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(54) APPARATUS FOR ELECTROLYSIS OF MOLTEN OXIDES

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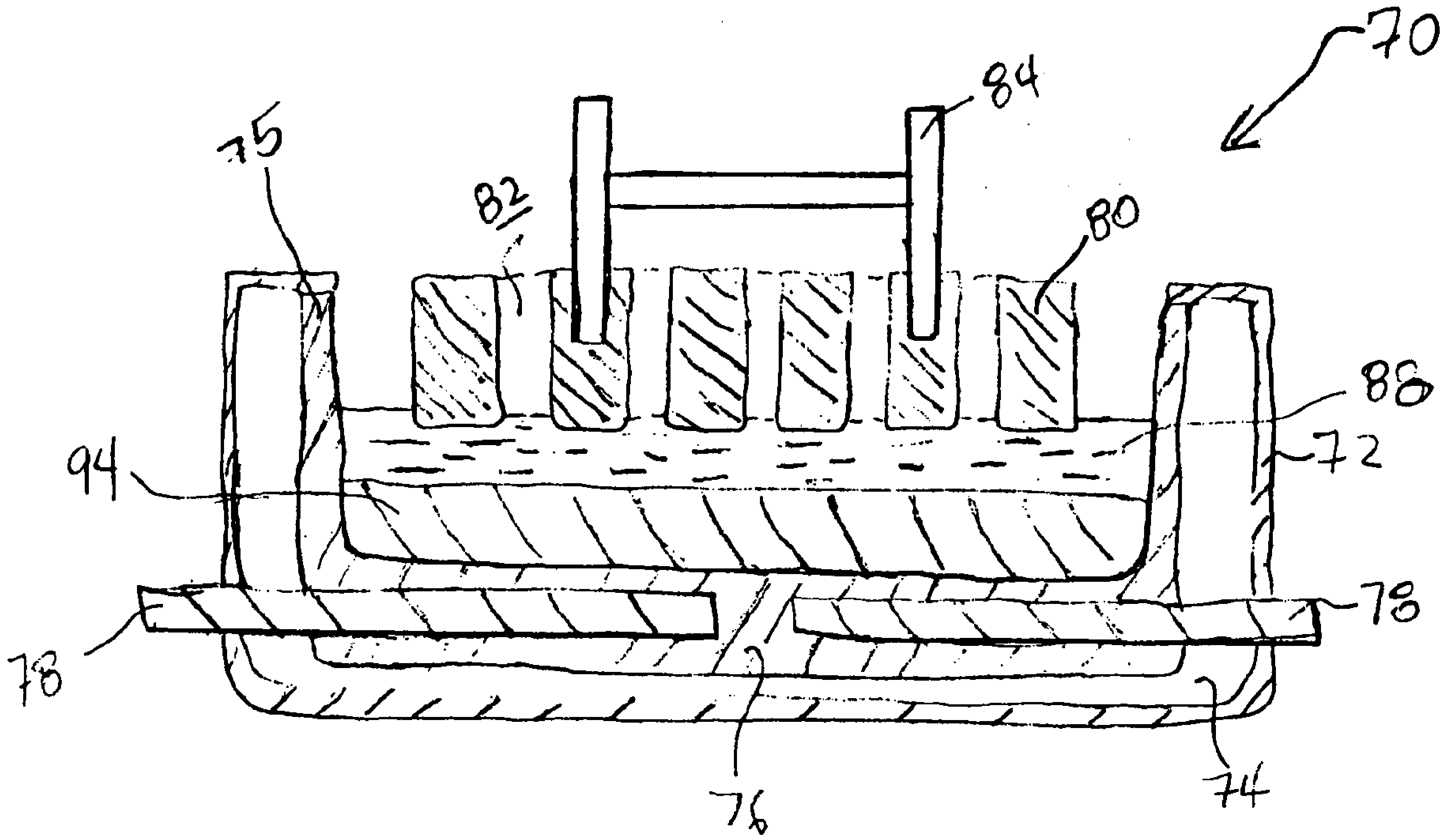
(57) ABSTRACT

The invention provides improved electrodes for electrolytic cells operating with molten salt electrolytes. Nonconsumable iridium-based anodes of the invention facilitate the release of gaseous oxygen from oxide-containing melts, for example in the electro-chemical production of liquid or gaseous reactive metals from oxides. Cathode substrates of the invention are constructed of a tungsten-based alloy and enable deposition of an overlying liquid-metal cathode. Incorporation of the anode and cathode substrate of the invention into molten-oxide cells establishes a novel method for electrolytic extraction of titanium and other reactive metals.



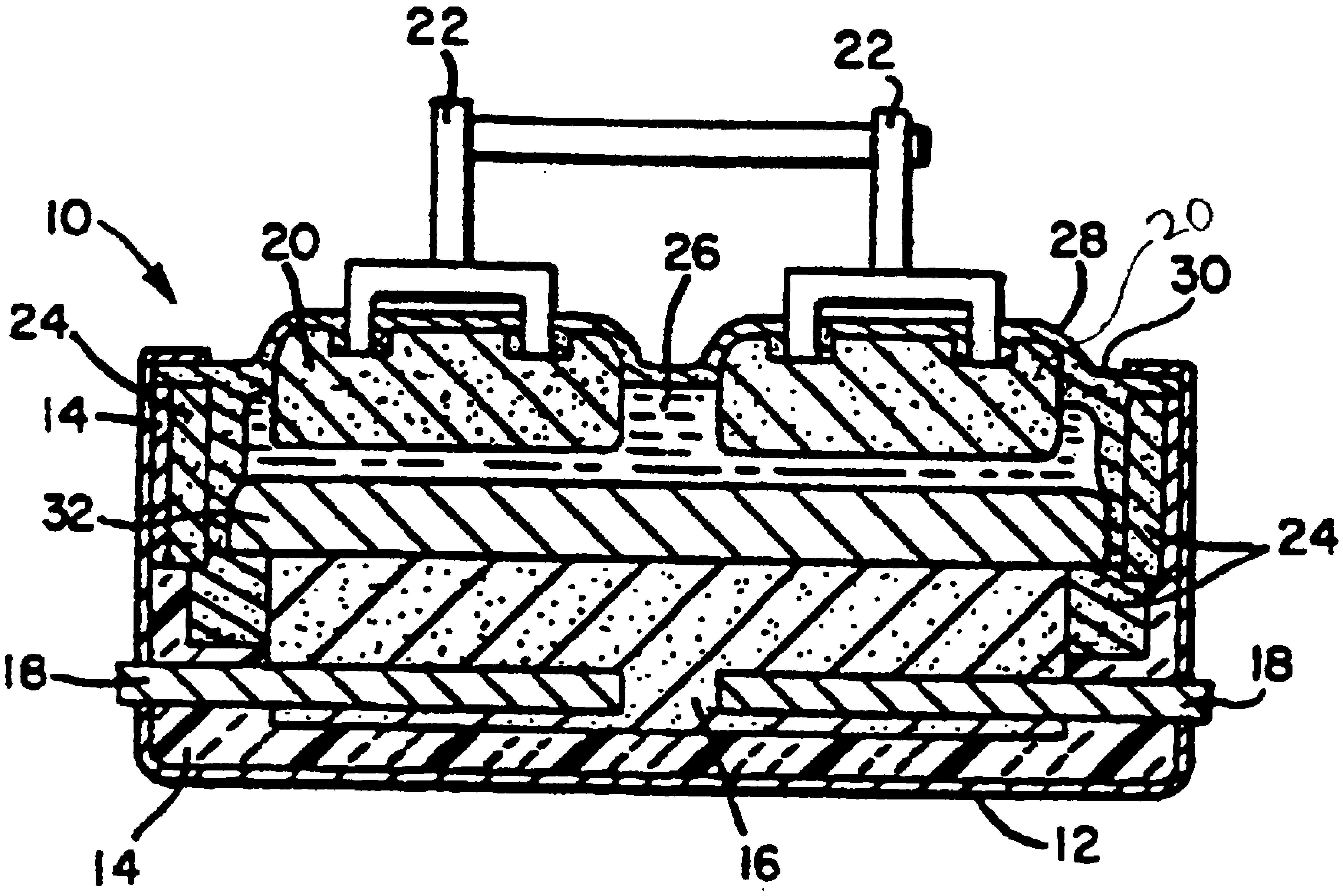


Fig. 1

(prior art)

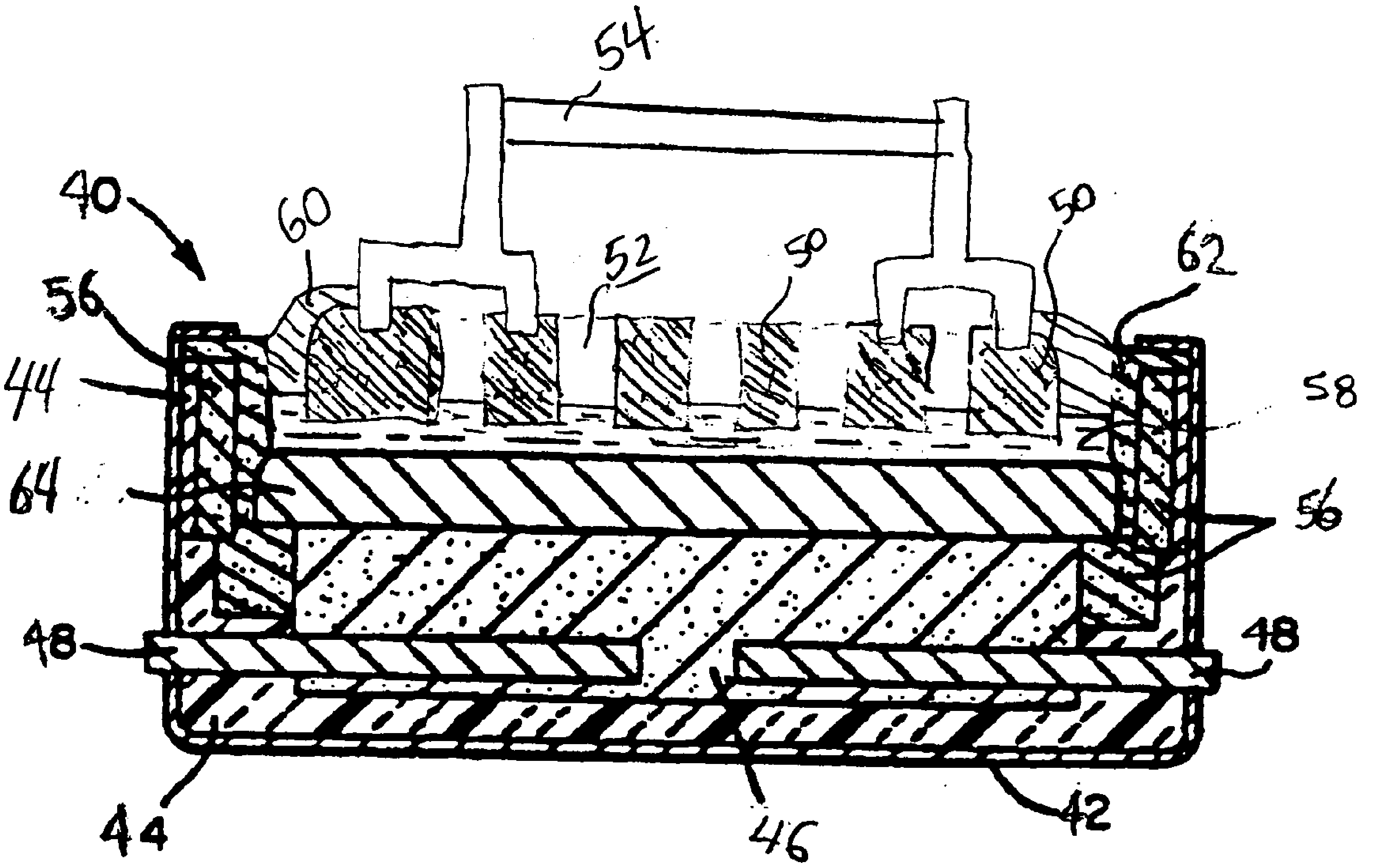


FIG. 2

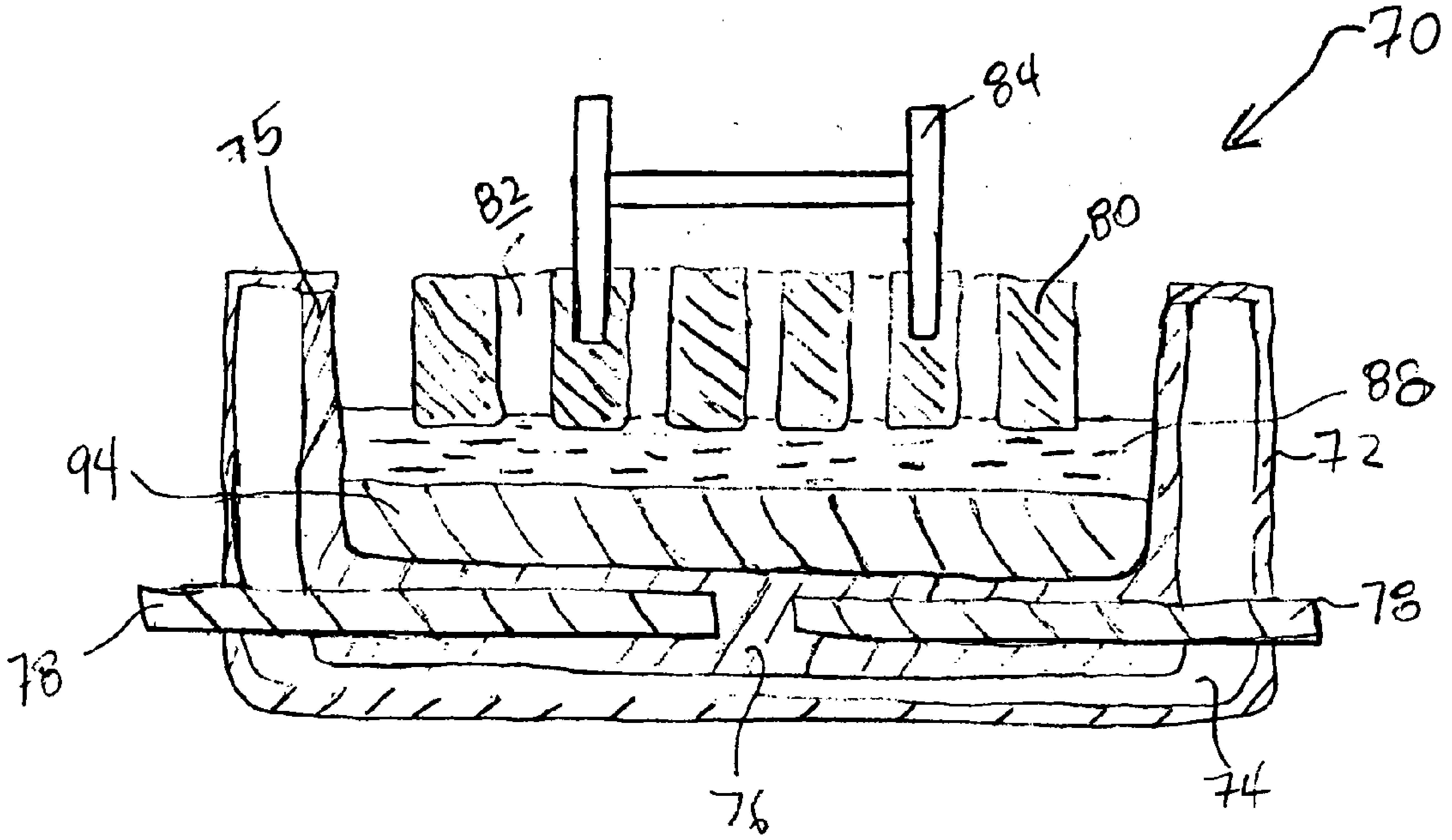


FIG. 3

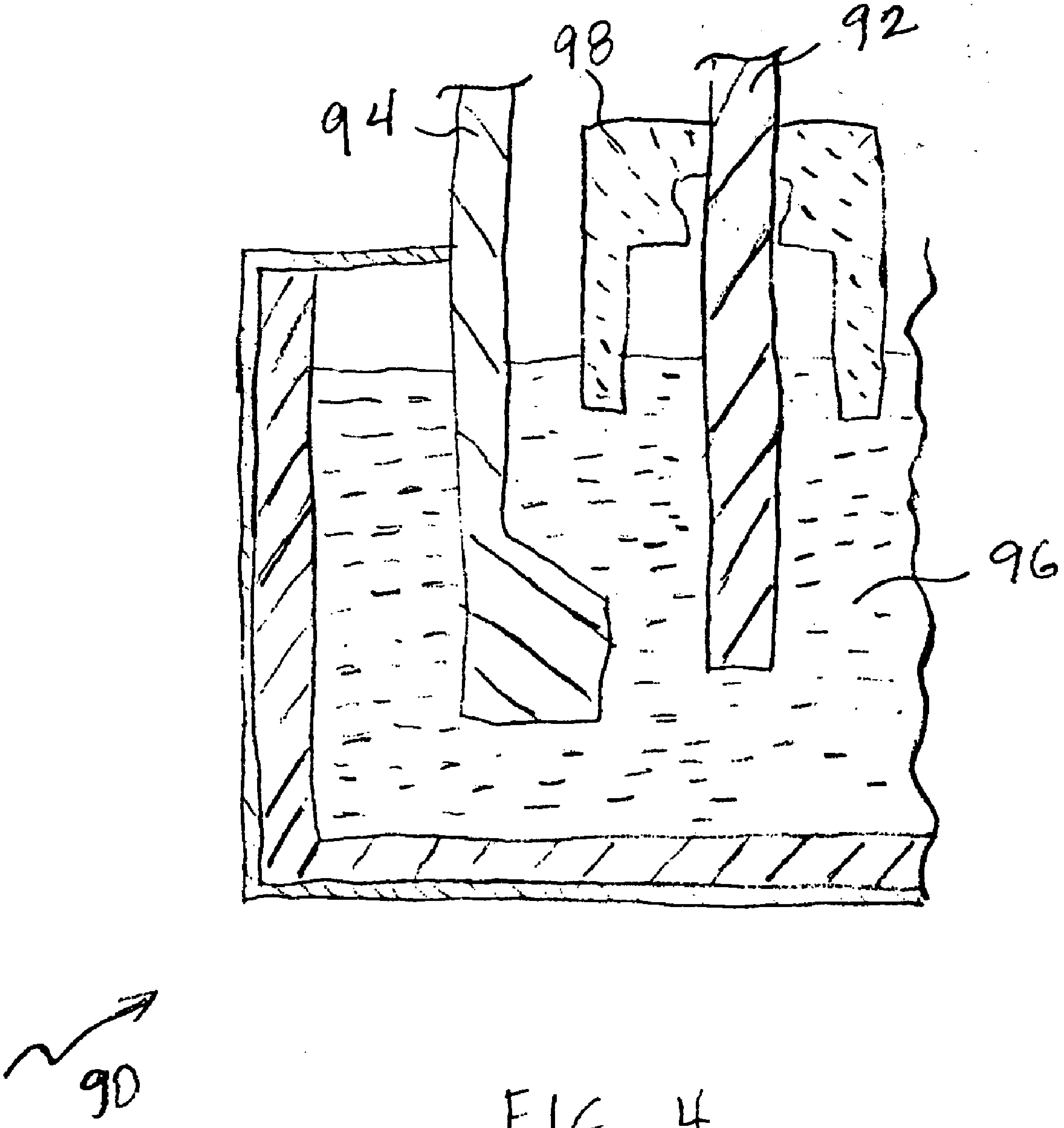


FIG. 4

APPARATUS FOR ELECTROLYSIS OF MOLTEN OXIDES

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to electrolytic cells for the production of metals from molten electrolytes. In particular, this invention provides novel anodes and cathode substrates for use with oxide melts and liquid or gaseous metal products. More particularly, an electrochemical technique for deposition of liquid titanium from titanium dioxide is described.

[0003] 2. Background Information

[0004] Electrolytic processes acting on molten salt electrolytes have been used to produce several important metals, examples of which are given in U.S. Pat. No. 5,185,068, the entire disclosure of which is incorporated by reference.

[0005] Electrolytic reduction in extractive metallurgy has seen its greatest commercial success in the production of aluminum. The invention of the Hall-Héroult process in the 1880s gave birth to a new industry and transformed aluminum from a precious metal into a ubiquitous material, commonplace in construction, transportation, packaging, and electrical devices.

[0006] This process functions by passing an electric current through a molten fluoride electrolyte containing alumina at about 1000° C. (The electrochemical extraction of aluminum by the Hall-Héroult process is discussed in U.S. Pat. No. 4,999,097, the entire disclosure of which is incorporated by reference.) The Hall-Héroult process has persisted as the only commercial production method for aluminum with little change in its components since early implementations. For example, the anode at which oxygen from the melt is oxidized is made of carbonaceous materials as were the first Hall-Héroult cell anodes. Carbon has several useful properties that have allowed the Hall-Héroult process to become a tonnage provider of aluminum. Carbon anodes are solid at the cell operating temperatures, well above the melting point of aluminum, so that the aluminum can be retrieved in liquid form. Also, the electrical conductivity of carbon is sufficiently high that the massive amperages required for practicable production rate can be conveyed to the melt without excessive voltages.

[0007] However, significant problems also attend the use of carbon anodes, related to their preparation and to their consumption during aluminum smelting. Carbon anodes typically are fabricated by baking carbonaceous feedstocks such as coal tar, petroleum coke and pitch at high temperatures for extended periods of time. Arranging these materials for treatment exposes workers to injurious carbon dust. Then, during this prebake process the anode outgases undesirable by-products such as hydrocarbons, polychlorinated biphenyls and sulfur dioxide. Consequently, anode fabricators must undertake expensive filtering, collecting and treatment operations. Furthermore, anode outgassing generally persists throughout the active lifetime of the electrode.

[0008] Moreover, interactions between the anode and the molten electrolyte during cell operation consume the anode. Although, ideally, the anode reaction should be the oxidation of oxide ions to gaseous oxygen, the carbon anode is not inert in the aggressive high-temperature chemical environment of the cell. Anode material is removed from the electrode as oxygen in the bath combines with carbon to form volatile carbon monoxide and carbon dioxide. Similarly, perfluorocarbon compounds, mainly tetrafluoromethane and hexafluoroethane, are produced during operation at low alumina concentration, so that aluminum smelting is the greatest single contributor to perfluorocarbon compound emissions in the United States.

[0009] Anode consumption is problematic for several reasons. First, it makes cell operation more difficult. It is difficult to maintain uniform anode current loading during operation due to the continuously changing topology of the electrolyte-anode interface. Due to uncertainty in the position of the anode's inconstant surface, the anode-cathode spacing is maintained at a cautiously large value to preclude electrical shorting between the anode and cathode so that a greater cell voltage must be applied to the cell to drive current through the electrolyte. The anode must be continually repositioned to maintain contact with the bath as its vertical dimension shrinks. Anode changes are labor intensive and disturb the thermal balance and electrical current distribution in the cell. Gases produced by the consumption reaction can remain trapped under the anode surface and contribute additional ohmic drops to the operating voltage. With about one-half pound of solid carbon being converted to so-called greenhouse gases for every pound of aluminum produced by the Hall-Héroult process, environmental concerns about electrolytic aluminum smelting as historically practiced have become more prominent.

[0010] Due to these problems, considerable research has been directed toward finding an alternate anode material. In addition to maintaining the desirable characteristics of the currently used anode material, the ideal electrode would be nonconsumable, serving mainly as an electron sink. Such an electrode would not react with oxygen formed at the anode and would not dissolve in the molten electrolyte. Despite substantial effort, no fully satisfactory inert anode has been identified.

[0011] Owing to the great advantages of the electrolytic process over alternative aluminum smelting schemes, the Hall-Héroult cell has persisted despite the longfelt need for an alternative to carbon. While an inert anode has been viewed as a highly desirable target, its discovery would provide an enhancement to an already-workable system—not a pre-requisite for a viable process. However, the identification of such an oxide-compatible, high-temperature-stable electrode for aluminum extraction could also make possible new processes for extraction of other metals from their oxide compounds.

[0012] The example of titanium is instructive. The main sources of titanium are ilmenite and rutile, in both of which titanium is bound to oxygen. Nonelectrolytic industrial processes for titanium extraction act on titanium chlorides and so require an additional preliminary unit operation, the carbochlorination of titanium dioxide—which generates carbon dioxide—for rendering titanium chloride feed for the final reduction. For example, the principal commercial route by which titanium is produced is the Kroll process, a batch metallothermic reduction of titanium tetrachloride by magnesium. The titanium sponge product is contaminated with excess magnesium and magnesium chloride.

[0013] Of the electrolytic titanium-smelting processes that have been evaluated, most do not directly reduce a titanium-oxygen compound but rather begin with a chlorinated compound. For example, the Dow-Howmet process dissolves titanium dichloride, produced from the tetrachloride, in a potassium and lithium chloride molten electrolyte. With an operating temperature of about 520° C., the Dow-Howmet cell, like other electrolytic titanium producing operations, deposits titanium well below its melting temperature (1670° C.), resulting in dendritic solid deposits into which electrolyte is entrained. The product must be washed and then remelted to render metal ingot.

[0014] The Fray, Farthing, & Chen (FFC) process differs in that it uses titanium dioxide feedstock in the form of a reactive cathode immersed in a molten chloride electrolyte containing calcium chloride. By passage of current, oxygen is electrochemically removed from the TiO_2 cathode leaving behind elemental titanium. On the anode, oxygen reacts as it does in the Hall cell to produce CO_2. Although the FFC process moves in the right direction by obviating chlorination of titanium dioxide it is nonetheless environmentally suspect due to the halide electrolyte. The formation of unacceptable, albeit small, amounts of dioxin and furans undoubtedly attends the evolution of carbon dioxide on the carbon anode in such an environment. Also, the FFC process has not become economically viable owing to the long times required to remove all the oxygen from the cathode, solid-state diffusion being extremely slow.

[0015] Identification of an inert anode stable in a molten oxide environment at temperatures in the liquid range of titanium would eliminate the need for carbon and molten halides in the electrolytic extraction titanium. Using such an anode, liquid titanium could be obtained directly from an oxide source with gaseous oxygen as a byproduct. However, such high temperatures and highly corrosive conditions constitute a set of design constraints even more stringent than those for an inert anode for the comparatively benign physicochemical climate of the Hall-Héroult cell. Even if the standard noble metals—gold, silver and platinum—were not conventionally regarded as prohibitively expensive for large-scale industrial applications, they would not be suitable candidates for use in a liquid titanium cell owing to either their relatively low melting temperatures (silver and gold) as compared with that of titanium or, in the case of platinum, to its lack of structural integrity.

[0016] Beyond designating an inert anode, the design of apparatus for electrolytic extraction from oxide media poses many challenges not faced in the Hall-Héroult cell. For example, another essential component with rigorous materials requirements is the cathode substrate upon which the metal is deposited, the deposit subsequently acting as the cathode.

[0017] An ideal cathode substrate would have the following qualities: first, the cathode substrate material must be solid at the operating temperature of the electrolytic cell. Considering titanium again as an illustrative example, materials that may be serviceable at aluminum's relatively low melting temperature may well lack structural integrity at the higher temperatures—exceeding 1700° C.—required for deposition of titanium metal in liquid form.

[0018] Another requirement of the cathode substrate material is that it not react chemically with the molten electrolyte or the liquid metal product. The carbon substrate of the Hall-Héroult cell is not compatible with reactive metals such as titanium in this instance because these metals react, to an undesirable extent, with carbon to form carbides.

[0019] A third requirement concerns the electronic conductivity of the cathode substrate material. The rate of electrolytic metal deposition is proportional to the flow of electrons through the cathode substrate. If the electronic conductance of this element is too low, metal deposition at a commercially acceptable rate will be achieved only by application of a large voltage, which in turn will translate into unacceptably high electric power cost. Thus, in order to maintain an economical energy efficiency for metal extraction, the substrate material must be reasonably conductive.

[0020] Materials from the class of compounds known as refractory hard metals (RHMs) have been considered as candidate materials for the cathode substrate in liquid metal electrodeposition apparatus based on these criteria. However, RHMs have other properties that detract from their suitability for cathode support in electrolytic cells: RHMs are expensive and also mechanically brittle and therefore difficult to shape.

[0021] To date, no material has been shown to meet the performance and practical requirements for a cathode substrate in a cell containing an oxide melt at temperatures exceeding 1700° C.

DESCRIPTION OF THE INVENTION

OBJECTS OF THE INVENTION

[0022] An object of the present invention is, accordingly, an apparatus for extraction of metal from an oxide feedstock without use of carbon-based electrodes.

[0023] Another object of the invention is an electrochemical apparatus for depositing liquid titanium from titanium dioxide feedstock.

[0024] Another object of the invention is the electrochemical extraction of metals, in liquid or gaseous form, above their melting temperatures.

[0025] Another object of the invention is metal smelting with significantly reduced emission of greenhouse gases.

[0026] Another object of the invention is nonconsumable anodes for electrochemical extraction of metals.

[0027] Still another object of the invention is an anode shaped with channels for ducting evolved oxygen.

[0028] Another object of the invention is a means for electrochemical production of oxygen by the action of electric current through an electrode immersed in a molten electrolyte containing a source of oxygen.

[0029] Another object of the invention is to provide conductive cathode substrates compatible with liquid reactive metals and molten reactive-metal precursors.

BRIEF SUMMARY OF THE INVENTION

[0030] The invention relates to the discovery that materials heretofore not considered useful for electrodes and electrode substrates of cells for the electrolytic production of metals from oxide-based feedstocks in a molten electrolyte can serve as such, thereby providing improved electrolytic cells and novel methods for metal production.

[0031] In one aspect, the invention provides nonconsumable iridium anodes for accepting electrons from oxide-containing melts, thereby facilitating the oxidation of precursors in the electrolyte, with evolution of gaseous oxygen. The anodes of the invention comprise an iridium-based body having a continuous iridium surface, such that substantially the entire anodic surface in contact with the electrolyte in the cell is an iridium-based material.

[0032] As used herein, the term iridium-based denotes a material comprising iridium sufficiently concentrated and voluminous to establish a substantially continuous iridium surface over a contact interface—defined to be the entire anode-electrolyte interface—and also to confer mechanical integrity and chemical properties of the same order as those of pure bulk iridium. In one embodiment, the anode is substantially pure iridium. In another embodiment, the anode comprises an electrode foundation of a less-expensive material overlaid by a continuous film of iridium-based material. In yet another embodiment, the anode is made of an iridium-based alloy having an iridium content of at least 80%.

[0033] With a melting point of 2446° C., iridium metal can withstand service temperatures for electrolytic smelting of reactive metals without degradation of its mechanical properties. Its excellent high-temperature oxidation resistance allows it to serve in the aggressive molten oxide environment required to achieve the objects of the invention.

[0034] The electrodes disclosed herein eliminate the need for the expensive dedicated anode-preparation shop necessary to maintain a smelting facility using carbon anodes. Being essentially nonconsumable, the anodes are replaced less frequently, and operating costs are reduced. The stable anode contour permits closer approach to the metal product so the cell can function at lower voltage and hence lower power cost per unit of metal product.

[0035] The mechanical properties of iridium make possible a variety of anode geometries greatly advantageous over the block design used for carbon anodes. In one embodiment, the anode is formed with channels for conveying oxygen evolving at the anode-electrolyte interface out of the cell, preventing the aggregation of large bubbles that reduce cell efficiency. A similar advantage is provided by another embodiment in which the anode has a comb-like structure.

[0036] In one embodiment, the inert anode of the invention is incorporated into a conventional Hall-Héroult cell for aluminum extraction and replaces carbon-based anodes of the prior art, with improved performance with respect to difficulty of operation and undesirable emissions.

[0037] In another embodiment, the iridium-based anode contacts a molten electrolyte containing titanium and oxygen precursors as part of a cell producing titanium metal, preferably operating at a temperature sufficient for production of liquid titanium. In a preferred embodiment, the anode is used with an electrolyte comprising titanium dioxide—derived, for example, from anatase or rutile—dissolved in a molten oxide solvent containing at least one member of the group consisting of beryllium oxide, magnesium oxide, calcium oxide, aluminum oxide, and lithium oxide.

[0038] In yet another embodiment, the iridium-based electrode of the invention serves as anode in an apparatus evolving gaseous oxygen, for example in conjunction with deposition of a reactive metal. Candidate reactive metals for liquid-phase deposition include beryllium, aluminum, silicon, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, yttrium, zirconium, hafnium, indium, tin, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, actinium, thorium, protactinium and uranium. The anode of the invention could similarly serve in an electrolysis apparatus for vapor-phase production of reactive metals such as lithium, sodium, magnesium, potassium, calcium, rubidium, strontium and cesium.

[0039] In this embodiment, the anode of the invention is equally suitable for cell configurations incorporating one or more vertically oriented, dipping cathodes, which furnish electrons for the electrochemical reduction of ions in the electrolyte but do not act as a substrate supporting the accumulated metal deposit. Such a configuration may be more satisfactory in cells operating so as to produce a vapor-phase metal since the proximity of the cathode to the upper surface of the electrolyte simplifies collection of the metal product, which can readily exit the cell at the top. Dipping electrodes may be similarly desirable in the case of a liquid metal product lower in density than the molten oxide electrolyte. Cells may additionally include a protective wall between anode and cathode for shielding products of the respective electrodes from one another to prevent recombination or electrical shorting. Such design considerations are well known to those skilled in the art of electrochemical extraction of metals.

[0040] In another aspect, the invention provides tungsten-based cathode substrates—having a tungsten content of at least 50%—for deposition of liquid reactive metals. The cathode substrate furnishes electrons to the molten electrolyte, either directly or through a liquid metal layer, during cell operation. Cathode substrates constructed of a tungsten-based alloy enable deposition of an overlying liquid reactive-metal cathode without continual formation of carbides to an extent that would erode the cathode substrate. Such materials are resistant to alloying with liquid titanium and are solid at the temperature range of interest. Furthermore, unlike elemental tungsten, they resist oxidation at high temperatures. In a preferred embodiment, the tungsten-based alloy contains at least 15% rhenium by weight; an example is W-25Re, comprising 75% tungsten and 25% rhenium, which has a melting temperature above 3000° C.

[0041] Incorporation of the anode and cathode substrate of the invention into an electrolysis cell containing molten-oxide electrolyte establishes a novel method for electrolytic extraction of reactive metals. In a preferred embodiment, the iridium-based anode and tungsten-based cathode substrate co-operate in a cell for optimum production of liquid titanium metal directly from an oxide feedstock. Titanium production according to the invention proceeds without release of greenhouse gases: Because the metal is reduced directly from oxide, preparatory processing is much cleaner and simpler. Since the invention deposits titanium in liquid form, subsequent treatment is far easier than in current methods.

BRIEF DESCRIPTION OF THE DRAWINGS

[0042] The foregoing discussion will be understood more readily from the following detailed description of the invention, when taken in conjunction with the accompanying drawings, in which like reference numerals indicate identical or functionally similar elements, of which:

[0043] FIG. **1** is a vertical section showing a Hall-Héroult cell such as is employed commercially for aluminum extraction;

[0044] FIG. **2** is a vertical section illustrating one embodiment of a Hall-Héroult cell modified to employ a nonconsumable anode of this invention, the single anode having venting channels;

[0045] FIG. **3** is a vertical section illustrating one embodiment of a Sadoway cell for titanium extraction according to the invention; and

[0046] FIG. **4** is a vertical section illustrating the anode of the invention used in a cell having a dipping cathode.

DETAILED DESCRIPTION OF THE INVENTION

[0047] With reference to FIG. **1**, a conventional Hall-Héroult cell **10**, of the prior art, has a steel outer shell **12** lined by overlying thermal insulation **14**. A carbon cathode substrate **16** positioned at the bottom of the cell **10** contains metallic current collector bars **18**. Carbon anodes **20** are formed by prebaking carbon blocks suspended from steel anode rods **22** which supply electrical current to the anodes **20**. A cell lining **24** is also formed from carbon blocks.

[0048] Molten electrolyte **26** contains dissolved alumina, which is continually supplied by breaking an alumina crust **28** and adding fresh alumina. The alumina crust **28** forms on frozen electrolyte and helps to minimize heat loss from the top of the cell **10**. Since cryolite, Na_3AlF_6, has the capacity to dissolve alumina, it is the principal constituent of the electrolyte **26**. Additionally, certain fluoride salts are present in the electrolyte **26**. Calcium fluoride, CaF_2, decreases the freezing point of cryolite. Aluminum fluoride, AlF_3 contributes to the freezing point depression and also improves current efficiency in the cell **10**.

[0049] The operating temperature of the cell is about 1000° C. As electric current passes from the carbon anodes **20** through the molten electrolyte **26** to the cathode **16**, dissolved alumina is reduced to form a molten aluminum layer **32** over the cathode substrate **16** at the bottom of the cell **10**. Gas consisting principally of carbon dioxide and carbon monoxide is generated at the anode **20**. The carbon anode **20** is consumed during this reaction.

[0050] Contact between the molten electrolyte **26** and the carbon cell lining **24** would result in a chemical attack on the cell lining **24** due to the formation of intercalation compounds. In order to prevent such contact the cell **10** is operated under conditions that cause a frozen electrolyte layer **30** to form between the carbon cell lining **24** and the molten electrolyte **26**. The molten electrolyte **26** is surrounded by the shell of frozen electrolyte **30** and supported by the molten aluminum layer **32**. The need to maintain the frozen electrolyte layer **30** complicates control of the cell because the location of the interface between the molten and frozen electrolyte phases varies with operating conditions of the cell **10**.

[0051] In practice, the carbon cathode substrate **16** is covered with a deep pool of molten aluminum so that aluminum deposits onto the molten aluminum layer **32** rather than onto carbon. Thus, the molten aluminum layer **32** provides electrons to the molten electrolyte and functions as cathode in the cell **10**. This arrangement prevents the degradation of the cathode substrate **16** by creation and dissolution into the electrolyte of aluminum carbide, which is formed when aluminum is electrodeposited onto carbon.

[0052] With reference to FIG. **2**, in a preferred embodiment of the invention, an electrolysis cell **40** configured for the extraction of aluminum has a steel outer shell **42** lined by overlying thermal insulation **44**. A carbon cathode substrate **46** positioned at the bottom of the cell **40** contains metallic current collector bars **48**. A single anode **50** is constructed from iridium metal and formed with channels **52** for venting oxygen to the extetior of the cell **40**. The anode **50** is connected to a supply of electric current by an anode rod **54**, which may be of iridium or of some other conductive material. Cell lining **56** is also formed from carbon blocks.

[0053] The cell contains molten electrolyte **58** covered with a frozen alumina layer **60**. Electrolyte compositions capable of dissolving alumina, such as are found in conventional Hall-Héroult cells, are compatible with the cell of the invention. Accordingly, the cell **40** is operated so as to maintain a frozen electrolyte layer **62**.

[0054] The operating temperature of the cell is about 1000° C. As electric current passes from the iridium anode **50** through the molten electrolyte **58** to the cathode substrate **46**, dissolved alumina is reduced to build a molten aluminum layer **64** over the cathode substrate **46** at the bottom of the cell **40**. Gas consisting principally of oxygen is generated at the inert, nonconsumable anode **50** and passes through the channels **52**, thus exiting the cell **40**.

[0055] With reference to FIG. **3**, in another preferred embodiment of the invention, an electrolysis cell **70**, configured for the extraction of titanium has a tungsten-rhenium outer shell **72** lined by overlying thermal insulation **74**. A tungsten-rhenium cell interior, comprising sidewalls **75** and a cathode substrate **76**, nests inside the thermal insulation **74**. The cathode substrate **76** positioned at the bottom of the cell **70** contains metallic current collector bars **78**. A single anode **80** is constructed from iridium metal and formed with channels **82** for venting oxygen to the exterior of the cell **70**. The anode **80** is connected to a supply of electric current by an anode rod **84**, which is of some electrically conductive material.

[0056] The cell contains molten electrolyte **88** acting as a solvent for titanium dioxide. The electrolyte **88** is preferably one or more molten oxides, the precise composition of which is selected for its capability of dissolving titanium dioxide as well as other physical and chemical properties known to those skilled in the art of molten salt electrochemistry.

[0057] The operating temperature of the cell is about 1700° C. As electric current passes from the iridium anode **80** through the molten electrolyte **88** to the cathode substrate **76**, dissolved titanium dioxide is reduced to build a liquid titanium layer **94** over the cathode substrate **76** at the bottom of the cell **70**. Gas consisting principally of oxygen is generated at the inert, nonconsumable anode **80** and passes through the channels **82**, thus exiting the cell **70**.

[0058] With reference to FIG. **4**, in yet another embodiment of the invention, an electrolysis cell **90** has an iridium anode **92** and a cathode **94** which are suspended above the cell **90** and dip into a molten electrolyte **96**. During cell operation, gaseous oxygen evolves on the anode **92**. The cathode **94** provides electrons to the electrolyte **96**, thereby extracting a reactive metal, which, depending on its boiling temperature, leaves the cell **90** as a vapor or remains in the cell in the liquid phase. A protective wall **98** interposed between the anode **92** and the cathode **94** shields products of the respective electrodes from one another to prevent recombination or electrical shorting.

[0059] Although specific features of the invention are included in some embodiments and drawings and not in others, it should be noted that each feature may be combined with any or all of the other features in accordance with the invention.

[0060] It will therefore be seen that the foregoing represents a highly advantageous approach to providing anodes and cathodes for high-temperature molten-oxide metal extraction. The terms and expressions employed herein are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. An apparatus for extracting liquid titanium metal from titanium dioxide by electrolysis, the apparatus comprising:
- a. a cathode substrate of a tungsten-based material, the liquid titanium metal forming a deposit over the cathode substrate;
- b. an anode of iridium-based material upon which gaseous oxygen evolves;
- c. a molten electrolyte containing the titanium dioxide, the electrolyte being in contact with the anode over a contact interface, the contact interface being a substantially continuous iridium surface, the titanium dioxide being dissolved in the molten electrolyte.

2. The apparatus of claim **1** wherein the tungsten-based material contains rhenium.

3. The apparatus of claim **1** wherein the tungsten-based material is W-25Re.

4. The apparatus of claim **1** wherein the molten electrolyte comprises a molten oxide solvent.

5. The apparatus of claim **4** wherein the molten oxide solvent comprises at least one member of the group comprising beryllium oxide, magnesium oxide, calcium oxide, aluminum oxide, and lithium oxide.

6. The apparatus of claim **1** wherein the iridium-based material contains at least 80% iridium.

7. The apparatus of claim **1** wherein the apparatus has an exterior, the anode being constructed with channels for conveying the oxygen from the substantially continuous iridium surface to the exterior.

8. The apparatus of claim **1** wherein the iridium-based material is substantially pure iridium.

9. An apparatus for extracting a reactive metal from an oxide feedstock by the action of electric current, the apparatus comprising:
- a. a cathode substrate of a tungsten-based material, the reactive metal forming a deposit over the cathode substrate;
- b. a molten electrolyte in which the feedstock is dissolved.

10. The apparatus of claim **9** wherein the reactive metal is titanium.

11. The apparatus of claim **10** wherein the deposit is liquid titanium.

12. The apparatus of claim **9** wherein the reactive metal is a member of the group comprising beryllium, aluminum, silicon, scandium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, yttrium, zirconium, hafnium, indium, tin, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, actinium, thorium, protactinium and uranium.

13. The apparatus of claim **9** wherein the tungsten-based material contains rhenium.

14. The apparatus of claim **9** wherein the tungsten-based material is W-25Re.

15. An apparatus for producing oxygen by the action of electric current, the apparatus comprising:
- a. a molten electrolyte containing a source of the oxygen;
- b. an anode of an iridium-based material contacting the electrolyte over a contact interface, the contact interface being a substantially continuous iridium surface, the oxygen evolving on the anode.

16. The apparatus of claim **15** wherein the electrolyte contains an oxide source of a reactive metal, the apparatus further comprising a cathode substrate, a liquid deposit of the reactive metal deposit forming over the cathode substrate by the action of the electric current.

17. The apparatus of claim **16** wherein the reactive metal is aluminum.

18. The apparatus of claim **16** wherein the reactive metal is titanium.

19. The apparatus of claim **16** wherein the reactive metal is a member of the group comprising beryllium, aluminum, silicon, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, yttrium, zirconium, hafnium, indium, tin, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, actinium, thorium, protactinium and uranium.

20. An apparatus for extracting a reactive metal from an oxide feedstock by the action of electric current, the apparatus comprising:
- a. a molten electrolyte in which the oxide feedstock is dissolved;
- b. a cathode contacting the electrolyte;
- c. an anode of an iridium-based material contacting the electrolyte over a contact interface, the contact interface being a substantially continuous iridium surface, the oxygen evolving on the anode.

21. The apparatus of claim **20** wherein the reactive metal is extracted as a vapor.

22. The apparatus of claim **20** wherein the reactive metal is extracted as a liquid.

23. An apparatus for extracting liquid aluminum from an aluminum oxide feedstock by electrolysis, the apparatus comprising:
- a. a molten electrolyte in which the feedstock is dissolved;
- b. an anode of iridium-based material contacting the electroyte over a contact interface, the contact interface being a substantially continuous iridium surface.

24. The apparatus of claim **1** wherein the titanium dioxide is derived from anatase.

25. The apparatus of claim **1** wherein the titanium dioxide is derived from rutile

26. The apparatus of claim **21** wherein the reactive metal is a member of the group comprising lithium, sodium, magnesium, potassium, calcium, rubidium, strontium and cesium.

27. The apparatus of claim **22** wherein the reactive metal is a member of the group comprising beryllium, aluminum, titanium silicon, scandium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, yttrium, zirconium, hafnium, indium, tin, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, actinium, thorium, protactinium and uranium.

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