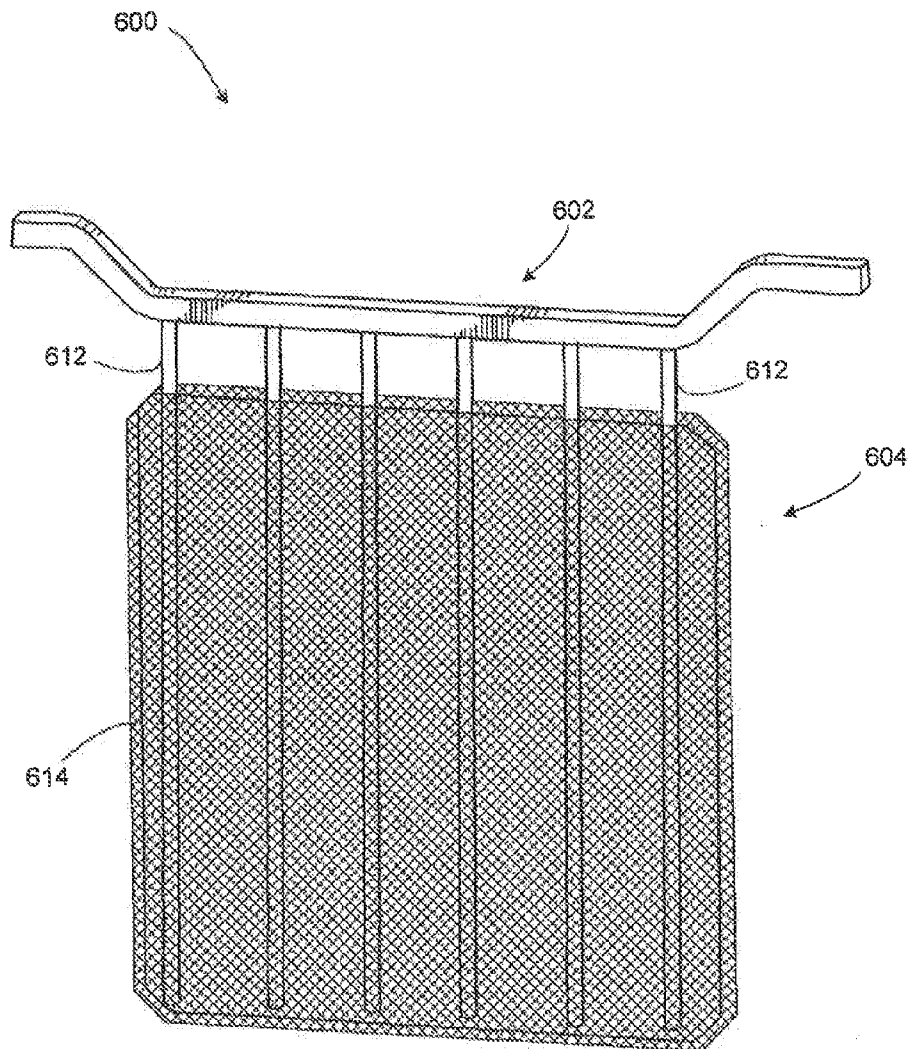




US 20130126341A1

(19) **United States**(12) **Patent Application Publication**
Sandoval et al.(10) **Pub. No.: US 2013/0126341 A1**(43) **Pub. Date: May 23, 2013**(54) **ANODE STRUCTURE FOR COPPER
ELECTROWINNING**continuation of application No. 12/432,473, filed on
Apr. 29, 2009, now Pat. No. 8,038,855.(71) Applicant: **FREEPORT-MCMORAN
CORPORATION**, Phoenix, AZ (US)**Publication Classification**(72) Inventors: **Scot P. Sandoval**, Morenci, AZ (US);
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C25B 11/02 (2006.01)
(52) **U.S. Cl.**
CPC **C25B 11/02** (2013.01)
USPC **204/286.1; 29/825**(73) Assignee: **FREEPORT-MCMORAN
CORPORATION**, Phoenix, AZ (US)(57) **ABSTRACT**(21) Appl. No.: **13/739,865**(22) Filed: **Jan. 11, 2013****Related U.S. Application Data**(63) Continuation of application No. 13/248,244, filed on
Sep. 29, 2011, now Pat. No. 8,372,254, which is a

An electrode for use in producing copper in either a conventional electrowinning cell or the direct electrowinning cell is provided. The electrode includes a hanger bar and an electrode body coupled with the hanger bar. The electrode body includes at least one conductor rod having a core and an outer layer surrounding the core and a substrate coupled with the conductor rod.



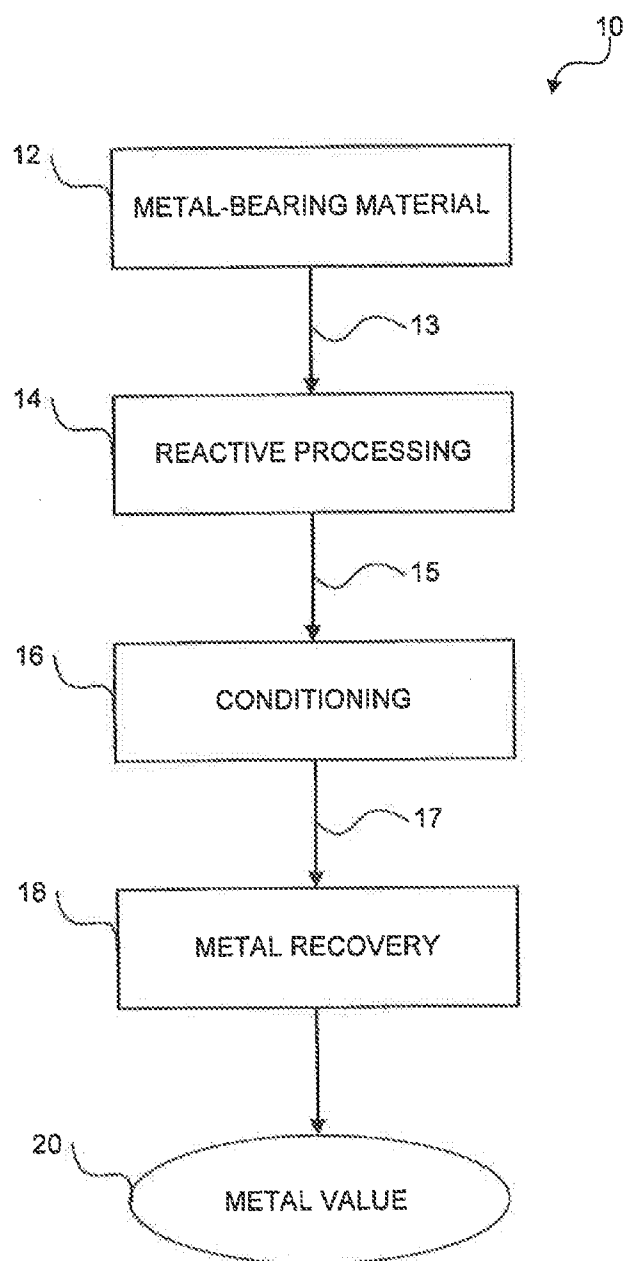


FIG. 1

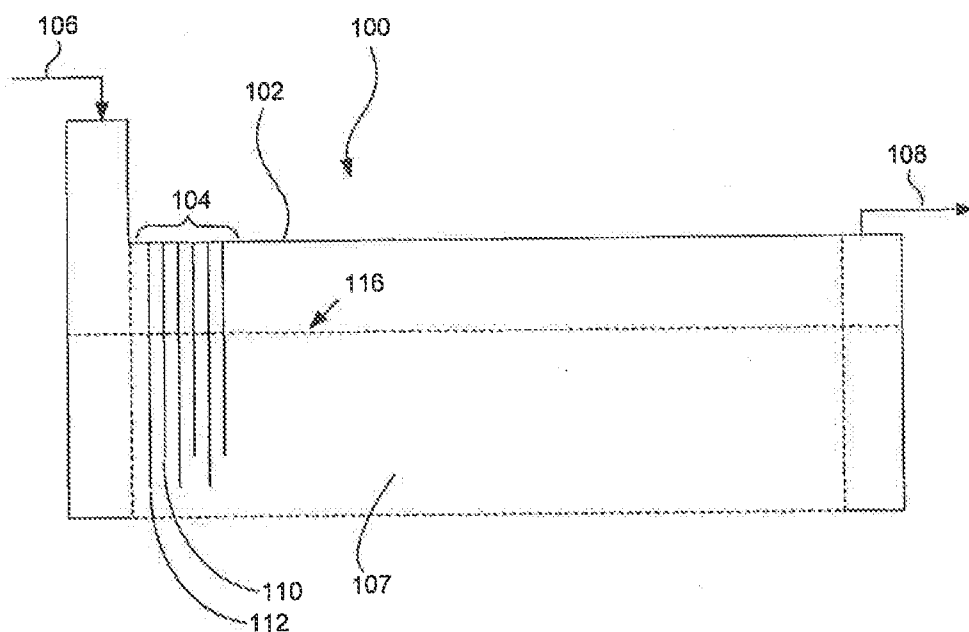


FIG. 2

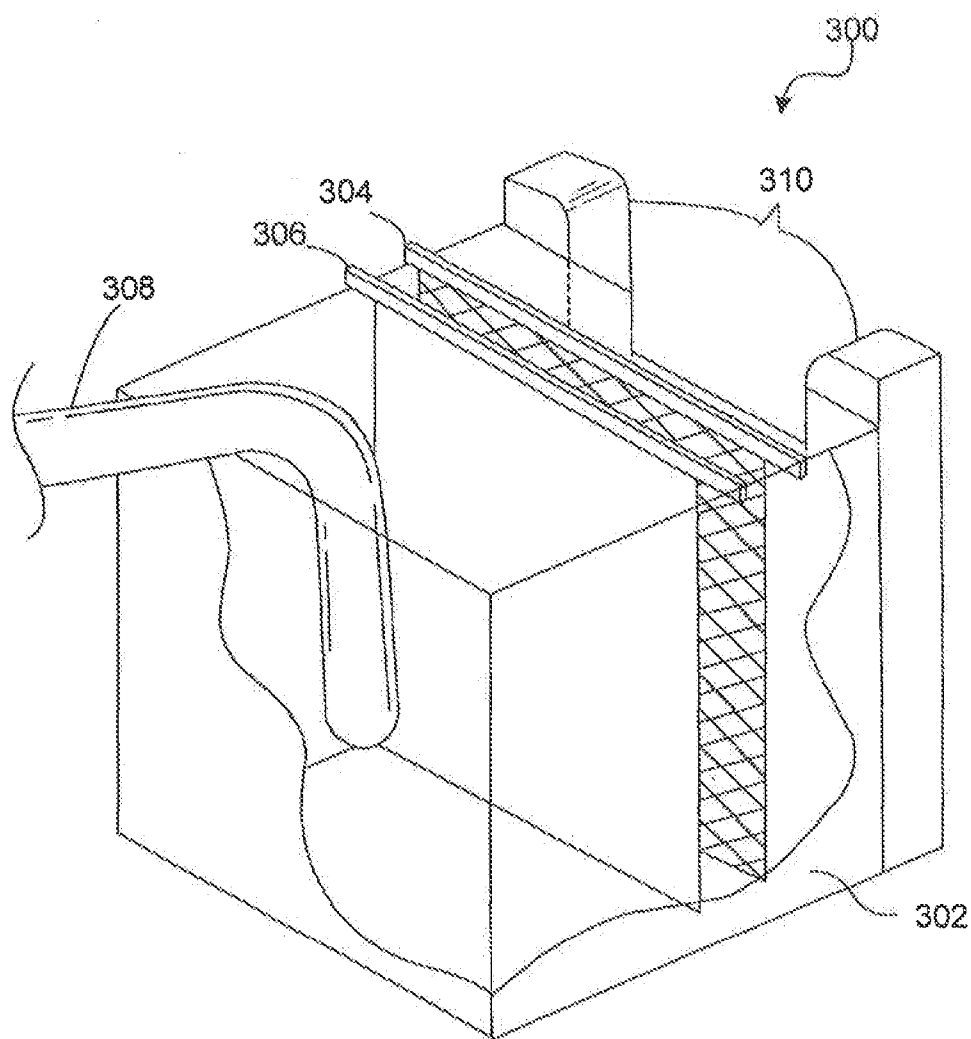


FIG. 3

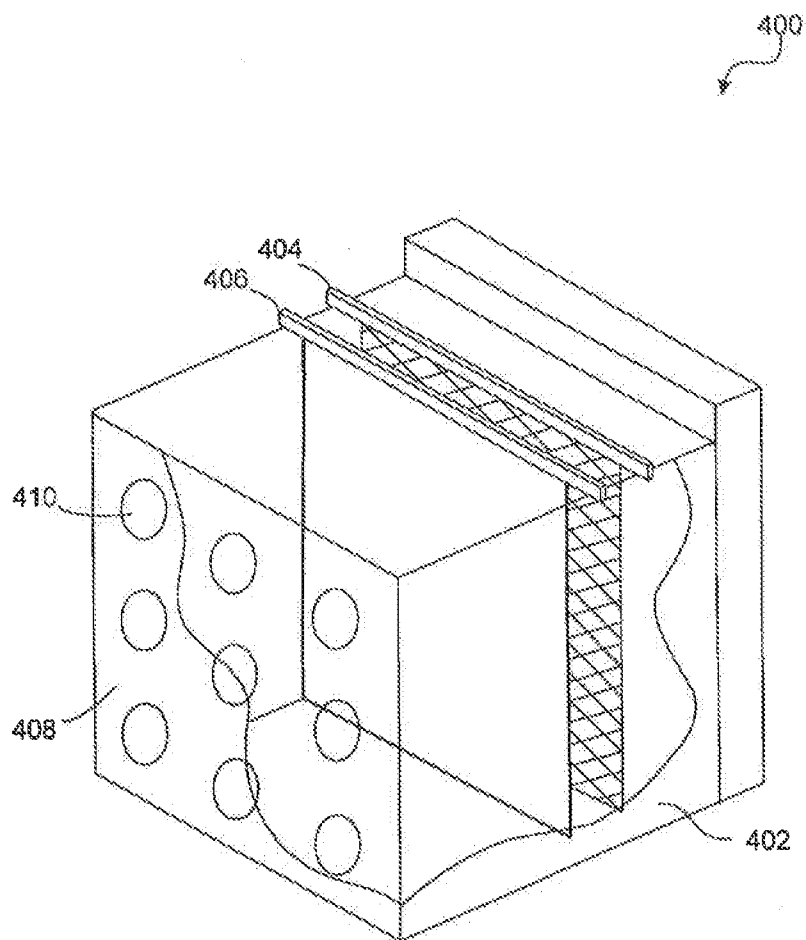


FIG. 4

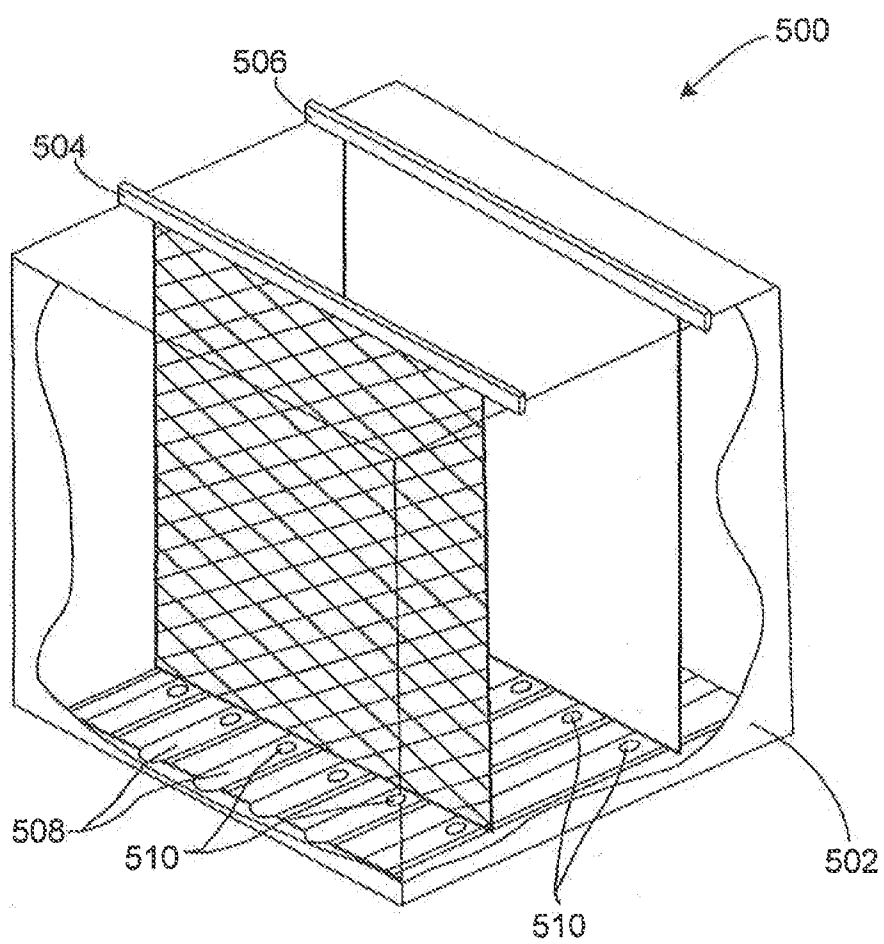


FIG. 5

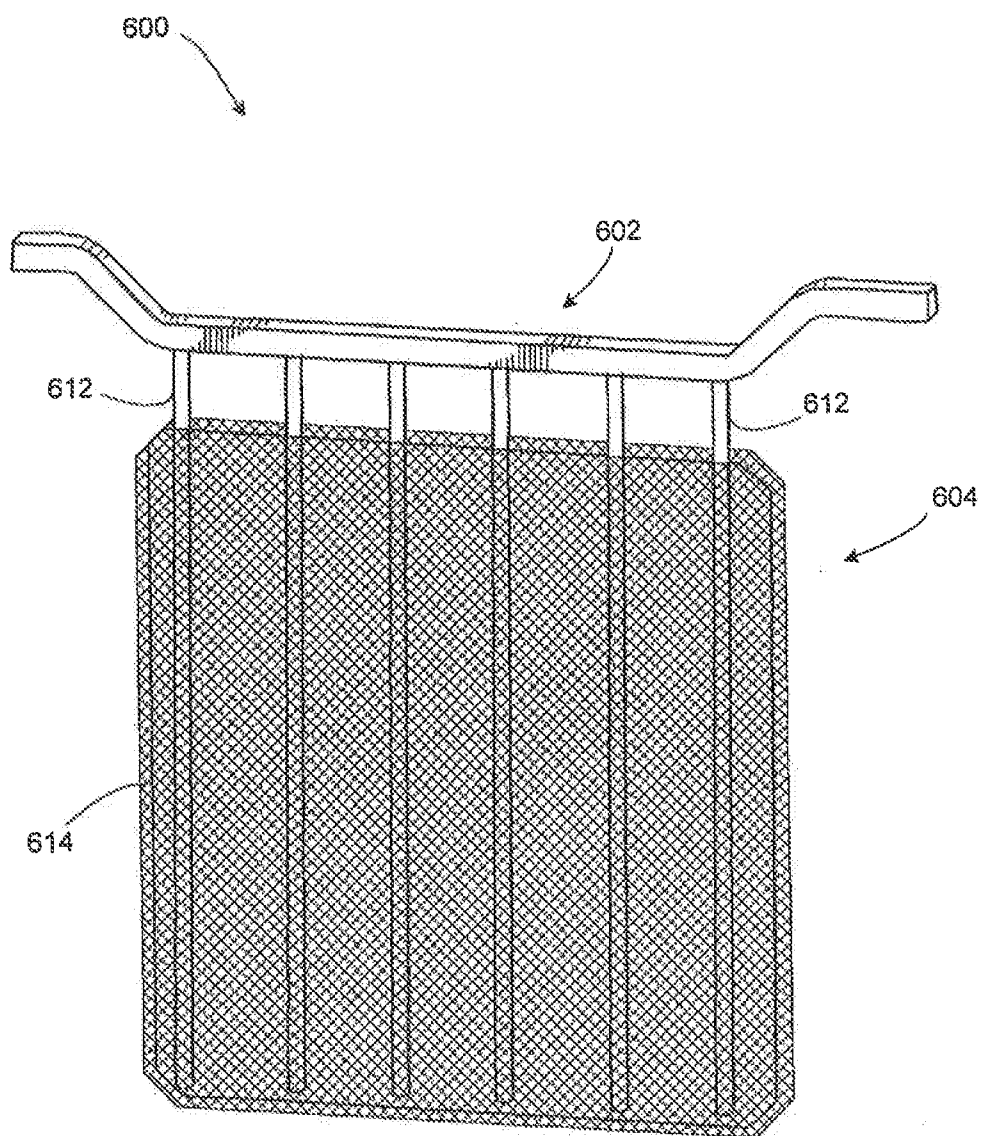


FIG. 6

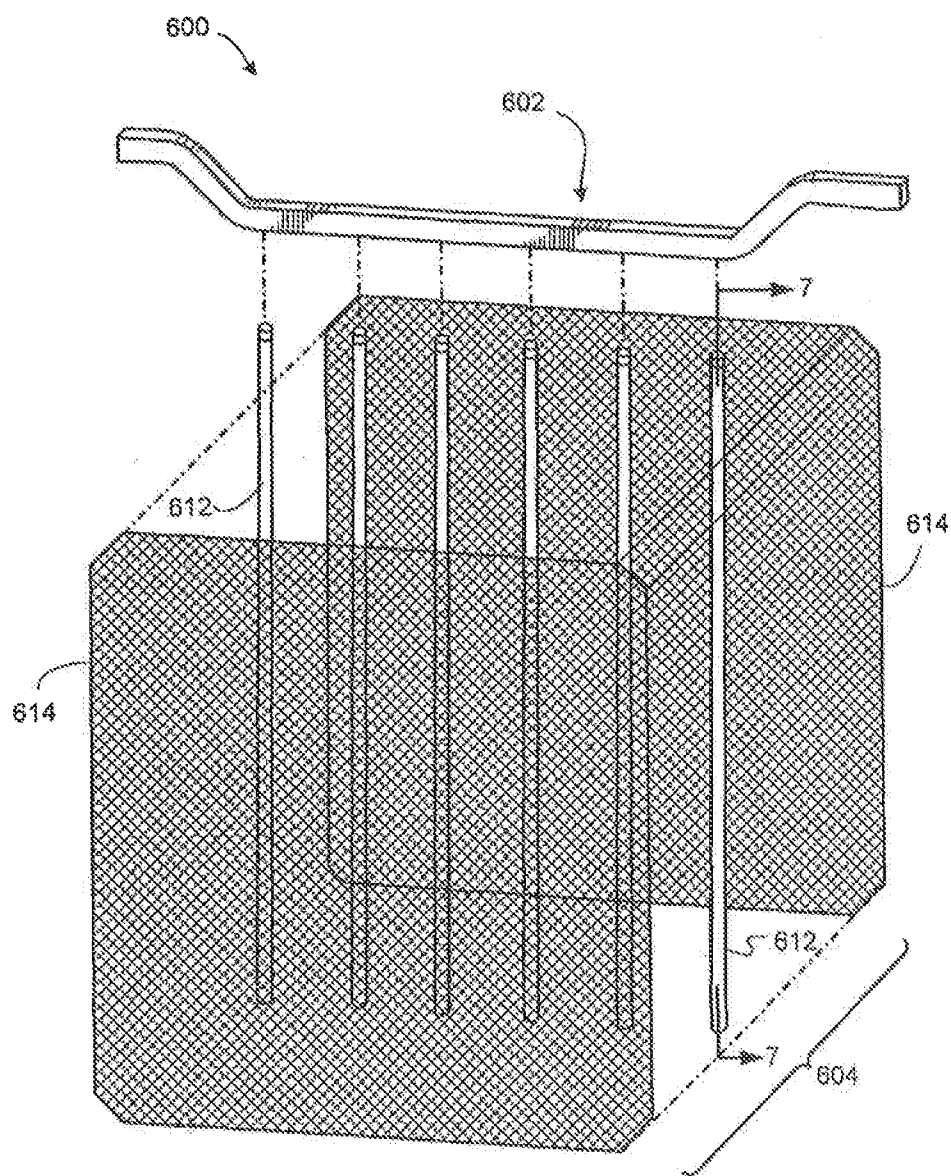


FIG. 7

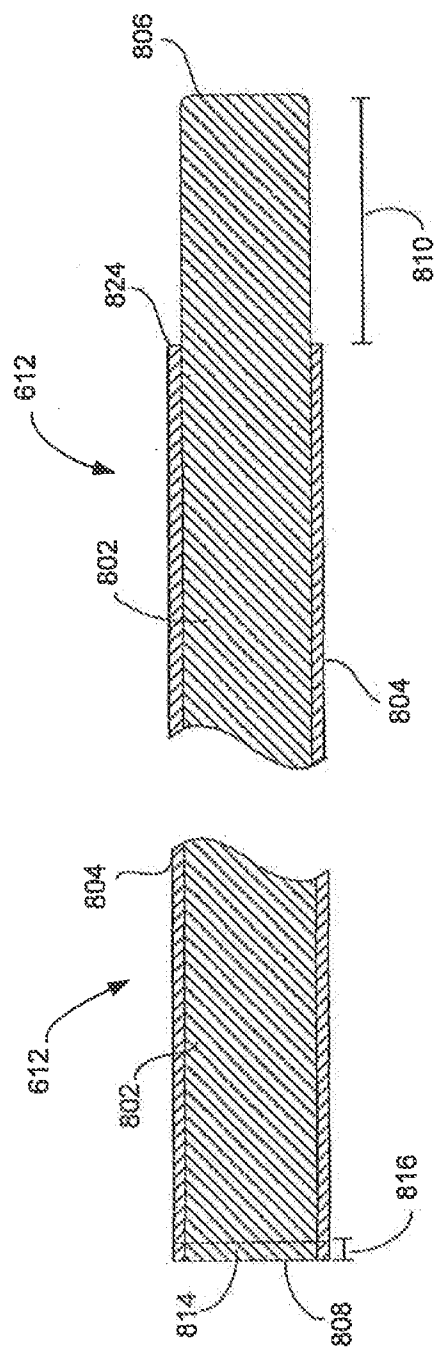


FIG. 8A

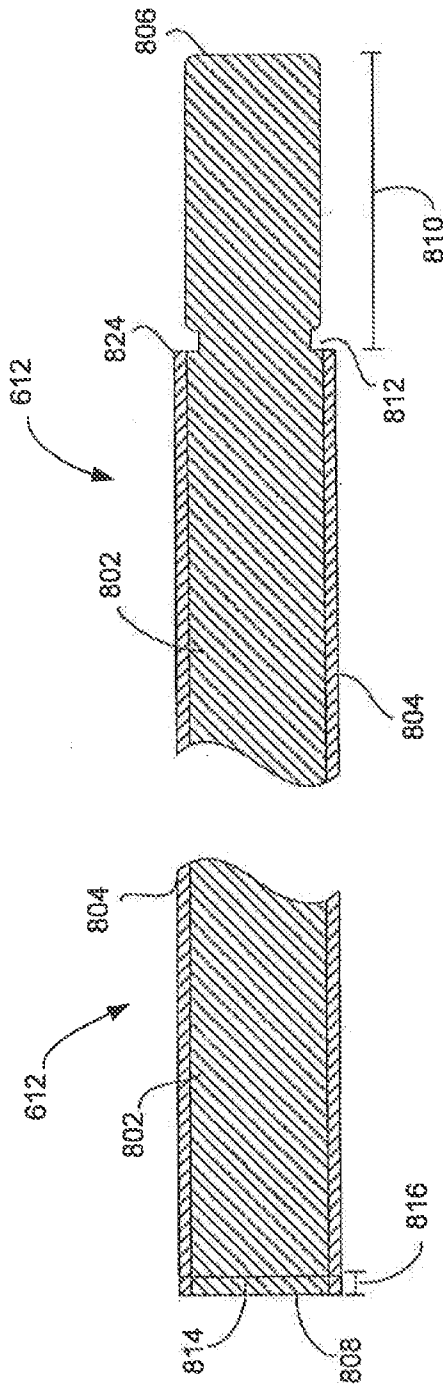


FIG. 8B

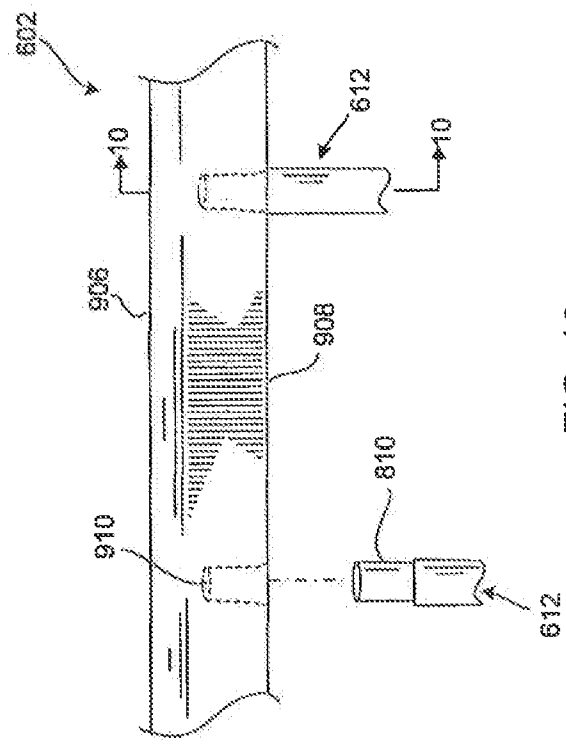
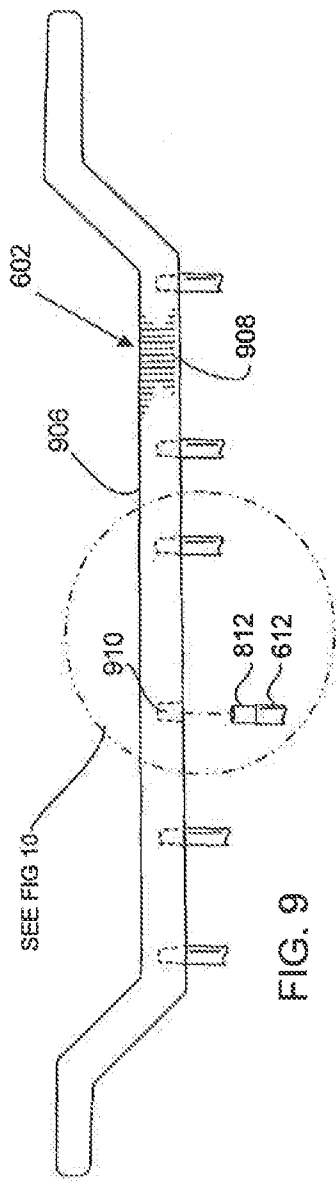


FIG. 10

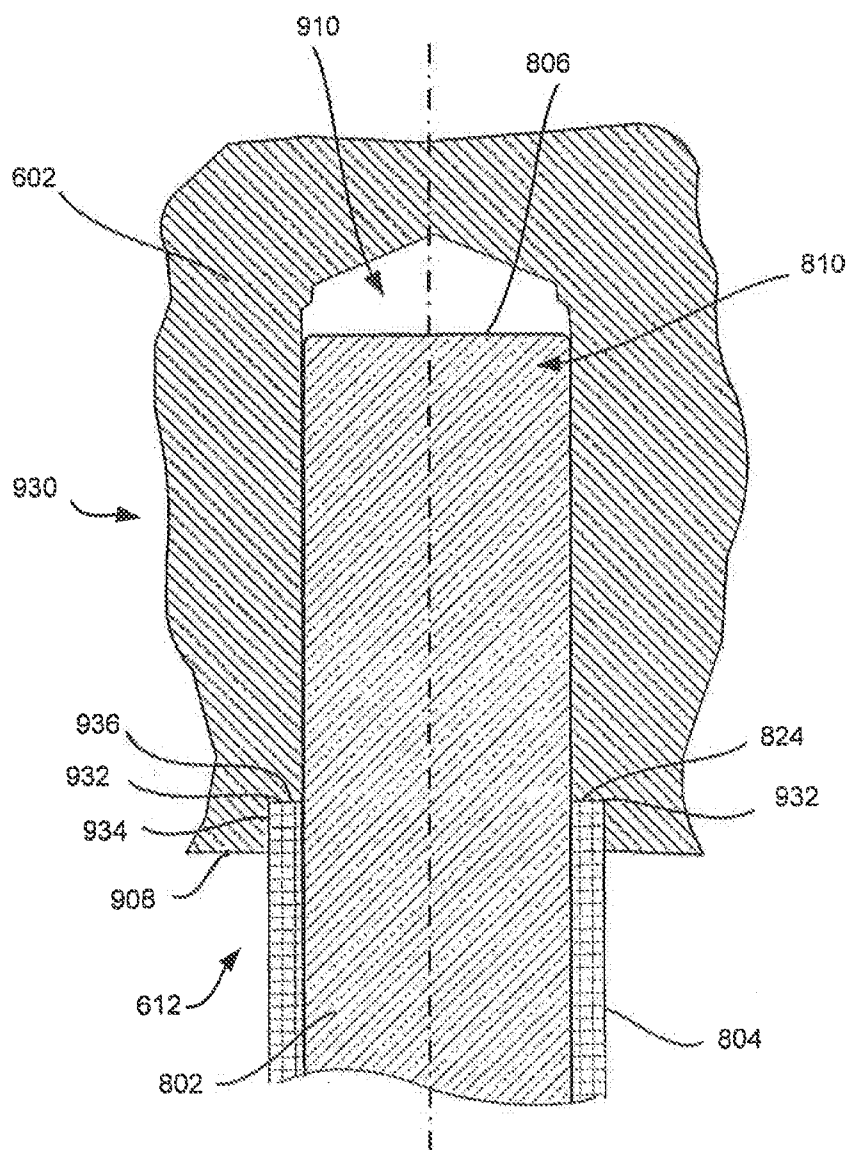


FIG. 11A

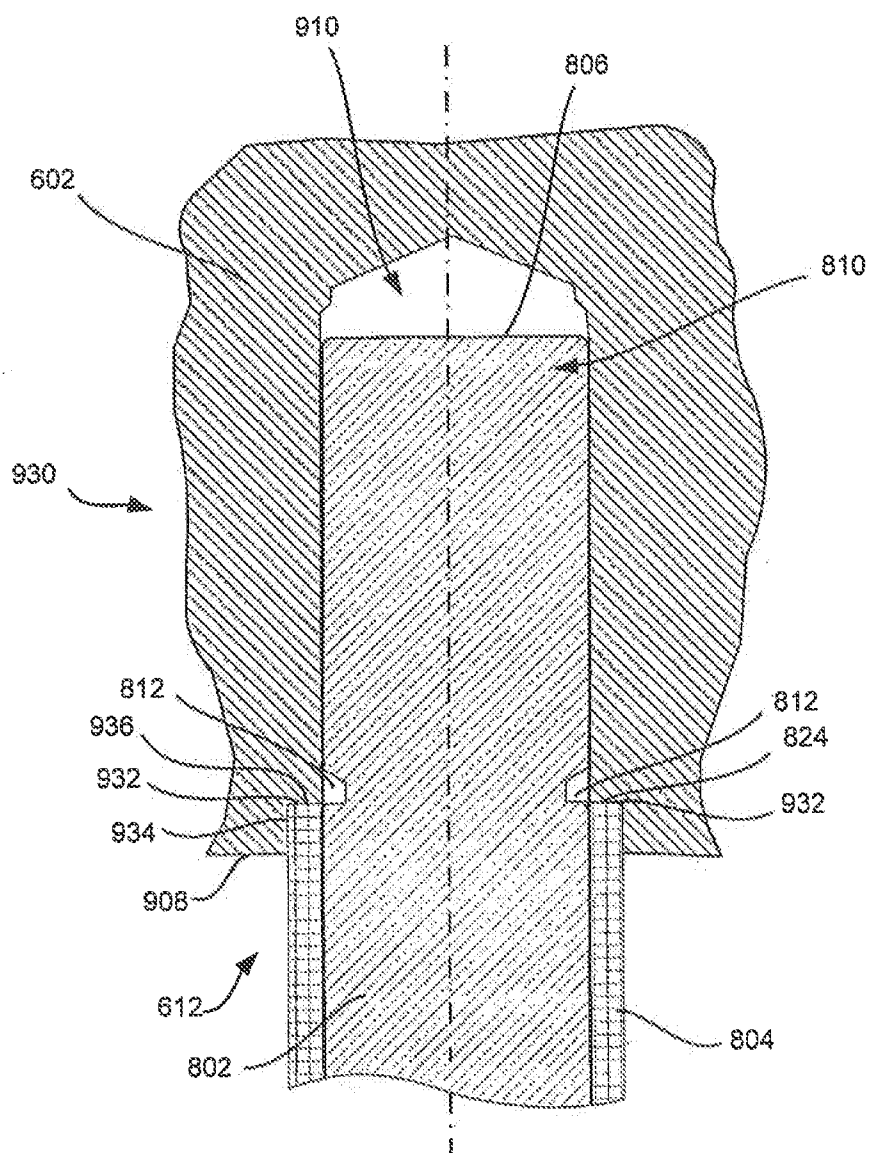


FIG. 11B

ANODE STRUCTURE FOR COPPER ELECTROWINNING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and is a continuation of U.S. patent application Ser. No. 13/248,244 entitled, "ANODE STRUCTURE FOR COPPER ELECTROWINNING" and filed on Sep. 29, 2011. The '244 Application claims priority to and is a continuation of U.S. patent application Ser. No. 12/432,473 entitled, "ANODE STRUCTURE FOR COPPER ELECTROWINNING" which was filed on Apr. 29, 2009, now U.S. Pat. No. 8,038,855 issued Oct. 18, 2011. All the aforementioned applications are hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention generally relates to an apparatus for producing copper using electrowinning, and relates more specifically to an electrode apparatus for use in an electrowinning cell.

BACKGROUND

[0003] Efficiency and cost-effectiveness of copper electrowinning is, and for a long time has been, important to the competitiveness of the copper industry. Research and development efforts in this area have thus focused, at least in part, on mechanisms for decreasing the total cost for anodes used in copper electrowinning, which directly impact the cost-effectiveness of the electrowinning process.

[0004] One type of anode employed in an electrowinning operation typically comprises a lead or a lead alloy, such as, for example, Pb—Sn—Ca. One significant disadvantage of using such anodes is lead contamination of the copper cathodes. Specifically, during the electrowinning operation, small amounts of lead are released from the surface of the anode and ultimately cause the generation of undesirable sediments, sludges, particulates suspended in the electrolyte, other corrosion products, or other physical degradation products in the electrochemical cell and contamination of the copper product. Another disadvantage of using lead anodes in conventional electrowinning processes is the need to add cobalt sulfate to the copper electrolyte to help stabilize lead-based anodes for at least one of control of surface corrosion characteristics of the anode, control of formation of lead oxide, and/or prevention of deleterious effects of manganese in the system. Improvements are needed in the materials used for anodes useful for electrochemical reactions, as well as in the construction of the anodes.

SUMMARY

[0005] Accordingly, in various embodiments, the present invention provides a new design for an anode structure for use in electrowinning cells. In an aspect of an exemplary embodiment, the present invention provides an anode for an electrowinning cell that accommodates flow-through anodes and conventional cathodes. This allows for the production of high quality copper from copper-containing solutions using either a conventional electrowinning process or a direct electrowinning process.

[0006] In accordance with various embodiments, the present invention provides an electrode for producing copper in an electrowinning cell. The electrode includes a hanger bar

and an electrode body including at least one conductor rod and a substrate, a connection coupling the hanger bar and the at least one conductor rod, and a seal isolating the connection. In an exemplary embodiment, the at least one conductor rod has an inner core and an outer layer surrounding a portion of the inner core. In an exemplary embodiment, at least one perforated substrate can be coupled to the at least one conductor rod. The present invention offers significant economic benefits in manufacturing and/or electrode lifetime as compared to prior art electrodes without sacrificing functionality.

[0007] Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way. The present invention will become more fully understood from the detailed description and the accompanying drawings wherein:

[0009] FIG. 1 is a flow chart illustrating a process of metal value recovery, according to various embodiments of the present invention;

[0010] FIG. 2 is a cross sectional view illustrating an electrowinning cell, in accordance with various embodiments of the present invention;

[0011] FIG. 3 is a prospective view illustrating a flow-through electrowinning cell, in accordance with an exemplary embodiment of the present invention;

[0012] FIG. 4 is a prospective view illustrating a flow-through electrowinning cell, in accordance with an exemplary embodiment of the present invention;

[0013] FIG. 5 is a prospective view illustrating a flow-through electrowinning cell, in accordance with an exemplary embodiment of the present invention;

[0014] FIG. 6 is a prospective view illustrating a flow-through anode, in accordance with various embodiments of the present invention;

[0015] FIG. 7 is an exploded prospective view of the flow-through anode illustrated in FIG. 6, in accordance with various embodiments of the present invention;

[0016] FIG. 8A is a cross-sectional view of a conductor rod taken along line 7-7 of FIG. 7, in accordance with an exemplary embodiment of the present invention;

[0017] FIG. 8B is a cross-sectional view of a conductor rod taken along line 7-7 of FIG. 7, in accordance with an exemplary embodiment of the present invention;

[0018] FIG. 9 is a front exploded view illustrating a hanger bar and a portion of a plurality of conductor rods, in accordance with various embodiments of the present invention;

[0019] FIG. 10 is an enlarged view of the portion highlighted in FIG. 9, in accordance with various embodiments of the present invention;

[0020] FIG. 11A is a partial cross-sectional view taken along line 10-10 of FIG. 10, in accordance with an exemplary embodiment of the present invention; and

[0021] FIG. 11B is a partial cross-sectional view taken along line 10-10 of FIG. 10, in accordance with an exemplary embodiment of the present invention.

DETAILED DESCRIPTION

[0022] The following description is merely exemplary in nature and is not intended to limit the present invention, its applications, or its uses. It should be understood that throughout the drawings, corresponding reference numerals indicate like or corresponding parts and features. The description of specific examples indicated in various embodiments of the present invention are intended for purposes of illustration only and are not intended to limit the scope of the invention disclosed herein. Moreover, recitation of multiple embodiments having stated features is not intended to exclude other embodiments having additional features or other embodiments incorporating different combinations of the stated features.

[0023] Various embodiments of the present invention are an improvement to a conventional electrode for an electrolytic cell. The present invention exhibits significant advancements over prior art apparatus, enables significant improvements in copper product quality and process efficiency, and/or provides economic benefits. Moreover, existing copper recovery processes that utilize lead-based anodes or conventional titanium anodes in conventional electrowinning apparatus may, in many instances, be retrofitted to exploit the many commercial benefits that the present invention can provide.

[0024] An electrowinning cell as described herein may be configured for the extraction of a variety of metal values. In the case of electrowinning, a current is passed through an anode through the electrolyte solution or metal-bearing solution containing the metal value so that the metal value is extracted as it is deposited in an electroplating process onto the cathode. In general, electrowinning metal values can include, but are not limited to, copper, gold, silver, zinc, nickel, chromium, cobalt, manganese, rare earth metals, and alkaline metals. Although various examples included in this disclosure discuss the use of an anode in the electrowinning of copper, the anode described herein, in accordance to the present invention, may be used in the electrowinning of any metal value.

[0025] Referring to FIG. 1 in accordance with various aspects of the present invention, a metal-bearing material **12** is provided for processing in accordance with metal recovery process **10**. Metal-bearing material **12** may be an ore, a concentrate, or any other material from which metal values may be recovered. Metal values such as, for example, copper, gold, silver, zinc, platinum group metals, nickel, cobalt, molybdenum, rhenium, uranium, rare earth metals, and the like may be recovered from metal-bearing material **12** in accordance with various embodiments of the present invention. Various aspects and embodiments of the present invention, however, prove especially advantageous in connection with the recovery of copper from copper sulfide ores, such as, for example, chalcopyrite (CuFeS_2), chalcocite (Cu_2S), bornite (Cu_5FeS_4), covellite (CuS), enargite (Cu_3AsS_4), digenite (Cu_9S_5), mixtures thereof and/or concentrates thereof. In addition, various aspects and embodiments of the present invention also prove advantageous in connection with the recovery of copper from copper oxide ores and/or concentrates thereof. Still further, various aspects and embodiments of the present invention prove advantageous in the recovery of any of the electrowinning metals, as listed herein, such as for example cobalt or zinc, from ores and/or concentrates thereof. Thus, in various embodiments, metal-bearing material **12** is a copper ore or concentrate, and in an exemplary

embodiment, metal-bearing material **12** is a copper sulfide ore or a copper oxide ore, mixture thereof, or concentrates thereof.

[0026] In various embodiments, processed metal-bearing material **15** may comprise metal-bearing material **12** prepared for metal recovery process **10** in any manner that enables the conditions of processed metal-bearing material **13** to be suitable for a chosen processing method, as such conditions may affect the overall effectiveness and efficiency of processing operations. Desired composition and component concentration parameters may be achieved through a variety of chemical and/or physical processing stages, the choice of which will depend upon the operating parameters of the chosen processing scheme, equipment cost and material specifications. For example, metal-bearing material **12** may undergo comminution, flotation, blending, and/or slurry formation, as well as chemical and/or physical conditioning to produce processed metal-bearing material **13**. In an exemplary embodiment, processed metal-bearing material **13** is a concentrate.

[0027] With continued reference to FIG. 1, after metal-bearing material **12** has been suitably prepared, processed metal-bearing material **13** is subjected to reactive processing step **14** to put a metal value or metal values in processed metal-bearing material **13** in a condition for later metal recovery steps, namely metal recovery **18**. For example, exemplary suitable processes include reactive processes that tend to liberate the desired metal value or metal values from the metal-bearing material **12**.

[0028] In accordance with an exemplary embodiment of the present invention, reactive processing step **14** may comprise leaching. Leaching can be any method, process, or system that enables a metal value to be leached from processed metal-bearing material **13**. Typically, leaching utilizes acid to leach a metal value from processed metal-bearing material **13**. For example, leaching can employ a leaching apparatus such as for example, a heap leach, a vat leach, a tank leach, a pad leach, a leach vessel or any other leaching technology useful for leaching a metal value from processed metal-bearing material **13**.

[0029] In accordance with various embodiments, leaching may be conducted at any suitable pressure, temperature, and/or oxygen content. Leaching can employ one of a high temperature, a medium temperature, or a low temperature, combined with one of high pressure, or atmospheric pressure. Leaching may utilize conventional atmospheric or pressure leaching, for example but not limited to, low, medium or high temperature pressure leaching. As used herein, the term "pressure leaching" refers to a metal recovery process in which material is contacted with an acidic solution and oxygen under conditions of elevated temperature and pressure. Medium or high temperature pressure leaching processes for chalcopyrite are generally thought of as those processes operating at temperatures from about 120° C. to about 190° C. or up to about 250° C. In accordance with various embodiments of the present invention, reactive processing step **14** may comprise any type of reactive process to put a metal value or values in processed metal-bearing material **13** in a condition to be subjected to later metal recovery steps.

[0030] In various embodiments, reactive processing step **14** provides a metal-bearing slurry **15** for conditioning **16**. In various embodiments, conditioning **16** can be, for example, but is not limited to, a solid liquid phase separation step, an additional leach step, a pH adjustment step, a dilution step, a

concentration step, a metal precipitation step, a filtering step, a settling step, and the like, as well as combinations thereof. In an exemplary embodiment, conditioning 16 can be a solid liquid phase separation step configured to yield a metal-bearing solution 17 and a metal-bearing solid.

[0031] In other various embodiments, conditioning 16 may be one or more leaching steps. For example, conditioning 16 may be any method, process, or system that further prepares metal-bearing material 12 for recovery. In various embodiments, conditioning 16 utilizes acid to leach a metal value from a metal-bearing material 12. For example, conditioning 16 may employ a leaching apparatus such as for example, a heap leach, a vat leach, a tank leach, a pad leach, a leach vessel or any other leaching technology useful for leaching a metal value from a metal-bearing material 12.

[0032] In accordance with various embodiments, conditioning 16 may be a leach process conducted at any suitable pressure, temperature, and/or oxygen content. In such embodiments, conditioning 16 may employ one of a high temperature, a medium temperature, or a low temperature, combined with one of high pressure, or atmospheric pressure. Conditioning 16 may utilize conventional atmospheric or pressure leaching, for example but not limited to, low, medium or high temperature pressure leaching. Medium or high temperature pressure leaching processes for chalcopyrite are generally thought of as those processes operating at temperatures from about 120° to about 190° C. or up to about 250° C.

[0033] In various embodiments, conditioning 16 may comprise dilution, settling, filtration, solution/solvent extraction, ion exchange, pH adjustment, chemical adjustment, purification, concentration, screening, and size separation. In various embodiments, conditioning 16 is a high temperature, high pressure leach. In other embodiments, conditioning 16 is an atmospheric leach. In further embodiments, conditioning 16 is a solid liquid phase separation. In still further embodiments, conditioning 16 is a settling/filtration step. In various embodiments, conditioning 16 produces metal-bearing solution 17.

[0034] In various embodiments, metal-bearing solution 17 may be subjected to metal recovery 18 to yield metal value 20. In exemplary embodiments, metal recovery 18 can comprise electrowinning metal-bearing solution 17 to yield recovered metal value 20 as a cathode. In one exemplary embodiment, metal recovery 18 may be configured to employ conventional electrowinning processes and include a solvent extraction step, an ion exchange step, an ion selective membrane, a solution recirculation step, and/or a concentration step. In one preferred embodiment, metal recovery 18 may be configured to subject metal-bearing solution 17 to a solvent extraction step to yield a rich electrolyte solution, which may be subject to an electrowinning circuit to recover a desired metal value 20. In another exemplary embodiment, metal recovery 18 may be configured to employ direct electrowinning processes without the use of a solvent extraction step, an ion exchange step, an ion selective membrane, a solution recirculation step, and/or a concentration step. In another preferred embodiment, metal recovery 18 may be configured to feed metal-bearing solution 17 directly into an electrowinning circuit to recover a desired metal value 20. In an especially preferred embodiment, metal value 20 is copper.

[0035] For the sake of convenience and a broad understanding of the present invention, an electrowinning circuit useful in connection with various embodiments of the present inven-

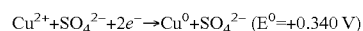
tion may comprise an electrowinning circuit, constructed and configured to operate in a conventional manner. The electrowinning circuit may include a plurality of electrowinning cells, each cell may be constructed as an elongated rectangular tank or vessel containing alternating cathodes and anodes, arranged perpendicular to the long axis of the tank. A metal-bearing solution may be provided to the tank, for example at one end, to flow perpendicular to the plane of the parallel anodes and cathodes. With the application of current from a power supply, a metal value, such as for example, copper, can be deposited at the cathodes, and water can be electrolyzed to form oxygen and protons at the anodes.

[0036] With initial reference to FIG. 2, an exemplary electrowinning cell 100 is illustrated in accordance with various embodiments of the present invention. Electrowinning cell 100 comprises vessel 102 configured to hold a series of electrodes 104. Power supply (not pictured) can be coupled to series of electrodes 104. In various embodiments, series of electrodes 104 can comprise a plurality of alternating anodes 112 and cathodes 110. As understood by one of ordinary skill in the art, any number of anodes 112 and/or cathodes 110 may be utilized. In addition an electrowinning circuit may comprise an individual electrowinning cell 100 or a plurality of electrowinning cells 100 connected in series or in parallel.

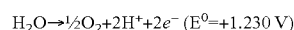
[0037] Typically, metal-bearing electrolytic solution 107 enters through entry port 106 at one end and flows through cell 100 (and thus past electrodes 104), during which a metal value is electrowon from metal-bearing electrolytic solution 107 onto cathode 110. An active surface or area of each of the series of electrodes 104 is the portion of each of the series of electrodes 104 that is immersed in metal-bearing electrolytic solution 107 up to solution fill level 116. In an exemplary embodiment, metal-bearing electrolytic solution 107 is metal-bearing solution 17. In a preferred embodiment, metal-bearing electrolytic solution 107 comprises at least copper. Lean electrolyte (metal-bearing electrolytic solution 107 having a reduced concentration of metal value) exits at exit port 108 of cell 100 at a distal end. In accordance with one aspect of an exemplary embodiment of the present invention, at least a portion of lean electrolyte may be returned to cell 100. In another aspect of an exemplary embodiment, at least a portion of lean electrolyte can be returned to at least one of reactive processing 14 and conditioning 16.

[0038] The general process of copper electrowinning, wherein copper is plated from a copper electrolyte, such as for example metal-bearing electrolytic solution 107, to a substantially pure cathode in an aqueous electrolyte is believed to occur by the following reactions:

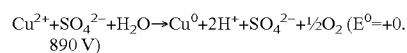
[0039] Cathode Reaction:



[0040] Anode Reaction:



[0041] Overall Cell Reaction:



[0042] Conventional copper electrowinning operations use either a copper starter sheet or a stainless steel “blank” or titanium “blank” as the cathode 110. In accordance with one aspect of an exemplary embodiment of the present invention, the cathode 110 is configured as a metal sheet. The cathode 110 may be formed of copper, copper alloy, stainless steel, titanium, or another metal or combination of metals, alloys,

and/or other suitable materials. As illustrated in FIG. 2 and as is generally well known in the art, cathode 110 is typically suspended from the top of electrochemical cell 100 such that a portion of cathode 110 is immersed below solution fill level 116 in metal-bearing electrolytic solution 107, as discussed above. This active surface is the portion of cathode 110 onto which a metal value, such as copper, is plated during electrowinning.

[0043] In general, electrowinning chemistry and electrowinning apparatus for copper value recovery are known in the art. As with conventional electrowinning cells, the rate at which direct current can be passed through cell 100 is effectively limited by the rate at which copper ions can pass from the copper-bearing solution to the cathode surface. This rate, also known as the limiting current density, is a function of factors such as copper concentration, diffusion coefficient of copper, cell configuration, and level of agitation of the aqueous copper-bearing solution. Conventional electrowinning operations typically operate at current densities in the range of about 220 to about 380 Amps per square meter (" A/m^2 ") or of about 20 Amps per square foot (" A/ft^2 ") of active cathode, and more typically in the range of about 300 A/m^2 and about 350 A/m^2 or of about 28 A/ft^2 and about 32 A/ft^2 . Use of an electrolytic solution flow system, which can provide additional electrolyte circulation and/or air injection into an electrochemical cell 100, can allow for higher current densities to be achieved.

[0044] In accordance with an exemplary embodiment of the present invention, overall cell voltage in a range of from about 0.75 Volts (" V ") to about 3.0 V can be achieved, preferably less than about 1.9 V, and more preferably less than about 1.7 V. The overall cell voltage achievable can be dependent upon a number of factors, including spacing of the series of electrodes 104, the configuration and materials of construction of the series of electrodes 104, acid concentration and metal value concentration in the electrolytic solution 107, current density, electrolytic solution 107 temperature, electrolytic solution 107 conductivity, and, to a smaller extent, the nature and amount of any additives to the electrowinning process (such as, for example, flocculants, smoothing agents, and/or surfactants).

[0045] Generally speaking, as the operating current density in the electrochemical cell 100 increases, the metal value plating rate onto cathode 110 increases. Stated another way, as the operating current density increases, more cathode 110 of the metal value, for example, copper, is produced for a given time period on cathode active surface area than when a lower operating current density is achieved. Alternatively, by increasing the operating current density, the same amount of the metal value may be produced in a given time period, but with less active cathode surface area (i.e., fewer or smaller cathodes 110, which corresponds to lower capital equipment costs and lower operating costs).

[0046] In accordance with one aspect of an exemplary embodiment of the present invention, the temperature of metal-bearing electrolytic solution 107 in electrowinning cell 100 is maintained at from about 40° F. to about 150° F. In accordance with one preferred embodiment, metal-bearing electrolytic solution 107 is maintained at a temperature of from about 90° F. to about 140° F. Higher temperatures may, however, be advantageously employed. For example, in direct electrowinning operations, temperatures higher than 140° F. may be utilized. Alternatively, in certain applications, lower temperatures may advantageously be employed. For

example, when direct electrowinning of dilute copper-containing solutions is desired, temperatures below 85° F. may be utilized.

[0047] The operating temperature of metal-bearing electrolytic solution 107 in electrowinning cell 100 may be controlled through any one or more of a variety of means well known in the art, including, for example, heat exchange, an immersion heating element, an in-line heating device (e.g., a heat exchanger), or the like, preferably coupled with one or more feedback temperature control means for efficient process control.

[0048] In accordance with an exemplary embodiment of the present invention, the acid concentration in the metal-bearing electrolytic solution 107 for electrowinning may be maintained at a level of from about 5 grams to about 250 grams of acid per liter of metal-bearing electrolytic solution 107. In accordance with one aspect of a preferred embodiment of the present invention, the acid concentration in the metal-bearing electrolytic solution 107 is advantageously maintained at a level of from about 150 grams to about 205 grams of acid per liter of metal-bearing electrolytic solution 107, depending upon the upstream process.

[0049] In accordance with an exemplary embodiment of the present invention, the copper concentration in metal-bearing electrolytic solution 107 for electrowinning is advantageously maintained at a level of from about 5 grams of copper per liter (" g/L ") to about 40 g/L of metal-bearing electrolytic solution 107. Preferably, the copper concentration is maintained at a level of from about 10 g/L to about 35 g/L of metal-bearing electrolytic solution 107. However, various aspects of the present invention may be beneficially applied to processes employing copper concentrations above and/or below these levels, with lower copper concentration levels of from about 0.5 g/L to about 5 g/L and upper copper concentration levels of from about 40 g/L to about 50 g/L being applied in some cases.

[0050] While various configurations and combinations of anodes 112 and cathodes 110 in the electrochemical cell 100 may be used effectively in connection with various embodiments of the present invention, a flow-through anode can be used, and electrolytic solution flow system can include an electrolyte flow manifold capable of maintaining satisfactory flow and circulation of electrolyte within the electrowinning cell.

[0051] Generally speaking, any electrolytic solution pumping, circulation, or agitation system capable of maintaining satisfactory flow and circulation of metal-bearing electrolytic solution 107 between the series of electrodes 104 in an electrowinning cell 100 such that the process specifications described herein are practicable and may be used in accordance with various embodiments of the present invention.

[0052] In accordance with an exemplary embodiment of the present invention, the metal-bearing electrolytic solution 107 flow rate is maintained at a level of from about 0.05 gallons per minute per square foot of active cathode 110 to about 30 gallons per minute per square foot of active cathode 110. Preferably, the metal-bearing electrolytic solution 107 flow rate is maintained at a level of from about 0.1 gallons per minute per square foot of active cathode 110 to about 0.75 gallons per minute per square foot of active cathode 110. It should be recognized that the optimal operable metal-bearing electrolytic solution 107 flow rate useful in accordance with the present invention will depend upon the specific configuration of the process apparatus as well as the electrolyte

chemistry employed, and thus flow rates in excess of about 30 gallons per minute per square foot of active cathode **110** or less than about 0.05 gallons per minute per square foot of active cathode **110** may be optimal in accordance with various embodiments of the present invention. Moreover, metal-bearing electrolytic solution **107** movement within electrowinning cell **100** may be augmented by agitation, such as through the use of mechanical agitation and/or gas/solution injection devices, to enhance mass transfer.

[0053] Referring now to FIG. 3, an electrochemical cell in accordance with various aspects of an exemplary embodiment of the present invention is illustrated. Electrochemical cell **300** generally comprises vessel **302** configured to hold at least one anode **304**, at least one cathode **306**, electrolyte injection inlet **308**, and outlet port **310**. Although an angled electrolytic solution injection inlet configuration is illustrated in FIG. 3 for purposes of reference, any number of configurations of an electrolytic solution injection inlet **308** may be possible. Electrolyte injection inlet **308** preferably may be configured to substantially distribute flow of metal-bearing electrolytic solution **107** evenly across the active surfaces of at least one anode **304** and at least one cathode **306**.

[0054] Referring now to FIG. 4, an electrochemical cell in accordance with various aspects of an exemplary embodiment of the present invention is illustrated. Electrochemical cell **400** generally comprises vessel **402** configured to hold at least one anode **404**, at least one cathode **406**, and distributor plate **408** comprising a plurality of injection holes **410**. Although an approximately horizontal electrolytic solution injection configuration is illustrated in FIG. 4 for purposes of reference, any number of configurations of differently directed and spaced injection holes **410** may be possible. For example, although injection holes **410** illustrated in FIG. 4 are approximately parallel to one another and similarly directed, configurations comprising a plurality of opposing injection streams or intersecting injection streams may be beneficial in accordance with various embodiments of the present invention. Preferably, distributor plate **408** can be configured to substantially distribute flow of metal-bearing electrolytic solution **107** evenly across the active surfaces of at least one anode **404** and at least one cathode **406**.

[0055] Injection velocity of the metal-bearing electrolytic solution **107** into an electrochemical cell may be varied by changing the size and/or geometry of the holes or slots through which electrolyte enters the electrochemical cell **400**. For example, with reference to FIG. 4 wherein electrolytic solution **107** feed is sent through distributor plate **403** configured having a plurality of injection holes **410**, if the diameter of injection holes **410** is decreased, the injection velocity of the electrolytic solution **107** is increased, resulting in, among other things, increased agitation of the electrolytic solution **107**. Moreover, the angle of injection of electrolytic solution **107** into electrochemical cell **400** relative to the cell walls and the electrodes, such as anode **404** and cathode **406**, may be configured in any way desired, through any number of cell walls.

[0056] Referring now to FIG. 5, an electrochemical cell in accordance with various aspects of an exemplary embodiment of the present invention is illustrated. Electrochemical cell **500** generally comprises vessel **502** configured to hold at least one anode **504**, at least one cathode **506**, and electrolyte flow manifold **508** comprising a plurality of injection holes **510** distributed throughout at least a portion of vessel **502**. As can be seen in FIG. 5, electrolytic solution flow manifold **508**

is a "floor mat" type manifold that is located on the floor of vessel **502**. Flow manifold **508** preferably is configured to substantially distribute flow of metal-bearing electrolytic solution **107** evenly across the active surfaces of at least one anode **504** and at least one cathode **506**.

[0057] In accordance with various embodiments of the present invention, exemplary electrochemical cells **300**, **400**, and **500** comprise examples of apparatus useful for implementation of an electrowinning step in an electrowinning cell **100**, as illustrated in FIG. 2. These and other exemplary aspects are discussed in greater detail herein below.

[0058] In accordance with exemplary embodiments of the present invention, a flow-through anode, such as anodes **304**, **404**, and **504** illustrated in FIGS. 3-5, can be incorporated into any of exemplary cells **100**, **302**, **402** and **502** illustrated in FIGS. 1 and 3-5. Likewise, in accordance with exemplary embodiments of the present invention, a flow-through cathode, such as cathode **306**, **406**, and **506** illustrated in FIGS. 3-5, can be incorporated into any of exemplary cells **100**, **302**, **402** and **502** illustrated in FIGS. 1 and 3-5.

[0059] Referring now to FIGS. 6-11, an electrode for an electrolytic cell is illustrated in accordance with various embodiments of the present invention. An exemplary embodiment of the electrode can be a flow-through anode **600** which will be discussed in detail. It should be understood that the anode **600** discussed below in detail can be incorporated into exemplary cells **300**, **400**, and **500** as anodes **304**, **404**, and **504** respectively or into exemplary cell **100** as anodes **112**.

[0060] In accordance with various embodiments, anode **600** can comprise hanger bar **602** and at least one conductor rod **612**. Anode **600** may comprise hanger bar **602** and anode body **604**. Anode body **604** may comprise at least one conductor rod **612** and at least one substrate **614** coupled to at least one conductor rod **612**. In accordance with an exemplary embodiment, hanger bar **602** is made from copper. In accordance with an exemplary embodiment, anode body **604** is suspended from hanger bar **602**. Preferably, during use, substantially all of anode body **604** is immersed in an electrolyte solution (i.e., below electrolyte fill level **116**, as illustrated in FIG. 2).

[0061] In accordance with an exemplary embodiment, anode body **604** comprises substrate **614**, as illustrated in FIGS. 6 and 7. Preferably, in accordance with an exemplary embodiment, substrate **614** comprises a mesh screen, perforated sheet or an expanded metal sheet. For example in constructing substrate **614**, an expanded sheet may be made by putting slits through a metal sheet then pulling the metal sheet from all sides to create an expanded sheet having a plurality of substantially diamond-shaped holes. Substrate **614** may be constructed of any conductive material, for example, those as described herein. In various embodiments, substrate **614** comprises a valve metal or a combination of valve metals or alloys comprising at least one valve metal. In an exemplary embodiment, substrate **614** comprises titanium.

[0062] In other embodiments, anode body **604** may comprise substrate **614** configured in the form of a mesh-like substrate. In an exemplary embodiment, substrate **614** comprises a woven wire screen with about a 100×100 strand per square inch to about a 10×10 strand per square inch, preferably from about an 80×80 strand per square inch to about a 30×30 strand per square inch, and more preferably about a 60×60 strand per square inch to about a 40×40 strand per square inch. However, other various rectangular and irregular

geometric mesh configurations may be used. In various embodiments, substrate **614** may be somewhat more porous, for example, a strand every square inch. Any strand pitch may be used for construction of substrate **614**. In various embodiments, substrate **614** uses an irregular pattern in which there is not a consistent pitch from side to side.

[0063] In accordance with various embodiments, substrate **614** may be fastened to conductor rods **612**, and such fastening methods are well known in the art and may include, for example, welding, adhesives, braided wire, fasteners, staples, and the like. Any means now known or hereafter developed in the future that may hold substrate **614** to rods **612** may be used as long as a portion of the substrate **614** is in electrical conductive contact to at least one of the conductor rods **612**. In accordance with one exemplary embodiment, substrate **614** may be welded to conductor rods **612**.

[0064] Conductor rods **612**, which are coupled to hanger bar **602**, can be of any number. In an aspect of the present invention, the number of conductor rods can be from about 4 to about 12, or from about 6 to about 8, or about 6, or about 8. In various embodiments, at least two of substrate **614** can be coupled to either side of conductor rods **612**, then the edges of the at least two of substrate **614** can be coupled together. In such a configuration, the at least two of substrate **614** create an envelope around a plurality of conductor rods **612**. The coupling of the edges of the at least two of substrate **614** can increase rigidity and/or increase lifetime of anode body **604**. In addition, the coupling of the edges of the at least two of substrate **614** can improve the coupling of substrate **614** to conductor rods **612** and/or improve conductivity of anode body **604**.

[0065] In accordance with another aspect of an exemplary embodiment of the present invention, substrate **614** may comprise any electrochemically active coating on a surface of substrate **614**. Exemplary coatings include those provided from platinum, ruthenium, iridium, or other Group VIII metals, Group VIII metal oxides, or compounds comprising Group VIII metals, and oxides and compounds of titanium, molybdenum, tantalum, and/or mixtures, alloys and combinations thereof. A mixture of tantalum oxide and iridium oxide can be used as an electrochemically active coating on substrate **614**. Preferably, in accordance with one exemplary embodiment, substrate **614** comprises a titanium mesh with a coating comprised of a mixture of iridium oxide and tantalum oxide.

[0066] In accordance with various embodiments, conductor rod **612** contains core **802** and outer layer **804**, as illustrated in FIG. **8A**, which is a cross-sectional view of conductor rod taken along line 7-7 of FIG. **7**. Outer layer **804** can cover essentially the entirety of core **802** below hanger bar **602**. Core **802** comprises a conductive material, for example, but not limited to, copper, copper alloy, aluminum, copper aluminum alloy, stainless steel, titanium, gold, combinations thereof, or any other electrically-conductive materials suitable for core **802**.

[0067] Outer layer **804** can be any conductive metal, such as, for example, a valve metal. Outer layer **804** can be formed of one of the so-called valve metals, including titanium, tantalum, zirconium, and niobium. For example, titanium may be alloyed with nickel, cobalt, iron, manganese, or copper can form a suitable outer layer **804**. In an exemplary embodiment, outer layer **804** comprises titanium because, among other things, titanium is rugged and corrosion-resistant and in that regard can extend the lifetime of anode **600**. In accordance

with an exemplary embodiment, outer layer **804** can be made from titanium and may be cold rolled onto core **802** or clad thereon.

[0068] In accordance with an exemplary embodiment, conductor rod **612** includes first end **806** and second end **808** which is distal to first end **806**. First end **806** includes attachment portion **810**. Attachment portion **810** includes exposed core **802** and does not include outer layer **804** of conductor rod **612**. In an exemplary embodiment, if core **806** has outer layer **804** that has been cold-rolled over the surface of core **804**, a portion of outer layer **804** may be cut near first end **806** to create attachment portion **810**.

[0069] Second end **808** of conductor rod **612** contains cap **814**. Cap **814** fits within removed portion **816** of core **802**. Removed portion **816** of core **802** may be removed by any suitable method. In accordance with an exemplary embodiment, removed portion **816** of core **802** is removed by contacting it with an acid. As will be apparent to those skilled in the art, cap **814** may comprise a myriad of different configurations as compared to that in FIG. **8A**. For example, cap **814** may be a disc, having a diameter equal to the outer diameter of conductor rod **612** and attached to the end of conductor rod **612** using means known to those skilled in the art or hereafter developed, such as for example, an adhesive, welding, fasteners, combinations thereof, and the like. Other configurations for cap **814** can include an edge that is greater than the diameter of conductor rod **612**. In such configurations, cap **814** can be fastened using threads, forced on, crimped, adhesives, welding, fasteners, combinations thereof, and the like. Any configuration of cap **814** known to those skilled in the art or developed in the future may be used at second end **808** of conductor rod **612**. Use of cap **814** is advantageous to prevent acid from eating away core **802** of conductor rod **612** when anode **600** is used in electrowinning applications.

[0070] In accordance with another aspect of an exemplary embodiment of the present invention, conductor rod **612** may also optionally comprise any electrochemically active coating. Exemplary coatings include those provided from platinum, ruthenium, iridium, or other Group VIII metals, Group VIII metal oxides, or compounds comprising Group VIII metals, and oxides and compounds of titanium, molybdenum, tantalum, and/or mixtures, alloys and combinations thereof. A mixture of tantalum oxide and iridium oxide can be used as an electrochemically active coating on conductor rod **612**.

[0071] In accordance with various embodiments, conductor rod **612** contains core **802** and outer layer **804**, as illustrated in FIG. **8B**, which is a cross-sectional view of conductor rod taken along line 7-7 of FIG. **7**. Core **802** and outer layer **804** comprise any materials discussed herein. In accordance with an exemplary embodiment, core **802** can comprise copper and outer layer **804** can be made from titanium and may be cold rolled onto core **602** or clad thereon.

[0072] In accordance with an exemplary embodiment, conductor rod **612** includes first end **806** and second end **808** which is distal to first end. First end **806** includes attachment portion **810**. Attachment portion **810** includes exposed core **802** and does not include outer layer **804** of conductor rod **612**.

[0073] In an exemplary embodiment, circumferential groove **812** may be inscribed in core **802** adjacent to outer layer **804**. More specifically, the circumferential groove **812** may be machined into core **802**. If core **802** has outer layer **804** that has been cold-rolled over the surface of core **802**, a portion of outer layer **804** may be cut near first end **806** to

create attachment portion **810**. Once outer layer **804** is cut, a portion of outer layer **804** may be removed and the cutting of outer layer **804** may create groove **812**. In an exemplary embodiment, outer layer **804** can be cold-rolled or clad onto core **802** up to groove **812**. Using such a method, groove **812** may be used as a guide for rolling outer layer **804** over core **802** such that a length of attachment portion **810** is essentially equivalent across a plurality of conductor rods **612**. In an exemplary embodiment, grooves can be configured to hold a seal member (not shown) for example a synthetic rubber O-ring type seal, or a fluoropolymer elastomer O-ring type seal.

[0074] Referring now to FIGS. 9 and 10, hanger bar **602** will be discussed. In accordance with an exemplary embodiment, hanger bar **602** can be a "steerhead" configuration, which is configured to be positioned horizontally in an electrowinning cell. Other configurations for hanger bar **602** may, however, be utilized, such as, for example, substantially straight configurations, multi-angled configurations, offset configurations and the like. In accordance with an exemplary embodiment, hanger bar **602** contains an upper surface **906** and a lower surface **908**. In accordance with an exemplary embodiment, the lower surface **908** contains a plurality of recessed holes **910** that extend within the hanger bar, upwardly along a vertical axis.

[0075] In accordance with an exemplary embodiment, at least one conductor rod **612** can be coupled with hanger bar **602** and suspended therefrom, as illustrated in FIGS. 6, 9 and 10. In accordance with an exemplary embodiment, attachment portion **810** of conductor rod **612** can be inserted into recessed hole **910** of hanger bar **602**. Preferably, in accordance with an exemplary embodiment, attachment portion **810** of conductor rod **612** is press fit within recessed hole **910**. Attachment portion **810** can be inserted such that core **802** is flush within recessed hole **910** thereby providing for a suitable electrically conductive connection between core **802** and hanger bar **602**.

[0076] With reference to FIGS. 11A and 11B, connection **930** is illustrated as a cross sectional view along the line 10-10 of FIG. 10. Connection **930** comprises one of the plurality of recessed holes **910** and attachment portion **810** fastened in the one of the plurality of recessed holes **910**. In an exemplary embodiment, connection **930** can be a press fit attachment of attachment portion **810** into one of plurality of recessed holes **910** such that attachment portion **810** is forced into one of plurality of recessed holes **910**.

[0077] Referring now to FIGS. 11A and 11B and in accordance with an exemplary embodiment, attachment portion **810** of conductor rod **612** is inserted into recessed hole **910** of hanger bar **602**. Preferably, in accordance with an exemplary embodiment, attachment portion **810** of conductor rod **612** is press fit within recessed hole **910**. Attachment portion **810** is inserted such that core **802** is flush within recessed hole **910** thereby providing for a suitable electrically conductive connection between core **802** and hanger bar **602**.

[0078] In another aspect of an exemplary embodiment, attachment portion **810** may be tapered, making it easier to form connection **930** when meeting an end of the end of the forward end of attachment portion **810** into one of plurality of recessed holes **910**. In addition, tapering of attachment portion **810** can be advantageous when connection **930** is a press fit since a force is only necessary when the taper is equal to or greater than the diameter of the one of the plurality of recessed holes **910**. In an exemplary embodiment, attachment

portion **810** is made out of copper and, as such, may be malleable under pressure during a press fit for connection **930**. In addition, hanger bar **602** may be made of copper and, as such, may be somewhat malleable which may be advantageous in creating a press fit for connection **930**. In an exemplary embodiment, connection **930** comprising attachment portion **810** and one of the plurality of recessed holes **610** creates an electrical conductive interface between hanger bar **602** and conductor rod **612**.

[0079] Other attachment means may be used for connection **930**, for example, threads, barbed surfaces, chamfer surfaces, lock-tight fittings, and combinations thereof. In addition, secondary materials, such as adhesives, welds, splints, deformable members, and the like can be used to reinforce connection **930**.

[0080] With continual reference to FIGS. 11A and 11B, seal **932** is illustrated in accordance with another aspect of exemplary embodiments of the present invention. Seal **932** can be created during a press fit of connection **930** between attachment portion **810** and one of the plurality of recessed holes **910**. In an exemplary embodiment, plurality of recessed holes **910** comprises notch **934**. Notch **934** can be an indentation in lower surface **908** of hanger bar **602** having end **936** of notch **934** which is substantially parallel to the plane of lower surface **908**. Notch **934** typically has a diameter which is greater than the diameter of the plurality of recessed holes **910**. In an aspect of an exemplary embodiment, a diameter of notch **934** is greater than an outer diameter of outer surface **804** of conductor rod **612**.

[0081] In accordance with another aspect of an exemplary embodiment, seal **932** is at an interface of end **936** of notch **934** and forward edge **824** of outer surface **804**. Forward surface **824** of outer surface **804** is essentially perpendicular to the length of conductor rod **612**. As will be appreciated by those skilled in the art, to optimize performance of seal **932**, a surface of forward edge **824** of outer surface **804** and a surface of end **936** of notch **934** should be essentially smooth and flat. If an angle is used for either the forward edge **824** of the outer surface **804** or end **936** of notch **934**, as will be appreciated by those skilled in the art, such angles should be complimentary to optimize seal **932**.

[0082] Seal **932** essentially isolates connection **930**. For example, if anode **600** is utilized in electrowinning for copper, seal **932** can isolate connection **930** from acid fumes from the electrolytic cell. It is advantageous to isolate connection **930** from acid fumes so that the integrity of connection **930** is not affected by etching effects of acid fumes to the inter wall of one of the plurality of recessed holes **910** and/or outer surface of attachment portion **810**. In this regard, use of seal **932** can ensure greater lifetime of anode **600**. Seal **932** can include a compressible ring, a polymeric ring or grommet, or any other such seal interfaces that are now known to those skilled in the art or hereafter developed. As will be appreciated by those skilled in the art, if such a seal interface is employed between end **936** of notch **934** and leading edge **824** for seal **932**, it is preferred that such a seal interface impermeable to whichever solution or gas from which seal **932** is isolating connection **930**, or at least the seal interface does not communicate such solution or gas into connection **930**.

[0083] With reference to FIG. 11B, in an exemplary embodiment, groove **812** assists in press fit of connection **930** such that attachment portion **810** may be deformed as it is press fit into one of plurality of recessed holes **910** and as such the deformation of attachment portion **810** may move some

material into groove **812**. In an exemplary embodiment, groove **812** can be configured to hold a seal member, such as, for example, a synthetic rubber O-ring type seal or a fluoropolymer elastomer O-ring type seal.

[0084] According to various embodiments, the present invention provides methods of making an electrode useful for electrowinning a metal value. In various embodiments, the method can include cladding core **802** with outer layer **804** and exposing an attachment portion to **810**. As discussed herein, outer layer **804** can be cold-rolled over core **802**. In another exemplary embodiment of the present invention, core **802** may be dipped in a solution to create outer layer **804**. Exposing attachment portion **810** can include cutting a portion of outer layer **804** and removing the cut portion of outer layer **804** to expose attachment portion **810** of core **802**. In various embodiments, the method can include capping an end of conductor rod **612**. The capped end is distal to attachment portion **810**. In an exemplary embodiment, the method can include etching a portion of core **802** distal to attachment portion **810**. The etching of core **802** creates a portion that is removed to provide space for attachment of cap **814**. The method can also include welding cap **814** to conductor rod **612**. In various embodiments, the method can include creating a plurality of recessed holes **910** in hanger bar **602**. Creating a plurality of recessed holes **910** can include drilling, machining, etching, and the like. In an exemplary embodiment of the present invention, the method can include creating a recessed notch **934** around a circumference of each of the plurality of recessed holes **910**.

[0085] In various embodiments, the method can include connecting at least one conductor rod **612** to hanger bar **602**. In an exemplary embodiment, the method can include press fitting attachment portion **810** into one of plurality of recessed holes **910**. The method can include creating connection **930** by mating attachment portion **810** with one of plurality of recessed holes **910**. The method can include reinforcing connection **930** and such reinforcement can include applying an adhesive, inserting a shim, welding, applying a fastener, and combinations thereof.

[0086] In an exemplary embodiment, the method can include creating seal **932**. Seal **932** can be created by interfacing front surface **824** of outer layer **804** with end **936** of notch **934**. In an exemplary embodiment, the method can include isolating connection **930**. Seal **932** can essentially isolate connection **930**. In various embodiments, the method can include coating conductor rod **612** with an electrochemically active coating.

[0087] In various embodiments, the method can include attaching at least one substrate **614** to at least one conductor rod **614**. In an exemplary embodiment, the method can include coating at least a portion of substrate **614**. Attaching substrate **614** to at least one conductor rod **612** can include welding, braiding, stapling, fastening, and/or combinations thereof. In an exemplary embodiment, the method can include attaching a second substrate **614** to at least one conductor rod **612**. The method can include coating at least a portion of substrate **614** with an electrochemically conductive coating.

[0088] The present invention has been described above with reference to a number of exemplary embodiments. It should be appreciated that the particular embodiments shown and described herein are illustrative of the present invention and its best mode and are not intended to limit in any way the

scope of the present invention as set forth in the claims. Those skilled in the art having read this disclosure will recognize that changes and modifications may be made to the exemplary embodiments without departing from the scope of the present invention. For example, various aspects and embodiments of this invention may be applied to electrowinning of metals other than copper, such as nickel, zinc, cobalt, and others. Although certain preferred aspects of the present invention are described herein in terms of exemplary embodiments, such aspects of the present invention may be achieved through any number of suitable means now known or hereafter devised. Accordingly, these and other changes or modifications are intended to be included within the scope of the present invention.

1. An electrode comprising:
a conductor bar having a recess;
a conductor rod comprising a core clad in a valve metal and an attachment portion having an exposed core; and
wherein the conductor rod is press fit into the recess.
2. The electrode according to claim 1, further comprising a substrate coupled to the conductor rod.
3. The electrode according to claim 1, wherein the core is selected from the group consisting of copper and aluminum.
4. The electrode according to claim 1, wherein the valve metal is titanium.
5. The electrode according to claim 2, wherein the substrate comprises titanium.
6. The electrode according to claim 2, wherein the substrate comprises an electrochemically active coating.
7. The electrode according to claim 6, wherein the electrochemically active coating comprises a mixture of tantalum oxide and iridium oxide.
8. The electrode according to claim 7, wherein the substrate comprises a titanium mesh.
9. The electrode according to claim 1, wherein the conductor bar is a hanger bar.
10. The electrode according to claim 9, wherein the hanger bar has a steerhead configuration.
11. The electrode according to claim 1, wherein the attachment portion is tapered.
12. The electrode according to claim 1, further comprising a seal disposed at the interface of the attachment portion and the conductor bar.
13. The electrode according to claim 12, wherein the seal comprises at least one of a compressible ring, a polymeric ring and a grommet.
14. A method for constructing an electrode comprising:
exposing a core at a first end of a conductor rod, wherein the conductor rod comprises the core clad in a valve metal; and
press fitting the first end of the conductor rod into a recess of a conductor bar.
15. The method according to claim 14, further comprising coupling a substrate to the conductor rod.
16. The method according to claim 15, further comprising coating a portion of a surface of the substrate with an electrochemically active coating.
17. The method according to claim 14, further comprising disposing a seal at the junction between the conductor rod and the conductor bar.
18. The method according to claim 14, further comprising capping a distal end of the conductor rod.