

- [54] **ELECTRODES HAVING SILICON BASE MEMBERS**
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References Cited

UNITED STATES PATENTS

- 546,328 9/1795 Hoepfner 204/290 R

1,302,959	5/1919	Page.....	204/290 R
3,491,014	1/1970	Bianchi et al.	204/290 F
3,654,121	4/1972	Keith et al.	204/290 F
3,657,102	4/1972	Keith et al.	204/290 F
3,672,990	6/1972	Beck et al.	204/290 F

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[57] **ABSTRACT**

An electrode is disclosed having an electroconductive surface on an electroconductive silicon substrate. Also disclosed is an electrolytic cell containing an anode having an electroconductive surface on an electroconductive silicon substrate and an electrolytic process for the electrolysis of brines utilizing such an anode.

89 Claims, No Drawings

ELECTRODES HAVING SILICON BASE MEMBERS

This application is a continuation-in-part of U.S. application for U.S. Pat. of Howard H. Hoekje, Ser. No. 260,790, filed June 8, 1972 and is directed to divisional subject matter disclosed in said application.

BACKGROUND OF THE INVENTION

In the past, electrodes for the electrolysis of brines, whether for production of chlorine or alkali metal chlorate, generally have been bulk graphite slabs or plates. While these graphite slabs and plates had satisfactory electroconductivity, they were subject to attack by the electrode products, to erosion, and to ultimate destruction in service.

To a significant extent, the bulk graphite slabs of the prior art have been replaced by metallic electrodes. In their common form metallic electrodes have a valve metal base or substrate with an electroconductive surface usually of noble metal or oxide thereof. Electroconductive substrates that have been suggested include titanium, tantalum, tungsten, niobium and zirconium. Most frequently titanium substrates have been used.

Such coated metal electrodes are, however, characterized by high cost because of the high cost of the titanium metal base as well as the high cost of the noble metal. Attempts to find a lower cost metallic anode have typically been directed to reducing the cost of the electroconductive surface of the electrode. Some attempts have been made, however, to find lower cost substrates. One such attempt is disclosed in U.S. Pat. No. 3,419,014 to G. Bianchi et al involving a base of silicon iron alloy containing 14 through 16 percent silicon. This alloy would appear to be largely Fe_3Si or Fe_2Si , both being iron silicides. Since the alloy itself did not resist the attack of the solution Bianchi proposed addition of small amounts of chromium or molybdenum.

The problem of providing a silicon containing base for anodes used in electrolysis of alkali metal halide brine is complicated by the fact that many of the conductive silicon alloys or silicides are not resistant to anodic attack by the brine solution undergoing electrolysis. Thus, according to the above identified Bianchi patent, the iron silicon (Example 5) alloy had a corrosion rate of 4 mg/hr./cm² when heated in chlorinated brine.

Further, it has been found according to this invention that while pure elemental silicon is sufficiently inert for the purpose it is a very poor conductor of electricity. Thus, despite the relatively low cost of silicon metal, it does not appear to be used in commercial electrolytic production of chlorine.

SUMMARY OF THE INVENTION

It has now been found that silicon in elemental state can be provided with sufficient electroconductivity without impairing seriously its chemical inertness and thus can be effectively used as an electrode substrate for the electrolysis of brine and consequent production of elemental chlorine or alkali metal chlorate. This can be accomplished most satisfactorily by adjusting the composition of the elemental silicon to improve its electroconductivity and by providing the electroconductive silicon with an inert surface or coating which has a low chlorine overvoltage, for example, below 0.25 volt at a current density of 200 amperes per square foot. Such a surface may for example be a coat-

ing of metallic platinum or other metal of the platinum group or ruthenium oxide or other oxide of the platinum group or other electroconductive oxide or other material which does not lose its electroconductivity as electrolysis proceeds over a substantial period of time, say 3 through 12 months or more.

The desired electroconductivity may be imparted to the silicon by doping the silica with electron donor atoms such as phosphorous and/or electron acceptor atoms such as boron. Also conductive silicides may be dispersed in the elemental silicon to achieve electroconductivity. At the same time the presence of impurities or contaminants such as iron, which are soluble or leachable from the electrode during use must be held low enough so that the elemental silicon remains inert.

DESCRIPTION OF THE INVENTION

According to this invention, an electrode is provided having a low overvoltage which comprises an electrolyte resistant electroconductive surface such as metallic platinum or ruthenium oxide on an electroconductive substrate composed partially or completely and preferably predominantly of silicon in elemental state (as distinguished from silicides which may be regarded as compounds of silicon and another metal). While the silicon is in elemental state it contains impurities, doping agents or additives, e.g., boron, phosphorous, etc. or silicides of certain metals dispersed through the silicon which impart conductivity and/or strength to the silicon. The elemental silicon generally is a continuous phase with the other agents dissolved or dispersed therein. However, mixtures of the elemental silicon particles, preferably but not necessarily containing a doping agent, may be fritted or sintered or otherwise bonded together with silicides of other metals. Such an electrode is useful as an anode in the electrolysis of brines, particularly aqueous solutions of the alkali metal chlorides such as sodium chloride, lithium chloride and potassium chloride and is inert to the anodic attack of such solutions. Such electrolysis may be conducted to produce alkali metal chlorate or chlorine. These anodes may be used in either diaphragm cells or mercury cells to produce alkali metal hydroxide and elemental chlorine.

This silicon substrate should be electroconductive and should be at least as electroconductive as graphite, e.g., silicon should have a bulk electrical conductivity in excess of $10^2(\text{ohm-centimeters})^{-1}$ and preferably $10^4(\text{ohm-centimeters})^{-1}$ or higher. Substantially pure silicon, e.g., silicon having a purity in excess of 99.995 atomic percent, is at most a poor conductor, and may even be characterized as a non-conductor having a resistivity of only about 1 ohm-centimeters. It is known that by incorporating small, even trace amounts of boron, phosphorous or other materials, the resulting silicon composition will be electroconductive. According to this invention it has been found that with proper precaution the silicon substrate can be provided in a form which is inert to anodic attack and such substrates can be effectively used to support the conductive surface.

Elemental silicon containing up to 2 percent or even up to 5 percent boron or up to 2 percent phosphorous and negligible amounts of other impurities have been found, according to this invention, to have the desired inertness to anodic attack by aqueous sodium chloride.

The same is true even if the iron content of the elemental silicon is one half to one percent by weight. If, however, an electrode contains enough soluble contaminant, for example iron, substantial anodic attack can occur and the silicon composition is not inert. This attack is evidenced by color development in the electrolyte and even disintegration of the silicon substrate or etching of the surface thereof. Thus, Bianchi U.S. Pat. No. 3,491,014 reports that an iron silicon alloy containing about 16 percent silicon (apparently as iron silicide) when exposed to the sodium chloride solution produced a yellow color. See Bianchi Example II.

I have observed similar coloration using an iron-silicon alloy containing about 65 percent Si and 35 percent Fe by weight. This attack appeared to be reduced when a small amount of boron or phosphorous (about 1 to 2 percent by weight) was introduced into this alloy. However, the iron content of the electrode should rarely be allowed to exceed 40 percent by weight. More resistant substrates are obtained when the elemental silicon concentration is higher; for example, an alloy containing about 75 percent Si and 25 percent Fe contains about 50 percent elemental silicon and is more resistant.

Since many commercial silicon metals contain such soluble or leachable impurities or other metals, care must be taken not to permit contamination of the elemental silicon or to avoid use of elemental silicon contaminated with soluble contaminants to such an extent that the inertness of the substrate or at least of the substrate surface of interface between the electroconductive surface and the electrode interior is impaired.

The required degree of inertness may be readily demonstrated by coating the elemental silicon with a ruthenium oxide coating as in Example 4 below and testing the anode thus produced in the cell and according to the procedure described in Example 4, continuously for at least one week with chlorine being continuously evolved at a current density of 200 amperes per square foot calculated on the area of the coated surface of the sample. If the coated and uncoated sides and the solution do not show readily visible corrosion within this time, the elemental silicon composition may be considered inert for the purpose herein contemplated.

This silicon substrate preferably should further have some physical strength in order to be resistant to impact and abrasion. The physical strength of relative pure silicon metal may be improved by the presence of small amounts of alloying agents such as aluminum, gallium, manganese, and the like. Alternatively, the silicon may be reinforced with iron or other metals which are stronger and less brittle although less resistant to anodic attack of chloride electrolyte so long as these reinforcing materials are covered and protected by the elemental silicon and electrolyte cannot penetrate the elemental silicon to attack the reinforcement.

Particularly desirable substrates are those containing from about 85 atomic percent to about 99.99 atomic percent elemental silicon, and preferably from about 90 atomic percent to about 99.5 atomic percent elemental silicon. By elemental silicon is meant silicon that is present as the metal or element itself having a zero formal valence. In contrast, the silicon of a metal silicide such as FeSi while metallic in character is regarded as a silicon compound. As previously noted, the electrode may contain silicides of other metals. In such a case the elemental silicon content may be lower, for

example as low as 5 to 10 percent by weight although the entire silicon content (elemental and as silicide) may be in excess of 50 percent by weight, preferably above 75 percent by weight.

Preferably either an electron donor such as phosphorous, arsenic, antimony or bismuth, or an electron acceptor such as boron, aluminum, gallium, or the like is present as an additive or dopant in the silicon crystal lattice to impart electroconductivity thereto. When either an electron donor or an electron acceptor is present, it should be present in an amount greater than about 0.01 percent by weight of silicon, e.g., up to 15 percent based on the weight of the electrode. Amounts of such dopants in excess of 10 to 15 percent by weight of the electrode rarely are resorted to because the conductivity required to be imparted can be achieved with amounts in the range of 0.1 to 5 percent by weight of the dopant. However, added amounts of the dopant may be advantageous for other purposes or convenience. Often it is advantageous to hold the concentration of the dopant below 0.5 percent in order to avoid loss in physical strength.

By the presence of small amounts of impurities or doping agents, the electroconductivity of the silicon is increased to in excess of about 10^2 (ohm-centimeters)⁻¹ and preferably to in excess of about 10^4 (ohm-centimeters)⁻¹ or even higher, which is comparable or superior to graphite (and at least as good as metallic conductors such as titanium metal). The presence of electron acceptor atoms such as boron appears also to increase the inertness of the silicon substrate.

The substrate may also contain alloying agents alloyed with or dissolved in or in physical or chemical combination with the elemental silicon, such as silver, aluminum, arsenic, gold, boron, copper, iron, gallium, indium, lithium, manganese, titanium, nickel, zirconium, tin, chromium, antimony, sulfur, or zinc. Such alloying agents are included to provide increased physical strength, easier castability and/or electroconductivity to the silicon base member. Many of them are present as silicides.

Preferably, alloying agents such as aluminum, gallium, and manganese are present in the silicon lattice. Such materials, when present in an amount up to about one half percent by weight and preferably up to about one percent by weight but not greatly in excess of about one and one half percent by weight, increase the ease with which metallic silicon can be cast. Additional amounts thereof do not have a significant impact on castability of the silicon. Furthermore, amounts of aluminum, gallium, and manganese sufficient to result in the formation of large portion of a second, or aluminum or gallium or manganese-rich phase should be avoided as such phase is particularly susceptible to attack by the electrolyte, resulting in a porous, weakened electrode. While the concentration at which such a susceptible phase appears depends on the metallurgical history of the silicon, especially the heating and cooling rates and the working thereof, aluminum, gallium, or manganese concentrations in excess of one and one half percent by weight normally should be avoided or special metallurgic precaution taken to prevent the appearance of such a second phase. Iron in amounts up to 40 percent by weight improve castability and can be present if the tendency of iron to cause disintegration of the anode is overcome as described above.

Various silicides may be present in and/or on the surface of the silicon substrate herein contemplated or generated therein serve to impart electroconductivity to the elemental silicon substrate of the electrodes of this invention or to strengthen or to impart other desirable properties to the elemental silicon. Such silicides include the electroconductive silicides of various metals such as silicides of magnesium, phosphorous, calcium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, copper, arsenic, rubidium, strontium, niobium, molybdenum, platinum, ruthenium, rhodium, palladium, tellurium, cesium, barium, the rare earth metals such as cerium or other metals such as hafnium, tantalum, tungsten, rhenium, osmium and iridium. Of especial value for this purpose are the disilicides of zirconium, titanium, chromium, tantalum, molybdenum, tungsten and vanadium.

Particularly desired silicides which may be present in the substrate of the anode herein contemplated and/or on the surface thereof are the electrolyte resistant, highly electroconductive silicides, such as the silicides of metals of Group IV, V and VI, e.g., $TiSi_2$, $ZrSi_2$, VSi_2 , $NbSi_2$, $TaSi_2$, and WSi_2 and the heavy metal silicides, e.g. Cr_3Si , Cr_5Si_3 , $CrSi$, $CrSi_2$ and $MoSi_2$ as well as cobalt silicides $CoSi_2$. When it is necessary or advisable to avoid reducing too greatly the physical strength of the silicon base member, the amount of silicide present is kept to a minimum (inasmuch as some silicides incorporated in the silicon lattice or dispersed through the silicon reduce physical strength) and may reduce the chemical inertness even though silicides have the benefit of increasing the bulk electroconductivity of the silicon bases. For such reasons, silicide concentrations of less than about 5 weight percent of the silicon base member, and preferably less than about 2 weight percent of the silicon base member are contemplated.

On the other hand, some silicides such as chromium silicides or the silicides of nickel, cobalt, vanadium, or tungsten may be used in higher amounts, for example up to 50 to 75 percent by weight so long as a substantial amount of elemental silicon is present. Such silicides being highly conductive impart enough electroconductivity to the silicon that electron donor atoms or acceptor atoms may not be needed. Such silicide-elemental silicon mixtures may contain in excess of 60 percent preferably above 75 percent Si even though elemental Si may be as low as 10 to 25 percent.

The silicon substrates useful in providing the anodes of this invention may be in the form of single castings of the elemental silicon or composition containing elemental silicon or rolled sheet, screen or other conventional anode form thereof. Castings should have a thickness sufficient to impart mechanical strength to the anode. This will vary with the strength of the metallic silicon. Even for relatively brittle silicon a thickness of a quarter of an inch or more and preferably up to about 2 or more inches rarely above 3 inches is adequate. Such castings should have sufficient surface area to provide economical electrodes, and may range from about 2 to about 6 feet in the longer dimension and from about 1 to about 4 feet in the shorter dimension. Electrodes of larger size may be cast and utilized if suitable support means are provided therefor. When the bulk silicon castings are coated with a suitable electroconductive surface, as will be described hereinafter, and installed in an electrolytic cell, e.g., of the diaphragm type, they provide a very satisfactory anode for

the evolution of chlorine. They also may be used as anodes for mercury cells commonly used to produce chlorine and alkali metal amalgam.

Alternatively, the silicon substrates useful in providing the anodes of this invention may be in the form of an internally reinforced silicon. Such reinforced silicon slabs or structures will typically contain a mesh work, lattice work, rods, wires, fibers or bars of suitable reinforcing material stronger, or at least less brittle than elemental silicon within the metallic silicon. The reinforcing material may be elemental or metallic titanium, zirconium, steel, iron, cobalt, nickel, molybdenum, or copper. Fibrous quartz can also be used. Such materials should have a higher melting point than metallic silicon around which the metallic silicon may be cast or to which the elemental silicon may be applied as a coating. Preferably the reinforcing material is one having a rate of formation of the silicide at the temperatures of molten silicon (about 1,420°C.) that is minimal or at least silicide formation is minimized by holding the reinforcing material at a temperature below silicide formation by recourse to external cooling.

According to still another exemplification of this invention, the silicon may be a laminate on a suitable electroconductive material. For example, the silicon may be present as a thin film, for example, up to about one-thirty-second or one-sixteenth of an inch or greater on a suitable stronger or less brittle metallic base. The base may be metallic iron, steel, cobalt, nickel, titanium, molybdenum or copper or other less costly base. Alternatively the base member may be "INVAR," an alloy of iron and nickel containing approximately 40 percent nickel and 60 percent iron, and having a thermal coefficient of expansion approximately the same as that of silicon. Conveniently the silicon may be present as a sheet suitably bonded to a metallic substrate to form a laminate.

In all of these cases the electroconductive coating (or the innermost undercoating thereof where a plurality of coatings are applied) is in contact with silicon of the substrate.

For most purposes, the silicon substrates useful in providing the electrodes of this invention are substantially impervious to the electrolyte. That is, the silicon itself is characterized by the substantial absence of pores and interstices such that the interior of the silicon mass and certainly any reinforcing material therein is not wet by the electrolyte. However, the silicon itself may have some surface roughness and some porosity at or near the surface. Moreover, the electrodes of this invention may be in the form of arrays of rods and bars, or in the form of mesh, or perforate or foraminous sheets or even coarse particles or fritted coarse particles thereby allowing the passage of electrolyte around the bulk silicon masses. Such electrodes, while themselves macroscopically electrolyte permeable to the bulk flow of electrolyte have members that are microscopically impermeable to the flow of electrolyte within the interior of the substrate mass itself.

Elemental silicon, when used as an anode for electrolysis of brine displays only slight electrochemical action or effect — even at relatively high voltage. Even this slight electrochemical activity rapidly diminishes as electrolysis is continued. This is probably due to formation of a film of silicon dioxide and/or other oxides or suboxides of silicon on the exposed portions of the sili-

con base rendering the exposed silicon portions of the base non-conductive.

For this reason, a suitable inert electroconductive surface is provided on any silicon exposed to the electrolyte. This surface may cover that portion which is otherwise uncoated with platinum or other electroconductive coating.

The preferred materials used for the electroconductive coating are those which are electroconductive, chemically inert or resistant to anodic attack. They are known and used in the art for the evolution of chlorine. Many of these materials have a low chlorine overvoltage, e.g. less than 0.25 volts at a current density of 200 amperes per square foot.

A suitable method of determining chlorine overvoltage is as follows;

A two-compartment cell constructed of polytetrafluorethylene with a diaphragm composed of asbestos paper is used in the measurement of chlorine overpotentials. A stream of water-saturated Cl_2 gas is dispersed into a vessel containing saturated NaCl , and the resulting Cl_2 -saturated brine is continuously pumped into the anode chamber of the cell. In normal operation, the temperature of the electrolyte ranges from 30° to 35°C ., most commonly 32°C ., at a pH of 4.0. A platinized titanium cathode is used.

In operation, an anode is mounted to a titanium holder by means of titanium bar clamps. Two electrical leads are attached to the anode; one of these carries the applied current between anode and cathode at the voltage required to cause continuous generation of chlorine. The second is connected to one input of a high impedance voltmeter. A Luggin tip made of glass is brought up to the anode surface. This communicates via a salt bridge filled with anolyte with a saturated calomel half cell. Usually employed is a Beckman miniature fiber junction calomel such as catalog No. 39270, but any equivalent one would be satisfactory. The lead from the calomel cell is attached to the second input of the voltmeter and the potential read.

Calculation of the overvoltage, η , is as follows:

The International Union of Pure and Applied Chemistry sign convention is used, and the Nernst equation taken in the following form:

$$E = E_0 + 2.303 RT/nF \log [\text{oxidized}]/[\text{reduced}]$$

Concentrations are used for the terms in brackets instead of the more correct activities.

E_0 = the standard state reversible potential = +1.35 volts

n = number of electrons equivalent $^{-1}$ = 1

R , gas constant, = 8.314 joule deg $^{-1}$ mole $^{-1}$

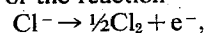
F , the Faraday = 96,500 coulombs equivalent $^{-1}$

Cl_2 concentration = 1 atm

Cl^- concentration = 5.4 equivalent liter $^{-1}$ (equivalent to 305 grams NaCl per liter)

$T = 305^\circ\text{K}$

For the reaction



$$E = 1.35 + 0.060 \log 1/5.4 = 1.30$$

This is the reversible potential for the system at the operating conditions. The overvoltage on the normal hydrogen scale is, therefore,

$$\eta = V - [E - 0.24]$$

where

V is the measured voltage,

E is the reversible potential,

1.30, 0.24 is the potential of the saturated calomel half cell.

The preferred materials are further characterized by their chemical stability and resistance to chlorine attack or to anodic attack in the course of electrolysis.

Suitable coating materials include the platinum group metals, platinum, ruthenium, rhodium, palladium, osmium, and iridium. The platinum group metals may be present in the form of mixtures or alloys such as palladium with platinum or platinum with iridium. An especially satisfactory palladium-platinum combination contains up to about 15 percent platinum and the balance palladium. Another particularly satisfactory coating is metallic platinum with iridium, especially when containing from about 10 to about 35 percent iridium. Other suitable metal combinations include ruthenium and osmium, ruthenium and iridium, ruthenium and platinum, rhodium and osmium, rhodium and iridium, rhodium and platinum, palladium and osmium, and palladium and iridium. The production or use of many of these coatings on other substrates are disclosed in U.S. Pat. Nos. 3,630,768, 3,491,014, 3,242,059, 3,236,756 and others.

The electroconductive material also may be present in the form of an oxide of a metal of the platinum group such as ruthenium oxide, rhodium oxide, palladium oxide, osmium oxide, iridium oxide, and platinum oxide. The oxides may also be a mixture of platinum group metal oxides, such as platinum oxide with palladium oxide, rhodium oxide with platinum oxide, ruthenium oxide with platinum oxide, rhodium oxide with iridium oxide, rhodium oxide with osmium oxide, rhodium oxide with platinum oxide, ruthenium oxide with platinum oxide, ruthenium oxide with iridium oxide, and ruthenium oxide with osmium oxide.

There may also be present in the electroconductive surface, oxides which themselves are non-conductive or have low conductivity. Such materials, while having low bulk conductivities themselves, may nevertheless provide good conductive films with the above mentioned platinum group oxide and may have open or porous structures thereby permitting the flow of electrolyte and electrical current therethrough or may serve to more tightly bond the oxide of the platinum metal to the silicon base. For example, aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, niobium oxide, hafnium oxide, tantalum oxide, or tungsten oxide may be present with the more highly conductive platinum group oxide in the surface coating. Where a plurality of oxide coatings are applied it is advantageous to apply the outer coatings as mixtures of the type here described. Carbides, nitrides and silicides of these metals or of the platinum group metals also may be used to provide the electroconductive surface. For example, an electrode may be provided having an elemental silicon base or substrate with a surface thereon containing a mixed oxide coating comprising ruthenium dioxide and titanium dioxide, or ruthenium dioxide and zirconia, or ruthenium dioxide and tantalum dioxide. Additionally, the mixed oxide may also contain metallic platinum, osmium, or iridium. Oxide coatings suitable for the purpose herein contemplated are described in U.S. Pat. No. 3,632,408 granted to H. B. Beer.

According to a further embodiment, the silicon base electrodes of this invention may have a surface composed at least partially or even wholly of an electroconductive inert metal silicide such as silicide of a platinum

group metal. The electroconductive silicide surface of the electrode may be provided by those silicides having a satisfactory electroconductivity, and further, having chemical resistance to the anolyte and the evolved anodic product. Such a silicide-containing surface may, moreover, be a combination of two or more silicides, both characterized by their substantial resistance to chemical attack by the anolyte and the evolved anodic product, but only one of the silicides having a high electrical conductivity and a low chlorine overvoltage effect in the evolution of chlorine.

Especially good electroconductive, electrolyte-resistant silicides for this purpose include silicides of the platinum group metals, that is, platinum silicide, palladium silicide, iridium silicide, rhodium silicide and ruthenium silicide. Many such silicides have the formula M_xSi_y , where M is the metal and x and y each are 1 to 5. Other silicides having sufficiently high conductivity and fairly good chemical resistance to the anolyte products include the chromium silicide CrSi, Cr_5Si_3 and $CrSi_2$, cobalt silicide CoSi, nickel silicide NiSi, titanium silicide TiSi₂, vanadium silicide VSi₂, zirconium silicide ZrSi₂, niobium silicide, hafnium silicide tantalum silicide TaSi₂, and tungsten silicide.

As a general rule several coatings of the conductive material (platinum or the like) are deposited successively one upon the other in order to build up the thickness of the coating and reduce its permeability to electrolyte. Because of the high cost of the noble metal however, the coating is comparatively thin, usually being less than 0.001 inches, rarely over a few thousandths of an inch in thickness. Consequently, the coatings are porous and permeable to electrolyte and thus the silicon of the substrate, which contacts the conductive inner layer or layers, itself becomes exposed to anodic attack as it is used. It is especially for this reason that this silicon must be inert; otherwise the support for the coating becomes etched away and the coating flakes off the electrode.

According to a very effective embodiment, the first undercoating may be composed of a mixture of a platinum group silicide and a platinum group metal or oxide thereof or alternatively, all of the platinum group metal in such undercoating may be in the form of a silicide. This may be effectively accomplished by applying the platinum group metal or metal oxide coating to the silicon base and then heating, for example at 500°–1,100°C. until the silicon has reacted with the coating to form a silicide of the platinum group metal e.g., PtSi₂, PdSi₂, or RuSi₂. Thereafter subsequent coatings of the platinum group metal or platinum group metal oxides may be applied. Alternatively, the outer coatings may be deposited as silicides, for example by applying to the silicon base coatings a solution of silicon resinate or other silicon ester and platinum resinate or other platinum group resinate and heating the resulting coating at 350°–500°C. to cause production of platinum metal and the platinum silicide. In similar way, an ethyl alcohol solution of silicon tetrachloride and platinum group chloride may be applied and heated to deposit a silicide coating.

The proportion of platinum group silicide to metal or metal oxide may be varied by varying the amount of silicon resinate or other silicon ester. Generally about one equivalent of silicon resinate to 2 to 5 equivalents of platinum resinate is used and the coating ranges from

10 to 50 percent platinum silicide, the balance being platinum metal.

Other electroconductive coatings which may be deposited on the silicon base are the bimetal and trimetal spinels. Such spinels include $MgFeAlO_4$, $NiFeAlO_4$, $CuAl_2O_4$, $CoAl_2O_4$, $FeAl_2O_4$, $FeAlFeO_4$, $NiAl_2O_4$, $MoAl_2O_4$, $MgFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, $CdFe_2O_4$, $PbFe_2O_4$, $MgCo_2O_4$, $ZnCo_2O_4$, and $NeNi_2O_4$. The preferred bimetal spinels are the heavy metal aluminates, e.g. cobalt aluminate ($CoAl_2O_4$), nickel aluminate ($NiAl_2O_4$) and the iron aluminates ($FeAlFeO_4$, $FeAl_2O_4$). The bimetal spinels may be present as discrete clusters on the surface of the silicon substrate. A particularly satisfactory electrode is provided by an outer surface containing discrete masses of cobalt aluminate on a silicon substrate having an underlying platinum coating thereon from 2 to 100 or more micro-inches thick disposed on the substrate. The bimetal spinels may also be present as a porous, external layer, with a conductive layer of platinum group metal or platinum group metal oxide, e.g. ruthenium oxide or platinum interposed between the base and the spinel coating. The bimetal spinel layer, having a porosity of from about 0.70 to about 0.95, and a thickness of from about 100 micro-inches to about 400 or more micro-inches thick provides added sites for surface catalyzed reactions. A particularly satisfactory electrode may be provided according to this exemplification having an electroconductive silicon substrate, an intermediate layer of platinum from 10 to 100 micro-inches thick, and a layer of cobalt aluminate spinel having a porosity of from about 0.70 to about 0.95 and a thickness of from about 100 to about 400 micro-inches thick. Alternatively, especially for mercury cathode cell service, ruthenium dioxide may be substituted for the platinum, providing an electrode having a silicon substrate, a ruthenium dioxide layer in electrical and mechanical contact with the silicon substrate, and a layer of spinel on the ruthenium dioxide layer.

As stated above, the electrodes of this invention are utilized as anodes in electrolytic cells for the electrolysis of brines. In one embodiment of this exemplification, anodes are used in monopolar diaphragm cells of the type characterized as Hooker type cells. In Hooker type cells, the anodes in the form of slabs are held vertically and bonded to a base or bottom members of the cell. Typically, this bonding is accomplished by embedding the silicon base anodes of this invention in a pool of molten lead on the upper surface of the base member of the cell, and in contact with the base member. When the electrodes of this invention are used in such diaphragm type cells, the silicon base anodes may be thick slabs on the order of from about ½ inch to about 2 inches in thickness. In this way since they have approximately the same dimensions as graphite electrodes, they may be used in presently existing Hooker type cells without expensive reconstruction or redesign of the cells or the cell bottom.

According to an alternative exemplification, the silicon base anode may be bolted, welded, or metallurgically joined to the base member of the monopolar diaphragm cell. The metal base of the cell, most commonly iron or steel, may then be covered with a suitable electrolyte resistant material, e.g., asphalt or rubber to protect the base from the electrolyte. In this way the lead surface of the electrolytic cell base may be dispensed with.

According to an embodiment of this invention desired doping agents, e.g., boron, phosphorus, etc., may be readily incorporated in the silicon by mixing the elemental silicon with a compound of the doping agent, particularly a compound of such agent which melts with the silicon or reacts with molten elemental silicon. To incorporate a small amount of boron into the elemental silicon it is convenient to melt the silicon with a readily meltable boron compound or flux such as boric oxide or alkali metal borates, e.g., sodium borate or sodium tetraborate. In the course of melting, the mixture stratifies into a silicon metal layer and a layer or scum of the boron compound or the silicon reaction product thereof. However, the silicon picks up boron from the boron flux and thus becomes electroconductive. At the same time the alkali metal borate is at least partially converted to silicate. Similar results are obtained with other boron compounds.

Similarly when an alkali metal phosphate or other solid or liquid phosphorous compound such as trisodium phosphate is melted with the silicon the elemental silicon takes up phosphorus from the phosphorus compound.

Thus these compounds may be used both as a flux to facilitate melting and/or to protect the surface of molten silicon from attack by the surrounding atmosphere, and a source of the donor atom or acceptor atom. The flux may be added to the silicon prior to melting and/or casting.

Other fluxes which decrease the surface tension of the molten silicon, and either form a protective layer over the molten silicious glass in the presence of silicon or react with oxygen-containing compounds of silicon to form a low density melt, and are slightly basic, such as alkali metal carbonates, sodium carbonate and sodium bicarbonate, may be used to facilitate casting and to remove oxygen and other impurities, or to protect the silicon from oxidation.

The amount of flux added is dependent on the amount of oxide present and is a matter of simple testing. Generally, the flux powder used should be at least enough to provide at least a one millimeter (usually not over 10 millimeters thick coating of powder on the surface of the element silicon particles and/or to provide a liquid flux layer over the top of the molten silicon. As a rule the amount of flux is at least 5 percent by weight of the silicon and generally is in the range of 10 to 20 percent of such weight. The depth of the flux layer rarely exceeds the depth of the metal layer.

It is convenient to introduce the boron or like material into the silicon by reacting part of the elemental silicon with a compound of the donor or acceptor element. In general the reaction should take place either before or during the melting of the silicon so that the resulting donor or acceptor atom may be uniformly dispersed in the residual molten elemental silicon. So long as the element is below silicon in the electromotive series (considering sodium adjacent the upper end and gold adjacent the lower end of the series) the desired metal may be introduced by reacting a compound of such metal with part of the elemental silicon leaving the remainder of the elemental silicon to absorb and take up, possibly as a silicide, the desired metal.

In this way the amount of the desired metal to be introduced in the silicon may be controlled simply by limiting or controlling the amount of compound of the desired metal or element which is to be introduced rela-

tive to the elemental silicon present. In the case of acceptor or donor atoms, very small amounts for example 0.005 weight percent or more may be introduced into the silicon. Larger amounts, ranging up to 2 percent or even higher may be required or desired. The amount of such atoms rarely is in excess of 10 percent by weight unless the element imparts further desirable properties such as strength, chemical resistance, etc., to the elemental silicon composition.

Of course the donor or acceptor atoms may be added in metallic state. For example, metallic boron may be melted with elemental silicon.

As has been noted physical and/or electrical properties may be enhanced by incorporating in the elemental silicon amounts of metals such as aluminum, gallium, chromium, manganese or other metals. Most of these, which are below silicon in the electromotive series also may be incorporated by contacting the elemental silicon with a compound thereof in the same way as has been described above. Alternatively the metals as such may be mixed and melted with the silicon in melted state. The result in any event is to produce a mixture of the element with the resulting silicide of the added metal the elemental silicon usually being the continuous phase in which the silicide is dissolved or dispersed. Such products may contain as low as 5 to 10 percent of elemental silicon although the total silicon as element and silicide usually is in excess of 50 percent by weight — generally in excess of 75 percent by weight.

Further enhancement of the mechanical and electrical properties of the silicon may be obtained by various metallurgical means. For example, the silicon after casting may be hot rolled. Hot rolling should be carried out above the softening point of the silicon, e.g., above about 600°C.

The silicon substrate may also be in the form of a sheath having a less inert core containing less silicon or even no silicon, for example, a layer of silicon metal. It may be deposited upon a copper, a steel or iron core by any of the means known in the art such as vapor phase deposition, vacuum sputtering, ion bombardment, metal cementation, thermal decomposition of silicon tetrachloride and hydrogen on the core. The core members themselves are materials that are more electroconductive than metallic silicon, but not necessarily as resistive to the electrolyte as the silicon. Such core materials include the valve metals, titanium, tantalum, tungsten, vanadium, hafnium, and zirconium. Such materials also include iron, steel, cobalt, nickel, copper, aluminum and INVAR among others. Furthermore, the base member may also be graphite. As described hereinbefore, the surface of silicon substrates of this invention have an electroconductive surface thereon.

Electroconductive surfaces on the silicon member may be provided by any of a number of expedients well known in the art or as described in the above identified patents. For example, salts of the precious metals may be thermally decomposed on the surface of the silicon to yield the electroconductive surface. In this manner, coatings of ruthenium chloride, rhodium chloride, platinum chloride, platinum resinate, ruthenium resinate or other organic or inorganic platinum group compound may be deposited on the surface of the silicon and decomposed by heating at 300°–600°C. in air or in an

inert atmosphere to provide a suitable electroconductive surface thereon.

Before applying the coatings to the silicon surface it is necessary to prepare the silicon for coating by etching or pickling with a suitable acid. Best results are obtained by subjecting the base to the action of hydrogen fluoride in aqueous solution or an acidic solution containing fluoride. Suitable acid pickling solutions include solutions of a mineral acid such as HCl or HNO₃ containing a small amount of fluoride ions conveniently as hydrofluoric acid.

The surface also may be pickled in an alkaline solution such as an aqueous solution of alkali metal fluoride and alkali metal hydroxide. Alternatively the conductive metal coating may be applied to the silicon by electrodeposition, electroless deposition, cathodic electrophoresis, vacuum sputtering, metallic cementation, or powder metallurgy.

According to a suitable method of applying silicide coatings of high silicide concentration to the electrode substrate of this invention, the metal used in preparing the electroconductive, electrocatalytic silicide, e.g., platinum may be sputtered onto the silicon substrate. Thereafter, the silicon substrate may be heated at 500° - 1,100°C. to obtain the proper amount of electroconductive silicide. Thereafter, the remaining metal may be back-sputtered from the silicon-based electrode, thereby providing a silicide electrode surface which contains little or only a small amount of free metal on a silicon base.

The electrodes thus obtained are capable of use without corrosion or decomposition for long periods of time and particularly for the production of chlorine both in diaphragm type and mercury cells. However, it is not limited to such use. The anodes herein contemplated may be used in electrochemical reactions wherever a corrosion-resistant anode or at least one having long life is desired. Thus, electrodes can be used for production of alkali metal chlorate. Alternatively, the electrolyte in the cell may be a salt of a metal, e.g., copper or nickel chloride, nitrate or sulfate from which copper or nickel may be electrodeposited by electrolysis of the solution between the elemental silicon base anode and a cathode to electrodeposit the metal on the cathode. Copper, nickel, iron, manganese, and the like may be so deposited from these salts.

The electrolytic oxidation of organic compounds, e.g., propylene to propylene oxide or propylene glycol may be performed using such anodes. Moreover, metal structures such as ships' hulls may be cathodically protected using these anodes. In each case, the cell comprises the anode having the elemental silicon substrate herein contemplated, a cathode, and means to impose an external voltage or electromotive force between the anode and cathode whereby the anode is positively charged with reference to the cathode. The following examples are illustrative.

EXAMPLE I

An electrode was prepared having a ruthenium dioxide surface on a rough metallic silicon substrate. An irregular piece of elemental silicon containing 99.5 percent by weight silicon, and approximately 0.25 weight percent each of iron and aluminum, and measuring approximately 2 inches by 1½ inches by ½ inch was etched in a 2 percent hydrofluoric acid solution in

percent hydrochloric acid for 10 minutes. Thereafter, it was rinsed with water and dried.

A solution was prepared containing 2 grams of RuCl₃ · 3H₂O in 18 grams of ethyl alcohol. Four coats of this solution were brushed onto one surface of the silicon piece. After each coat was applied, the silicon piece was heated at the rate of 50°C. for 5 minutes to a temperature of 350°C. and maintained thereat for 10 minutes. After the fourth coat the chunk was heated at the rate of 50°C. for 5 minutes to a temperature of 450°C. and maintained thereat for 40 minutes.

Thereafter, the silicon was inserted in a laboratory diaphragm cell. The laboratory diaphragm cell was a 2 liter beaker containing a catholyte compartment. The catholyte compartment was a plastic cube open to the atmosphere at the top and having one side open. An asbestos diaphragm of approximately 1/16 inch thickness was across the open side. The cathode of the laboratory diaphragm cell was a platinized titanium coupon.

The anolyte was brine containing 310 grams per liter of sodium chloride adjusted to a pH of 3.5 by the addition of hydrochloric acid. Electrolysis was commenced at a current of 0.65 amperes and chlorine was observed to be evolved on the anode. The cell voltage was 3.20 volts. At a current of 1.30 amperes the cell voltage was 4.40 volts. The ruthenium dioxide-coated surface of the silicon-based anode was estimated to be approximately 6.5 square centimeters.

EXAMPLE II

An electrode was prepared having a silicon substrate with a platinum surface. Silicon of the type described in Example I in the form of irregular pieces measuring approximately 2 inches by 2 inches by ½ inch, and containing approximately 99.5 weight percent silicon and approximately 0.25 weight percent each of iron and aluminum was placed in a graphite crucible. Sodium tetraborate powder was added to the silicon. Sufficient sodium tetraborate powder was added to provide approximately 1 cubic centimeter of powder per square centimeter of surface area of the silicon. The crucible containing the silicon was heated to a temperature of approximately 1,500°C. and maintained thereat for approximately 30 minutes. While the silicon was still liquid it was poured into graphite molds, cast into silicon coupons 4¼ inches long by ¾ inch wide by 5/16 inch thick. It contained about 1 percent by weight of boron.

The resulting coupon was cleaned with emery cloth and thereafter with Comet. It was then rinsed in distilled water and etched in a solution of 5 percent sodium fluoride and 2 percent potassium hydroxide in water for 15 minutes. It was then rinsed in water and dried. The coupon was masked with "Teflon" (TM) tape, leaving one exposed surface.

A solution was prepared containing 525 milliliters of absolute ethyl alcohol, 125 milliliters of concentrated sulfuric acid, 70 milliliters of toluene, 17.8 grams of chloroplatinic acid, and 2.0 grams of rhodium trichloride. The silicon coupon was inserted in the platinum solution and plated as a cathode at a current density of 30 amperes per square foot for 45 minutes. Thereafter, the platinum-plated coupon was removed from the solution, rinsed in water, and dried. The platinum-plated coupon was then placed in an oven exposed to the atmosphere and heated to 350°C. in 7 minutes. The coupon was maintained at 350°C. for 30 minutes.

Thereafter, the silicon electrode having a metallic platinum surface thereon was inserted in a laboratory diaphragm cell. The diaphragm cell had an iron mesh cathode separated from the anode by a 1/16 inch thick asbestos paper diaphragm. The anolyte was brine containing 310 grams per liter of sodium chloride adjusted to a pH of 3.5 by the addition of hydrochloric acid. Electrolysis was commenced at a current density of 200 amperes per square foot and chlorine was seen to be evolved. The initial cell voltage was 2.85 volts. After 24 hours of electrolysis the cell voltage stabilized at 2.94 volts. After 49 days of electrolysis the cell voltage was 2.94 volts.

EXAMPLE III

A silicon coupon was prepared having a platinum surface thereon.

Pieces of silicon measuring approximately 2 inches by 2 inches by 1/8 inch and containing approximately 99.5 percent silicon and the balance iron and aluminum, were placed in a graphite crucible and sufficient sodium tetraborate powder was added to provide a film of approximately 1/10 of a cubic centimeter of sodium tetraborate per square centimeter of surface area of the silicon. To this was added aluminum pellets constituting about 1 percent by weight of total aluminum and silicon in the crucible. The crucible containing the silicon, with sodium tetraborate and metallic aluminum added, was then placed in an electric-resistant furnace open to the atmosphere. The crucible-containing silicon was heated to approximately 1,520°C. and maintained thereat for approximately 30 minutes. Thereafter, the crucible was removed from the furnace and the silicon poured into quartz molds. The resulting piece measuring 3.8 centimeters by 0.7 centimeters by 1.8 centimeters was removed from the mold and permitted to cool. Thereafter it was etched in a 5 weight percent sodium fluoride, 2 weight percent potassium hydroxide solution in water. It was then rinsed in distilled water, dried, rinsed in acetone and dried.

A solution was prepared containing 525 milliliters of absolute ethyl alcohol, 125 milliliters of concentrated sulfuric acid, 70 milliliters of toluene, 17.8 grams of chloroplatinic acid, and 2.0 grams of rhodium trichloride. The coupon was inserted in this solution and made the cathode of an electrolytic cell. Platinum was plated from the organic platinum bath described above onto the silicon cathode. Electroplating was conducted at a current density of 30 amperes per square foot for 20 minutes. Thereafter the coupon was removed from the electroplating solution, rinsed in water, and dried. It was then placed in an oven and heated to 350°C. for 15 minutes. The coupon was kept at 350°C. for 15 minutes. Thereafter the coupon was masked with "Teflon" (TM) tape except for an area measuring 1.4 centimeters by 1.2 centimeters. The coupon was placed in a laboratory diaphragm cell described in EXAMPLE I hereinabove. At a current density of approximately 100 amperes per square foot chlorine was observed to be evolved and the cell voltage varied between 2.5 and 2.7 volts. After 22 hours of electrolysis cell voltage varied between 3.5 and 3.7 volts.

EXAMPLE IV

The silicon metal used in this example had the following composition:

		percent by weight
Manganese	0.017	do.
Magnesium	0.009	do.
Iron	0.31	do.
Chromium	less than 0.002	do.
Aluminum	0.05	do.
Calcium	0.009	do.
Vanadium	0.05	do.
Titanium	0.04	do.
Copper	0.098	do.
Nickel	0.01	do.
Zirconium	less than 0.002	do.

the balance being elemental silicon. It had a resistivity of about one ohm centimeters.

Four-hundred grams of the silicon metal in the form of pieces about 1/2 inch in diameter was mixed with 20 grams of powdered sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and 20 grams of powdered sodium acid phosphate (Na_2HPO_4). The resulting mixture was heated in a crucible to 1570°C. for 90 minutes and the mixture melted to form a layer of molten silicon with a slag on top. The molten silicon metal was poured into the cavity of a graphite mold preheated to 650°C. for 90 minutes. The mold had a cavity of 1 inch by 1 inch by 5 1/4 inches and after the silicon metal had been poured in, the mold was allowed to stand until it had cooled to room temperature. A good silicon casting containing about one percent phosphorous and about one percent boron was obtained. It had a resistivity of about 4×10^{-4} ohm-centimeters.

The casting was cut in two to obtain a rectangular piece 5 inches by 3/4 inches by 7/32 inches. The cut piece was immersed in 2.5 Normal NaOH aqueous solution at 98°C. for 30 minutes. Then the sample was washed with distilled water, dried and coated on its uncut side by brush with a solution of 1.5 grams of ruthenium chloride (RuCl_3) containing 38.26 percent by weight of Ru (the balance being chloride and water of crystallization) in 9 grams of ethyl alcohol and the coated piece was heated at 350°C. for 8 minutes and allowed to cool to room temperature. The cooled piece was recoated and reheated in the same way.

The coated side was given four additional coats in the same way using a solution of:

1.2 grams of	RuCl_3 solution containing 1 gram of the above ruthenium chloride in 4 grams of methanol.
2 grams of	TiCl_3 solution containing 8 percent by weight of TiCl_3 in 15 percent by weight HCl aqueous solution.
0.5 grams of	Aqueous hydrogen peroxide containing 30 percent H_2O_2 .
1 gram	Methanol

After each coating, the coated piece was heated to 350°C. for 8 minutes. After the fourth coating the coated piece was further heated to 450°C. and held at 450°C. for 30 minutes.

The coated piece was placed as an anode in a glass container having vertically mounted therein a cylindrical iron screen cathode about 2 inches in diameter and 5 1/2 inches high, the piece being hung vertically with a coated face thereof opposite the outer side of the cathode. The cathode had an asbestos diaphragm on its outer side. The spacing between anode and cathode 1/4 to 1/2 inch.

An aqueous solution containing 305 grams of sodium chloride per liter of solution and having a pH of 10 was

continuously fed into the cell at a rate of 350 milliliters per hour and a voltage sufficient to cause a flow of current at an anode current density of 200 amperes per square foot calculated on the area of the coated face of the piece opposite the cathode was imposed between anode and cathode. Sodium hydroxide solution was continuously withdrawn from within the cathode cylinder. The relative flows of sodium chloride solution introduced and sodium chloride-sodium hydroxide withdrawn was adjusted to obtain decomposition of about fifty percent of the sodium chloride introduced into the cell. Chlorine was evolved at the surface of the casting and was separately collected on the anolyte side and withdrawn.

The initial voltage between the anode and cathode was 2.94. This electrolysis was continued for sixty-two days during which the voltage rose to 3.54 volts. The acidity of the anolyte stabilized at about pH 4 to 4.5. The silicon base still appeared to be largely unattacked by the evolved chlorine or the electrolyte and it appeared that the increased voltage was due primarily to flaking off of part of the coating.

In another test a silicon base of the above type containing about 5 percent by weight of molybdenum had at the most recent inspection operated with no rise in voltage for 115 days.

In some other tests the anodes fractured or broke during use. This is believed to be due to flaws in the casting rather than to corrosion of elemental silicon. One anode of this type operated at the above current density for over 100 days before breaking.

Other fluxes which have been used in the melting operation have included sodium tetraborate alone or disodium acid phosphate alone, boric acid, a mixture of sodium tetraborate and sodium hydroxide Na_2WO_4 , Na_2WO_4 plus B_2O_3 , LiAlO_3 plus Al_2O_3 , LiAlO_3 plus B_2O_3 , B_2O_3 plus Cr_2O_3 , AlPO_3 plus $\text{Na}_2\text{B}_4\text{O}_7$ plus V_2O_5 , soda lime glass, soda lime glass plus sodium tetraborate, fused borax plus metallic tungsten, molybdenum or cobalt powder.

The result in these cases was to introduce the metal (boron, phosphorous, cobalt, etc.) into the elemental silicon roughly in the proportion that these metals where in the added flux or metal.

EXAMPLE V

To test the effects of boron contents on the electroconductivity of the silicon anode bases, a series of anodes were prepared having ferrosilicon bases containing varying amounts of boron. These electrodes were given ruthenium dioxide coatings, and their electroconductivities and chlorine overvoltages were determined.

A. Twelve Weight Percent Iron

Three electrodes were prepared having ferro-silicon bases containing 12 weight percent iron. Two of the electrode bases contained 0.5 weight percent boron. The third contained no boron.

The ferro-silicon used in this test was Ohio Ferro Alloys Ferro Silicon having a nominal iron content of 15 weight percent and an actual iron content of 12 weight percent.

Seven hundred grams of the ferro-silicon was placed in a No. 10 graphite crucible. The crucible of ferro-silicon was heated to $1,580^\circ\text{C}$. for approximately one hour. The molten ferro-silicon was then poured into a

$\frac{1}{4}$ inch $\times$ 1 inch $\times$ 6 inch graphite mold that had been preheated to $1,000^\circ\text{C}$. After the ferro-silicon solidified and cooled, its electroconductivity was measured using a Weston Model 911 Milliammeter with power supplied through a Kokour Company Silicon Rectifier. The electrical conductivity was found to be (ohm-centimeter) $^{-1}$.

Two electrodes were prepared having bases containing twelve weight percent iron, 0.5 weight percent boron, and the balance silicon. In preparing these electrodes, 1800 grams of ferro-silicon and 42 grams of fused sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) were placed in a No. 10 graphite crucible. The crucible was placed in a furnace and heated to $1,580^\circ\text{C}$. for approximately one hour. Then the molten ferro-silicon, containing boron, was poured into a preheated, $\frac{3}{4}$ inch $\times$ 1 inch $\times$ 6 inch graphite mold.

After the metal had solidified and cooled, two 5 inch $\times$ $\frac{3}{4}$ inch $\times$ $\frac{1}{4}$ inch samples were cut from the ingot. The uncut surface of each sample was sandblasted and washed with "Comet" (TM) household cleanser. Each sample was then etched for five minutes in a 2.5 normal sodium hydroxide solution at 90°C ., rinsed in water, and air dried.

Three coats of an undercoating solution of two grams of Englehard Industries Ruthenium Trichloride in 18 grams of U.S. Industrial Chemical Absolute Ethyl Alcohol were applied to the uncut surface of each sample. After each coat, the sample was heated to 350°C . for 10 minutes.

Thereafter three coats of an outer coating solution were applied above the undercoating solution. The outer coating solution was prepared by dissolving 18.1 grams of K and K Laboratories Titanium chloride in 51.5 grams of a 15 weight percent aqueous solution of Fisher Scientific Company hydrochloric acid. Two grams of this solution were mixed with one gram of Mallinckrodt Absolute Methyl Alcohol and 0.5 grams of Baker and Adams 30 weight percent hydrogen peroxide. This solution was then mixed with 1.2 grams of a solution that had been prepared from 1 gram of Englehard Industries Ruthenium Trichloride and 4 grams of Mallinckrodt Absolute Methyl Alcohol. Three coats of this solution were applied to the previously undercoated surfaces of each sample. After each of the first two coats the electrode was heated to 350°C . for 10 minutes. After the last coat, each electrode was heated to 450°C . for 30 minutes.

The resulting electrodes had bulk electroconductivities of 1500 (ohm-centimeter) $^{-1}$. Each of the electrodes had a chlorine overvoltage of 0.08 to 0.10 volts at 200 amperes per square foot in a chlorinated solution containing 315 grams per liter of sodium chloride.

B. Nineteen Weight Percent Iron

Two electrodes were prepared having ferro-silicon bases containing nineteen weight percent iron. One contained 0.5 weight percent boron; and the balance silicon. The other contained no boron.

The ferro-silicon used in this test was Ohio Ferro Alloys Ferro-Silicon having a nominal iron content of 15 weight percent and an actual iron content of 12 weight percent.

Seven hundred grams of the ferro-silicon was placed in a No. 10 graphite crucible. The crucible of ferro-silicon was heated to $1,580^\circ\text{C}$. for approximately one hour.

The molten ferro-silicon was then poured into a 3/4 inch $\times$ 1 inch $\times$ 6 inch graphite mold that had been preheated to 1000°C. After the ferro-silicon solidified and cooled, its electroconductivity was measured using a Weston Model 911 Milliammeter was power supplied through a Kokour Company Silicon Rectifier. The electrical conductivity was found to be 19 (ohm-centimeter)⁻¹.

A second electrode was prepared having a base containing nineteen weight percent iron, 0.5 weight percent boron, and the balance silicon. In preparing these electrodes, 1800 grams of ferro-silicon and 42 grams of fused sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) were placed in a No. 10 graphite crucible. The crucible was placed in a furnace and heated to 1,580°C. for approximately seventy-five minutes. Then the molten ferro-silicon, containing boron, was poured into a preheated, 3/4 inch $\times$ 1 inch $\times$ 6 inch graphite mold.

After the metal had solidified and cooled, a 5 inch $\times$ 3/4 inch $\times$ 1/4 inch sample as cut from the ingot. The uncut surface of the sample was sandblasted and washed with "Comet" (TM) household cleanser. The sample was then etched for 5 minutes in a 2.5 normal sodium hydroxide solution at 90°C., rinsed in water, and air dried.

Three coats of an undercoating solution of two grams of Engelhard Industries Ruthenium Trichloride in 18 grams of U.S. Industrial Chemical Absolute Ethyl Alcohol were applied to the uncut surface of each sample. After each coat the sample was heated to 350 C. for 10 minutes.

Thereafter three coats of an outercoating solution were applied above the undercoating solution. The outercoating solution was prepared by dissolving 18.1 gram of K and K Laboratories Titanium chloride in 51.5 grams of a 15 weight percent aqueous solution of Fisher Scientific Company hydrochloric acid. Two grams of this solution were mixed with one gram of Mallinckrodt Absolute Methyl Alcohol and 0.5 grams of Baker and Adams 30 weight percent hydrogen peroxide. This solution was then mixed with 1.2 grams of a solution that had been prepared from 1 gram of Engelhard Industries Ruthenium Trichloride and 4 grams of Mallinckrodt Absolute Methyl Alcohol. Three coats of this solution were applied to the previously undercoated surface of the sample. After each of the first two coats, the electrode was heated to 350°C. for 10 minutes. After the last coat the electrode was heated to 450°centigrade for 30 minutes.

The resulting electrode had bulk electroconductivities of 970 (ohm-centimeters)⁻¹. The electrodes had a chlorine overvoltage of 0.03 volts at 200 amperes per square foot in a chlorinated solution containing 315 grams per liter of sodium chloride.

C. Thirty Weight Percent Iron

Nine electrodes were prepared having ferro-silicon bases containing thirty weight percent iron. Two of the electrode bases contained 2 weight percent boron, two of the electrode bases contained 1 weight percent boron, one electrode base contained 0.5 weight percent boron, two of the electrode bases contained 0.1 weight percent boron, and two of the electrode bases contained no boron.

The ferro-silicon used in this test was Ohio Ferro Alloys Ferro-Silicon having a nominal iron content of 35 weight percent and an actual iron content of 30 weight percent.

Seven hundred grams of the ferro-silicon was placed in a Number 10 graphite crucible. The crucible of ferro-silicon was heated to 1,500°C. for approximately 65 minutes. The molten ferro-silicon was then poured into a 1/4 inch $\times$ 1 inch $\times$ 6 inch graphite mold that had been preheated to 1,000°C. After the ferro-silicon solidified and cooled its electroconductivity was measured using a Weston Model 911 Milliammeter was power supplied through a Kokour Company Silicon Rectifier. The electrical conductivity was found to be 32 (ohm-centimeter)⁻¹.

Eight electrodes were prepared having bases containing thirty weight percent iron, from 0.1 to 2 weight percent boron, and the balance silicon. In preparing these four melts, 700 grams of ferro-silicon and fused sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) in the amount as shown below were placed in a No. 10 graphite crucible:

WEIGHT OF $\text{Na}_2\text{B}_4\text{O}_7$ MELTED WITH
700 GRAMS OF FERRO-SILICON

Weight of $\text{Na}_2\text{B}_4\text{O}_7$ (grams)	Weight Percent of B in Melt
3.25	0.1
16.25	0.5
32.50	1.0
65.00	2.0

Each crucible was placed in a furnace and heated to 1,580°C. for approximately one hour. Then the molten ferro-silicon, containing boron, was poured into a preheated, 1 inch $\times$ 1 inch $\times$ 5 3/4 inch graphite mold.

After the metal had solidified and cooled, 5 inch $\times$ 3/4 inch $\times$ 1/4 inch samples were cut from each ingot. The uncut surface of each samples was sandblasted and washed with "Comet" (TM) household cleanser. Each sample was then etched for five minutes in a 2.5 normal sodium hydroxide solution at 90°C., rinsed in water, and air dried.

Three coats of an undercoating solution of two grams of Engelhard Industries Ruthenium Trichloride in 18 grams of U.S. Industrial Chemical Absolute Ethyl Alcohol were applied to the uncut surface of each sample. After each coat the sample was heated to 350°C. for 10 minutes.

Thereafter, three coats of an outer coating solution were applied above the undercoating solution. The outer coating solution was prepared by dissolving 18.1 grams of K and K Laboratories Titanium Chloride in 51.5 grams of 15 weight percent aqueous solution of Fisher Scientific Company hydrochloric acid. Two grams of this solution were mixed with one gram of Mallinckrodt Absolute Methyl Alcohol and 0.5 grams of Baker and Adams 30 weight percent hydrogen peroxide. This solution was then mixed with 1.2 grams of a solution that had been prepared from 1 gram of Engelhard Industries Ruthenium Trichloride and 4 grams of Mallinckrodt Absolute Methyl Alcohol. Three coats of this solution were applied to the previously undercoated surfaces of each sample. After each of the first two coats the electrode was heated to 350°C. for 10 minutes. After the last coat the electrode was heated to 450°C. for 30 minutes.

The anodes were tested as anodes for the electrolysis of brines, and the following chlorine overvoltages and bulk electroconductivities were obtained.

CHLORINE OVERVOLTAGE AND BULK
ELECTROCONDUCTIVITIES
FOR ANODES HAVING A 30 WEIGHT PERCENT IRON FERRO-
SILICON BASE

Weight percent boron	Chlorine overvoltage (volts)	Bulk Electro- conductivity (ohm-cm) ⁻¹
0.0	—	32
0.0	0.76	32
0.1	0.06	457
0.1	0.05	457
0.5	0.05	775
1.0	—	807
1.0	0.03	807
2.0	0.05	895
2.0	0.04	895

Electrodes of the above type have good durability when used as described in the above examples. It is also to be understood that they may be used in lieu of graphite as electrodes in alkali metal chlorate cells for producing alkali metal chlorate.

The present invention has been described with special reference to electrodes in which the substrate is silicon metal in which the silicon content is at least about 85 percent by weight of the electrode. Such substrates are especially effective because of their inertness and because they are predominantly (usually over) elemental silicon. However, other substrates containing as low as 50 percent or even as low as ten percent by weight of elemental silicon (as distinguished from metallic silicide) may be used. For example, substrates containing both elemental silicon and silicides of titanium or zirconium may be used. Typical such substrates may contain about 10 to 99 percent elemental silicon and 1 to 45 percent by weight of nickel, cobalt, chromium, titanium or zirconium, probably as the silicides NiSi₂, CoSi₂, CrSi₂, TiSi₂ or ZrSi₂. Ferrosilicon alloys having in excess of about 60 percent by weight of silicon contain 10 to 99 percent by weight of elemental silicon, the balance being iron, probably as FeSi₂. These mixtures to the extent that they remain inert may be used as substrates, the required electroconductivity being obtained by incorporation of boron, phosphorous or the like as described above. In general, the total silicon content including silicides and elemental silicon of the substrate is at least about 50 percent, preferably above 75 percent by weight thereof.

It is to be understood that although the invention has been described with specific reference to specific details of particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

I claim:

1. An electrode having an electroconductive surface on a metallic base comprising at least 50 weight percent silicon, which base contains a dopant chosen from the group consisting of phosphorous, arsenic, antimony, bismuth, boron, aluminum, and gallium in an amount sufficient to provide said base with an electroconductivity greater than 100 (ohm-centimeters)⁻¹.

2. The electrode of claim 1 wherein the electroconductive surface has a chlorine overvoltage in aqueous alkali metal chloride which is below 0.25 volt at a current density of 200 Amperes per square foot.

3. The electrode of Claim 2 wherein the electroconductive surface comprises an electrocatalytic material.

4. The electrode of claim 3 wherein the electroconductive surface comprises a platinum group metal.

5. The electrode of claim 3 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

6. The electrode of claim 1 wherein at least part of the silicon is in the form of an alloy.

7. The electrode of claim 6 wherein the metallic base comprises at least 85 weight percent silicon.

8. The electrode of claim 6 wherein the metallic base comprises at least 10 weight percent elemental silicon.

9. The electrode of claim 6 wherein at least part of the silicon is present as an alloy with materials shown from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, rion, tungsten, and vanadium.

10. The electrode of claim 1 wherein the base contains from about 0.1 to about 5 weight percent of the dopant.

11. An electrode having an electroconductive surface on a metallic base comprising at least 50 weight percent silicon, which base contains from 0.1 to 5 weight percent of a dopant to provide said base with an electroconductivity greater than 100 (ohm-centimeters)⁻¹.

12. The electrode of claim 11 wherein at least part of the silicon is in the form of an alloy.

13. The electrode of claim 12 wherein the metallic base comprises 50 weight percent silicon.

14. The electrode of claim 12 wherein the metallic base comprises 10 weight percent elemental silicon.

15. The electrode of claim 12 wherein at least part of the silicon is present as an alloy with materials chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

16. The method of claim 11 wherein the electroconductive surface has a chlorine overvoltage in aqueous alkali metal chloride which is below 0.25 volt at a current density of 200 Amperes per square foot.

17. The electrode of claim 16 wherein the electroconductive surface comprises an electrocatalytic material.

18. The electrode of claim 16 wherein the electroconductive surface comprises a platinum group metal.

19. The electrode of claim 16 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

20. The electrode of claim 11 wherein the dopant is chosen from the group consisting of boron, aluminum, gallium, phosphorous, arsenic, antimony, and bismuth.

21. An electrode comprising:

A. a metallic silicon base comprising at least 50 weight percent silicon, which base contains a dopant chosen from the group consisting of phosphorous, arsenic, antimony, bismuth, boron, aluminum, and gallium in an amount sufficient to provide said base with an electroconductivity greater than 100 (ohm-centimeters)⁻¹; and

B. an electroconductive surface thereon which has a chlorine overvoltage in aqueous sodium chloride of

less than 0.25 volt at a current density of 200 Amperes per square foot.

22. The electrode of claim 21 wherein at least part of the silicon is in the form of an alloy.

23. The electrode of claim 22 wherein the metallic silicon base comprises at least 85 weight percent silicon.

24. The electrode of claim 22 wherein the metallic silicon base comprises at least 10 weight percent elemental silicon.

25. The electrode of claim 22 wherein at least part of the silicon is present as an alloy with materials chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

26. The electrode of claim 21 wherein the base contains from about 0.1 to about 5 weight percent of the dopant.

27. The electrode of claim 21 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

28. The electrode of claim 21 wherein the electroconductive surface comprises a conductive material and a nonconductive material.

29. An electrode comprising:

A. a metallic base comprising at least 50 weight percent silicon, which base contains from 0.1 to 5 percent by weight of a dopant to provide said base with an electroconductivity greater than 100 (ohm-centimeters)⁻¹; and

B. an electroconductive surface thereon which has a chlorine overvoltage in aqueous sodium chloride of less than 0.25 volt at a current density of 200 Amperes per square foot.

30. The electrode of claim 29 wherein at least part of the silicon is in the form of an alloy.

31. The electrode of claim 30 wherein the metallic base comprises at least 85 weight percent silicon.

32. The electrode of claim 30 wherein at least part of the silicon is present as an alloy with materials chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

33. The electrode of claim 29 wherein the dopant is chosen from the group consisting of boron, aluminum, gallium, phosphorous, arsenic, antimony, and bismuth.

34. The electrode of claim 29 wherein the metallic base comprises at least 10 weight percent elemental silicon.

35. The electrode of claim 29 wherein the electroconductive surface comprises a platinum group metal.

36. The electrode of claim 29 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

37. An electrode comprising:

A. a metallic base having an electroconductivity greater than 100 (ohm-centimeters)⁻¹ and comprising 50 weight percent silicon and at least 0.01 weight percent of a dopant chosen from the group consisting of phosphorous, arsenic, antimony, bismuth, boron, aluminum, and gallium; and

B. an electroconductive surface thereon.

38. The electrode of claim 37 wherein at least part of the silicon is in the form of an alloy.

39. The electrode of claim 38 wherein some of the silicon is present as a silicide.

40. The electrode of claim 39 wherein the silicides are chosen from the group consisting of titanium silicide, zirconium silicide, niobium silicide, tantalum silicide, chromium silicide, molybdenum silicide, and tungsten silicide.

41. The electrode of claim 38 wherein the metallic base comprises 50 weight percent silicon.

42. The electrode of claim 38 wherein the metallic base comprises 10 weight percent elemental silicon.

43. The electrode of claim 38 wherein at least part of the silicon is present as an alloy with materials chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

44. The electrode of claim 37 wherein the electroconductive surface has a chlorine overvoltage in aqueous alkali metal chloride which is below 0.25 volt at a current density of 200 Amperes per square foot.

45. The electrode of claim 44 wherein the electroconductive surface comprises an electrocatalytic material.

46. The electrode of claim 44 wherein the electroconductive surface comprises a platinum group metal.

47. The electrode of claim 44 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

48. The electrode of claim 44 wherein the electroconductive surface comprises a conductive material and a nonconductive material.

49. The electrode of claim 48 wherein the nonconductive material is SiO₂.

50. The electrode of claim 37 wherein the metallic base is hot rolled.

51. The electrode of claim 37 wherein the metallic base contains internal reinforcing means.

52. The electrode of claim 37 wherein the electrode comprises an electroconductive metallic substrate; an electrolyte impermeable silicon layer on said substrate; and an electroconductive surface on said silicon layer.

53. An anode useful for the electrolysis of brines comprising:

an electroconductive, electrolyte impermeable silicon substrate comprising 50 weight percent elemental silicon, having dispersed therethrough more than 10 parts per million of a dopant, and having an electrical conductivity of greater than 10² (ohm-centimeters)⁻¹; and

an electroconductive coating thereon having a chlorine overvoltage less than 0.25 volt at 200 Amperes per square foot, chosen from the group consisting of the platinum group metals and oxygen-containing compounds of the platinum group metals.

54. In an electrolytic cell which comprises means for feeding brine to the electrolytic cell, an anode, a cathode, and means for externally imposing an electromotive force between said anode and said cathode of said cell whereby an electrical current is caused to flow from said anode to said cathode, the improvement wherein said anode comprises:

an electrolyte impermeable, electrolyte resistant metallic base having an electroconductivity greater than 10² (ohm-centimeters)⁻¹ and comprising a 50

weight percent silicon and at least 0.01 weight percent of a dopant; and
an electroconductive surface thereon.

55. The electrolytic cell of claim 54 wherein the electroconductive surface has a chlorine overvoltage in aqueous alkali metal chloride which is below 0.25 volt at a current density of 200 Amperes per square foot.

56. The electrolytic cell of claim 55 wherein the electroconductive surface comprises an electrocatalytic material.

57. The electrolytic cell of claim 56 wherein the electroconductive surface comprises a platinum group metal.

58. The electrolytic cell of claim 56 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

59. The electrolytic cell of claim 56 wherein the electroconductive surface comprises a conductive material and a nonconductive material.

60. The electrolytic cell of claim 56 wherein the nonconductive material is SiO_2 .

61. The electrolytic cell of claim 54 wherein some of the silicon is present as a silicide.

62. The electrolytic cell of claim 61 wherein the silicides are chosen from the group consisting of titanium silicide, zirconium silicide, niobium silicide, tantalum silicide, chromium silicide, molybdenum silicide, and tungsten silicide.

63. The electrolytic cell of claim 54 wherein at least part of the silicon is in the form of an alloy.

64. The electrolytic cell of claim 63 wherein the metallic base comprises 85 weight percent silicon.

65. The electrolytic cell of claim 63 wherein the metallic base comprises at least 10 weight percent elemental silicon.

66. the electrolytic cell of claim 63 wherein at least part of the silicon substrate is present as an alloy with a metal chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

67. The electrolytic cell of claim 54 wherein the dopant if chosen from the group consisting of phosphorous, arsenic, antimony, bismuth, boron, aluminum, and gallium.

68. The electrolytic cell of claim 54 wherein the base is hot rolled.

69. The electrolytic cell of claim 54 wherein the base contains internal reinforcing means.

70. The electrolytic cell of claim 54 wherein the anode comprises an electroconductive metallic substrate; an electrolyte impermeable silicon layer on said substrate; and an electroconductive surface on said silicon layer.

71. In an electrolytic cell which comprises means for feeding brine to the electrolytic cell, an anode, a cathode, and means for externally imposing an electromotive force between said anode and said cathode of said cell whereby an electrical current is caused to flow from said anode to said cathode, the improvement wherein said anode comprises:

an electrolyte impermeable, electrolyte resistant base having an electroconductivity greater than 10^2 (ohm-centimeters) $^{-1}$ and comprising 50 weight percent silicon and at least 0.01 weight percent of a dopant chosen from the group consisting of phosphorous, arsenic, antimony, bismuth, boron, aluminum, and gallium; and

an electroconductive surface thereon.

72. In a method of electrolyzing brine which comprises the steps of feeding brine to an electrolytic cell and externally imposing an electromotive force between an anode and a cathode of said cell whereby an electrical current is caused to flow from said anode to said cathode, the improvement wherein said anode comprises:

a metallic base having an electroconductivity greater than 10^2 (ohm-centimeters) $^{-1}$ and comprising 50 weight percent silicon and at least 0.01 weight percent of a dopant; and

an electroconductive surface thereon.

73. The method of claim 72 wherein at least part of the silicon is in the form of an alloy.

74. The method of claim 73 wherein some of the silicon is present as silicides.

75. The method of claim 74 wherein the silicides are chosen from the group consisting of titanium silicide, zirconium silicide, niobium silicide, tantalum silicide, chromium silicide, molybdenum silicide, and tungsten silicide.

76. The method of claim 73 wherein the metallic base comprises 85 weight percent silicon.

77. The method of claim 73 wherein the metallic base comprises at least 10 weight percent elemental silicon.

78. The method of claim 73 wherein at least part of the silicon is present as an alloy with materials chosen from the group consisting of aluminum, gallium, iron, cobalt, nickel, molybdenum, chromium, manganese, iron, tungsten, and vanadium.

79. The method of claim 72 wherein the electroconductive surface has a chlorine overvoltage in aqueous alkali metal chloride which is below 0.25 volt at a current density of 200 Amperes per square foot.

80. The method of claim 79 wherein the electroconductive surface comprises an electrocatalytic material.

81. The method of claim 80 wherein the electroconductive surface comprises a conductive material and a nonconductive material.

82. The method of claim 81 wherein the nonconductive material is SiO_2 .

83. The method of claim 80 wherein the electroconductive surface comprises a platinum group metal.

84. The method of claim 80 wherein the electroconductive surface comprises an oxygen-containing compound of a platinum group metal.

85. The method of claim 72 wherein the dopant is chosen from the group consisting of boron, aluminum, gallium, phosphorous, arsenic, antimony, and bismuth.

86. The method of claim 72 wherein the base is hot rolled.

87. The method of claim 72 wherein the base contains internal reinforcing means.

88. The method of claim 72 wherein the anode comprises an electroconductive metallic substrate; an electrolyte impermeable silicon layer on said substrate; and an electroconductive surface on said silicon layer.

89. In a method of electrolyzing brine which comprises the steps of feeding brine to an electrolytic cell and externally imposing an electromotive force between an anode and a cathode of said cell whereby an electrical current is caused to flow from said anode to

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said cathode, the improvement wherein said anode comprises:
a metallic base having an electroconductivity greater than 10^2 (ohm-centimeters)⁻¹ and comprising 50 weight percent silicon and at least 0.01 weight per-

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cent of a dopant chosen from the group consisting of boron, aluminum, gallium, phosphorous, arsenic, antimony, and bismuth; and an electroconductive surface thereon.
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,852,175 Dated December 3, 1974

Inventor~~(s)~~ Howard H. Hoekje

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At Column 22, Claim 9, line 20, "rion" should be "iron".

Signed and sealed this 18th day of February 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks