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The History of Progress in Dimensionally Stable Anodes

Paul Duby

This article provides a brief history of dimensionally stable anodes by reviewing innovations in the chlor-alkali industry, electroplating and electrogalvanizing, and electrowinning. These anodes are attractive for numerous reasons (e.g., long life and reduced energy consumption), but they must still overcome the hurdle of cost to gain wider acceptance for applications in the metallurgical process industries.

INTRODUCTION

A nonconsumable anode is preferred for many electrolytic processes. Technological and economic considerations dictate the selection of a suitable material. In the past, graphite, iron, lead, and various alloys were found acceptable, notwithstanding some corrosion and mechanical wear resulting in the release of impurities, loss of geometrical shape, and eventual replacement of the electrode. A dimensionally stable anode is one for which the degradation processes are much slower and limited to the electro-active surface layer. Since the shape and structural integrity of the electrode are preserved, the surface layer, usually a coating with appropriate catalytic properties, can be regenerated.

The first insoluble anode proposed as a substitute for the graphite electrode is the platinized titanium anode or, more generally, an electroplated platinum-group metal (PGM) or alloy applied to a valve metal electrode. It was developed in the late 1950s, primarily for use in the metal-finishing industry.[1] Platinum-clad titanium electrodes were tested for use in the chlor-alkali industry, but their cost, combined with unacceptable wear rate and increasing passivation, discouraged further development for that particular application.[2] The accomplishment that led to large-scale use of dimensionally stable anodes came in the 1960s when Henri Beer invented the titanium electrode coated with precious-metal oxides.[3]

CHLOR-ALKALI INDUSTRY

The development of dimensionally stable anodes for the chlor-alkali industry is an example of a very successful innovation. A brief discussion of its history as well as the technological experience gained in the process is relevant to assess the prospects for metallurgical-industry applications.

In an address delivered in 1980 before the Electrochemical Society,[4] Henri Beer reviewed his research and the subsequent industrial development of various types of titanium anodes. His aim was to find an appropriate electrocatalyst for the production of chlorine to be applied to an electrode capable of carrying high current densities for long periods of time without being consumed or changing its geometrical dimensions. He started by working with coatings obtained by electrodeposition of PGMs on titanium, for use in mercury cells. Like other investigators, he discovered the importance of the pretreatment of the titanium substrate and the improvement in adhesion and electrocatalytic activity obtained by replacing the electrodeposition process by a thermochemical one consisting of an application of a solution of salts of the desired metals followed by thermal decomposition. He also observed that the passivation and loss of platinum metal were greatly reduced by alloying the platinum with about 30 wt.% iridium.

Further attempts to reduce the overpotential for chlorine evolution, the wear of the coating, and its cost led to experimentation with PGM oxides. In 1967, Beer succeeded in preparing more electroactive and stable coatings by thermochemical coprecipitation of PGM oxides with oxides of titanium or the other valve metals. These anodes were registered under the trademark DSA®. Since that time, many patents have appeared describing various mixtures of metal oxides as the active coatings on valve metal substrates. The dimensionally stable anode in use today for chlorine production is made of a titanium structure of rods or expanded metal with a coating of doped, mixed oxides of ruthenium and titanium having a high electrocatalytic activity and electrical conductivity.

It is worthwhile to note that the change from graphite anodes to coated metal anodes was not a simple substitution, as it required modifications to the cell design and large capital expenditures. At first, the current and cell output were significantly increased with a modest (about 5%) decrease in power consumption per tonne of chlorine gas. Later, the new anodes led to the design of a new generation of improved diaphragm cells and made possible the development of membrane cells. Over the decade of the 1970s, DSA-type electrodes revolutionized the chlorine industry with resulting savings of about 20% in the specific energy requirement. Holden and Kolb reviewed the state of the art of manufacturing and applications of the metal anodes to the chlor-alkali industry.[5]

The success of the industrial applications of the ruthenium oxide-coated electrode was based only on a limited investigation of its overpotential for chlorine evolution and its stability for continuous operation as an anode. These were empirically related to the morphology and the preparation process.[6] Research of a more fundamental nature followed later. Trasatti and O'Grady reviewed the work carried out on the properties of ruthenium oxide electrodes during the 1970s.[7] Trasatti also edited reviews of all electrodes of conductive metal oxides.[8] A better understanding of the physico-chemical properties of the single- and mixed-oxide films, in turn, generated ideas for further improvement of electrodes for practical applications. More recently, for instance, ion implantation has been used to modify and characterize the properties of mixed ruthenium-titanium oxide films.[9] Tilak et al.[10] presented a more fundamental analysis of the factors influencing the kinetics of oxygen versus chlorine evolution on ruthenium oxide-based anodes. They suppressed oxygen evolution by operating with low surface areas and by adding dopants.

Progress is continuing to improve the design of the structure and coating of the electrodes.[11–13] For diaphragm electrolyzers, the coatings consist mainly of ruthenium and titanium oxides, and service life is reported to be more than 14 years at 2 kA/m². For the membrane process, the conditions are more severe due to a larger current density, higher alkalinity, and a need to control the oxygen and chlorate. An improved coating consisting of ruthenium, titanium, and iridium oxides is expected to perform for more than ten years at 3 kA/m².[12]

A large number of variations in composition of oxide coatings have been investigated. For instance, palladium oxide can be used to reduce the iridium content.[14] The influence of coating composition has been investigated in order to optimize electrodes for the production of chlorate or hypochlorite.[15] Nonprecious metal oxides were also considered. Alpha-lead dioxide coated on titanium was suggested for the electrosynthesis of sodium perchlorate.[16] Burke and McCarthy found that thermally produced cobalt oxide (Co_3O_4), doped with RuO_2 to improve conductivity, is a promising anode material.[17] These oxides of the spinel type have been tested for chlorine evolution. Because of their longer service life in alkaline solutions, they were recommended on a nickel substrate for water electrolysis.

ELECTROPLATING AND ELECTROGALVANIZING

Inert anodes made by electrodeposition of platinum on titanium have been used successfully for some time in various baths for electroplating gold and other precious metals. Information on the electrocatalytic properties and behavior under different conditions has been reviewed.[1] Skomoroski et al.[18] investigated the performance of platinum-clad tantalum anodes and compared them favorably with electroplated platinized titanium electrodes in various electroplating baths. For these applications, the life of the electrodes and the costs are quite acceptable.

Until recently, soluble anodes of lead-silver alloy electrodes were used satisfactorily in sulfate solutions. They are no longer suitable for modern high-speed galvanizing lines that produce a pure metal or a zinc alloy exempt of lead contamination. Platinum-clad titanium anodes suffer from high wear and, thus, high costs. The chemical stability of ruthenium oxide is limited in a sulfuric acid solution and the RuO_2-TiO_2 coating used successfully for chlorine evolution is not commercially viable for oxygen evolution in sulfate electrolyte because of its high wear rate. Electrodes based on iridium oxide by itself or mixed with other oxides and applied atop a dense conducting layer between the titanium substrate and the electrocatalyst have an excellent lifetime and are standard anodes for new strip electrogalvanizing plants.[19,20]

McIntyre[21] reported that iridium oxide coatings tested for use as anodes during cathodic electrodeposition of organic coatings showed no degradation and an estimated service life of four years, while in similar tests, ruthenium oxide coatings were marginal and cobalt oxide coatings were unsatisfactory. Hine et al.[22] tested a platinized titanium sheet loaded with thermally deposited iridium oxide for use in chromium electroplating. Hardee et al.[23] have reviewed the use of DSA-type anodes for high-speed electroplating and electrogalvanizing. They discussed the failure modes: loss of catalyst by dissolution or erosion, passivation of the valve metal substrate, and various types of damage caused by impurities in the electrolyte.

ELECTROWINNING

Electrowinning is only one of the steps of complex metallurgical flow sheets, and a significant modification of one unit operation often affects all the others. The successful application of dimensionally stable electrodes for chlorine evolution is critical for the development of chloride hydro-electrometallurgy. A dimensionally stable anode with good service life facilitates the design of permanent anodic compartments and chlorine removal systems for safe operation of the tankhouse. Given the successful commercial application of solvent extraction to the treatment of chloride solutions of nickel and cobalt, there is an incentive to develop an efficient chloride electrowinning process for these metals.

In 1975, Sumitomo Metals and Mining Company reported the use of DSA anodes on a commercial scale for the electrowinning of nickel and cobalt from chloride electrolytes.[24] The electrodes had been selected after being found much superior to graphite anodes in earlier stages of process development. At the same time, Falconbridge, in Norway, was phasing out the Hybinette electrorefining process for nickel and cobalt, replacing it by chlorine leach, solvent extraction, and electrowinning.[25] The tankhouse section was equipped with DSA-type anodes made of a titanium structure coated with an electroactive layer of a noble metal oxide. The structure is fitted with a hood to which the diaphragm bag is attached. The conversion to the chlorine leach process resulted in a doubling of the production per tank and a significant improvement of the working conditions in the plant.

Most other commercial electrowinning processes, however, are carried out in sulfate electrolytes, and oxygen-evolving anodes are required. Given the relatively low cost of the ruthenium oxide coating and its success in the chlor-alkali industry, it is logical to consider it for use in sulfate solution, although available thermodynamic data indicate that it is not stable in the potential range required for oxygen evolution in acid solution. Lodi et al.[26] investigated the effect of chemical composition and surface morphology on oxygen evolution in acid solution. They found that the active layer of ruthenium oxide was being corroded over a wide range of pH. Their results were confirmed by other investigators, and an extensive review was published by Trasatti et al.[8]

Baboian[27] reported the results of electrowinning tests in acid sulfate solutions using platinum-clad anodes made of titanium, tantalum, and niobium clad with a platinum foil. The platinum loss, however, was too high for commercial applications. Wensley and Warren[28,29] carried out extensive experiments with PGM-coated anodes. They also found significant loss of coating under the typical conditions for sulfate electrowinning. In particular, when investigating the 70 wt.% Pt-30 wt.% Ir applied via a thermal decomposition process, they found evidence of preferential dissolution of platinum. They also observed increased corrosion rates in the presence of thiourea and other organic additives commonly used in electrowinning electrolytes. Scarpellino and Fisher[30,31] tested various precious metal coatings in an all-sulfate nickel electrowinning electrolyte. They reported that multilayer coatings with an Ru-Ir alloy as the electrocatalyst were expected to operate for at least 20,000 hours as an energy-efficient insoluble anode.

Since iridium oxide has been known to be the electroactive component for oxygen evolution, considerable effort has been devoted to formulating mixed coatings with less-expensive metal oxides and subcoatings to prevent or decrease the rate of loss of active material. These electrodes are now commercially available from several manufacturers. Although they have been described in the patent literature, exact compositions and coating procedures are often trade secrets. Ferron[32] has carried out laboratory tests of an iridium oxide-coated titanium anode in a copper electrowinning cell. The initial operating potential was about 300 mV lower than that of a lead anode under the same conditions; it increased linearly at a rate of 220 mV per year, which was correlated to the rate of electrochemical corrosion of the coating.[33] Minor amounts of lead in solution deposited anodically above a critical potential. Glue had no effect, but thiourea caused faster degradation of the coating.[34] Among mixed-oxide coatings, iridium oxide and tantalum oxide have been considered. Rolewicz et al.[35] and Comminellis[36] have found no evidence of a true solid solution. They observed that the catalytic activity and the lifetime were related to the quantity of iridium oxide while the tantalum oxide reduced the corrosion rate. At the optimal composition of 70% IrO_2 and 30% Ta_2O_5, the degradation proceeded uniformly.

Progress has been made toward reducing the cost and extending the service life of electrodes. Beer disclosed the invention of an activated lead anode composed of titanium sponge coated with ruthenium oxide and pressed into a lead-calcium substrate.[37] Field tests in pilot cells for copper electrowinning demonstrated that an average 300 mV savings could be maintained for an expected catalytic life time of about three years.[38] The lead content of the electrowon copper was significantly lower than with the lead-calcium anodes. Koziol and Wenk[39] discussed tests made with different anode designs: massive or corrugated sheet, lamellar or mesh box, mesh or corrugated mesh, and others. Bewer et al.[40,41] discussed the characteristics and the test results obtained with activated sintered-titanium anodes.

Tests of DSA-type anodes have been carried out in sulfate electrolytes for copper, zinc, nickel, cobalt, and manganese using commercially available as well as newly invented electrodes. For instance, graphite-based and ceramic-based RuO_2-TiO_2 electrodes were investigated for nickel and zinc electrowinning.[42] Anodes consisting of titanium, tungsten, or molybdenum nitride or carbide coatings on stainless steel were proposed for use in a zinc sulfate electrolyte.[43] Piron[44] found that nickel-iridium oxides with 2% iridium displayed good electrocatalytic activity for the alkaline electrowinning of zinc under high current densities. Ardelean et al.[45] ran small pilot-scale tests for high-intensity zinc electrowinning in a sulfate electrolyte and they found that DSA-type anodes were not practical due to the build-up of manganese dioxide.

CONCLUSION

The energy savings achieved with electrocatalytic DSA-type anodes have been well documented and they correspond to values suggested by Ettel[46] some time ago. The influence of impurities or additives present in electrowinning electrolytes on the electrocatalytic activity and service life of these electrodes needs further investigation, and a more fundamental understanding is required to direct the development of new coatings. Research should be aimed at noble and/or non-noble oxide materials.[47] The prohibitive cost factor remains the major hurdle. Operating life in pilot cells for copper electrowinning has been claimed to vary from one to two years with energy savings of 15–20%.[47] Warren[48] noted that the incremental investment allowable to achieve the expected savings is not high; it is much lower than in the chlor-alkali industry since the value of the annual production of chlorine per unit of anode area is about ten times the corresponding value of the copper output in a conventional electrowinning cell. Rolled anodes of lead-calcium-tin alloys are the state of the art in copper tankhouses.[49] Although lead contamination of the cathodes has been much reduced, it is still a problem in modern plants.[50] There is certainly a strong incentive for further research aimed at developing a dimensionally stable anode with economically acceptable service life in a sulfate electrolyte and with an improved design to fit a more efficient cell. The ruthenium oxide anode for chlorine evolution was a successful innovation that revolutionized the design of the chlor-alkali cells. More recently, it was important in the successful development of new hydro-electrometallurgical processes for nickel and cobalt, because it provided not only energy savings at an acceptable investment cost, but also it made possible a more efficient design and operation of the electrolysis cells.

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ABOUT THE AUTHOR

Paul Duby earned his Eng.Sc.D. in mineral engineering at Columbia University in 1962. He is currently a professor of mineral engineering at Columbia's Henry Krumb School of Mines. Dr. Duby is also a member of TMS.

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