United States Patent [19]

Hoekje

[11] **3,926,770**

[45] **Dec. 16, 1975**

[54] **ELECTROLYTIC CELL HAVING SILICON BIPOLAR ELECTRODES**

[75] Inventor: **Howard H. Hoekje,** Akron, Ohio

[73] Assignee: **PPG Industries, Inc.,** Pittsburgh, Pa.

[22] Filed: **Dec. 4, 1973**

[21] Appl. No.: **421,706**

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 260,790, June 8, 1972, abandoned, and Ser. No. 336,288, Feb. 27, 1973, Pat. No. 3,852,175, and Ser. No. 356,972, May 3, 1973, abandoned, said Ser. No. 336,288, and Ser. No. 356,972, is a continuation-in-part of Ser. No. 260,790, , said Ser. No. 356,972, is a continuation-in-part of Ser. No. 336,288.

[52] **U.S. Cl.** ..... **204/256;** 204/98; 204/254; 204/255; 204/268; 204/290 R; 204/291; 204/293

[51] **Int. Cl.**[2] **C25B 11/04**

[58] **Field of Search** ..... 204/254, 255, 256, 268, 204/290 R, 291

[56] **References Cited**

UNITED STATES PATENTS

546,328	9/1895	Hoepfner	204/290 R
1,172,887	2/1916	Halter	204/256
2,717,872	9/1955	Zdansky	204/256
3,441,495	4/1969	Colman	204/268
3,491,014	1/1970	Bianchi et al.	204/290 R X
3,497,433	2/1970	Weed	204/268 X

FOREIGN PATENTS OR APPLICATIONS

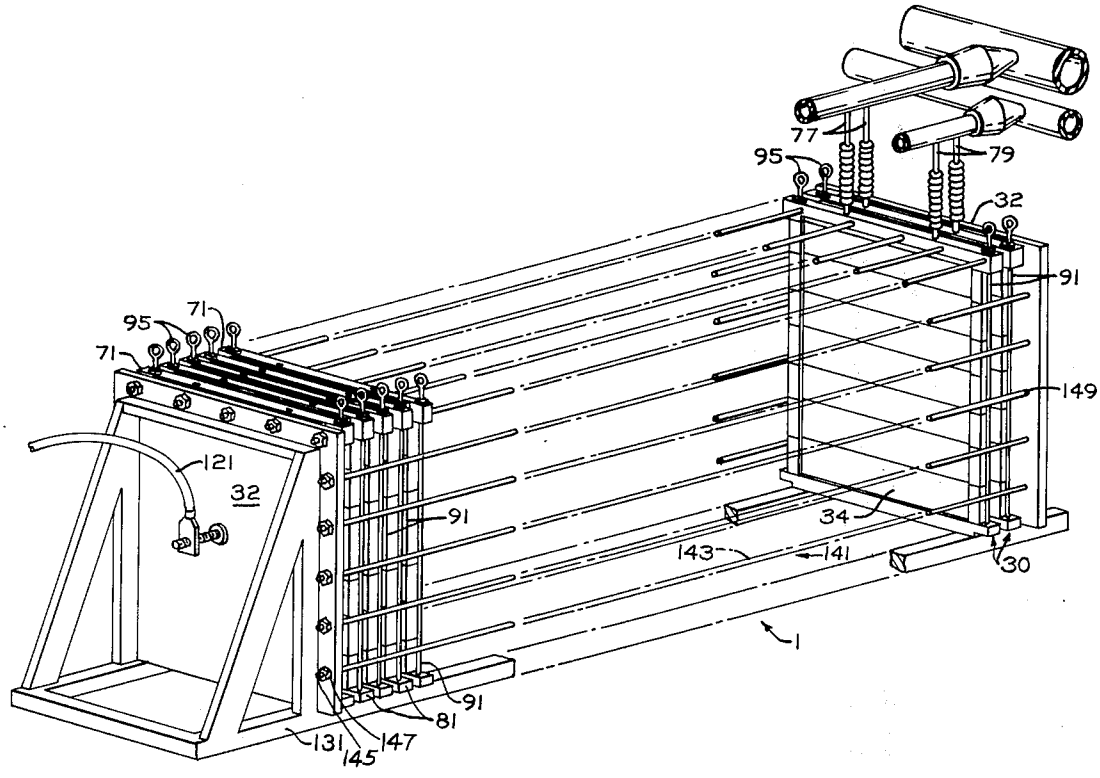
195,518	2/1907	Germany	204/291

Primary Examiner—John H. Mack
Assistant Examiner—W. I. Solomon
Attorney, Agent, or Firm—Richard M. Goldman

[57] **ABSTRACT**

Disclosed is a bipolar electrolyzer having a plurality of bipolar electrodes. The bipolar electrodes are electroconductive silicon metallic electrodes having an anodic surface on one side and a cathodic surface on the opposite side.

56 Claims, 4 Drawing Figures



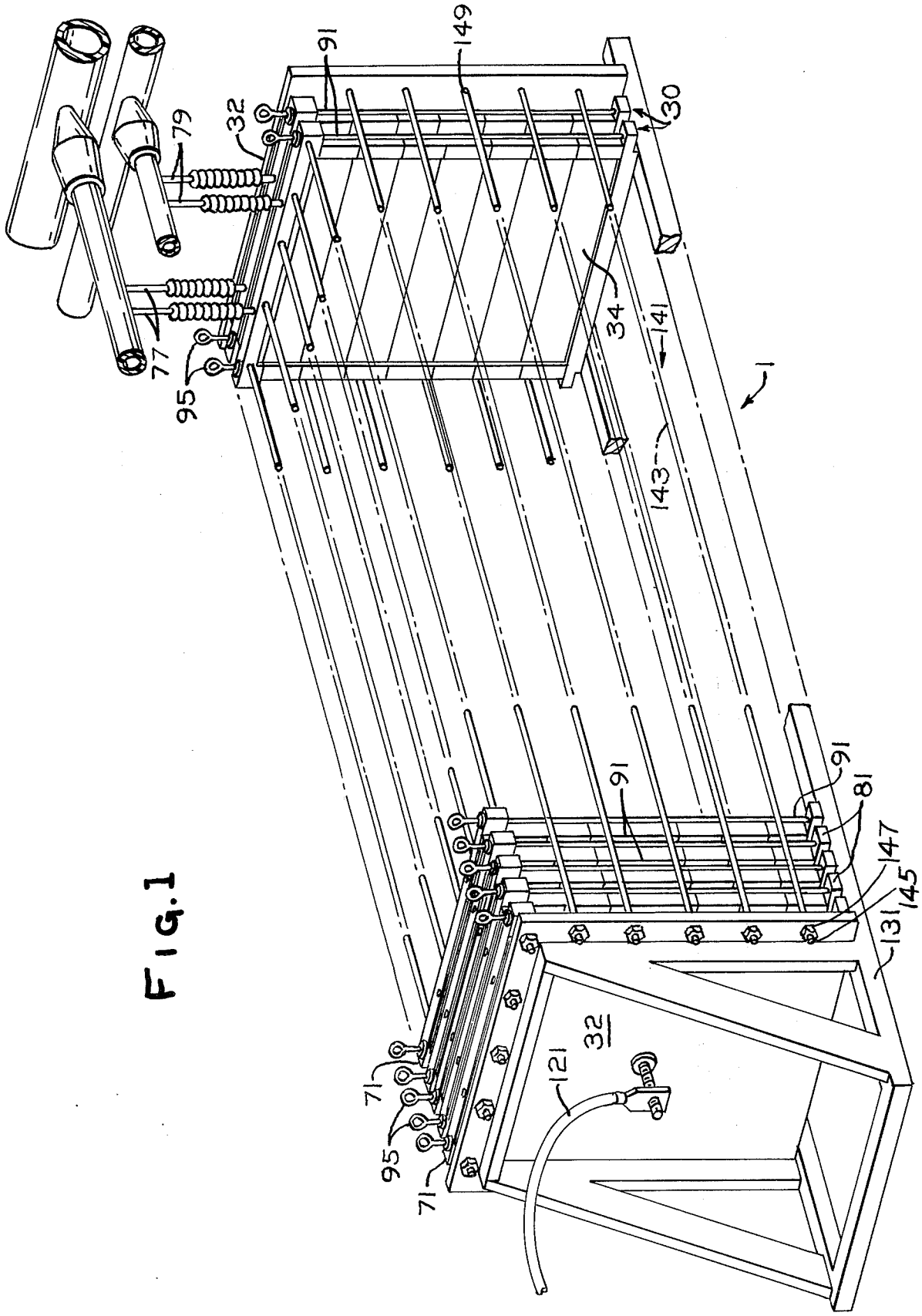

91
149
32
79
30
34
141
77
95
1
143
91
91
81
147
145
131
32
121
71
95
71

FIG. 1

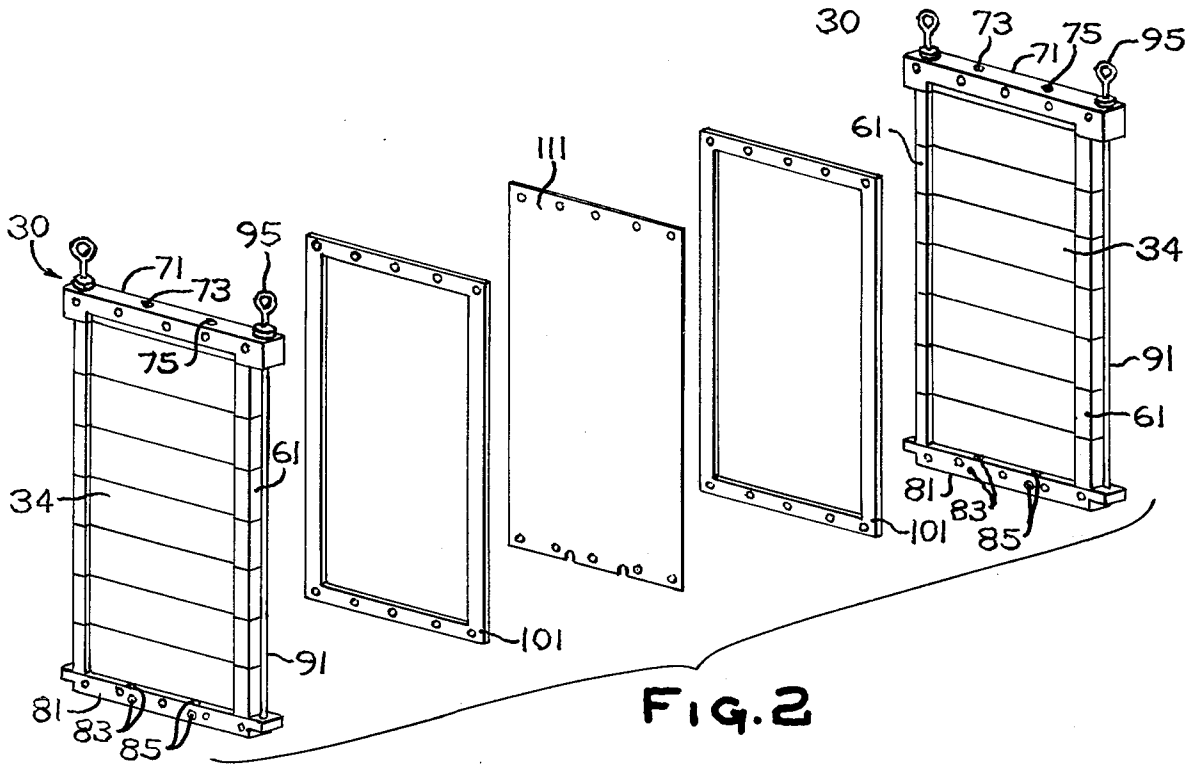


FIG. 2

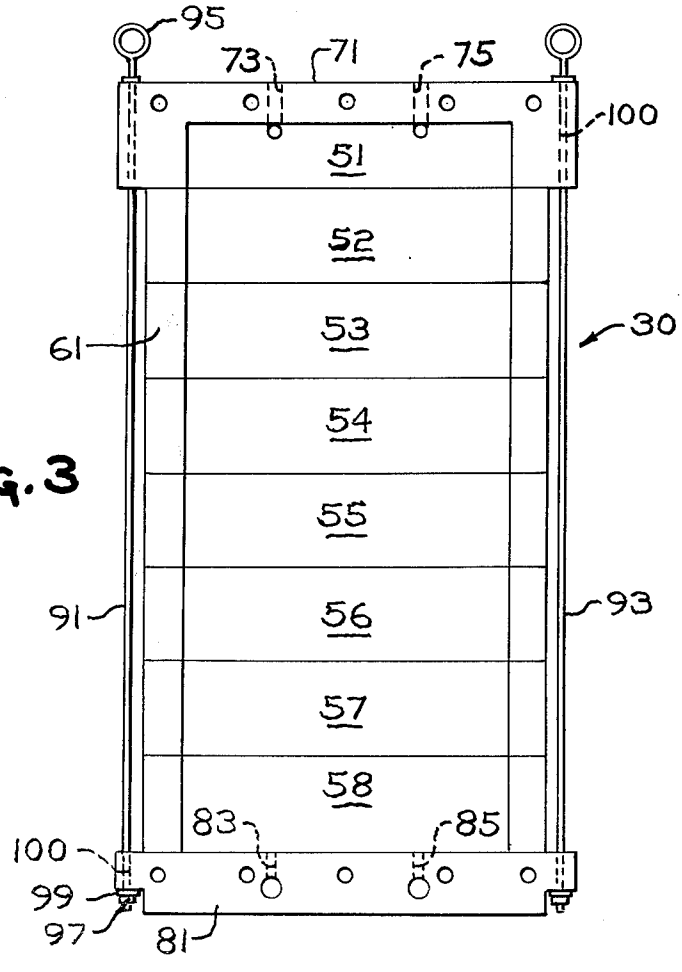


FIG. 3

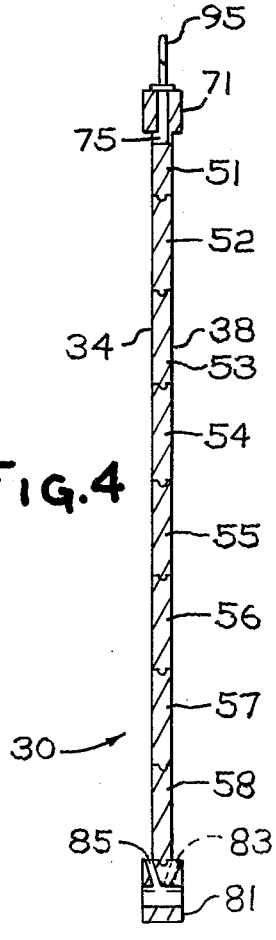


FIG. 4

ELECTROLYTIC CELL HAVING SILICON BIPOLAR ELECTRODES

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of my commonly assigned, copending U.S. application Ser. No. 260,790 filed June 8, 1972, now abandoned of my commonly assigned, copending U.S. application Ser. No. 336,288, filed Feb. 27, 1973, now U.S. Pat. No. 3,852,175, which is in turn a continuation-in-part of said U.S. application Ser. No. 260,790 and of my commonly assigned, copending U.S. application Ser. No. 356,972 filed May 3, 1973, now abandoned, which is in turn a continuation-in-part of said U.S. application Ser. No. 260,790 and Ser. No. 336,288.

BACKGROUND OF THE INVENTION

Brines, e.g., sodium chloride, potassium chloride, and the like, may be electrolyzed to yield the halogen, e.g., chlorine, at the anode and the alkali metal hydroxide, e.g., caustic soda, or potash, at the cathode. The anode reaction is reported in the literature to be:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The cathode reaction is reported in the literature to be:

$$2H^+ + 2e^- \rightarrow H_2$$

In halogen producing cells, with a barrier interposed between the anode and the cathode, e.g., an electrolyte permeable diaphragm or a permionic membrane, alkali metal ion and hydroxyl ion are present in the catholyte chamber. In such cells, the anolyte is acid, having a pH of from about **3.0** to about **5.0** while the catholyte is basic having a pH in excess of about **12,** e.g., and frequently as high as **14.**

In the production of alkali metal chlorate, as distinguished from the production of chlorine and alkali metal hydroxide, the anode product and the cathode product are not separated by a permeable barrier. The anode and cathode products are permitted to contact each other whereby the following reactions are reported in the literature to take place:

1. $3Cl_2 + 60H^- \rightarrow 3ClO^- + 3H_2O$
2. $2ClO^- + 2H^+ \rightarrow 2HClO$
3. $2HClO + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+$

This provides an overall reaction of:

$$3Cl_2 + 60H^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$$

In the production of alkali metal chlorate, the electrolyte is acidic, neutral, or slightly basic, that is, it has a pH of from about **3.5** to about **7.0** or **8.0** and preferably from about **4.5** to about **6.8.** An acidic electrolyte drives reaction (2) $2ClO^- + 2H^+ \rightarrow 2HClO$, i.e., an acidic electrolyte favors the formation of HClO.

In the electrolytic cells of the prior art, electrolysis was carried out with graphite anodes and steel cathodes. However, graphite anodes were characterized by deterioration according to the following anodic reactions:

$$2ClO^- \rightarrow Cl_2 + O_2$$
$$C + O_2 \rightarrow CO_2$$

Furthermore, graphite anodes, in addition to deteriorating under cell conditions, were characterized by a high chlorine overvoltage, e.g., in excess of about **0.25** volt at an anode current density of **125** Amperes per square foot in chlorinated brine.

The graphite anodes of the prior art have been gradually replaced by metal anodes. Such metal anodes typically have a valve metal base with an electroconductive coating thereon. Valve metals are those metals which form an oxide film when subjected to anodic conditions in aqueous acidic media. Typically, the valve metals used in fabricating anodes according to the prior art are titanium, tantalum, tungsten, zirconium, hafnium, niobium, and the like. Most commonly, titanium was used in fabricating anodes according to the prior art. The coating on the valve metal base was typically a platinum group metal, e.g., ruthenium, rhodium, palladium, osmium, iridium, or platinum, or an oxide of a platinum group metal, such as ruthenium oxide, or an oxygen-containing compound of a platinum group metal. Generally, the platinum group metal or oxide thereof was present with an oxide of a film-forming metal, such as titanium dioxide, thereby providing a surface on the valve metal, e.g., ruthenium dioxide and titanium dioxide. Additionally, materials such as magnetite, Fe_3O_4, and lead dioxide have been used with satisfactory results. However, electrolytic cells having precious metal coated valve metal basis are characterized by a high cost per unit of electrode area.

SUMMARY OF THE INVENTION

It has now surprisingly been found that a particularly outstanding bipolar electrode useful for the electrolysis of brines is a silicon metal bipolar electrode containing small amounts of a dopant, having a suitable anodic coating on the anodic surface thereof, and having a suitable cathodic coating or film on the cathodic surface thereof.

DESCRIPTION OF THE INVENTION

The electrolytic cell contemplated herein may be more fully understood by reference of the Figures:

FIG. **1** is an isometric, partial schematic view of the bipolar electrolyzer of this invention.

FIG. **2** is an exploded view of an individual cell of the bipolar electrolyzer of this invention.

FIG. **3** is a front elevation of an individual bipolar electrode of the electrolytic cell of this invention.

FIG. **4** is a cutaway side elevation of a bipolar electrode useful in the electrolytic cell of this invention.

The bipolar electrolytic cell of this invention may either be a chlorine cell, characterized by a permeable barrier between the anode and cathode of an individual cell thereof, or it may be a chlorate cell, characterized by the absence of such a permeable barrier, and the presence of the anode and cathode of a cell within the same electrolyte chamber.

A bipolar cell of this invention is an electrolytic cell having a plurality of individual cells in bipolap mechanical and electrical configuration, each individual cell being separated from the prior adjacent cell and the subsequent adjacent cell of the electrolyzer by common structural members. The common structural member is variously known as a "cell unit", a "backplate", or a "bipolar electrode". It is to be understood that these terms are equivalent and may be used interchangeably. In a bipolar electrolytic cell, the backplate or bipolar electrode includes the cathode of one cell and the anode of the next adjacent cell, and is electroconductive so as to provide for a low IR voltage drop between the cathode of one cell and the anode of the next adjacent cell. Preferably, in a diaphragm cell, the bipolar electrode is electrolyte impermeable, so as to

prevent the migration of ions from one cell to the adjacent cell.

The electrolytic cell shown in FIGS. **1** through **4** includes a plurality of bipolar electrodes **30** between a pair of end electrodes **32, 32.** Each individual bipolar electrode **30** has a cathodic surface **34** and an anodic surface **38.**

The individual bipolar electrodes **30** are maintained in a spaced relationship to each other so that the anodic surface **38** of one bipolar electrode **30** and the cathodic surface **34** of the next adjacent bipolar electrode **30** in the electrolyzer define an electrolyte volume of an individual electrolytic cell therebetween. In this way, an individual electrolytic cell is defined by the anodic surface **38** of one bipolar electrolyzer **30** and the cathodic surface **34** of the next adjacent bipolar electrode **30** in the electrolyzer **1.**

An individual bipolar electrode **30** includes a gas header means **71.** The gas header means **71** extends beyond the cathodic surface **34** and the anodic surface **38** of the bipolar electrode **30.** The gas header means **71** includes a chlorine outlet **73** for recovering chlorine from the anolyte chamber in contact with the anodic surface **38** of the bipolar electrode **30,** and for feeding the chlorine to the chlorine recovery system **77.**

The gas header **71** also includes a hydrogen outlet **75** for recovering hydrogen from the catholyte chamber in contact with the cathodic surface **34** of the bipolar electrode **30.** The hydrogen outlet **75** is in communication with the hydrogen recovery system **79.**

The individual bipolar electrode **30** also includes a liquid header means on the bottom thereof. The liquid header means **81** extends beyond the cathodic surface **34** and the anodic surface **38** of the bipolar electrode **30.** A brine feed means **83,** communicating with a brine line, extends through the header **81** to the anodic side **38** of the bipolar electrode **30** while an alkali-metal hydroxide recovery means **85** extends from the cathodic side **34** of the bipolar electrode **30** to the cell liquor recovery system.

The gas header **71** and liquid header **81** may be metallurgically joined to the bipolar electrode **30.** This may be accomplished by a copper weld, a nickel weld, or a lead weld, as will be described more fully hereinafter.

Alternatively, the gas header means **71** and the liquid header means **81** may be mechanically joined to the bipolar electrode **30.** For example, compressive means **91** may compress the gas header means **71** and liquid header means **81** onto the bipolar electrode **30.** A pair of compressive means **91** extend from the gas header means **71** alongside the bipolar electrode **30** to the liquid header means **81.** In a preferred exemplification of the compressive means **91,** a threaded rod **93** passes through an aperture **100** in the gas header means **71,** from the gas header means **71,** alongside the bipolar electrode **30,** to the liquid header means **81,** and passes through an aperture **100** in the liquid header means **81.** The upper end of the threaded rod **93** may include an eye-bolt **95.** The lower end typically includes a nut **97** and washer **99.**

The individual bipolar electrodes **91** typically contain peripheral walls or side walls **61** along the vertical surfaces thereof. These side walls and the extensions of the gas header means **71** and liquid header means **81** define a single plane. A gasket means **101** may be interposed between adjacent bipolar electrodes **30** so as to provide an electrolyte tight seal between the first or anodic bipolar electrode or bipolar unit **30** of an individual cell and the second bipolar unit or cathodic bipolar electrode **30** of the individual cell. In this way, a substantially electrolyte tight chamber is provided.

The bipolar electrode **30** may be cast as a single silicon member. Alternatively, the bipolar silicon electrode **30** may be cast as a plurality of individual silicon castings **51, 52, 53, 54, 55, 56, 57,** and **58.** When the silicon bipolar electrode **30** is cast as a plurality of individual silicon castings **51** through **58,** the content of transition metal silicide is not critical as some thermal expansion upon solidification may be tolerated. However, if the silicon bipolar electrode **30** is cast as a single casting, continuous casting techniques, heat treating techniques, or measured amounts of transition metal silicides must be provided, in order to prevent or relieve thermal stresses.

When the silicon bipolar electrode **30** is cast as individual silicon castings **51** through **58,** the individual castings may be suitably joined together, for example, at tongue and groove joints by compressive means **91** as shown in the figures. Alternatively, various metallurgical techniques may be used, such as providing an adherent surface, e.g., nickel or copper, on the surface of the silicon castings **51** through **58** to be joined. Thereafter, a molten flux of aluminum, nickel, copper, lead, tin, or lead-tin alloy may be provided between the nickel or copper coated surfaces, i.e., within the tongue and groove, to effect a metallurgical bond.

In a chlorine cell configuration, a barrier **111** is provided between the anode **38** and cathode **34** of an individual cell. The permeable barrier may be an electrolyte permeable barrier, i.e., a diaphragm, such as is described in Sconce, Chlorine: Its Manufacture, Properties and Uses (A.C.S. Monograph 154), Reinhold Publishing Co., New York (1962), at pages 81 to 126, especially pages 105 to 108. Such an electrolyte permeable barrier permits the passage of alkali metal halide, or halide ion, through the barrier so as to provide a catholyte product containing in excess of 7 weight percent alkali metal chloride, and frequently as high as 10 or 12 or even 15 percent alkali metal chloride.

Alternatively, the barrier (**111**) may be a permionic membrane. A permionic membrane, such as described in U.S. Pat. No. 2,967,807 to S. G. Osborne et al for "Electrolytic Decomposition of Sodium Chloride," and in U.S. Pat. No. 3,438,897 to M. S. Kircher et al for "Protection of PermSelective Diaphragm During Electrolysis," is electrolyte impermeable but permeable to cations. Typically, a permionic membrane permits the recovery of a catholyte liquor substantially free of alkali metal halide, i.e., a catholyte liquor containing less than one percent alkali metal halide, and frequently one-tenth of a percent or even less of alkali metal halide. Such catholyte liquor frequently contains 10, 20, or even 50 percent alkali metal hydroxide.

In one exemplification of the electrolytic cell of this invention where the cathode **34** is a surface of the backplate **30,** and the barrier **111** is unsupported, the barrier **111** may be provided with reinforcement means. Typical reinforcement means include catholyte liquor resistant mesh, such as steel mesh or fluorocarbon thread mesh. When the barrier **111** is a diaphragm, the diaphragm may be an asbestos paper diaphragm, e.g., electrolytic asbestos paper.

The individual bipolar electrodes **30** are maintained in a spaced relationship, with electrolyte tight seals therebetween, by suitable compressive means. Typical means for maintaining the bipolar electrolyzer in an op-

erating condition are compressive means **141** including a threaded rod **143** having nuts **145** and washers **147** at the opposite ends thereof, thereby applying a compressive force upon all the individual bipolar electrodes **30** of the electrolyzer. Preferably the rod **143** is insulated so as to avoid short circuiting the cell. The rod **143** may pass through apertures **149** in the individual bipolar electrodes **30.** Alternatively, the rod **143** may pass alongside the individual bipolar electrodes **30.** The electrolyzer is supported on the support **131.**

In the electrolytic cell of this invention, power is supplied to an anodic end cell **32** of the electrolyzer from an electric power supply by electrical conduction means **121** and recovered from a cathodic half cell **32** through electrical conduction means **121** at the opposite end of the electrolyzer **1.**

In the electrolytic cell contemplated herein, the electrodes are electroconductive members fabricated of silicon. The silicon used in fabricating the bipolar electrodes should be electroconductive and preferably at least as electroconductive as graphite, e.g., silicon having a bulk electrical conductivity in excess of 100 $(\text{ohm-centimeters})^{-1}$ or even 1000 $(\text{ohm-centimeters})^{-1}$ or more.

Substantially pure silicon, e.g., silicon having a purity in excess of 99.99 atomic percent, is at most a poor conductor or even a semiconductor or non-conductor. The silicon useful in providing the bipolar electrodes contemplated herein, typically has an electroconductivity in excess of 100 $(\text{ohm-centimeters})^{-1}$.

The silicon useful in providing the bipolar electrodes contemplated herein has chemical resistance to the electrolyte and to products of the electrolytic process. This chemical resistance is typically provided by the formation of a film or a layer of a silicon oxide, e.g., SiO_2, or suboxides thereof, on the areas of the silicon exposed to the electrolyte.

Additionally, silicon electrodes contemplated herein for use in bipolar electrodes should have physical strength in order to be resistant to impact and abrasion. Physical strength may be provided by the presence of small amounts of alloying agents.

The electrical conductivity may be provided either by the presence of a dopant, i.e., an electron donor or an electron acceptor. Suitable electron donors are phosphorous, arsenic, antimony, and bismuth. Suitable electron acceptors are boron, aluminum, gallium, and the like. For electrochemical applications, i.e., for use as electrodes in electroconductive media, electron acceptors appear to impart chemical resistance to the silicon.

The dopant used in providing improved electrical conductivity, which dopant may either be an electron acceptor or an electron donor, should be present in an amount greater than 0.01 weight percent of the silicon, and preferably in an excess of about 0.1 percent of the silicon. Generally, the dopant should be less than about 3 weight percent of the silicon, and almost always less than about 5 weight percent of the silicon. The presence of small amounts of the dopant increases the electrical conductivity from about 10 $(\text{ohm-centimeters})^{-1}$ or less which is characteristic of semi-conductor and rectifier grades of silicon to in excess of 100 (ohm-centimeters) and preferably to in excess of 1000 or even 10,000 (ohm-centimeters) or even higher which is comparable to graphite and conventional metallic conductors.

Particularly good results are obtained when the dopant is an electron acceptor, preferably boron, and the concentration of boron is from about 0.1 weight percent of the silicon to about 1.5 or even 2 weight percent of the silicon.

Increased physical strength and castability may be provided by alloying agents such as aluminum, gallium, manganese, iron, cobalt, nickel, chromium, or molybdenum. These alloying agents, when present, may be present in total concentration, i.e., as a silicide and as the metal, in excess of one-half percent by weight, preferably in excess of about 8 percent by weight, frequently as high as 30 percent by weight or even more, but generally not greatly in excess of about 40 percent by weight. These alloying agents serve to increase the malleability and ductility of the elemental silicon. Elemental silicon as the term is used herein is silicon having a formal valence of 0.

In addition to elemental silicon, the various silicides may be present within and on the surface of the bipolar electrode useful in the bipolar electrolyzer of this invention. While the term silicide is used herein, it is to be understood that such term also encompasses metallic solid solutions of silicon and the metal referred to as being present as a silicide, metallic solid solutions of silicon and the silicide, and metallic solutions of the silicides. Additionally, it is to be understood that when silicides and alloying agents are referred to, they may be present in a complex metallurgical system of substantially pure silicon phases, substantially pure silicide phases, and phases which are a metallic solid solution of various silicides and metallic solid solutions of silicon and various silicides. The silicides serve to provide additional electroconductivity to the silicon bipolar electrodes of this invention. Such silicides include the electroconductive silicides of various metals such as lithium silicide, boron silicide, sodium silicide, magnesium silicide, phosphorous silicide, hafnium silicide, calcium silicide, titanium silicide, vanadium silicide, chromium silicide, iron silicide, cobalt silicide, copper silicide, arsenic silicide, rubidium silicide, strontium silicide, zirconium silicide, niobium silicide, molybdenum silicide, ruthenium silicide, rhodium silicide, palladium silicide, tellurium silicide, cesium silicide, barium silicide, silicides of the rarer metals, tantalum silicide, tungsten silicide, rhenium silicide osmium silicide, iridium silicide, and platinum silicide.

The silicides themselves, while providing increased electroconductivity to the elemental silicon base members have fairly poor mechanical properties and, when present as a dominant phase, may serve to decrease the ductility of the silicon base member. For this reason, they will generally not be the major fraction of the material present within the electrode nor will they be present as the metallurgically dominant phase. Generally, silicides when present, should be less than about 50 percent of the total weight of the electrode. Most frequently, the silicide will be less than 20 weight percent of the total electrode and frequently less than about 5 weight percent of the total electrode.

When silicides are present in the electrodes of this invention, they will most commonly be the silicides of the dopants and additives, such as arsenic, boron, copper, iron, cobalt, nickel, manganese, and phosphorous; the silicides of the valve metals such as titanium, tantalum, tungsten, zirconium, hafnium, vanadium, niobium; and the silicides of the platinum group metals,

ruthenium, rhodium, palladium, osmium, iridium, and platinum.

Particularly desired silicides which may be present within the bipolar electrode of this invention and on the surfaces thereof, especially on the anodic surface of the bipolar herein contemplated are the highly electroconductive silicides such as the silicides of the platinum group metals, e.g., Pt_3Si, Pd_3Si, Ir_3Si_2, Rh_3Si_2, and Ru_3Si_2; the silicides of the valve metals, e.g., $TiSi_2$, $ZrSi_2$, VSi_2, $NbSi_2$, $TaSi_2$, and WSi_2; and the silicides of the heavy metals, e.g., Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$, $CoSi_2$, and $MoSi_2$.

A particularly outstanding silicon alloy which may be used to provide the electroconductive bipolar electrode of this invention is the silicon alloy containing sufficient dopant to provide an electrical conductivity in excess of 100 (ohm-centimeters), and sufficient total transition group metal, either as a metal or as an alloy with silicon, or as a silicide, to provide a volumetric coefficient of expansion upon solidification of less than about 10 percent and preferably as low as 1.0 percent or less, balance silicon. Alloys of this type, which are described in commonly assigned copending U.S. application Ser. No. 391,118 filed Aug. 27, 1973 now Pat. No. 3,854,940 for "Electroconductive Corrosion Resistant High Silicon Alloys" are characterized by the substantial absence of thermal stresses upon solidification and have a coefficient expansion upon solidification of plus **5** percent or less. The alloys described therein generally contain sufficient silicon so that a silicon-rich metallurgical phase is maintained as a metallographically predominant phase within the alloy with about two-thirds and preferably three-quarters or more of the silicon being present in the silicon-rich phase. Generally, the alloys therein described contain from about 4 to about 14 weight percent iron or from about 9 to about 12 weight percent total cobalt, or from 1 to about 7 weight percent total nickel, or from about 1 to about 7 weight percent chromium, or from about 1 to about 6 weight percent manganese, or from about 1 to about 18 weight percent scandium, yttrium, or a lanthanide, or from about 1½ to about 7 weight percent titanium, zirconium, or hafnium, or from about 1 to about 16 atomic percent vanadium, columbium, or tantalum, or about 1 atomic percent tungsten or from 1 to about 20 atomic percent copper, silver, or gold. Additionally, the alloy contains from about 0.2 to about 2 weight percent boron. The particular alloys described therein are generally present as a three-phase system containing a transition metal or transition metal silicide-rich phase, a dopant or dopant silicide-rich phase, and a silicon rich-phase. The silicon-rich phase is the metallurgically predominant phase and is substantially discontinuous, broken into numerous individual regions of silicon-rich phase. Transition metal-rich phase forms rivulets around the boundaries of the regions of the silicon-rich phase, and preferably the rivulets are substantially continuous around all the regions of silicon-rich phase. Dopant-rich phases are present as nodules at the boundaries between the phases and within the individual phases.

The preferred silicon alloys useful in providing bipolar electrodes contain from 0.01 to about 5 percent of a dopant, as defined above, from no alloying elements, to about 50 percent alloying elements, including silicides, and generally from about 5 to about 30 percent alloying elements, including silicides, as defined above, and the balance predominantly silicon, e.g., from about 45 to about 99 percent, and preferably from about 67 to about 94 percent total silicon.

A suitable electroconductive material should be provided on the anodic surface **38** of the bipolar electrode **30.** The electroconductive material may cover from about one-quarter of one percent of the anodic surface of the bipolar electrode **30** up to about 98 or 99 percent of the anodic surface of the bipolar electrode **30** or even all of the exposed surface of the bipolar electrode **30,** with oxides or silicon forming on those areas of the silicon exposed to the anodic reaction.

The preferred electroconductive materials are those electroconductive materials that are known in the art as suitable materials for the evolution of chlorine, and are characterized by a low chlorine overvoltage, e.g., less than 0.125 volt at a current density of 200 Amperes per square foot. The preferred materials are further characterized by their chemical stability and resistance to attack by chlorine.

The material on the anodic surface **38** of the silicon bipolar electrode **30** may be either an electrocatalyst, or an electroconductive material, or an electroconductive material having electrocatalytic properties. As used herein, an electrocatalyst or material with electrocatalytic properties is a material which may participate in the process of the absorption of the halide ion on the electrode or in the electron transfer from the halide ion to the electrode to form neutral halogen atoms, or in the combination of neutral halogen atoms to form neutral halogen molecules, or in the desorption of the neutral halogen molecules into the electrolyte. Electrocatalytic properties, as the term is used herein, are evidenced by either decreased halogen overvoltage or decreased dependence of overvoltage on current density, or both.

The preferred materials used for the electroconductive coating of the anodic surface **38** of the bipolar electrode **30** are those materials 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 volt 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 polytetrafluoroethylene 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:

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

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

E_o = 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 couloumbs equivalent^{-1}

Cl_2 concentration = 1 atm

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

T = 305°K

For the reaction

$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$,

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

This is the reversible potential for the system at the operating conditions. The overvoltage on the normal hydrogen scale is, therefore, $\eta = V - [E - 0.2]$ where V is the measured voltage, E is the reversible potential, **1.30, 0.24** is the potential of the saturated calomel half cell.

Suitable materials useful in coating the anodic portion of the bipolar electrode herein contemplated include the platinum group metals, e.g., platinum, ruthenium, rhodium, palladium, osmium, and iridium. The platinum group metals may be present in the form of mixtures or alloys such as platinum and palladium. An especially satisfactory platinum and palladium combination contains up to about **15** weight percent platinum and the balance palladium. Another particularly satisfactory coating is platinum and iridium. An especially satisfactory platinum-iridium combination is one containing from about **10** to about **35** weight percent iridium. Other suitable 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.

Alternatively, the material present on the surface of the anodic member of the electrode pair may be present in the form of an oxide of a precious metal such as ruthenium oxide, rhodium oxide, palladium oxide, osmium oxide, iridium oxide, and platinum oxide. The oxides may also be a mixture of the 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 surfaces of the anode member of the electrode pair herein contemplated nonconductive oxides and oxides of low conductivity. Such materials, while of low conductivity may be catalytic in the sense of providing surface area or available *d* shell electrons for further catalysis of the electrode products. Such materials, while having low bulk electroconductivities themselves, may nevertheless have open or porous structures thereby permitting the flow of electrolyte and electrical current therethrough. For example, aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, niobium oxide, hafnium oxide, tantalum oxide, or tungsten oxide may be present on and in the electroconductive surface in combination with the high conductivity, low chlorine overvoltage material. Additionally, other nonconductive materials, and materials of low conductivity may be present with a more highly conductive material present on the surface coating of the anode portion of the silicon electrode. Additionally, there may also be present on the surface of the anodic member of the electrode herein contemplated the electroconductive low overvoltage silicides of the platinum group metals. These silicides, e.g., platinum silicide, palladium silicide, iridium silicide, rhodium silicide and ruthenium silicide, especially Pt_3Si, Pd_3Si, Ir_3Si_2, Rh_3Si_2, and Ru_3Si_2 provide an electrolyte-resistant low overvoltage coating.

The surface of the anodic portion of the electrode herein contemplated may also include a combination of the oxides and silicides of the platinum group metals, e.g., ruthenium silicide with ruthenium dioxide or palladium silicide with palladium oxide.

The cathodic member of the electrode herein contemplated may be bulk elemental silicon. Elemental silicon has a hydrogen overvoltage of 0.5 volt at 200 Amperes per square foot. Alternatively, the cathodic member of the electrode pair herein contemplated may include substantial amounts of alloying agents, e.g., ferro-silicon, magnesium silicide, manganese silicide, cobalt silicide, molybdenum silicide, and the like. Thus, the cathodic member of the electrode pair herein contemplated may contain elemental silicon as well as substantial amounts, e.g., 75 percent or more by weight of electrolyte-resistant, electroconductive silicides. The cathode portion of the electrode may additionally, unlike the anodic member, be porous to the flow of electrolyte and gases, thereby permitting the introduction of oxygen or an oxygen-bearing gas.

Additionally, the cathodic surface may also be coated as described hereinbefore for the anodic surface. Any of the materials described above may be used, including the platinum group metals, the oxides and oxygen-containing compounds of the platinum group metals, the platinum group metal-rich silicides of the platinum group metals, and various other cathodically active, metal oxides resistant to basic media as spinels and bronze oxides.

Alternatively, the cathodic surface may be provided by material resistant to evolved hydrogen and to hydroxyl ion, OH^-, and having a low hydrogen overvoltage, e.g., less than about 0.35 volt at a current density of about 125 Amperes per square foot. Such materials include iron, cobalt, nickel, manganese, and the like. The surface may be present as a thin sheet, film, or layer, or even as a porous film on the silicon.

Such surfaces serve to lower the voltage of the cathode against a standard calomel electrode, e.g., to about 1.25 to 1.30 volts at 100 Amperes per square foot for a ruthenium oxide coated silicon cathode, as well as to protect the cathode against attack by the basic electrolyte. Only a small amount of coating is necessary to protect the silicon, e.g., less than one-tenth of one percent of the surface area need be coated to obtain a high degree of protection.

Although this invention has been described with particular reference to electrolytic cells for the electrolysis of aqueous alkali metal solutions to produce chlorine or chlorates, it is not limited to such use. The electrodes herein contemplated may be used in electrochemical reactions wherever a corrosion-resistant electrode pair having long life is required and the service is such that the pH of the electrolyte is greater than about 3.5 and less than about 10.0. Thus, the electrolyte in the cell may be a salt of a metal which may be electrodeposited and the electrolyte electrolyzed between the coated silicon anode and a silicon cathode. Alternatively, the electrode pair herein described may be used for the electrolytic oxidation of organic compounds. The electrode pair herein contemplated may further be understood by reference to the following Examples.

EXAMPLE I

A silicon bipolar electrode was prepared containing 0.5 weight percent boron as dopant. The electrical properties of the cathode surface of the bipolar electrode were tested, and thereafter the electrode is utilized as a bipolar electrode.

The electrode was prepared by placing 2700 grams of Ohio Ferro Alloys Corporation silicon pieces having a nominal silicon content of 100 weight percent, and an actual silicon content of 99.5 weight percent, and 63 grams of Fisher Scientific Company fused sodium tetraborate in a Number 10 graphite crucible. The crucible was placed in an electric resistance furnace and heated to 1540°C for 1½ hours. The resulting molten silicon was then poured into a graphite mold that had been preheated to 1000°C. The molten silicon in the mold was slowly cooled to 300°C over a period of 4 hours.

An electrode measuring 5 inches by ¾ inch by ¼ inch was cut from the ingot. This electrode was tested as a cathode in an aqueous solution of 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium dichromate. The pH of the electrolyte solution was 7, and the temperature of the electrolyte solution was 40°C. The cathode voltage was measured against a standard calomel electrode, and was found to be:

Current Density (Amperes per square foot)	Voltage (Volts)
50	1.87
100	1.87
200	1.89

Thereafter, a ruthenium oxide-titanium oxide surface is applied to one surface of the silicon electrode.

This is accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution is prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating are applied with heating to 350°C for 10 minutes after all three coats.

Then an outer-coating solution is applied above the undercoating. The outer-coating is prepared by dissolving 18.1 grams of titanium trichloride in 51.5 grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution were mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydrogen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution are applied on top of the under-coating. The electrode is heated to 350°C for 10 minutes after each first two coats and heated to 450°C for 30 minutes after the third coat. Thereafter the electrode is utilized as a bipolar electrode between two monopolar electrodes. The cells are divided into diaphragm cells by asbestos paper diaphragms on minus **80** mesh Teflon (TM) felt mats. A brine containing 315 grams per liter is fed into the two anolyte compartments, a cell liquor containing 150 grams per liter of sodium chloride and 100 grams per liter of sodium hydroxide is fed into the catholyte chambers. Electrolysis is commenced and gas is seen to be evolved from both surfaces of the silicon bipolar electrode.

EXAMPLE II

A ferro-silicon bipolar electrode was prepared containing 0.5 weight percent boron as dopant. The electrical properties of the cathode surface of the bipolar electrode were tested, and thereafter the electrode is utilized as a bipolar electrode.

The electrode was prepared by placing 1800 grams of Ohio Ferro Alloys Corporation ferro-silicon pieces having a nominal silicon content of 85 weight percent, a nominal iron content of 15 weight percent, an actual silicon content of 88.2 weight percent, and an actual iron content of 11.2 weight percent, and 42 grams of Fisher Scientific Company fused sodium tetraborate in a Number 10 graphite crucible. The crucible was placed in an electric resistance furnace and heated to 1540°C for 1 hour. The resulting molten ferro-silicon was then poured into a graphite mold that had been preheated to 1000°C. The molten ferro-silicon in the ingot mold was slowly cooled to 300°C over a period of **4** hours.

An electrode measuring 5 inches by ¾ inch by ¼ inch was cut from the ingot. This electrode was tested as a cathode in an aqueous solution of 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium dichromate. The pH of the electrolyte solution was 7, and the temperature of the electrolyte solution was 40°C. The cathode voltage was measured against a standard calomel electrode, and was found to be:

Current Density (Amperes per square foot)	Voltage (Volts)
50	1.78
100	1.84
200	1.88

Thereafter, a ruthenium oxide-titanium oxide surface is applied to one surface of the silicon electrode.

This is accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution is prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating were applied with heating to 350°C for 10 minutes after all three coats.

Then an outer-coating solution is applied above the undercoating. The outer-coating is prepared by dissolving 18.1 grams of titanium trichloride in 51.5 grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution were mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydro-

gen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution are applied on top of the under-coating. The electrode is heated to 350°C for 10 minutes after each first two coats, and to 450°C for 30 minutes after the third coat. Thereafter the electrode is utilized as a bipolar electrode between two monopolar electrodes. The cells are divided into diaphragm cells by asbestos paper diaphragms on minus 80 mesh Teflon felt mats. A brine containing 315 grams per liter is fed into the two anolyte compartments, a cell liquor containing 150 grams per liter of sodium chloride and 100 grams per liter of sodium hydroxide is fed into the catholyte chambers. Electrolysis is commenced and gas is seen to be evolved from both surfaces of the silicon bipolar electrode.

EXAMPLE III

A ferro-silicon bipolar electrode was prepared containing 0.15 weight percent boron as dopant. The electrical properties of the cathode surface of the bipolar electrode were tested, and thereafter the electrode is utilized as a bipolar electrode.

The electrode was prepared by placing 1800 grams of Ohio Ferro Alloys Corporation ferro-silicon pieces having a nominal silicon content of 75 weight percent, a nominal iron content of 25 weight percent, an actual silicon content of 80.8 weight percent, and an actual iron content of 19.2 weight percent, and 42 grams of Fisher Scientific Company fused sodium tetraborate in a Number 10 graphite crucible. The crucible was placed in an electric resistance furnace and heated to 1540°C for 1¼ hours. The resulting molten ferro-silicon was then poured into a graphite mold that had been preheated to 1000°C. The molten ferro-silicon in the ingot mold was slowly cooled to 300°C over a period of 4 hours.

An electrode measuring 5 inches by ¾ inch by ¼ inch was cut from the ingot. This electrode was tested as a cathode in an aqueous solution of 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium dichromate. The pH of the electrolyte solution was 7, and the temperature of the electrolyte solution was 40°C. The cathode voltage was measured against a standard calomel electrode, and was found to be:

Current Density (Amperes per square foot)	Voltage (Volts)
50	1.77
100	1.80
200	1.84

Thereafter a ruthenium oxide-titanium oxide surface is applied to one surface of the silicon electrode.

This is accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution is prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating were applied with heating to 350°C for 10 minutes after all three coats.

Then an outer-coating solution is applied above the undercoating. The outer-coating is prepared by dissolving 18.1 grams of titanium trichloride in 51.5 grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution were mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydrogen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution are applied on top of the under-coating. The electrode is heated to 350°C for 10 minutes after each first two coats and heated to 450°C for 30 minutes after the third coat. Thereafter, the electrode is utilized as a bipolar electrode between two monopolar electrodes. The cells are divided into diaphragm cells by asbestos paper diaphragms on minus 80 mesh Teflon (TM) felt mats. A brine containing 315 grams per liter is fed into the two anolyte compartments, a cell liquor containing 150 grams per liter of sodium chloride and 100 grams per liter of sodium hydroxide is fed into the catholyte chambers. Electrolysis is commenced and gas is seen to be evolved from both surfaces of the silicon bipolar electrode.

EXAMPLE IV

A ferro-silicon bipolar electrode was prepared containing 0.5 weight percent boron as dopant. The electrical properties of the cathode surface of the bipolar electrode were tested, and thereafter the electrode is utilized as a bipolar electrode.

The electrode was prepared by placing 700 grams of Ohio Ferro Alloys Corporation ferro-silicon pieces having a nominal silicon content of 65 weight percent, a nominal iron content of 35 weight percent, an actual silicon content of 69.8 weight percent and an actual iron content of 30.2 weight percent, and 16.25 grams of Fisher Scientific Company fused sodium tetraborate in a Number 4 graphite crucible. The crucible was placed in an electric resistance furnace and heated to 1540°C for 1 hour. The resulting molten ferro-silicon was then poured into a graphite mold that had been preheated to 1000°C. The molten ferro-silicon in the ingot mold was slowly cooled to 300°C over a period of 4 hours.

An electrode measuring 5 inches by ¾ inch by ¼ inch was cut from the ingot. This electrode was tested as a cathode in an aqueous solution of 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium dichromate. The pH of the electrolyte solution was 7, and the temperature of the electrolyte solution was 40°C. The cathode voltage was measured against a standard calomel electrode and was found to be:

Current Density (Amperes per square foot)	Voltage (Volts)
50	1.71
100	1.75
200	1.85

Thereafter a ruthenium oxide-titanium oxide surface is applied to one surface of the silicon electrode.

This is accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution is prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating are applied with heating to 350°C for 10 minutes after all three coats.

Then an outer-coating solution is applied above the under-coating solution. The outer-coating is prepared by dissolving 18.1 grams of titanium trichloride in 51.5

grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution are mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydrogen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution are applied on top of the under-coating. The electrode is heated to 350°C for 10 minutes after each first two coats, and to 450°C for 30 minutes after the third coat. Thereafter, the electrode is utilized as a bipolar electrode between two monopolar electrodes. The cells are divided into diaphragm cells by asbestos paper diaphragms on minus 80 mesh Teflon felt mats. A brine containing 315 grams per liter is fed into the two anolyte compartments, a cell liquor containing 150 grams per liter of sodium chloride and 100 grams per liter of sodium hydroxide is fed into the catholyte chambers. Electrolysis is commenced and gas is seen to be evolved from both surfaces of the silicon bipolar electrode.

EXAMPLE V

A ruthenium oxide coated ferro-silicon bipolar electrode was prepared containing 0.5 weight percent boron as dopant. The electrical properties of the cathode surface of the bipolar electrode were tested, and thereafter the electrode is utilized as a bipolar electrode.

The electrode was prepared by placing 1200 grams of Ohio Ferro Alloys Corporation ferro-silicon pieces having a nominal silicon content of 85 weight percent, a nominal iron content of 15 weight percent, an actual silicon content of 88.2 weight percent, and an actual iron content of 11.8 weight percent, 600 grams of Ohio Ferro Alloys Corporation silicon, and 42 grams of Fisher Scientific Company fused sodium tetraborate in a Number 10 graphite crucible. The crucible was placed in an electric resistance furnace and heated to 1540°C for 1½ hours. The resulting molten ferro-silicon was then poured into a graphite mold that had been preheated to 1000°C. The molten ferro-silicon in the ingot mold was slowly cooled to 300°C over a period of 4 hours.

An electrode measuring 5 inches by ¾ inch by ¼ inch was cut from the ingot. A ruthenium oxide-titanium oxide exterior surface was applied to both 5 inches by ¾ inch surfaces of the bipolar electrode. This was accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution was prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating were applied with heating to 350°C for 10 minutes after all three coats.

Then an outer-coating solution was applied above the undercoating solution. The outer-coating was prepared by dissolving 18.1 grams of titanium trichloride in 51.5 grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution were mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydrogen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution were applied on top of the under-coating. The electrode was heated to 350°C for 10 minutes after each first two coats, and to 450°C for 30 minutes after the third coat. This electrode was tested as a cathode in an aqueous solution of 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium dichromate. The pH of the electrolyte solution was 7, and the temperature of the electrolyte solution was 40°C. The cathode voltage was measured against a standard calomel electrode and was found to be:

Current Density (Amperes per square foot)	Voltage (Volts)
50	1.25
100	1.29

Thereafter the electrode is utilized as a bipolar electrode between two monopolar electrodes. The cells are divided into diaphragm cells by asbestos paper diaphragms on minus 80 mesh Teflon (TM) felt mats. A brine containing 315 grams per liter is fed into the two anolyte compartments, a cell liquor containing 150 grams per liter of sodium chloride and 100 grams per liter of sodium hydroxide is fed into the catholyte chambers. Electrolysis is commenced and gas is seen to be evolved from both surfaces of the silicon bipolar electrode.

EXAMPLE VI

A bipolar chlorate electrolyzer was prepared having a silicon bipolar electrode dividing the electrolyzer into two separate electrolytic cells, and having silicon electrodes facing the bipolar electrode.

The silicon electrodes were prepared by melting silicon powder, and fused sodium tetraborate ($Na_2B_4O_7$) in a graphite crucible. Sufficient sodium tetraborate was added to the charge to provide an electrode containing one weight percent boron. The charge was heated to 1500°C for 16 hours. Thereafter, the molten silicon containing boron was poured into a graphite mold that had been heated to 1000°C. After the silicon had solidified and cooled, the ingot was cut into 3 pieces.

The silicon member intended for use as an anode and one surface of the silicon member intended for use as a bipolar electrode were coated to provide a ruthenium oxide-titanium dioxide surface.

This was accomplished by etching the surface and applying a ruthenium trichloride under-coating to the surface. The under-coating solution was prepared by dissolving 2 grams of ruthenium trichloride in 18 grams of ethyl alcohol. Three coats of the under-coating were applied with heating to 350°C for 10 minutes after all three coats.

Then, an outer-coating solution was applied above the undercoating. The outer-coating was prepared by dissolving 18.1 grams of titanium trichloride in 51.5 grams of a 15 weight percent aqueous solution of hydrochloric acid. Two grams of this solution were mixed with 1 gram of methyl alcohol, 0.5 grams of 30 percent hydrogen peroxide, and 1.2 grams of a solution prepared from 1 gram of ruthenium trichloride and 4 grams of methyl alcohol. Three coats of this outer-coating solution were applied on top of the under-coating. The electrode was heated to 350°C for 10 minutes after each first two coats, and to 450°C for 30 minutes after the third coat.

The silicon member intended for use as a bipolar electrode was then cemented into a plastic fitting.

The uncoated silicon member was inserted at one end of a plastic rectangular box, and the coated silicon

member intended for use as an anode was inserted at the opposite end of the plastic rectangular box. The member intended for use as a bipolar electrode, in its plastic fitting, was cemented into the rectangular plastic box with the ruthenium dioxide coated surface thereon facing the uncoated silicon member, and the uncoated surface facing the ruthenium dioxide coated silicon member. The bipolar electrode was spaced one inch from each of the monopolar electrodes.

A solution of brine containing 310 grams per liter of sodium is placed in the cell and electrolysis is commenced. Chlorine is seen to be evolved from the anode, hydrogen from the cathode.

The silicon cathode was removed from the electrolytic cell and tested as a cathode. The electrolyte used for testing the cathode contained 450 grams per liter of sodium chlorate, 150 grams per liter of sodium chloride, and 5 grams per liter of sodium chromate ($Na_2Cr_2O_7$). At a current density of 200 Amperes per square foot, the voltage versus a standard calomel reference electrode was 1.89 volts. At a current density of **100** Amperes per square foot, the voltage versus a standard calomel electrode is 1.87 volts. At a current density of 50 Amperes per square foot, the voltage versus a standard calomel reference electrode is 1.84 volts.

The hydrogen overvoltage of the silicon cathode was calculated to be 0.44 volt at 200 Amperes per square foot.

It is to be understood that although the invention has been described with reference to specific details of particular embodiments thereof, it is not to be so limited as 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. A bipolar electrolyzer having a plurality of bipolar electrodes mechanically and electrically in series, with an anodic surface of one bipolar electrode facing a cathodic surface of the next adjacent bipolar electrode and forming an electrolytic cell therebetween, at least one of said bipolar electrodes comprising an electroconductive metallic silicon member containing at least 45 weight percent silicon and sufficient dopant to provide said member with an electroconductivity greater than 100 $(\text{ohm-centimeters})^{-1}$ and having an anodic surface on one side of said member and a cathodic surface on the opposite side thereof.

2. The electrolyzer of claim **1** wherein said dopant is chosen from the group consisting of boron, aluminum, gallium, phosphorous, arsenic, antimony, and bismuth.

3. The electrolyzer of claim **1** wherein said metallic bipolar electrode contains from about 0.01 to about 5 weight percent of the dopant.

4. The electrolyzer of claim **1** wherein said metallic bipolar electrode contains from about 45 to about 99 weight percent silicon.

5. The electrolyzer of claim **1** wherein the anodic surface of the bipolar metallic electrode comprises a coating of an electrocatalytic material on the bipolar electrode.

6. The electrolyzer of claim **5** wherein said electrocatalytic material is characterized by a chlorine overvoltage of less than 0.25 volt when measured in chlorinated brine at a current density of 125 Amperes per square foot.

7. The electrolyzer of claim **1** wherein the cathodic surface of the bipolar metallic electrode comprises a coating of a material having a hydrogen overvoltage less than 0.35 volt at 125 Amperes per square foot.

8. The electrolyzer of claim **1** wherein the cathodic surface of the bipolar metallic electrode comprises a coating of a metal chosen from the group consisting of iron, cobalt, nickel, and manganese.

9. The bipolar electrolyzer of claim **1** wherein said metallic bipolar electrode comprises means for spacing said metallic bipolar electrode from the adjacent bipolar electrode while providing an electrolyte tight seal therebetween.

10. The bipolar electrolyzer of claim **9** wherein said spacing means comprise a peripheral wall.

11. The bipolar electrolyzer of claim **10** wherein said means for providing an electrolyte tight seal comprises gasket means between the peripheral walls of adjacent bipolar electrodes.

12. The bipolar electrolyzer of claim **1** wherein said metallic bipolar electrode includes gas header means.

13. The bipolar electrolyzer of claim **12** wherein said gas header means is mounted on top of the metallic bipolar electrode, extends beyond the anodic and cathodic surfaces thereof, and comprises means for the recovery of cathodic gases and means for the recovery of anodic gases.

14. The bipolar electrolyzer of claim **1** wherein said metallic bipolar electrode includes liquid header means.

15. The bipolar electrolyzer of claim **14** wherein said liquid header means is mounted on the bottom of the metallic bipolar electrode and extends beyond the anodic and cathodic surfaces thereof, and comprises means for feeding brine and means for recovering cell liquor.

16. The bipolar electrolyzer of claim **1** wherein said metallic bipolar electrode comprises:

a. peripheral wall spacing means on the vertical sides thereof to space said bipolar electrode from adjacent bipolar electrodes and provide electrolyte volumes therebetween;

b. gas header means on the top of and extending beyond the anodic and cathodic surfaces of the metallic bipolar electrode; and

c. liquid header means on the bottom of and extending anodic and cathodic surfaces of the metallic bipolar electrode.

17. The bipolar electrolyzer of claim **16** wherein the leading edges of said peripheral walls, gas header means, and liquid header means are substantially in a single plane.

18. The bipolar electrolyzer of claim **16** wherein compressive means extend from an end cell of said bipolar electrolyzer, through the metallic bipolar electrodes thereof, to an opposite end cell thereof.

19. The bipolar electrolyzer of claim **16** wherein said header means are metallurgically joined to said metallic bipolar electrode.

20. The bipolar electrolyzer of claim **16** wherein said header means are mechanically joined to said metallic bipolar electrode.

21. The bipolar electrolyzer of claim **20** wherein said header means are joined to said metallic bipolar electrode by compressive means extending from said gas header means to said liquid header means.

22. The bipolar electrolyzer of claim **1** wherein the electroconductive silicon bipolar electrode comprises a single silicon member.

23. The bipolar electrolyzer of claim 1 wherein the electroconductive silicon bipolar electrode comprises a plurality of individual silicon members having electrolyte tight seals between adjacent individual silicon members.

24. The bipolar electrolyzer of claim 23 wherein said individual silicon members are compressively held together to form an electrolyte tight metallic bipolar electrode.

25. The bipolar electrolyzer of claim 23 wherein said individual silicon members are metallurgically joined together to form an electrolyte tight metallic bipolar electrode.

26. The bipolar electrolyzer of claim 1 wherein permeable barrier means are interposed between said metallic bipolar electrode and an adjacent bipolar electrode.

27. The bipolar electrolyzer of claim 26 wherein said permeable means comprise electrolyte permeable diaphragm means.

28. The bipolar electrolyzer of claim 26 wherein said barrier means comprise ion permeable membrane means.

29. A bipolar electrolyzer having a plurality of individual electrolytic cells mechanically and electrically in series, at least one of said cells comprising:

a first silicon cell unit having an anodic surface thereon;

a second silicon cell unit spaced from said first cell unit and having a cathodic surface thereon facing the anodic surface of the first silicon cell unit;

said first cell unit and second cell unit defining an electrolyte chamber therebetween; and

each of said silicon cell units comprising at least 45 weight percent silicon and sufficient dopant to provide an electrical conductivity of at least 100 $(\text{ohm-centimeters})^{-1}$.

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

31. The electrolyzer of claim 29 wherein said silicon cell units contain from about 0.01 to about 5 weight percent of the dopant.

32. The electrolyzer of claim 29 wherein the surface of said first silicon cell unit comprises a coating of an electrocatalytic material on the silicon.

33. The electrolyzer of claim 32 wherein said electrocatalytic material is characterized by a chlorine overvoltage of less than 0.25 volt when measured in chlorinated brine at a current density of 125 Amperes per square foot.

34. The electrolyzer of claim 29 wherein the surface of said second silicon cell unit comprises a coating of a material having a hydrogen overvoltage less than 0.35 volt at 125 Amperes per square foot.

35. The electrolyzer of claim 29 wherein the surface of said second silicon cell unit comprises a coating of material chosen from the group consisting of iron, cobalt, nickel, and manganese.

36. The bipolar electrolyzer of claim 29 comprising spacing means and sealing means for maintaining an electrolyte tight seal between said first cell unit and said second cell unit while maintaining the anodic surface of the first cell unit spaced from cathodic surface of the second cell unit, thereby defining an electrolyte volume therebetween.

37. The electrolyzer of claim 36 wherein said spacing means comprise a peripheral wall on at least one of said cell units.

38. The electrolyzer of claim 37 wherein said spacing means comprises a peripheral wall on the edges of at least one of said cell units.

39. The electrolyzer of claim 38 wherein said sealing means comprises gasket means between said first cell unit and said second cell unit.

40. The electrolyzer of claim 29 wherein said first cell unit includes gas header means.

41. The electrolyzer of claim 40 wherein said gas header means is mounted on top of said first cell unit, extends beyond the anodic surface thereof, and comprises means for the recovery of chlorine from said cell.

42. The electrolyzer of claim 29 wherein said first cell unit includes liquid header means.

43. The electrolyzer of claim 42 wherein said liquid header means is mounted on the bottom of said first cell unit, extends beyond the anodic surface thereof, and includes means for feeding brine to said cell.

44. The electrolyzer of claim 29 wherein said second cell unit includes gas header means.

45. The electrolyzer of claim 44 wherein said gas header means is mounted on top of said second cell unit, extends beyond the cathodic surface thereof, and comprises means for the recovery of hydrogen from said cell.

46. The electrolyzer of claim 29 wherein said second cell unit includes liquid header means.

47. The electrolyzer of claim 46 wherein said liquid header means is mounted on the bottom of said second cell unit, extends beyond the cathodic surface thereof, and comprises means for the recovery of cell liquor from said cell.

48. The electrolyzer of claim 29 wherein:

a. said first cell unit comprises:

1. peripheral wall spacing means on the vertical sides thereof;
2. gas header means on top of and extending beyond the anodic surface of said first cell unit;
3. liquid header means on the bottom of and extending beyond the anodic surface of said first cell unit; and
4. the leading edges of said peripheral walls, gas header means, and liquid header means are substantially in a first single plane;

b. said second cell unit comprises:

1. peripheral wall spacing means on the vertical sides thereof;
2. gas header means on top of and extending beyond the cathodic surface of said second cell unit;
3. liquid header means on the bottom of and extending beyond the cathodic surface of said second cell unit; and
4. the leading edges of said peripheral walls, gas header means, and liquid header means are substantially in a second single plane; and

c. gasket means are interposed between said first cell unit and said second cell unit.

49. The electrolyzer of claim 48 wherein compressive means extend from an end cell unit through the individual cell units to an opposite end cell.

50. The electrolyzer of claim 48 wherein said header means are metallurgically joined to said cell units.

51. The electrolyzer of claim 48 wherein said header means are mechanically joined to said cell units.

52. The electrolyzer of claim **51** wherein said header means are joined to said cell units by compressive means extending from said gas header means to said liquid header means.

53. The bipolar electrolyzer of claim **29** wherein each electroconductive silicon cell unit comprises a single silicon member.

54. The bipolar electrolyzer of claim **29** wherein each electroconductive silicon cell unit comprises a plurality of individual silicon members having electrolyte tight seals between adjacent individual silicon members.

55. The bipolar electrolyzer of claim **54** wherein said individual silicon members are compressively held together to form an electrolyte tight metallic bipolar electrode.

56. The bipolar electrolyzer of claim **54** wherein said individual silicon members are metallurgically joined together to form an electrolyte tight metallic bipolar electrode.

* * * * *