METAL ANODES

1. Introduction

In electrolytic processes, the anode is the positive terminal through which electrons pass from the electrolyte. Anode design and selection of anode materials of construction have traditionally been the result of an optimization of anode cost and operating economics, in addition to being dependent on the requirements of the process. Most materials used in metal anode fabrication are characteristically expensive; use has, however, been justified by enhanced performance and reduced operating cost. An additional consideration that has had increasing influence on selection of the appropriate anode is concern for the environment (see ELECTROCHEMICAL PROCESSING).

Industrial metal anodes can generally be classified in one of two groups. The first group, chlorine-generating anodes, find application primarily in the manufacture of chlorine and caustic, sodium chlorate, and sodium hypochlorite (see ALKALI AND CHLORINE PRODUCTS; CHLORINE OXYGEN ACIDS AND SALTS). The second group, consisting of the oxygen-evolving anodes, do not generate a saleable product directly, but rather facilitate the desired cathodic reaction. Commercial uses include high speed electrogalvanizing of steel (qv), electrowinning of base metals, plating operations, cathodic protection, electrophoretic painting, copper (qv) foil treatment, and, more recently, the primary production of copper foil itself (see ELECTROPLATING; MACHINING METHODS, ELECTROCHEMICAL).

2. Historical Development

Anodes of zinc, lead, silver, and other metals have found commercial application in a variety of uses since the early 1900s. Then, in 1950, a breakthrough in coated anode technology took place when the development of jet aircraft and the birth of the space industry expanded the demand for and supply of titanium, bringing the price of this metal into a more affordable range (see TITANIUM AND TITANIUM ALLOYS). Whereas titanium [7440-32-6] was valued in air transport and space programs for its strength-to-weight characteristic, other attributes were important for usage as metal anodes in the chlor alkali industry. These are (*1*) titanium's self-oxidizing valve metal quality which passes current in one direction only; (*2*) titanium's excellent corrosion-resistance to a wet chlorine environment; and (*3*) titanium's superior conductivity when compared to graphite.

Because titanium is subject to oxidation under anodic conditions, an electrically resistive layer is formed on its surface. Thus this material is, in itself, not the complete answer to the search for a metal anode suitable for use in chlor-alkali service. The principal participants in the worldwide chlorine industry therefore embarked on programs to develop appropriate coatings (qv) that would make the use of the titanium structure more fully practical. These programs were predicated on the use of platinum-group metals (qv) as the active ingredient of the coating. Patents were issued in the late 1950s for platinized titanium anodes utilizing catalysts on titanium supports (1,2).

During the 1960s, a group of British patents were issued (3–5) wherein technology effective in maintaining the precious metal in the coating in its metallic rather than oxidized state was emphasized. Realization of this objective was achieved by the specification of a reducing atmosphere during thermodeposition, by use of reducing agents in the coating formulation, or by electrolytic deposition. Whereas these metallic coatings (qv) have found application in cathodic protection service and, to some extent, in the manufacture of sodium chlorate, these coatings have not proven commercially effective in chlorine manufacture.

Commercial metal anodes for the chlorine industry came about after the late 1960s when a series of worldwide patents were awarded (6–8). These were based not on the use of the platinum-group metals (qv) themselves, but on coatings comprised of platinum-group metal oxides or a mixture of these oxides with valve metal oxides, such as titanium oxide (see PLATINUM-GROUP METALS, COMPOUNDS; TITANIUM COMPOUNDS). In the case of chlor-alkali production, the platinum-group metal oxides that proved most appropriate for use as coatings on anodes were those of ruthenium and iridium.

Many competitive programs to perfect a metallic anode for chlorine arose. In one, Dow Chemical concentrated on a coating based on cobalt oxide rather than precious metal oxides. This technology was patented (9,10) and developed to the semicommercial state, but the operating characteristics of the cobalt oxide coatings proved inferior to those of the platinum-group metal oxide.

3. Commercial Uses

3.1. Chlorine-Generating Anode.

Chlorine and Chlorine Oxygen Salts. Coated metal anode technology finds its most dramatic industrial application in the chlorine industry. Metal anode technology for chlorine [7782-50-5], Cl_2, manufacture, commercialized as the dimensionally stable anode (DSA) (Electrode Corp.), replaced essentially all graphite anodes worldwide in chlorine plants between 1972 and 1982. Advantages to DSA users relative to the older graphite anode include lower power consumption resulting from low overpotential and dimensional stability; reduced cell renewal activity owing to long anode life; cleaner products of electrolysis; elimination of some environmentally detrimental materials used with the graphite anode; and more consistent and stable cellroom operation.

Success in the chlorine industry led to the incorporation of DSA in sodium chlorate [7775-09-9], $NaClO_3$, manufacture. The unique structural characteristics of the anode allowed for innovative designs in cell hardware, which in turn contributed to the extensive worldwide expansion of the sodium chlorate industry in the 1980s.

Just as straightforward was the incorporation of coated metal anodes into systems for the production of sodium hypochlorite [7681-52-9], NaClO. On-site production units fed with either salt brine or seawater are used in far-reaching applications, ranging from cooling water treatment, drinking water disinfection, wastewater treatment, swimming pool disinfection, and secondary oil recovery, to marine sewage treatment and bleach manufacture (see CHLORINE OXYGEN ACIDS AND SALTS, DICHLORINE MONOXIDE, HYPOCHLOROUS ACID, AND HYPOCHLORITES).

Cathodic Protection Systems. Metal anodes using either platinum [7440-06-4] metal or precious metal oxide coatings on titanium, niobium [7440-03-1], or tantalum [7440-25-7] substrates are extensively used for impressed current cathodic protection systems. A prime application is the use of platinum-coated titanium anodes for protection of the hulls of marine vessels. The controlled feature of these systems has created an attractive alternative to the use of sacrificial anodes and frequent dry docking for painting and repair (see COATINGS, MARINE). These cathodic protection systems are also used on deep-sea oil-drilling platforms (see PETROLEUM).

Metal anodes using platinum and precious metal oxide coatings are also incorporated into a variety of designs of impressed current protection for pipeline and deep well applications, as well as for protection of condenser water boxes in power generating stations (see PIPELINES; POWER GENERATION).

Electroplating. Platinized titanium-on-niobium anodes are preferred for use in electroplating precious metals. These anodes find wide application in the electronics industry and in the creation of fine jewelry.

3.2. Oxygen-Evolving Anode. Research efforts to incorporate the coated metal anode for oxygen-evolving applications such as specialty electrochemical synthesis, electrowinning, impressed current, electrodialysis, and metal recovery found only limited applications for many years.

Two specific uses of oxygen anodes that represent comprehensive and growing market demands have surfaced. In the first, occasioned by the commercialization of the high speed electrogalvanizing process (11), the electrolytic hardware was designed to utilize DSA rather than the traditional dimensionally unstable lead or zinc anodes. This Andritz Ruthner technology has been well accepted by the worldwide electrogalvanizing industry and has been incorporated into production plants in North America, Europe, and South America, creating an instant demand for the coated titanium metal anode. In addition, plants originally designed for the use of lead or zinc anodes have been converting to coated metal anodes. Advantages include electric power savings, consistency of operation, and elimination of many environmental concerns.

The second use involves the application of DSA coating on a titanium mesh for cathodically protecting steel reinforcing in concrete structures, such as highway bridges and parking garages (12). This technology finds value in geographic areas where salt is used to prevent roadway icing and in marine shore locations. In practice, salt solution finds its way through the concrete to the reinforcing bar and promotes oxidation of the steel (qv). The rust thus formed occupies a greater volume than the steel, creating stress and eventually cracking the concrete. This continuing process can lead to virtual destruction of the structure if maintenance is delayed. By embedding the coated titanium mesh between the reinforcing steel and the surface of the concrete and by supplying a potential on the mesh to maintain the reinforcing steel cathodic, this destructive process can be eliminated and structure life significantly extended. This technology is seen as having a significant future of widespread utilization.

Several more traditional materials have found specific though limited commercial application as metal anodes. Examples are lead [7439-92-1] and zinc [7440-66-6] in the electrogalvanizing practice. Lead dioxide [1309-60-0] and manganese dioxide [1313-13-9] anode technologies have also been pursued. Two industrial electrolytic industries, aluminum [7429-90-5] and electric arc steel, still use graphite anodes. Heavy investment has been devoted to research and development to bring the advantages of DSA to these operations, but commercialization has not been achieved.

The commercial status of metal anodes for oxygen-evolving applications may be summarized as follows:

Application	Anode used
electrogalvanizing	DSA, lead, zinc
cathodic protection	platinized titanium, DSA, zinc, magnesium, lead, silver, aluminum
electrolysis of sodium sulfate and other inorganic salts	DSA
electrophoretic painting	stainless steel, DSA
copper foil production	lead, DSA
copper foil treatment	DSA, steel, platinized titanium
zinc electrowinning	DSA, lead
copper electrowinning	lead
aluminum anodizing	DSA, lead
metal finishing/recovery	DSA, lead, platinized titanium
electroplating of precious metals	platinized titanium or niobium

4. Coating Structure and Morphology

The crystal structure of metal anode coatings has been investigated using x-ray diffraction studies, x-ray fluorescence analysis, and microprobe studies in conjunction with scanning electron micrographs (see MICROSCOPY; X-RAY TECHNOLOGY). However, the role of the titanium metal substrate, or that of the oxides formed when the substrate is anodized or heated in air, is not completely clear for coatings that contain titanium in their solution. Most coatings, even those not containing titanium in the formulation, exhibit traces of titanium dioxide, present either in rutile [1317-80-2] or anatase [1317-70-0] form.

4.1. Ruthenium–Titanium Oxides. The x-ray diffraction studies of ruthenium–titanium oxide coatings show that the coating components are present as the metal dioxides, each in the rutile form as well as in solid solution with each other (13). The development of the crystal structure begins to occur at a bake temperature of about 400°C. By following the d_{110} diffraction line for the rutile structure, an increase in crystallinity can be seen as temperatures are increased to the 600–700°C range. Above these temperatures, the d_{110} peak begins to separate into two separate peaks, indicative of phase separation into individual rutile oxides, one rich in ruthenium and one rich in titanium.

It appears that the titanium metal substrate on which the coating is deposited plays an important role in the structure and morphology of the coating. The surface layer of rutile titanium dioxide normally found on oxidized titanium metal apparently acts as a seed to initiate growth of the rutile form of the oxide, rather than the anatase form. Interfacial layers of titanium suboxides, known to be electrically conductive, also act to effect a gradual transition from pure metal to pure rutile oxides. Without this interfacial layer, the large stresses in the titanium crystal structure created in the transition of metal to oxide would occur over a sharp boundary and reduce the adhesion of the coating to the substrate. Thus careful control of the bake temperature and rate of change, ie, the temperature profile, are necessary to ensure optimum adhesion of the oxides to the base metal.

Additional x-ray studies indicate some degree of lattice distortion in coatings prepared from chloride-containing coating solutions. This correlates with an analysis of 3–5% chloride in the coating, which is reduced to near zero if the coating is heated to 800°C.

Coatings produced at bake temperatures of 400–600°C are incompletely crystallized solid solutions of rutile titanium dioxide and ruthenium dioxide [12036-10-1] having lattice defects caused by the presence of chloride. The high degree of crystalline disorder contributes greatly to the electrical conductivity of the coating, the presence of active catalytic sites, and the high surface area of the coating.

Scanning electron micrographs of ruthenium–titanium oxide coatings show a characteristic microcracked surface (13). This cracking occurs early in the coating preparation, as solvent evaporates from the surface to form a gel of unreacted ruthenium and titanium compounds. As the coating is baked at higher temperatures, the cracks increase in size because of volume contraction of the gel. A fully baked anode coating has the appearance shown in Figure 1 and a surface-area factor of 180 to 230 times the geometrical area, as measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption. This large surface area contributes to the low chlorine discharge potential of these coatings, providing a large number of catalytic sites for gas evolution while minimizing concentration polarization.

4.2. Iridium Oxide. Iridium dioxide [12030-49-8] coatings, typically used in combination with valve metal oxides, are quite similar in structure to those of ruthenium dioxide coatings. X-ray diffraction shows the rutile crystal structure of the iridium dioxide; scanning electron micrographs show the micro-cracked surface typical of these thermally prepared oxide coatings.

4.3. Platinum–Iridium. There are two distinct forms of 70/30 wt% platinum–iridium coatings. The first, prepared as prescribed in British patents (3–5), consists of platinum and iridium metal. X-ray diffraction shows shifted Pt peaks and no oxide species. The iridium [7439-88-5] is thus present in its metallic form, either as a separate phase or as a platinum–iridium intermetallic. The surface morphology of a platinum–iridium metal coating shown in Figure 2 is cracked, but not in the regular networked pattern typical of the DSA oxide materials.

The second form consists of Pt metal but the iridium is present as iridium dioxide. Iridium metal may or may not be present, depending on the baking temperature (14). Titanium dioxide is present in amounts of only a few weight percent. The analysis of these coatings suggests that the platinum metal acts as a binder for the iridium oxide, which in turn acts as the electrocatalyst for chlorine discharge (14). In the case of thermally deposited platinum–iridium metal coatings, these may actually form an intermetallic. Both the electrocatalytic properties and wear rates are expected to differ for these two forms of platinum–iridium-coated anodes.

4.4. Spinel Cobalt Oxides. The cobalt mixed oxide [1308-06-1], Co_3O_4, containing Co(II) and Co(III) ions, has the spinel structure. The x-ray analysis shows that divalent zinc ions substitute for Co(II) in the tetrahedral sites of the lattice, causing an expansion of the lattice and formation of a normal $Zn_xCo_{3-x}O_4$ spinel structure (15). In these coatings containing zirconium [7440-67-7], a separate, partially crystalline phase of zirconium dioxide [1314-23-4] occurs. The coating has large microscopic pores, providing a high surface area which appears to be related to the presence of zirconium. Spinel oxides applied without the presence of zirconium are dense and closely packed coatings. Thermal studies indicate that decomposition of zirconyl nitrate [13826-66-9], the source of zirconium in the coating, produces NO_2. This gas is released into the cobalt–zinc oxide as it forms, presumably producing the open-pore, spongy morphology of the coating. Surface-area measurements confirm this model. The presence of zirconium increases the surface-area factor from approximately 250 to 1880, determined by BET measurements (15).

5. Operating Performance of Coatings

The key yardstick of performance for a coated metal anode is the period of time, measured in ampere-hours, that the coating operates before it reaches an unacceptable voltage, as measured by the single electrode potential (SEP). This SEP is characteristically constant over an extended period of operating time, but at some point escalates at increased and varying rates, depending on specific operating conditions. Factors influencing this escalation include accumulated average lifetime, operating current density, electrolyte conditions, exposure to oxygen in the anolyte compartment, and cell design. The magnitude of this escalation dictates the point at which the anode coating is considered to have failed, ie, to have reached the end of its operable life, and requires replacement.

5.1. Chlorine Anodes. In chlorine manufacture, anode operating life is limited by coating wear. The wear rate varies according to cell type. The longest anode coating life has been achieved in diaphragm chlorine cells. When these were first commercialized, it was expected that 5–6 years would represent a fully acceptable anode coating life. In practice, however, lives of 10–15 years and, in some cases, beyond, have been realized. This extended performance has been achieved in spite of the incorporation of voltage-saving techniques that position the anode only a few millimeters from the cathode surface. In some plants, the anode has been allowed to bear directly on the diaphragm itself. Whether this latter arrangement shortens coating operating life has yet to be determined.

Because mercury (qv) chlorine cells operate at higher current densities and because the mercury cell anode can be adjusted during operation to minimize the anode-to-cathode gap, anode coating life in these cells is much shorter. Lifetimes range from less than one year at high current densities and using close gaps, to periods in excess of five years at lower current densities and using greater gaps. In cellrooms that have converted from the traditional mesh- or rod-type structures to the newer blade-type anode, anode coating lifetimes have been extended.

Because of limited commercial experience with anode coatings in membrane cells, commercial lifetimes have yet to be defined. Expected lifetime is 5–8 years. In some cases as of this writing (ca 1995), 10-years performance has already been achieved. Actual lifetime is dictated by the membrane replacement schedule, cell design, the level of oxygen in the chlorine gas, and by the current density at which the anode is operated.

Metal anode coatings commercially used for manufacture of sodium chlorate include not only the ruthenium oxide coatings, but also platinum–iridium coatings. Whereas ruthenium oxide coatings might be preferred for a longer performance life and higher resistance to process upsets, platinum–iridium coatings generally operate at higher efficiencies during the first months of operation. The sodium chlorate industry has experienced only a limited coating replacement requirement. It is generally expected that coating life in chlorate cells approximates 10 years. Poor electrolyte circulation patterns and exposure to impurities in the anolyte have been known to shorten this life dramatically.

5.2. Oxygen-Evolving Anodes. In the case of oxygen-evolving anodes employing iridium dioxide-based coatings, the most significant commercial experience has been in the electrogalvanizing industry where coated titanium anodes have supplanted lead and zinc anodes. The coated anodes have achieved operation at current densities as high as 15 kA/m^2, eliminating lead contamination of the product and waste streams (16). Similar anodes are also being utilized in other oxygen-evolving metal-plating systems, such as copper foil production, electrotinning, and electrowinning.

In contrast to the coating wear limitation on anode life experienced in chlorine cells, passivation of the substrate beneath the coating is typically the limiting factor for oxygen-evolving anodes. As a result, technology has been introduced to either maintain or modify the titanium surface (17,18) to increase coating adhesion and significantly improve lifetimes. Anodes having operating lives $>65,000\ \mathrm{kA \cdot h/m^2}$ are readily available (19). Care must be taken, however, to avoid both foreign deposits on the anode surface and operation in reverse current modes, if extended lifetimes are to be expected (20).

6. Structure Design

Each electrolytic application demands a unique approach to anode structure design and fabrication. Factors such as current distribution, gas release, ability to maintain structural tolerances, electrical resistance, and the practicality of recoating must be taken into account. At the outset, chlorine anodes were designed to assume the same configuration as that of a new graphite electrode so that retrofit challenges were minimized. But a variety of newer structure design concepts have been presented to achieve power savings by reduction of the electrolytic gap between the anode and cathode of diaphragm chlorine cells. The most commercially accepted design is that of the expandable anode (Fig. 3) (21).

An expandable anode involves compression of the anode structure using clips during cell assembly so as not to damage the diaphragm already deposited on the cathode (Fig. 3**a**). When the cathode is in position on the anode base, 3-mm diameter spacers are placed over the cathode and the clips removed from the anode. The spring-actuated anode surfaces then move outward to bear on the spacers, creating a controlled 3-mm gap between anode and cathode (Fig. 3**b**). This design has also been applied to cells for the production of sodium chlorate (22).

In mercury chlorine cells, anode surfaces were originally fabricated from expanded titanium mesh or from appropriately spaced titanium rods. More recently it was found that cells operate at lower voltages when fitted with anode structures comprised of triangular rods, as embodied in the runner technology, or of vertical blades (23). Various mercury cell anode designs are shown in Figure 4. In some cases anolyte circulation baffles are incorporated into the anode structure to achieve added power savings by maintaining a higher average brine strength in the electrolytic gap.

The dimensionally stable characteristic of the metal anode made the development of the membrane chlorine cell possible. These cells are typically arranged in an electrolyzer assembly which does not allow for anode-to-cathode gap adjustment after assembly. Also, very close tolerances are required. The latitude that titanium affords the cell designer has made a wide variety of monopolar and bipolar membrane cell designs possible.

When used in radial cells such as for the production of copper foil and in some electrogalvanizing operations, the anode must be curved to meet the shape dictated by the cathodic drum. The anode must also achieve exact tolerances to assure that a constant anode-to-cathode gap is created. Maintaining the dimensional stability of a rigid anode structure is nearly impossible when that unit must endure multiple cycles of high temperature through the coating bake operation. To remedy this situation, an anode plate substrate is fabricated with an arc somewhat greater than that of the drum to which it is to form a match. At this stage, close tolerances are not required, and coating this plate poses no dimensional stability problems. The anode support structure, on the other hand, is fabricated using appropriately demanding accuracy so that when the anode plate is fitted into the support, it can be drawn into position by studs extending from its rear, inactive surface. It thus assumes a fixed position which attains the exact arc that has been specified (24). This design is shown in Figure 5.

7. Manufacturing Technology

Manufacturing techniques for metal-coated anodes have been developed to a high level of sophistication. Whereas in the early 1970s, anode coatings were applied by hand and curing was achieved in batch ovens, by the mid-1990s commercial plants were producing or recoating in excess of 50,000 anodes annually.

This procedure requires continuous coating processes (qv) and the use of electrostatic spray application, robotics, and strict process control (qv). The high cost of the coating itself demands high utilization efficiency. Quality requirements include consistent coating distribution, strong adherence, and a good surface appearance.

The coating process, outlined in Figure 6, starts either with the specification of appropriate titanium substrate material for new anodes, or with removal of existing coating in the case of anode recoating. Coating removal is especially critical in the case of anodes intended for electrogalvanizing service. Using an inappropriate method to remove existing coating can distort or even destroy the anode structure. It can also render the substrate surface incapable of achieving an effective bond with the coating. In the next step, the structure is submitted to a sulfuric or hydrochloric acid etch to prepare the surface for receipt of the new coating. The application of an intermediate layer to inhibit passivation of the substrate may also be prescribed. This also is of importance in oxygen-evolving service.

The coating itself is applied in a series of thin layers. A baking step follows each coat. Strict attention is given to the thermal profile of the preheat/bake/post-cool cycle and to the oven atmosphere to assure effective oxidation. Coating formulations vary considerably, based on the desired use of the anode and upon the proprietary technology of the coating supplier. Traditionally, ruthenium oxide coatings and variations of these coatings have been used in the diaphragm and mercury chlorine cell anodes; iridium may be included to achieve longer coating life in membrane cells. Oxygen-evolving applications require iridium oxide coatings. There is also some latitude in selecting whether water- or alcohol-based solvents are to be used.

The series of high temperature baking steps requires that consideration be given to the dimensional stability of the anode structure. If it is not, thermal warping can render a structure useless or, at a minimum, necessitate excessive and expensive anode-straightening techniques. When the anode structure includes titanium-clad copper components for enhanced conductivity, it is also possible to thermally damage the copper–titanium bond, thus introducing a high resistance to the structure. In some cases, the anode surface to be coated, whether mesh, bar, plates, or screen, etc, must be removed and coated separately in order to avoid damage to the structure's integrity.

In order to ensure that an electrolysis plant maintains a high on-stream factor, continuous and ongoing anode recoating programs are utilized based on removing and recoating the anode prior to coating failure. Allowing coatings to suffer catastrophic failure while in operation can result in a difficult situation owing both to the logistics of anode replacement in the operating circuit as well as the amount of time consumed in reprocessing the structure at the recoating facility. Only a limited number of spare anodes are available. Because as many as 30,000 anodes are required at a world-scale chlorine-producing facility, coating replacement is necessarily an ongoing activity, especially when coating life is relatively short, as in mercury chlorine cells and in electrogalvanizing lines. In cases where coating life extends for a period of 10 years or more, as in diaphragm chlorine cells, coating replacement can involve the use of a periodic recoating program which should be instituted well in advance of any anticipated plant-wide coating failure. For a large chlorine plant, such a program might continue for a period of four to five years.

8. Environmental and Safety Factors

The environmental challenge at the metal anode fabricating and coating plant originates more from the outside than from within the plant itself. The coating plant's process systems must be, of course, designed and operated to control vent stack emissions and impurities in wastewater streams. Sludges containing precious metal must also be appropriately recycled. But the specific tasks and facilities involved in providing these are matters of straightforward shop design and housekeeping.

The primary environmental concern for the coating plant is actually the residual material on the anode structures being returned for recoating. Therefore the anode user must enact effective cleaning procedures prior to shipment. For example, anodes in chlorine use must be cleaned of all traces of mercury and asbestos (qv). Anodes used in electrogalvanizing or in copper-foil production must similarly be cleaned to remove all traces of process materials. If cleaning at the user's plant is not done effectively, the anode may well be shipped back to the user for appropriate action before it is considered for recoating.

Whereas DSA coating operations demand only normal shop procedures for safety and environmental concerns, the commercial realization of this technology has had a most positive impact in the user's plant environment. The replacement of graphite anodes created a cleaner chlorine product in both the diaphragm and mercury cell plants, eliminating both a purification step and a chlorinated sludge disposal problem. Moreover, the dimensionally stable characteristic and long life of the DSA has facilitated the utilization of polymeric, nonasbestos diaphragms and has led to realization of the membrane chlorine cell. This same stability has eliminated the need for frequent adjustment of mercury cell anodes to compensate for wear. Overall, the DSA has made chlorine manufacture cleaner, more consistent, simpler, and therefore safer.

In electrogalvanizing, copper foil, and other oxygen-evolving applications, the greatest environmental contribution has been the elimination of lead-contaminated waste streams through replacement of the lead anode. In addition, the dimensionally stable characteristic of the metal anode introduces greater consistency and simplification of the process, thus creating a measure of predictability, and a resultant increased level of safety.

9. Economic Aspects

For the most part, coated metal anodes are made available by long-term lease rather than through outright sale. There has been a single-source supply protected by patents in most geographic areas. In the majority of cases, the supplier is either a privately owned company or a small unit of a large, complex organization. As the cost-saving and environmental value of this technology continues to increase, upward expectation in respect to prices is created. However, the appearance of new anode producers, together with expiration of some early patents, has created a competitive situation in some applications. This competition can be expected in turn to create a counterbalancing pressure to lower prices.

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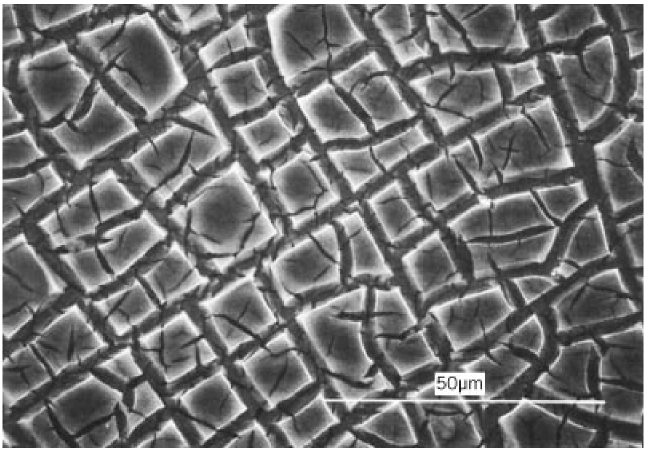

Fig. 1. Scanning electron microscope photograph of DSA ruthenium oxide coating, showing typical cracked surface.

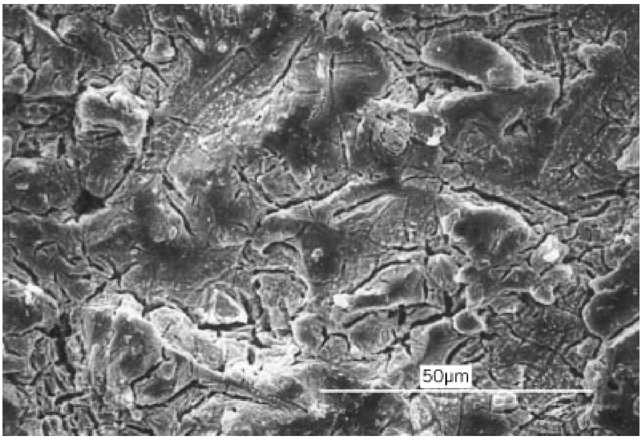

Fig. 2. Scanning electron microscope photograph of platinum–iridium metal coating on titanium.

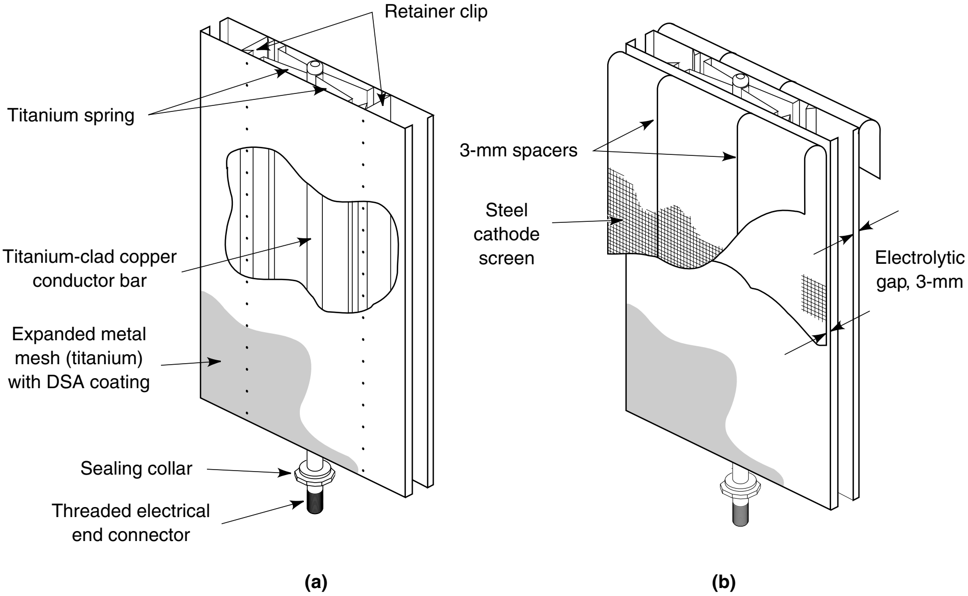

Fig. 3. Expandable anode for diaphragm chlorine cells: (**a**) clamped and (**b**) expanded.

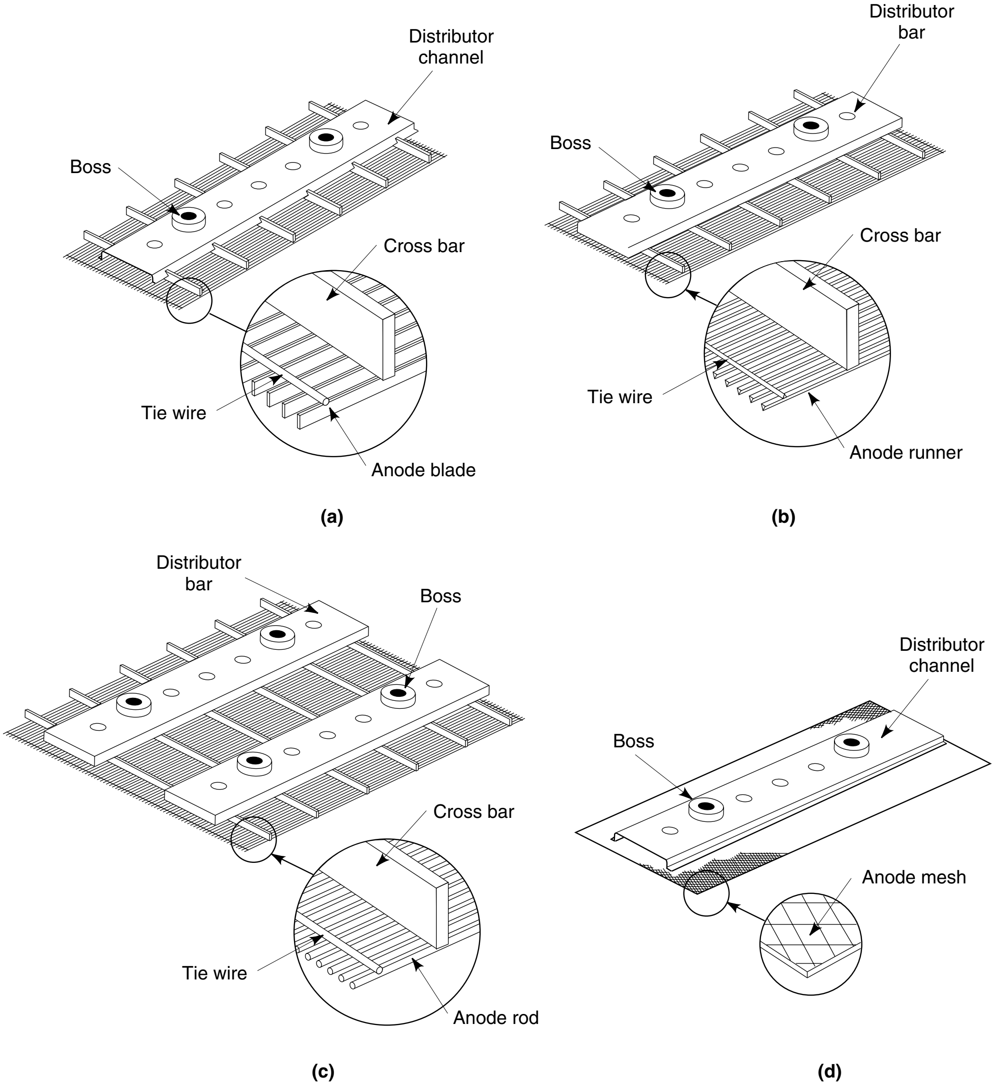

Fig. 4. Configurations of mercury chlorine cell anodes: (**a**) blade type; (**b**) runner technology; (**c**) rod type; and (**d**) mesh type.

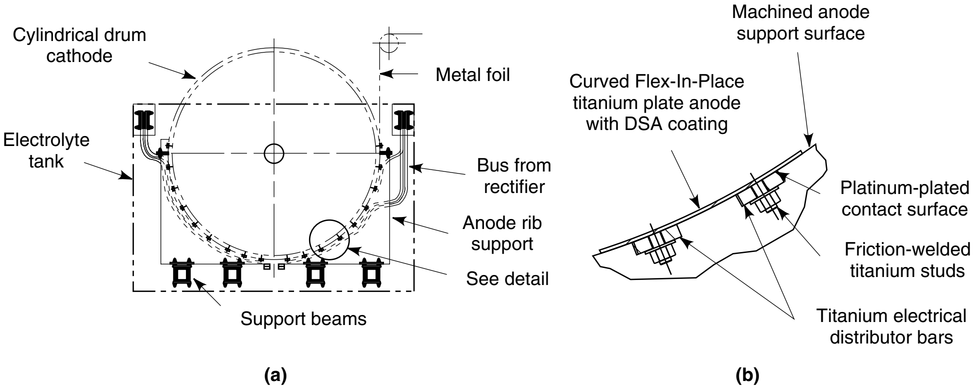

Fig. 5. Radial design for metal anode showing (**a**) cross-sectional view and (**b**) area of detail on drum rim.

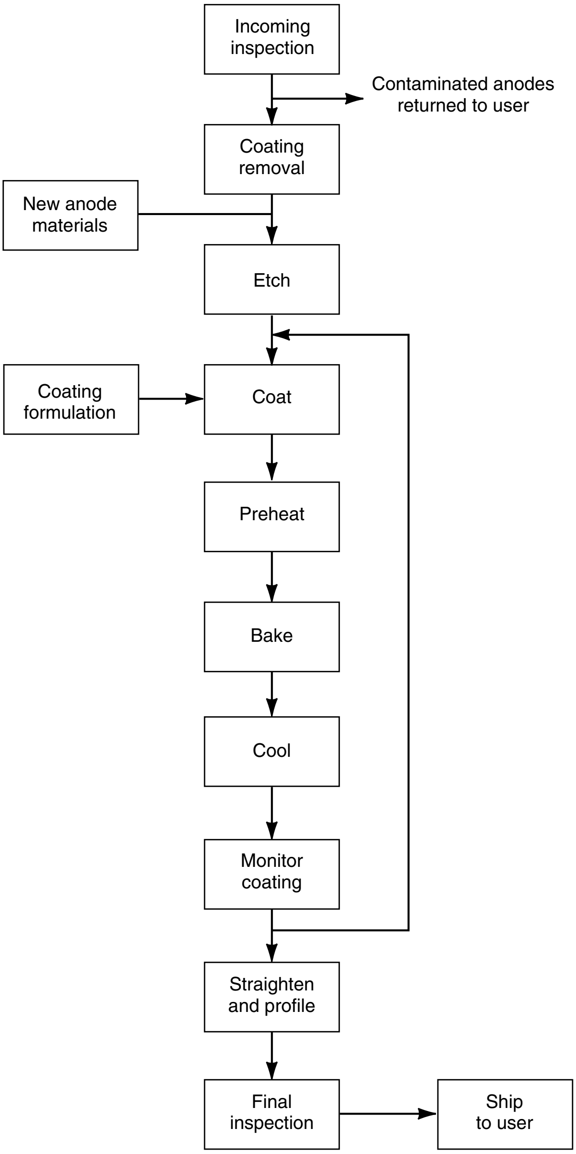

Fig. 6. Metal anode coating process.