrolyte, e.g., wetting agents and brighteners, shortened the lifetime of the anode, precluding use as an oxygen evolving electrode in electroplating.

In pursuing patent protection for the platinized titanium electrode ICI discovered that Henri Beer, an employee of Magneto Chemie in the Netherlands, had recently filed a patent describing a rhodium plated titanium electrode. An agreement was negotiated between the two companies to allow Henri Beer to pursue a variety of coating formulations, particularly to replace the graphite anode in chlorine cells. Data obtained in this program indicated that ruthenium oxide coatings were superior to the platinum or platinum/iridium electrodes that were already being used commercially, albeit on a limited scale. The chlorine industry and ICI were slow to change, forcing Henri Beer to join with DeNora (an Italian electrochemical company) to exploit the ruthenium oxide coatings. It was at this time that the first patent identifying MMO coatings was filed. This patent (British Patent 1,147,442: 1965) became known as the Beer 1 patent and is primarily directed to the co-deposition of oxides of ruthenium and titanium onto a titanium substrate. The coating is applied as a paint containing soluble compounds of the two metals and the paint is then thermally decomposed to form an adherent layer of mixed oxides. This $\text{RuO}_2\text{-TiO}_2$ coating on titanium was the first commercially successful MMO electrode.

It was later shown that the potentials at which chlorine and oxygen evolution occurred were dependent upon the concentration of ruthenium oxide in the coating. Hence, in 1967 a second patent (British Patent 1,195,871; 1967) was filed by Henri Beer, describing a coating containing a lower amount of ruthenium oxide, which became known as Beer 2. This second generation MMO electrode, costing less than the Beer 1 anode yet providing equivalent (if not better) performance, became the dominant coating used in commercial chlorine cells.

Since the 1970s MMO electrodes have transformed both technological and economic aspects for the production of chlorine, sodium chlorate and sodium hypochlorite. Modifications to the Beer 2 coating resulted in both longer lifetimes and reduced costs. The successful development of the membrane cell technology for large-scale production of chlorine and sodium hydroxide led to further modifications to the coating. RuO_2 was partly replaced with IrO_2 to counteract dissolution of the ruthenium oxide in the highly alkaline environment at the anode surface that can form in operating membrane cells. At high pH, oxygen evolution becomes the preferred anodic reaction and ruthenium dioxide is oxidized to a soluble ruthenium compound (RuO_4) and lost from the electrode surface.

Parallel development programs focused upon the use of MMO electrodes for processes involving oxygen evolution. The stability of iridium oxide and its' catalytic activity towards the oxygen evolution reaction made this platinum group metal oxide the preferred choice. The incorporation of tantalum oxide into the coating, rather than titanium oxide, provided superior extended performance by inhibiting the formation of TiO_2 at the coating/substrate interface.

Many combinations of oxides, particularly oxides of the platinum group metals and valve metals, were prepared and characterized in efforts to identify patentable coatings with comparable or superior performance to the Beer coatings and modified Beer coatings. However presently, only mixtures of TiO_2 - RuO_2 , TiO_2 - RuO_2 - IrO_2 , TiO_2 - RuO_2 - SnO_2 and TaO_2 - IrO_2 are used commercially. The development of the MMO electrodes significantly increased the stability, current efficiency and operating voltages of dimensionally stable electrodes and enabled the introduction of new electrochemical processes.

A Comparison of the MMO and Pt/Ti anodes

Platinized titanium electrodes have been almost entirely replaced by the MMO electrodes. The reason for the dominance of MMO electrodes for the commercial production of chlorine and sodium hydroxide is evident from the data shown below:

Table 1

Overpotential and Corrosion Data for Anode Materials used
in the Electrolysis of Sodium Chloride

Anolyte: 25% Sodium Chloride

Temperature: 90°C

Current Density: 3 KA/M₂

Anode Material	Chlorine Overpotential (mV)	Weight Loss from Anode (kilograms/ton Chlorine)
Graphite	≈ 400	2 - 3
Platinum	≈ 200	0.4 – 0.8
RuO ₂ – TiO ₂	≈ 50	< 0.03

Pt/Ti anodes are used in some small-scale electrosyntheses and for cathodic protection systems in seawater environments, e.g., on oil rigs and seawater intakes. Presently these anodes require the deposition of a layer of either Pt/Ir or a noble metal oxide onto the titanium substrate, upon which platinum is electrodeposited.

How do MMO Electrodes Work?

MMO coatings are stated to be electrocatalytic towards the evolution of hydrogen, oxygen and chlorine, reactions that are very important in industrial electrochemistry. What does this mean?

To carry out an electrochemical reaction the potential of the electrode is changed either anodically or cathodically to support current flow and therefore generation of the required product. This change in potential is known as the overpotential, i.e., the difference between the thermodynamically reversible potential for the particular reaction and the operating potential.

Electrocatalysis may be broadly defined as the ability of an electrode surface to influence the rate of the electrode reaction. It involves the physical and/or chemical interaction of the surface with the ions or molecules at that surface. It is this interaction that lowers the energy required to drive the reaction, i.e., it

reduces the overpotential required to sustain a practical current density. Hence, the use of electrocatalytic electrodes effectively reduces the cell voltage and therefore the power consumption for the electrolytic process.

Preparation of MMO Electrodes

The preparation of the MMO coating requires careful attention. The titanium substrate must be cleaned thoroughly and then etched under controlled conditions, to give the required substrate morphology. The etchant is typically a strongly reducing acid such as hydrochloric or sulfuric acid. The nature of the etched surface of the titanium substrate can markedly affect the performance of the electrode (particularly its' extended performance). The solvent and the type of precursor used in the coating solution also affect the coating. After cleaning and etching, A thin coat of "paint" (a solution containing soluble compounds of the noble metal platinum group metal) is applied. The coated structure is thermally treated at temperatures typically ranging from 400-600°C. The number of coats needed is dictated by the service and required lifetime but generally ranges from 5 – 20.

The temperature and time of thermal decomposition need to be carefully controlled. The catalyst "paints" are applied in many layers and heat treated after each coat. Photographs, obtained by scanning electron microscopy, have shown that the surface of the MMO coatings typically has a "mud-cracked" appearance (Figure 1), which significantly increases the active area of the electrode.

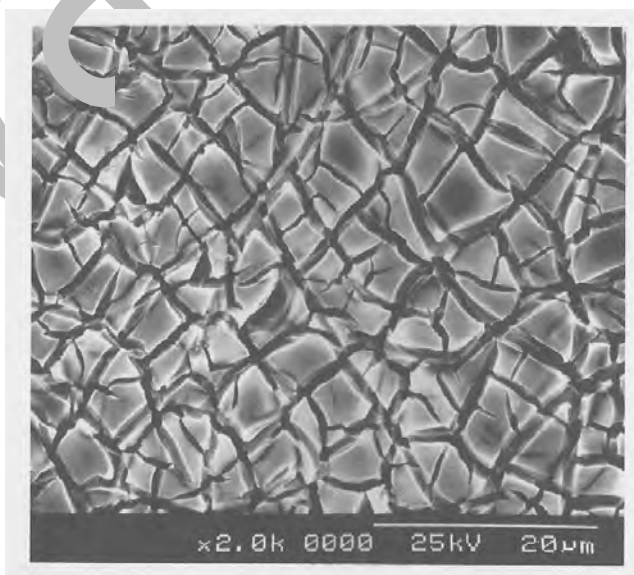
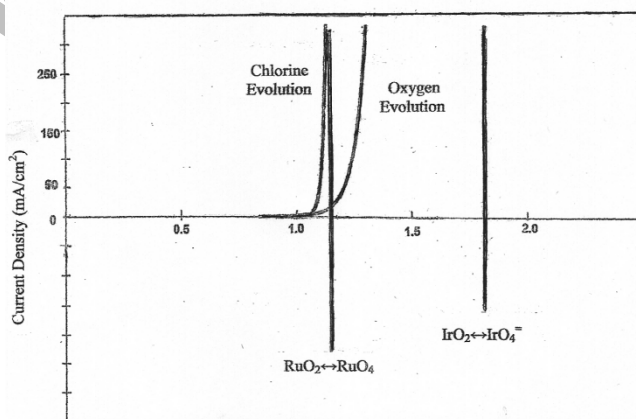


Figure 1: The “mud-cracked” appearance of the surface of an MMO coating, as shown by Scanning Electron Microscopy (SEM).

Selection of MMO Electrodes

When considering the electrooxidation of chloride ions in aqueous electrolytes thermodynamic data would predict that oxygen gas would be the major product of electrolysis. However, the oxygen evolution reaction is significantly more irreversible than the oxidation of chloride ions, resulting in high overpotentials at practical current densities. Thus, in fairly concentrated solutions of chloride ions, the evolution of chlorine is the dominant electrode reaction. Ruthenium oxide is an excellent electrocatalyst for chlorine evolution and RuO_2 - TiO_2 coated anodes are now widely (if not exclusively) used by the chlorine industry.

However, the oxygen evolution reaction cannot be totally suppressed and becomes a significant process (a) at high anolyte pH, (b) at temperatures approaching ambient and (c) at low concentration of chloride ions. Iridium oxide, which is less active for chlorine evolution, is electrocatalytic towards the oxygen evolution reaction and is significantly more stable than ruthenium oxide under all conditions. Figure 2 shows the current-potential curves for the two reactions and the potentials at which RuO_2 and IrO_2 begin to oxidize. The formation of the soluble compound RuO_4 , which dissolves from the coating, clearly limits the use of ruthenium based coatings when oxygen evolution occurs at the anode. Hence, for electrochemical processes where the anodic reaction is oxygen evolution, e.g., electroplating, electrowinning of metals from acid electrolytes or plating printed circuit boards, the preferred MMO coating is TaO_2 - IrO_2 . Also, pure RuO_2 coatings have generally been displaced for use in chloride concentrations less than about 28 gpl. These have been replaced by coatings that are mixtures of RuO_2 and IrO_2 .



Potential (Volts vs Std. Calomel Electrode)

Figure 2. Schematic Current-Potential Curves and Redox Potentials

How do MMO Electrodes Fail?

Extended operation of a MMO electrode leads to an increase in the overpotential of the anode. This loss of activity of the MMO coating may be attributed to one or more of several causes:

- (i) Dissolution of the platinum group metal oxide, particularly when ruthenium oxide is used in the coating As stated above the oxygen evolution reaction cannot be totally suppressed when using aqueous electrolytes and RuO_2 is slowly oxidized to the soluble species, RuO_4 . In membrane cells, the anode surface can become highly alkaline and this environment favors oxygen evolution. The resulting damage to a ruthenium-based MMO coating is shown in Figure 3.

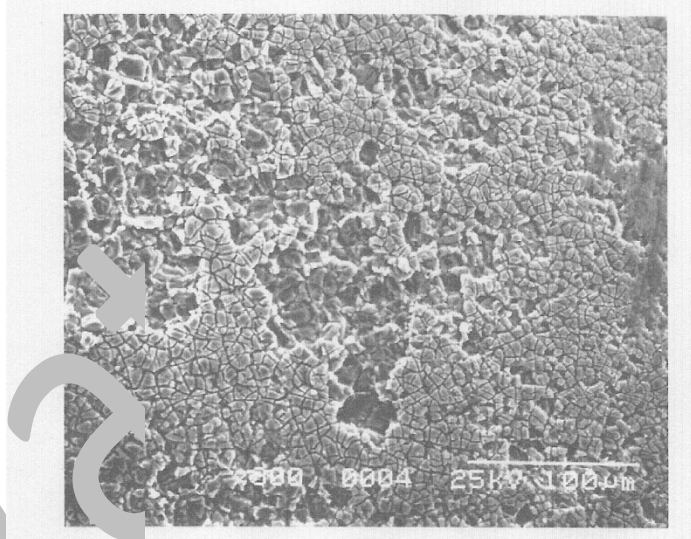


Figure 3. SEM photographs showing the results of caustic attack on an MMO coating used in a membrane chlorine cell.

- (ii) The turbulent hydrodynamic conditions at the electrode surface lead to erosion of the coating. The rapid evolution of gas from the coating generates significant pressures within the porous coating and can exacerbate the mechanical damage. Proper cell design that adequately removes gas from the electrode surface is critical to long term performance of MMO electrodes.

- (iii) Inorganic compounds such as SrSO_4 , BaSO_4 , PbSO_4 , MnO_2 , TiO_2 , iron oxides, alumina and silica accumulate at the surface of the anode, blinding the electroactive sites. This accumulation of insoluble compounds, which may involve either electrodeposition or electrophoresis, results in non-uniform current distribution. If the deposits are removed, it is possible that the electrode performance can be restored. However, in many cases the catalytic coating is removed with the adherent deposits.
- (iv) Organic impurities in the electrolyte may be partially oxidized and/or chlorinated at the anode and tend to adhere to the coating, again blinding the active sites and causing premature failure. Some chelating agents such as EDTA have been shown to bind to platinum group metal oxides, resulting in the extraction of the oxide from the valve metal matrix.
- (v) A non-conductive layer of TiO_2 can form at the coating-substrate interface, effectively passivating the anode due to the high resistivity of this oxide. This failure mechanism is almost entirely due to the formation of nascent oxygen at the surface of the electrode. This very aggressive form of oxygen readily attacks the titanium interface.
- (vi) The presence of fluoride or bromide ions in the anolyte leads to dissolution of the titanium substrate as fluorine and bromine are evolved. Titanium is not stable to the formation of these more aggressive halogen gases. The dissolution of the substrate undercuts the coating and it effectively “falls off” (Figure 4).

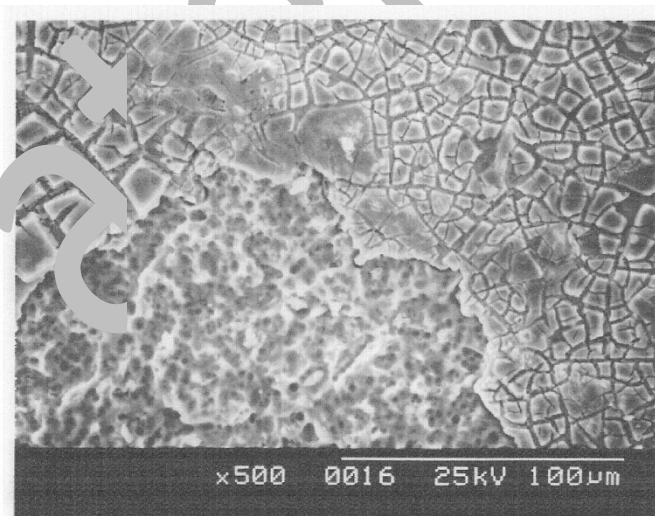


Figure 4. SEM photograph showing the effect of fluoride ions on an MMO coating

- (vii) Current reversal will have a significant effect on the lifetime of the electrode. This is commonly used in swimming pool chlorinators to remove the calcium and magnesium scale that forms due to hard water. While this is quite convenient for the operator since no routine acid wash is necessary, the coating lifetime is significantly reduced compared to MMO electrodes that are

continually held anodic. A major mode of failure is hydrogen attack of the titanium substrate to form the friable titanium hydride. This causes loss of coating. Also IrO_2 has been reported to be reduced to Ir_2O_3 which is somewhat soluble in acidic media.

Specifications for an Application for MMO electrodes

In order to provide the most suitable MMO for a given application the electrode manufacturer needs specific information about the intended use. For example:-

- (i) The Application: Is the electrode to be used in electroplating, electrowinning, printed circuit board plating or water treatment systems, where the dominant anodic reaction will be oxygen evolution? If the application involves disinfection or chlorination then both oxygen and chlorine evolution will occur at the anode.
- (ii) Electrolyte: The pH of aqueous electrolytes can determine the reactions occurring at the anode and is a significant factor in selecting a suitable coating. Detailed analyses of the electrolyte, and/or the water used to prepare it, will indicate what inorganic and organic impurities are present and in what concentrations. As is discussed above the presence of fluoride ions, barium and strontium sulfates, iron and manganese salts will compromise the performance and shorten the lifetime of the MMO electrode.
- (iii) Current Density: The current density at an electrode is usually expressed in Amps/Square Inch or Amps/Square Meter. The current density determines the potential at which the electrode operates. As discussed earlier, the stability of RuO_2 decreases markedly as the potential becomes more positive due to increasing the current density.
- (iv) Plating Applications: Plating baths contain additives such as brighteners and levelers that are typically organic compounds. These additives are critical to the plating process and must be protected against oxidation at the anode during operation. Special coatings are available to provide this protection.