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Emmett, Jr.

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[54] **CONTINUOUS ELECTROWINNING CELL**

[75] Inventor: **Robert Clarence Emmett, Jr.,** Dundee, Ill.

[73] Assignee: **Envirotech Corporation,** Salt Lake City, Utah

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[52] **U.S. Cl.** **204/281,** 204/10, 204/216

[51] **Int. Cl.** **B01k 1/00,** C22d 5/00, B23p 1/00

[58] **Field of Search** 204/10, 225, 216, 208, 204/281, 13

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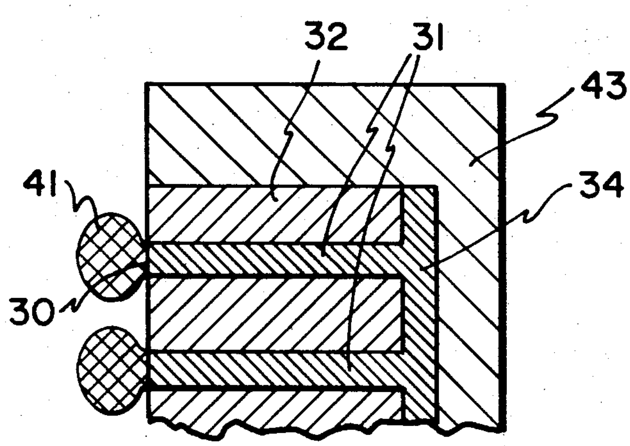
Primary Examiner—T. M. Tufariello
Attorney, Agent, or Firm—Robert R. Finch

[57] **ABSTRACT**

An electrolytic cell is formed with a housing enclosing a flat-faced cathode and anode in closely spaced face-to-face relationship. The cathode comprises a plurality of small diameter cathode elements held in spaced-apart relationship by an insulating matrix. Each of the elements terminates in a small diameter tip. Metal deposits on the tips in dendritric form and is scraped therefrom. The anode face is porous and connections are provided for withdrawing gaseous products from the face as they are formed. Operation is continuous, recovered metal being flushed from the cell in spent electrolyte as the latter is displaced by fresh electrolyte.

12 Claims, 8 Drawing Figures



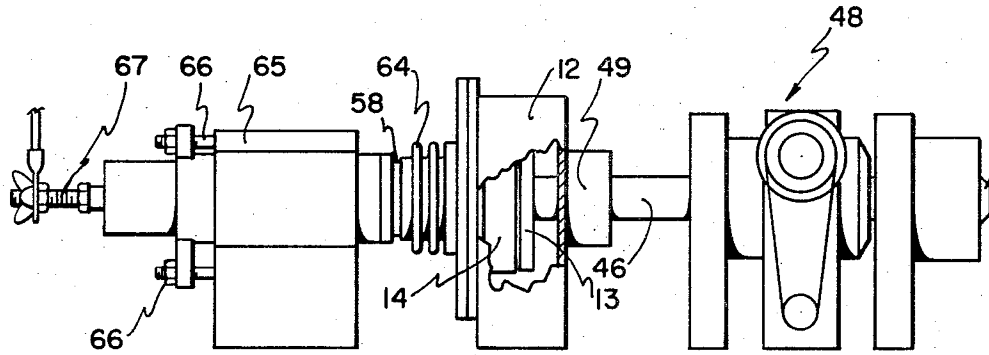

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FIG. 1

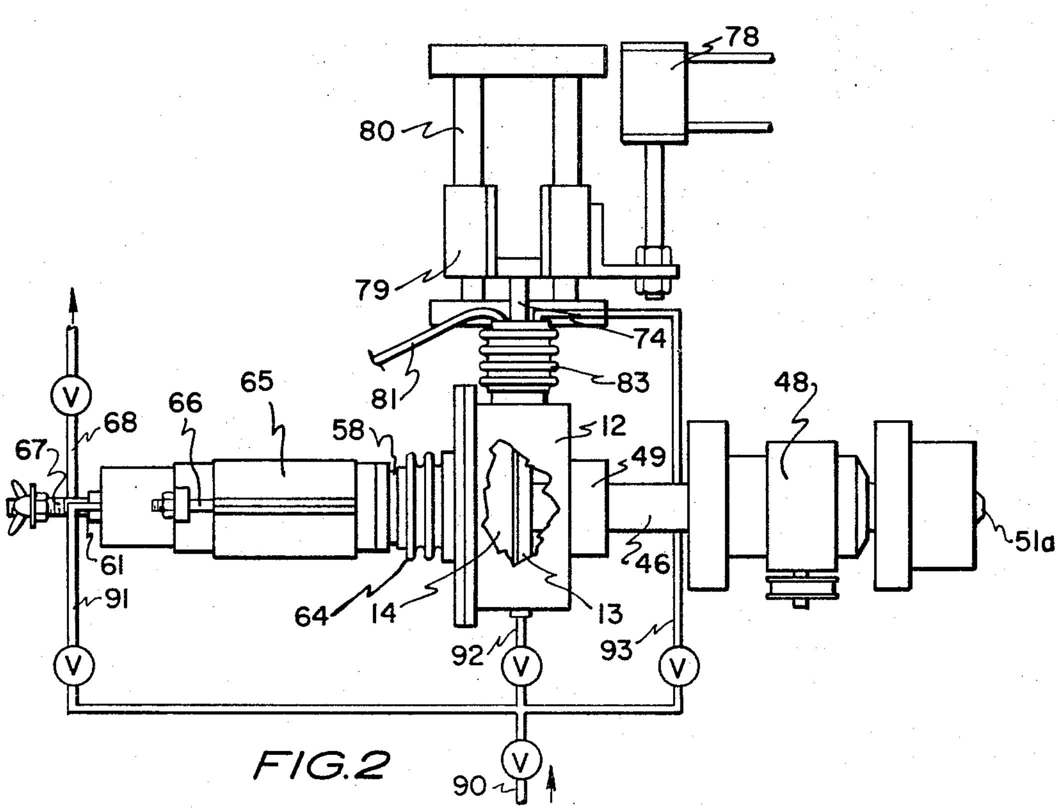
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FIG. 2

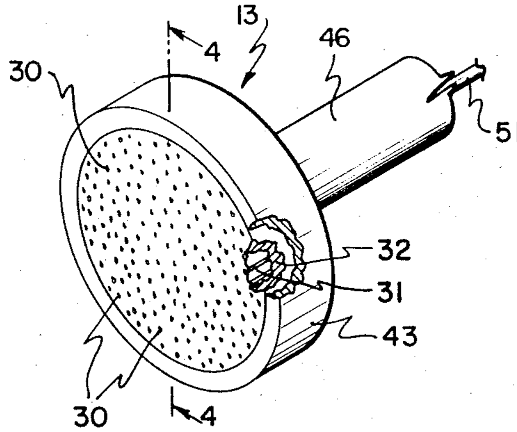

FIG. 3

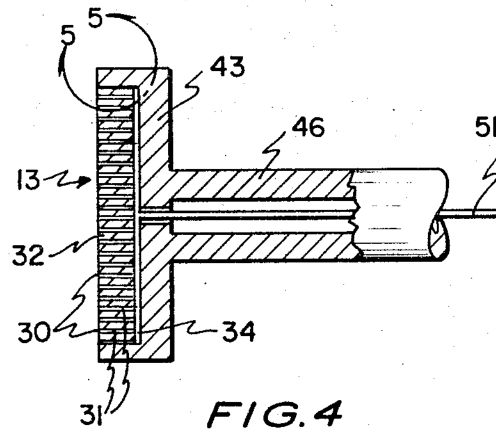

FIG. 4

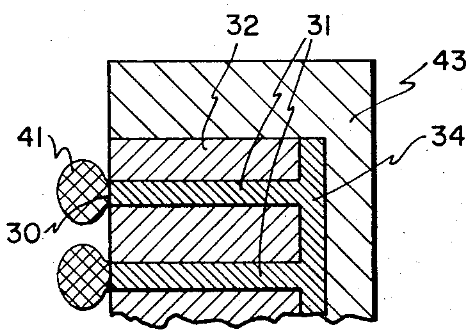

FIG. 5

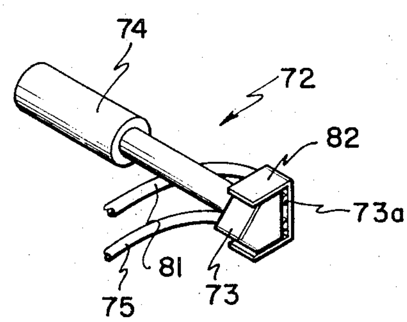

FIG. 8

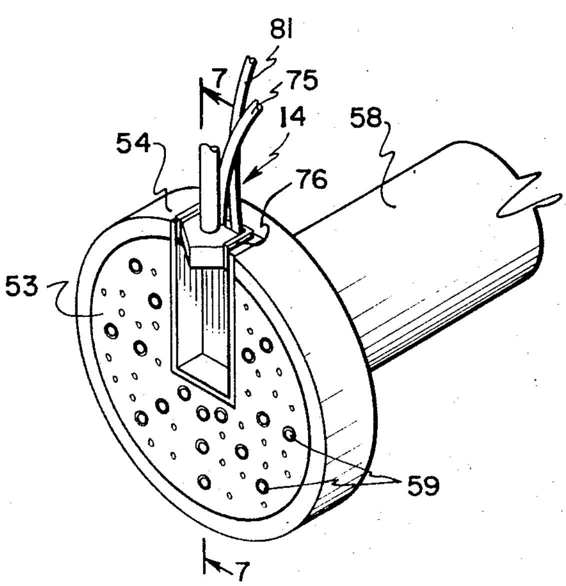

FIG. 6

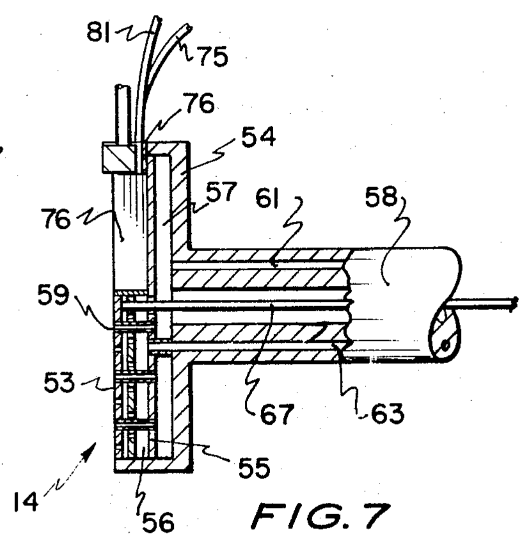

FIG. 7

CONTINUOUS ELECTROWINNING CELL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an apparatus and process for the continuous electrowinning of metal.

2. State of the Art

Electrowinning, a well-known process, utilizes an electric current to reduce an ionized metal for deposit as elemental metal on a cathode. The ionized metal is carried in an electrolyte usually yielded from an acid leach of a metal bearing ore or concentrate. A conventional electrowinning cell comprises a tank in which one or more sets of insoluble anodes and cathodes are immersed in an electrolyte. When a current passes through the electrolyte between the electrodes, metal is deposited on the cathode.

As currently practiced, electrowinning is a batch operation conducted in large tanks in which a plurality of cathodes and anodes are suspended. The anodes are usually chemically inert, typically, a lead alloy such as lead-antimony. The cathodes are usually thin starting sheets of the same metal as that which is to be recovered and are retained in the electrolyte for one to three weeks until a commercially usable quantity of metal builds on them.

Batch operations have several drawbacks. These include the need for a large amount of floorspace to achieve acceptable production rates and the fact that new starting cathodes must be supplied for each new batch.

Attempts have been made to improve on batch metallurgy. One proposal for doing so is the powder metallurgy technique in which very high current densities are employed under conditions such that the metal deposits on the cathode as a powder rather than a solid plate. In such form, the metal may often be scraped from the cathode while the latter is in place in the cell. Although powder metal is easy to harvest, it usually contains many occluded impurities and its granular characteristics, such as bulk density, are often unacceptable for use except with further purification.

SUMMARY OF THE INVENTION

This invention provides improved ways and means for continuous electrowinning of metal in commercial acceptable form. The mechanism includes a cathode of novel construction on which metal is deposited as small dense particles. Means are provided for continuously removing deposited metal while electrolysis continues.

The cathode is formed so that its exposed face comprises a plurality of small-area tips held in spaced-apart relationship by an insulating matrix. With this construction, each small-area tip functions as a separate cathode. The invention is predicated on the discovery that if the individual cathode tips have a small exposed area, metal will deposit thereon in a particular configuration and with such a fragile bond that it is subjected to easy harvesting without harming the tips. A harvesting means is provided to continuously remove deposited metal from the cathode tips, and means are also provided to remove the metal particles from the cell as they are harvested. A porous anode of special design is also provided to continuously withdraw gaseous products from the cell.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be more readily understood and carried into effect by reference to the following description and appended drawings which are offered by way of illustration and not in limitation of the invention, the scope of which is defined by the appended claims and equivalents thereof rather than by any separate description.

In the drawings:

FIG. **1** is a side view of an electrolytic cell embodying the invention. For purposes of illustrating internal components, a portion of the cell wall is shown as partially cut away;

FIG. **2** is a plan view of the cell illustrated in FIG. **1** with portions of the wall cut away for purposes of revealing internal components. Additionally, electrolyte supply piping is also illustrated;

FIG. **3** is a pictorial view, partially cut away, of the cathode employed in the cell illustrated in FIGS. **1** and **2**;

FIG. **4** is a sectional view taken in a plane passing through the line **4—4** of FIG. **3** and viewed in the direction of the arrows **4**;

FIG. **5** is an enlarged detailed view of that part of the cathode encompassed within the line **5—5** of FIG. **4**;

FIG. **6** is a pictorial view of an anode suitable for use in the cell illustrated in FIG. **1**;

FIG. **7** is a sectional view taken in a plane passing through the line **7—7** of FIG. **6** and viewed in the direction of the arrows **7**; and

FIG. **8** is a detailed view of a metal harvesting means adapted for use with the cell.

DETAILED DISCLOSURE

The electrowinning cell illustrated in FIGS. **1** and **2** generally comprises a housing **12** in which are mounted a cathode **13** and an anode **14** in face-to-face relationship. The housing **12** may be sealed to facilitate capture of gaseous products of electrolysis and prevent escape of corrosive vapors. The inner wall of the housing is electrically insulated, preferably with a corrosion-resistant material.

The cathode **13** is designed so that metal of proper characteristics will be efficiently deposited thereon at a high rate and in a form susceptible to continuous removal without damage to the cathode or interruption of the process. As shown in FIGS. **3–5**, the cathode **13** comprises a plurality of exposed electrically conductive tips **30**, each of which functions as a separate cathodic element. The tips are the terminal ends of thin conductors **31**, such as small-diameter wires, which are supported in spaced-apart relationship by a matrix of insulating material **32** held in an insulated holder **43** with only the tips **30** exposed. The other ends of the conductors **31** are all connected inside the holder to a common electrically conductive base **34**. The exposed surface or face of the cathode **13** should be smooth so that deposits on the individual cathode tips do not physically stick to the insulating matrix **32** and none of the sidewalls of the individual cathodic elements **31** are exposed. Thus, the conductive cathode surface may be described as being a smooth surface formed from the free ends of a plurality of electrical conductors held in spaced-apart relationship by a matrix of non-conducting material.

The cathode tips **30** are sufficiently small that the metal deposits thereon in a configuration which exhibits a weak bond and extends outwardly from the cathode face, thereby enhancing removal by a light scraping action. As illustrated, the cathode tips are flat, round surfaces about 0.025–0.15 mm in diameter (area = $0.0005 mm^2$ to $0.018 mm^2$) and the edges of the tips are spaced 0.25–0.6 mm apart at the closest points. As shown in FIG. **5**, metal deposits on the cathode tips **30** in the form of small outwardly extending clumps **41.** The clump-tip bond is small and easily broken. The small tips are important because if the diameter of the tip surface is increased appreciably, two undesirable things occur: first, the bonding area increases so that deposited metal adheres more firmly and, second, the deposited metal tends to spread radially about the tip and takes a disc-like configuration that is difficult to remove and which will also contribute to undesirable bridging between tips. As noted, the spacing between adjacent tips is also important and should be in the range of 0.25 to 0.6 mm to insure that deposited metal does not form a bridge between adjacent tips.

One technique for fabricating a suitable cathode is to first fix segments of relatively large diameter stainless steel wire to a base strip to provide a comb-like component. A number of such strips are fixed together to form a brush-like cluster. The diameters of the wires are then decreased by known etching techniques and the cluster is encapsulated in a suitable insulating material such as a ceramic, glass or appropriate plastic. The insulating material should be corrosion-resistant and of sufficient strength that it does not flex or permit working loose of the conductors to the extent that greater cathode areas are exposed lest the character of the metal deposits change and they become difficult to remove.

It is not necessary that the conductors **31** be wires or that they be round. Suitable cathodes have been formed where the individual tips have a rectangular configuration, say 0.025–0.1 mm by 0.5–2.5 mm (area = $0.0125 mm^2$ to $0.25 mm^2$), and with spacing between adjacent tips ranging from 0.25–0.6 mm at the closest points. Again, the spacing is important to avoid bridging between adjacent tips.

Referring again to the illustrated cathode, one end of an insulated shaft **46** is rigidly fixed to and extends from the rear face of the cathode holder **43** to extend through the adjacent endwall of the housing **12** where it connects to a suitable drive **48** adapted to effect slow rotation of shaft **46** and the cathode holder **43.** A conventional stuffing box **49** encircles the shaft where it exits the housing. An electrical conductor **51** (FIGS. **3** and **4**) extends from the common base **34** through the insulated shaft **46** to terminate outside the housing at a contactor **51***a* adapted to be connected to a direct current source, not shown, but which typically supplies a potential of about 2–8 volts across the electrodes. If the cell contains more than one pair of electrodes, the DC source should be capable of supplying 2–8 volts across each pair.

The anode **14** (FIGS. **6–7**) is designed to serve as the inlet for fresh electrolyte simultaneously with removal of gaseous electrolysis products. The anode includes a flat face plate **53** made from a perforated or otherwise porous material. For instance, the plate **53** may comprise two super-imposed layers of perforated titanium sheet which are coated with a metal or oxide capable of functioning as an inert anode whereby to promote oxygen release. When assembled in the housing, the anode face plate **53** forms the conductive anode surface and is in closely spaced parallel relationship to the conductive cathode surface **13.**

The face plate **53** fits over a hollow cylindrical holder **54** in which is fitted a solid divider **55** which divides the anode transversely into a front chamber or plenum **56,** just back of the anode face plate, and a back chamber or plenum **57** adjacent the rear of the holder. The holder and the divider should be made from non-conductive, anodic-corrosion-proof material. An insulated shaft **58** is connected and extends rearward from the holder. A suitable conductor **67** extends through the shaft to connect the face plates **53** to the D.C. source. A plurality of short, electrically non-conductive conduits **59** extend through the divider **55,** thence across the front chamber **56** and through the anode face plate **53** to thus provide communication between the rear chamber **57** through the face plate **53** into the interior of the housing **12.** A bore **61** in the shaft forms a conduit which connects the back chamber **57** to a source of electrolyte, all as more fully described hereinafter.

A second bore **63** extends longitudinally through the shaft **58** thence through the back chamber **57** and the divider **55** to provide communication between the front chamber **56** and the exterior of the anode whereby enabling withdrawal of gas through the porous anode face **53.** In some cases the withdrawal of gas may be facilitated by application of vacuum to the front chamber via conduit **63** in addition to the pressure differential created by introduction of electrolyte.

The electrolyte supply conduits **59** are sized and spaced on the anode face **53** to permit an adequate supply of fresh electrolyte into the housing **12** without unnecessary jetting that might result in premature removal of metal deposits from the face of the cathode **13.** Usually about 2 mm separates the two electrode faces but the distance can range from about 1 mm to 10 mm.

As previously mentioned, the shaft **58** connects to the rear of the anode assembly and extends through the wall of the housing **12.** Fluid leakage from the housing is contained by a flexible sleeve **64** (FIGS. **1** and **2**). The shaft **58** serves to support and adjust the anode **14** to selected positions within the housing. Adjustment of anode position is effected by mounting the shaft in a mechanism **65** outside the housing which enables adjustment in an axial direction. For fine adjustments of the anode position, use is made of simple draw bolts **66.**

As shown in FIG. **7**, an electrical conductor **67** extends from the anode face **53** through the shaft **58** to the electrical power source. It is insulated except where it contacts the plates **53.**

Metal-bearing electrolyte is introduced to the cell via a main feed line **90** and one or more of the valved branch lines **91, 92** and **93.** Of these, conduit **91** connects to passage **61** in shaft **58** to supply electrolyte through the anode face into the housing. Conduit **92** connects through the wall directly into the interior of the housing. Conduit **93** connects to special conduit **75** on the scraper blade assembly for purposes to be more fully explained hereinafter.

Free gases, primarily oxygen, liberated in the cell, are withdrawn through the conduit **68** which connects to passage **63** in the shaft **58.**

In the illustrated embodiment electrolyte will normally be supplied through both branches **91** and **92** to keep the housing, including the inter-electrode space, full without excessive liquid movement transverse to the electrode faces. Thus, in the normal operation, fresh electrolyte enters through the anode surface and through the housing wall. Some electrolyte is withdrawn through the anode face with the gas and the balance is withdrawn through the flush conduit with the harvested metal.

To accommodate special conditions, such as the deleterious high acid that could occur in the recovery of zinc, a further inlet conduit **75** is provided to supply low-acid content feed electrolyte to the harvesting blade area to assist in flushing out the loosened metal while diluting the acid content of the spent electrolyte in which the metal is flushed from the cell.

A harvester is provided for continuously removing deposited metal from the cathode points. The harvester **72** (FIGS. **6–8**) includes a blade **73** which is hooded, as hereinafter explained, and is fixed to a reciprocatable arm **74** which moves the blade and associated hood radially to-and-fro within a solid walled slot **76** formed in the anode face **53** (see FIG. **6**). The blade, enlarged in FIG. **8**, is much shorter than the slot **76.** The blade extends toward the cathode face and terminates close to the cathode face so that as the cathode **13** rotates, the edge of the blade **73** scrapes the metal deposits from the cathode tips. At the same time, the arm **74** moves the blade gradually toward the center of the electrode. The result is that the blade cuts a spiral path. When the limit of travel is reached the blade returns rapidly to the starting position near the edge and the cycle is repeated. Spacers **73***a* are provided to separate the blade **73** from the bottom of the hood thereby permitting liquid and metal to flow around the blade to discharge via a tube **81** that connects from the interior of the hood to a remote location outside the cell, whereby the mixture of spent electrolyte and metal particles may be continuously flushed from the blade area thus removing metal from the cell as soon as it is scraped from the cathode. Flow through the discharge conduit is induced by the pressure of incoming fresh electrolyte entering through the supply conduits. The slurry of metal particles is conveniently conducted to a filter or other separator for final recovery of the metal.

Although other blade arrangements may be used to scrape metal from the cathode, it is important that only a relatively small percentage of clean cathode tips be exposed at any one time and that the major part of the total cathode area is normally covered by deposited metal. If too much cathode tip area is exposed without a corresponding reduction in total current then undesirably high voltages will occur at the cathode tips with the result that hydrogen will deposit on the cathode in preference to metal thus seriously interferring with the operation.

FIGS. **1** and **2** illustrate portions of the harvester mechanism exterior to the housing. A reciprocal hydraulic ram **78** is mounted to drive a carriage **79** mounted on tracks **80.** The arm **74,** which carries the blade on one end, has its other end connected to the carriage to reciprocate therewith. The arm enters the housing through a flexible sleeve **83.** Controls (not shown), are provided to time the movement of the arm.

Electrolyte, such as an acid leach solution, is introduced via main conduit **90** and branches **91** and **92** into the housing thus feeding both through the anode face and the housing wall to maintain the cell substantially filled with electrolyte.

The electrolyte flow rate, the applied voltage and the distance between the electrode faces are all adjusted to obtain the desired rate and quality of deposit. Typical current densities will range from about 0.5 to about 2.0 amperes per square cm (about **460** amperes/ft.^{2} to about 1859 amperes/ft.^{2}). As used herein, current densities are computed on total surface area of the cathode face - not just the cathode tips. The configuration of metal deposits on the cathode, except for some very soft deposits obtained at high current densities, is that shown in FIG. **5.**

Simultaneously with the application of direct current, the cathode is rotated and the harvester blade actuated. The rate of cathode rotation and blade reciprocation are adjusted so that metal is scraped from the cathode tips fast enough to prevent bridging between adjacent deposits. Harvested metal and electrolyte are withdrawn from the cell via the conduit **81.** Recovered metal particles are filtered and, if desired, compacted or ground to a high density powder.

During operation on a copper sulfate solution, free oxygen is liberated at the anode **14.** A mixture of this oxygen and electrolyte is discharged through the porous anode face **53** thence through the conduit **68** to a separator and collector, not shown. The collected oxygen gas may be used as an oxidant in leaching or may be compressed for sale. Continuous removal of gas prevents polarization thus enabling electrolysis to proceed at minimum power consumption.

A test model constructed substantially as shown in the drawing was used for test work. In such model the cathode and anode were each 6 inches in diameter.

The cathode was formed from stainless steel wires, 0.075 to 0.125 mm in diameter × 2.5 mm length and were fixed in a flame sprayed ceramic matrix at an average spacing of 0.38 mm. Total cathode area, including the ceramic matrix, was 147 cm^2.

The anode was constructed as described in connection with FIGS. **6** and **7.** The anode face was formed from two layers of perforated titanium plate with 1.5 mm perforations. The plates were slightly spaced apart (1 mm) and the perforations were offset to create a tortuous path through the face. Twelve feed conduits **59** were provided in the anode face.

During tests, a purified electrolyte solution ranging from 10–35 g/l Cu and from 10–150 g/l H_2SO_4 was supplied to the cell.

In a typical run, 2.82 volts was applied at 120 amperes total current (0.82 amp./cm^2). Temperature was maintained at 86°C. The solution contained 130 g/l H_2SO_4 and 15 g/l copper at $CuSO_4$. Fresh solution was supplied to maintain these conditions and the test was run for 37 minutes during which time 79.6 grams of copper, at average particle size of 4–100 micron diameter, was collected. The copper exhibited a bulk density of 3.74 g/cc. Total power consumed was 0.208 Kwh and, under the test conditions, the power consumption rate was 2.68 Kwh/Kg Cu. Current efficiency was 90.8 percent.

These figures are contrasted with typical reported batch operations in conventional electrowinning in which current efficiencies as low as 72 percent and power consumption of 2.96 Kwh/Kg copper were attained at current density of 11 amperes/ft.^{2}.

Under the foregoing conditions the new cell recovered copper at a rate of 1.81 lb. of copper per square foot/hour.

Whereas the invention has been described only with reference to permanent electrodes, it is not limited to such an arrangement. For instance, sacrificial anodes may be employed. Obviously the cell may be used in electro refining as well as electrowinning and it may be used to recover any metal susceptible to electrowinning.

Although the illustrated embodiment includes only a single anode and cathode, a single cell may employ a plurality of pairs of anodes and cathodes. The anode-cathode pairs may, in the same cell, be connected either in series or in parallel. The series connection is more attractive economically.

Although the cell may be formed in an open tank, the use of a completely closed cell enables operation at elevated temperatures without the release of free steam. This is advantageous because high temperature operation is desirable since it reduces electrolyte resistance and thus power consumption. Also, at a constant current density and electrolyte composition, a higher temperature will yield a metal product of higher bulk density and improved flow-ability.

If an open tank is used the inlet and outlet will be arranged to accommodate continuous feed and discharge while maintaining a constant volume of solution to keep the electrodes submerged to the desired degree.

Obviously the electrodes may vary in overall size; however, the dimensions and cross-sectional areas of the individual cathode conductors as well as the tip spacing should remain within the specified limits in order to achieve the desired results.

While the conductive cathode and anode surfaces are shown as being flat, it will be appreciated that embodiments utilizing other forms may be constructed. For instance, the conductive cathode surface may be cylindrical so long as it is smooth and presents a plurality of small conductors held in spaced-apart relationship by a matrix of non-conductive material. Similar comments apply to the anode.

As is the case in any electrical device, precaution must be taken to insure that the several elements are insulated as necessary to avoid shock hazard, shorting and the like. For instance, it will be necessary to insulate the scraper from the reciprocating shaft **74.**

From the foregoing, it is evident that the present invention prevents novel ways and means for the continuous recovery of metal in electrolysis without interruption of the process.

I claim:

1. Apparatus for electrowinning of metal from a metal bearing electrolyte solution comprising a tank having an inlet and outlet and adapted to contain a substantially constant volume of electrolyte in continuous flow therethrough, an anode and a cathode mounted in said tank with conductive surfaces in functional relationship to each other, and said conductive surface of said cathode comprising a smooth surface formed from the free ends of a plurality of relatively small electrical conductors each of cross-sectional area in the range from $0.0005mm^2$ to $0.018mm^2$ and a matrix of non-conductive material holding said small conductors spaced-apart a distance of at least 0.25mm.

2. Apparatus according to claim **1** in which said conductors are wires of diameter in the range from 0.025–0.15 mm.

3. Apparatus according to claim **1** in which said conductors are rectangular in cross section of dimension in the range 0.025–0.1 mm by 0.5–2.5 mm.

4. Apparatus for electrolytic recovery of metal from a metal bearing electrolyte solution comprising a tank having an inlet and an outlet for receiving and discharging electrolyte solution and arranged to maintain in said tank a quantity of solution having a predetermined upper level, at least one flat-faced anode and one flat-faced cathode in said tank said flat faces being respectively the conductive anode and the conductive cathode surfaces, said anode and cathode being arranged with their conductive surfaces in closely spaced face-to-face relationship and at an elevation such that at least a portion of both said conductive surfaces are below said predetermined upper level of solution, said conductive cathode surface comprising an exposed smooth surface formed from the free ends of a plurality of electrical conductors each of a cross-sectional area not exceeding $0.25mm^2$ encapsulated in a matrix of non-conductive material to be held spaced apart at said surface a distance of at least 0.25mm, means connecting said conductive anode and cathode surfaces to opposite poles of a source of direct current while said tank contains electrolyte solution thereby to effect deposition of small particles of metal on said free ends of said conductors on said conductive cathode surface, and means for dislodging said particles from said conductive cathode surface.

5. Apparatus according to claim **4** in which said means for dislodging metal from said conductive cathode surface comprises a scraper and means to effect relative movement between said cathode surface and said scraper.

6. Apparatus according to claim **5** in which said scraper is positioned between said conductive anode and cathode surfaces and product discharge conduit means are provided for withdrawing a mixture of solution and dislodged metal from adjacent said scraper.

7. Apparatus according to claim **6** with the addition of means for introducing a supplemental supply of electrolyte into the tank adjacent the inlet to said product discharge conduit means to provide at least part of the solution making up the mixture discharged from adjacent said scraper.

8. Apparatus according to claim **7** in which said conductive anode surface is porous, a plenum underlies said surface, and conduit means connect said plenum to a source of reduced pressure whereby to withdraw gaseous products through said anode surface.

9. Apparatus according to claim **4** in which said inlet includes means for introducing solution into the space between said conductive anode and cathode surfaces.

10. Apparatus according to claim **6** in which a slot with solid walls is formed in said conductive anode surface, said scraper is positioned in said slot and a reciprocatable means connected to said scraper is provided to effect back and forth movement thereof in said slot.

11. Apparatus according to claim **5** in which said means effecting relative movement between said cathode and said scraper comprises rotatably journalled shaft means connected to said cathode, and means outside said tank for rotatably driving said shaft and cathode.

12. Apparatus according to claim **6** in which said tank comprises a closed vessel and said inlet and outlet are arranged to maintain said tank substantially filled with solution.

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