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(54) Title: ELECTROWINNING CELL AND PROCESS

(57) Abstract: An electrochemical cell and method for electrowinning a variety of multivalent metals including titanium is described. In one aspect, the invention provides an electrochemical cell comprising an anolyte chamber comprising an anode and configured for containing an anolyte, a catholyte chamber comprising a cathode and configured for containing a catholyte comprising a metal to be electrolytically produced, and a diaphragm separating the anolyte chamber and the catholyte chamber, the diaphragm configured to control the potential drop across the diaphragm so that it is below the potential difference required for inducing bi-polarity at the diaphragm.



ELECTROWINNING CELL AND PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to and the benefit of U.S. Utility Patent Application No. 13/947,342 entitled “Electrowinning Cell and Process,” filed on July 22, 2013, the entire disclosure of which is incorporated by reference herein in its entirety.

FIELD

[0002] The present invention relates to electrochemical cells, and in particular to an electrochemical cell that may be used for electrowinning processes.

BACKGROUND

[0003] The electrowinning process typically occurs in an electrochemical cell. In processes where a metal is electrowon from electrolytes containing metal salts, the metal is deposited at the cathode while, depending on the electrolyte composition, chlorine or oxygen may evolve at the anode. The electrowinning process may be used to extract many different types of metals, including, but not limited to titanium (Ti).

[0004] A permeable membrane or diaphragm is placed between the anode and cathode within the electrochemical cell to separate the electrolyte in the anode compartment (anolyte) from that in the cathode compartment (catholyte). In electrowinning processes involving multivalent metals, the diaphragm serves to retard the migration of metallic ions (cations) with lower oxidation states from the cathode to the anode. Without the diaphragm, cations with lower oxidation states will migrate to the anode and get oxidized at the anode, thereby degrading cell efficiency. In the case of electrowinning from chloride-containing electrolytes, the diaphragm also serves the purpose of confining the anodically generated chlorine to the vicinity of the anode and preventing the chlorine gas from interfering with processes at the cathode.

[0005] Presently, titanium is extracted from its ore using the Kroll process where the ore (TiO_2) is first chlorinated to TiCl_4 , and the TiCl_4 is then reduced to titanium using electrolytically produced magnesium (Mg) as the reducing agent. The

Kroll process is energy intensive (requiring about 100 KWh per kg of titanium), which is partly due to the need for electrowinning the reducing agent (such as magnesium) and separating the product (Ti) from the by-product (MgCl_2). In an alternative route, titanium can be electrowon directly from a molten salt electrolyte containing TiCl_4 in NaCl or KCl/LiCl.

[0006] Circumventing the need for electrowinning magnesium and separating titanium from the byproduct can save about 60 KWh of energy per kg of Ti. In spite of this advantage, attempts to commercialize Ti electrowinning (including, for example, attempts by the U.S. Bureau of Mines in the 1950s, TIMET in the 1970s, and Dow-Howmet in the 1980s) have failed. Porous ceramic diaphragms, diaphragms coated with metals, cathodic and anodic biased diaphragms – all exhibited early failure due to the uncontrollable deposition of titanium within the diaphragm, which clogged the diaphragm and halted cell operation.

[0007] At present, titanium cannot be electrowon due to plugging of the diaphragm used in the cell to separate the anolyte and catholyte. Titanium deposition within the diaphragm occurs due to the development of bipolarity at the diaphragm. Bipolarity causes electrochemical reactions at the diaphragm, including Ti deposition on the anolyte side of the diaphragm and oxidation of dissolved Ti ions on the catholyte side of the diaphragm. Bipolarity leads to cell efficiency loss and early diaphragm and cell failure.

SUMMARY

[0008] The present invention provides an electrochemical cell and method for electrowinning a variety of multivalent metals including titanium. In one aspect, the invention provides an electrochemical cell comprising an anolyte chamber comprising an anode and configured for containing an anolyte, a catholyte chamber comprising a cathode and configured for containing a catholyte comprising a metal to be electrolytically produced, and a diaphragm separating the anolyte chamber and the catholyte chamber, the diaphragm configured to control the potential drop across the diaphragm so that it is below the potential difference for bipolar reactions at the diaphragm.

[0009] In one embodiment, the diaphragm has a thickness lower than a thickness that allows the onset of bipolar reactions. In another embodiment, the diaphragm has a thickness l , such that the following inequality is satisfied: $il/\kappa < \Delta E$,

where i is the current density, κ is the effective electrolyte conductivity of an electrolyte in the cell, and ΔE is the reduction potential of the bipolar reactions at the diaphragm.

[0010] In one embodiment, the diaphragm may have a thickness of about 0.8 cm or less. In a different embodiment, the diaphragm may have a thickness of about 0.3 cm or less.

[0011] In one embodiment, the diaphragm comprises a plurality of diaphragms. The diaphragms may have the same thicknesses, differing thicknesses or a combination thereof. There may be a space between successive diaphragms of the plurality of diaphragms.

[0012] In one embodiment, each of the diaphragms in the plurality of diaphragms has a thickness lower than a thickness that allows the onset of bipolar reactions. In another embodiment, each of the diaphragms have a thickness l and satisfy the following inequality: $il/\kappa < \Delta E$, where i is the current density, κ is the effective electrolyte conductivity of an electrolyte in the cell, and ΔE is the reduction potential of the bipolar reaction at the diaphragm. In one embodiment, each diaphragm in the plurality of diaphragms has a thickness of about 0.8 cm or less. In one embodiment, the diaphragms each have a thickness l of about 0.3 cm or less. In one embodiment, the electrochemical cell may comprise 3 or 4 diaphragms each having a thickness of about 0.8 cm. In one embodiment, the electrochemical cell may comprise 3 or 4 diaphragms each having a thickness of about 0.3 cm.

[0013] In one embodiment, the diaphragm has a porosity that is larger than a porosity that allows for the onset of bipolar reactions for the given diaphragm thickness, electrolyte conductivity, and current density. In one embodiment, each diaphragm has the same porosity. In another embodiment, each diaphragm has a different porosity.

[0014] In one embodiment, the metal to be electrolytically produced is titanium.

[0015] In another aspect, the invention provides an electrowinning process for deposition of a metal from a solution comprising: providing an electrochemical cell comprising an anolyte chamber comprising an anode and an anolyte solution dispersed in the anolyte chamber, a catholyte chamber comprising a cathode and an cathode solution dispersed in the cathode chamber, the catholyte solution comprising a fluid

containing at least one metal dissolved therein, and a diaphragm separating the anolyte chamber and the catholyte chamber. The process further comprises establishing a predetermined voltage and current across the electrolytic cell sufficient to effect reduction and deposition of the at least one metal at the cathode and cause an oxidation reaction at the anode, wherein the diaphragm is configured to control the potential drop across the diaphragm so that it is below the onset potential for bipolarity.

[0016] In one embodiment, the diaphragm has a thickness lower than a thickness that allows bipolar reactions. In another embodiment, the diaphragm l satisfies the following inequality: $il/\kappa < \Delta E$, where i is the current density, κ is the effective electrolyte conductivity of an electrolyte in the cell, and ΔE is the reduction potential of the bipolar reaction for the at least one metal.

[0017] In another embodiment, the diaphragm comprises a plurality of diaphragms. The diaphragms may have the same thicknesses, differing thicknesses or a combination thereof. In one embodiment, there is a space separating successive diaphragms in the plurality of diaphragms. In one embodiment, the diaphragms each have a thickness l of less than 0.8 cm. In one embodiment, the diaphragms each have a thickness l of about 0.3 cm or less.

[0018] In one embodiment, the metal being deposited comprises titanium, chromium, iron, uranium, a trans-uranium metal, or a combination of two or more thereof.

[0019] In one embodiment, a constant or time-varying current or potential is applied to the diaphragm. In one embodiment, the catholyte and anolyte comprise aqueous or non-aqueous solutions. In another embodiment, the diaphragm is electrically conductive, and the method comprises applying a current or potential across the diaphragm to dissolve any metal deposits that form at the diaphragm. The current or potential applied across the diaphragm is chosen from a constant or a periodic current or potential. In one embodiment, the fluid is titanium tetrachloride in NaCl, LiCl-KCl, LiCl-KCl-NaCl, or LiCl-KCl-CaCl₂.

[0020] These and other aspects and embodiments of the present invention can be further understood with respect to the drawings and following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIGURE 1 is a schematic illustration of an electrochemical cell in accordance with an embodiment of the present invention; and

[0022] FIGURE 2 is a schematic illustration of an electrochemical cell in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION

[0023] The present invention provides an electrochemical cell suited for electrowinning of metals such as, for example, titanium. For the purposes of this application, the apparatus and process may be discussed with reference to titanium, but it will be appreciated that the electrochemical cell and process can also be used for the electrowinning of other metals, including, but not limited to, chromium, cobalt, niobium, iron, manganese, and others.

[0024] Figure 1 shows an electrochemical cell 100 suited to electrowin metal from a fused salt bath, e.g. titanium in a fused salt bath of compounds of titanium. The electrochemical cell 100 includes a body 102 adapted to hold the electrolytes including a fused salt bath comprising the metal ion or metal compound to be electrowon (e.g. titanium from titanium tetrachloride) without substantial adverse effects to the material of which the body 102 is constructed. Although a number of different materials are suitable, the body 102 can be, formed of a metal, such as steel, nickel, hastelloy, or any other suitable material.

[0025] The body 102 is internally divided into at least an anolyte chamber 104 and a deposition catholyte chamber 106. An anode 108 is disposed in the anolyte chamber 104 and adapted to be at least partially immersed in the bath during operation of the electrochemical cell 100. The material of which the anode 108 is formed is resistant to the corrosive effects of the bath and also to the elemental chlorine formed at the positive charged anode 108 during operation of the cell. Suitable anode 108 materials are, for example, carbon and graphite. However, it is not necessary for the invention that the anode 108 remains impervious to the electrolyte or non-reacting during the process. The invention can also be applied to cells and processes in which the anode 108 reacts and is consumed during the process, for example a carbon anode 108 that can react with oxygen to form carbon dioxide. The process can be used to extract a variety of metals from a solution. In one embodiment,

the metals can be chosen from titanium, chromium, iron, uranium, a trans-uranium metal, or a combination of two or more thereof.

[0026] A cathode 110 is suitably disposed within the catholyte chamber 106 to be at least partially immersed in the bath during operation of the electrochemical cell 100. The deposition cathode 110 is formed from a material such as carbon or a metal such as, for example, plain carbon steel, hastelloy, etc. onto which a metal of interest (e.g., metallic titanium) can be deposited or plated and subsequently recovered.

[0027] The cathode chamber 106 can also include a means (not shown) suitable to heat, cool, or otherwise maintain the contents of the electrochemical cell 100 at a desired temperature, and/or a feed means adapted to provide a feed material comprising the metal of interest (e.g., titanium) to the bath during operation of the electrochemical cell 100.

[0028] The anolyte chamber 104 and the catholyte chamber 106 are spaced apart from each other by at least one diaphragm 112. A diaphragm support (not shown) can optionally be combined with the diaphragm 112 to complement the diaphragm strength during operation of the electrochemical cell 100.

[0029] The diaphragm 112 may be formed of a metal screen, sheet, or film with a multiplicity of holes or pores extending through the thickness of the diaphragm 112. The diaphragm 112 substrate can be, for example, iron such as steel or stainless steel, and a metal, such as cobalt, nickel or an alloy of two or more. In one embodiment, the diaphragm 112 substrate comprise, at least about 50 weight percent cobalt or nickel, which is resistant to the corrosive environment within the body 102 and retains sufficient strength at predetermined operating temperature to act as a diaphragm 112. The pores can be formed by, for example, drilling, punching, weaving, sintering, and the like. The pores in the diaphragm 112 can be the same or different sizes. In one embodiment, the pores are of a substantially uniform size. The diaphragm 112 may have a consistent membrane porosity and tortuosity, or these factors may vary across the thickness of the diaphragm 112.

[0030] The diaphragm 112 can comprise a ceramic non-conductive material on which sufficient metal has been deposited by electrolytic or electroless procedures. Examples of suitable metals for coating the ceramic diaphragm 112 include, but are not limited to, cobalt, nickel, etc.

[0031] In accordance with the present technology, the diaphragm 112 is configured to control the potential drop across the diaphragm 112 so that is below the onset potential for bipolarity. That is, the diaphragm 112 is configured to prevent oxidation and reduction reactions, involving the metal of interest, from occurring at the diaphragm 112. The inventors have found that bipolarity can be prevented by controlling the potential drop across the diaphragm 112 to a lower value than that of the standard potential for the bipolar reaction which can take place at the diaphragm 112. It has been found that the potential drop across the diaphragm can be limited below the onset potential by keeping the diaphragm sufficiently thin, keeping the diaphragm sufficiently porous, keeping the current density across the diaphragm sufficiently low, or a combination of two or more thereof. In one embodiment, the electrochemical cell comprises one or more diaphragms, each having a thickness and porosity such that the ohmic potential drop ($\Delta\phi$) across the diaphragm is less than the difference in the reduction potentials (ΔE) for the bipolar reactions at the diaphragm. As used herein, the term “bipolar reaction” refers to the reduction/oxidation reaction at the diaphragm surface and within its pores that would result in the formation and deposition of solid species, e.g., metal at or within the diaphragm.

[0032] In one aspect, the diaphragm 112 has a thickness such that the following inequality is satisfied:

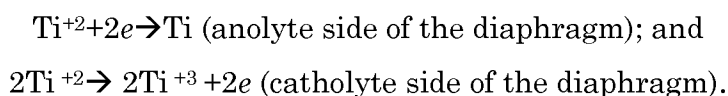
$$il/\kappa < \Delta E$$

where i is the current density, l is the thickness of the diaphragm 112, κ is the effective electrolyte conductivity within the diaphragm 112, and ΔE is the difference between the oxidation potential and the reduction potential the bipolar reactions at the diaphragm 112. The value il/κ is equal to the ohmic potential drop ($\Delta\phi$) across the diaphragm 112. It should be recognized that κ is the effective electrolyte conductivity within the diaphragm 112, and as such it is affected not only by the make-up of the electrolyte, but also by the porosity of the diaphragm 112 and the tortuosity of the pores. Higher porosity is achieved by providing more open space within the diaphragm 112, and lower tortuosity corresponds to having more straight and less convoluted pores; higher porosity and lower tortuosity correspond to a higher κ or lower diaphragm resistance, and hence to lower potential drop across the diaphragm 112. One method of measuring the diaphragm effective conductivity, κ , taking into account

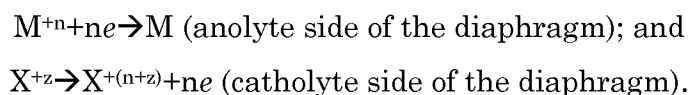
the effects of the porosity and tortuosity, is to (1) apply a certain measured current, I , across a diaphragm having an area, A , that is immersed into or soaked with an electrolyte, and (2) measure the voltage drop, V , across this diaphragm using a voltmeter. The diaphragm effective conductivity is $\kappa = I \cdot l / (A \cdot V)$, where l is the thickness of the diaphragm. This technique eliminates the need to determine independently the values of diaphragm porosity and tortuosity which can be difficult to directly measure. This experimentally determined effective conductivity κ incorporates already the effects of the porosity and tortuosity.

[0033] It should be further noted that the value of the ohmic drop across the diaphragm 112 can be controlled to be smaller than ΔE as indicated by the inequality above, by having a thin diaphragm 112, i.e., making the thickness, l , small, or having highly conductive electrolyte with highly porous diaphragm with minimal tortuosity leading to high effective conductivity κ , or by maintaining the average current density, i , at the diaphragm at a small value such that the inequality above is maintained.

[0034] Using titanium as an example, the bipolar reactions at the diaphragm 112 may be:



[0035] More generally, the bipolar reactions at the diaphragm may be:



In the latter equation, species X can be the metal M or any other oxidizable species. z is the initial oxidation number of species X

[0036] When bipolarity develops at the diaphragm 112, the diaphragm 112 can become plugged by deposits of the metal of interest, leading to efficiency loss and early failure. In accordance with the present technology, by keeping the voltage drop across the diaphragm 112 low, by, e.g. keeping the thickness of the diaphragm l at an appropriate low value, deposition of the metal at or within the diaphragm 112 can be prevented.

[0037] While one diaphragm 112 may be suitable for use, the diaphragm can be provided as a plurality of diaphragms 112 in a single electrochemical cell. In one

embodiment, the diaphragm 112 comprises a plurality of diaphragms 112. The diaphragms 112 are disposed adjacent to one another. In arranging and configuring the diaphragms 112, the diaphragms 112 must be oriented such there is a space or gap disposed between successive diaphragms 112 such that the individual diaphragms 112 in the stack do not touch one another. However, such gap may be filled or partially filled by an insulating porous non-conductive spacer. Figure 2 illustrates an embodiment of an electrochemical cell 100' comprising a plurality of diaphragms. The cell 100' is similar to the cell 100 of Figure 1 except that cell 100' comprises a plurality of diaphragms 112a, 112b, and 112c. The diaphragms 112 are arranged such that there is a space (e.g., 114, 116) disposed between successive diaphragms 112. The space (e.g., 114, 116) is maintained to avoid the individual diaphragms 112a, 112b and 112c from touching each other, which can compromise their electrical isolation from one another. The space (e.g., 114, 116) may comprise of an open space to be filled by an electrolyte, by a perforated insulating spacer, or a porous insulator.

[0038] In a cell comprising multiple thin diaphragms 112, the diaphragms are generally provided such that each diaphragm has a thickness whereby $il/\kappa < \Delta E$. In embodiments comprising a plurality of diaphragms, the thickness of each diaphragm 112 can be the same, or the diaphragms can have different thicknesses, providing however, that the inequality above is maintained for each individual diaphragm in the stack. The number of diaphragms 112, the thickness of each diaphragm l , and the space (e.g., 114, 116) between successive diaphragms can be individually chosen to provide a desired separation effect between the catholyte and the anolyte. The number of diaphragms is chosen to provide sufficient diffusion resistance to the migrating titanium ions so that they do not reach the anode 108 in excessive amounts.

[0039] The thickness of the diaphragms l may also depend on the metal of interest to be deposited from the solution. In one embodiment, the diaphragm 112 has a thickness of about 0.8 cm or less; about 0.6 cm; or less; about 0.4 cm or less; about 0.3 cm or less; even about 0.1 cm. In one embodiment, the diaphragm 112 has a thickness of from about 0.1 cm to about 0.8 cm; from about 0.2 cm to about 0.6 cm; even about 0.3 cm to about 0.4 cm. In still another embodiment, the diaphragm 112 has a thickness of from about 0.1 cm to about 0.3 cm. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-

disclosed ranges. As previously described, when a plurality of diaphragms 112 are employed, the thickness of the diaphragms 112 can be the same or different, and the space or distance between successive diaphragms 112 can be the same or different.

[0040] Further, an electrolyte flow may be maintained through the diaphragm 112 or the stack thereof, such that the flow further reduces the undesirable transport of species across the diaphragm 112 or diaphragm stack. The electrolyte on the two sides of the diaphragm or plurality of diaphragms can be maintained at the same or different levels.

[0041] Further, the diaphragms 112 can be electrically conductive and connected to a power source (not shown). The power source can be adjustable to provide a constant or periodic current or potential waveform to dissolve or remove any undesired bipolar reaction from accumulating on or within the diaphragms 112.

[0042] The source of the metal to be electrolytically produced and deposited at the cathode 110 can be chosen as desired. For example, titanium can be electrowon from materials such as titanium tetrachloride, titanium tetrabromide, titanium trifluoride, titanium carbide, titanium dioxide etc.

[0043] The salt may be chosen as desired for the metal of interest to be extracted. Such salts or mixtures thereof can be, for example, NaCl, LiCl-KCl, LiCl-KCl-NaCl, and LiCl-KCl-CaCl₂. When titanium is recovered from titanium tetrachloride, the fused salt bath desirably contains a mixture of alkali or alkaline earth metal halides, preferably lithium and potassium chlorides. A eutectic mixture of the salts employed in the bath is advantageous because of the low melting temperature of such mixture. Alternatively, when electrowinning at room temperature is desired, metal salts dissolved in aqueous medium may be employed as the electrolyte.

[0044] The electrowinning process is performed by applying a current across the electrodes to effectuate deposition of the metal of interest (e.g., titanium) at the cathode 110. In one embodiment, the method comprises (a) providing an electrochemical cell 100 comprising an anolyte chamber 104 comprising an anode 108; a catholyte chamber 106 comprising a cathode 110; and a diaphragm stack separating the anolyte chamber 104 and the catholyte chamber 106; (b) the catholyte solution comprising a fluid containing at least one metal dissolved therein; and (d) establishing a predetermined voltage or current across the electrolytic cell sufficient to

effect reduction and deposition of the at least one metal at the cathode 110 and cause an oxidation reaction at the anode 108, wherein the diaphragm 112 is configured to prevent bipolar reactions at the diaphragm 112.

[0045] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

CLAIMS

What is claimed is:

1. An electrochemical cell comprising:
an anolyte chamber comprising an anode and configured for containing an anolyte;
a catholyte chamber comprising a cathode and configured for containing a catholyte comprising a metal to be electrolytically produced; and
a diaphragm separating the anolyte chamber and the catholyte chamber, the diaphragm configured to control the potential drop across the diaphragm so that it is below the potential difference for the onset of bipolarity at the diaphragm.
2. The electrochemical cell of claim 1, wherein the diaphragm has a thickness lower than a thickness that allows bipolar reactions.
3. The electrochemical cell of claim 2, wherein the diaphragm comprises a plurality of diaphragms.
4. The electrochemical cell of claim 3, comprising a space between successive diaphragms of the plurality of diaphragms.
5. The electrochemical cell of claim 3, wherein the space between successive diaphragms comprises an open space to be filled by electrolyte or comprises a porous insulating spacer disposed in the space.
6. The electrochemical cell of claim 3, wherein each diaphragm has a different thickness.
7. The electrochemical cell of claim 2, wherein the metal to be electrolytically produced is titanium.
8. The electrochemical cell of claim 2, wherein the diaphragm has a thickness of about 0.8 cm or less.

9. The electrochemical cell of claim 2, wherein the diaphragm comprises a plurality of diaphragms, and each diaphragm in the plurality of diaphragms has a thickness of about 0.8 cm or less.

10. The electrochemical cell of claim 9, comprising a space disposed between successive diaphragms.

11. The electrochemical cell of claim 1, wherein the diaphragm has a porosity that is larger than a porosity that allows for the onset of bipolar reactions for a given thickness, electrolyte conductivity, and current density.

12. The electrochemical cell of claim 11, wherein the diaphragm comprises a plurality of diaphragms, and each diaphragm has a porosity that is larger than a porosity that allows for the onset of bipolar reactions for a given thickness, electrolyte conductivity, and current density.

13. The electrochemical cell of claim 12, wherein each diaphragm has a different porosity.

14. An electrowinning process for deposition of a metal from a solution comprising:

(a) providing an electrochemical cell comprising:

an anolyte chamber comprising an anode and an anolyte solution dispersed in the anolyte chamber;

a catholyte chamber comprising a cathode and an cathode solution dispersed in the cathode chamber, the catholyte solution comprising a fluid containing at least one metal dissolved therein;

and

a diaphragm separating the anolyte chamber and the catholyte chamber; and

(b) establishing a predetermined voltage and current across the electrolytic cell sufficient to effect reduction and deposition of the at least

one metal at the cathode and cause an oxidation reaction at the anode, wherein the diaphragm is configured to control the potential drop across the diaphragm so that it is below the onset potential for bipolarity.

15. The electrowinning process of claim 14, wherein the diaphragm has a thickness lower than a thickness that allows for the onset of bipolar reactions.

16. The electrowinning process of claim 14, wherein the diaphragm comprises a plurality of diaphragms.

17. The electrowinning process of claim 16, comprising a space separating successive diaphragms in the plurality of diaphragms.

18. The electrowinning process of claim 16, wherein the diaphragms each have a thickness lower than a thickness that allows for the onset of bipolar reactions.

19. The electrowinning process of claim 14, wherein a constant or time-varying current or potential is applied to the diaphragm.

20. The electrowinning process of claim 14, comprising depositing titanium, chromium, iron, uranium, a trans-uranium metal, or a combination of two or more thereof at the cathode.

21. The electrowinning process of claim 14, wherein the catholyte and anolyte comprise aqueous or non-aqueous solutions.

22. The electrowinning process of claim 14, wherein the diaphragm has a porosity that is larger than a porosity that allows for the onset of bipolar reactions for a given thickness, electrolyte conductivity, and current density.

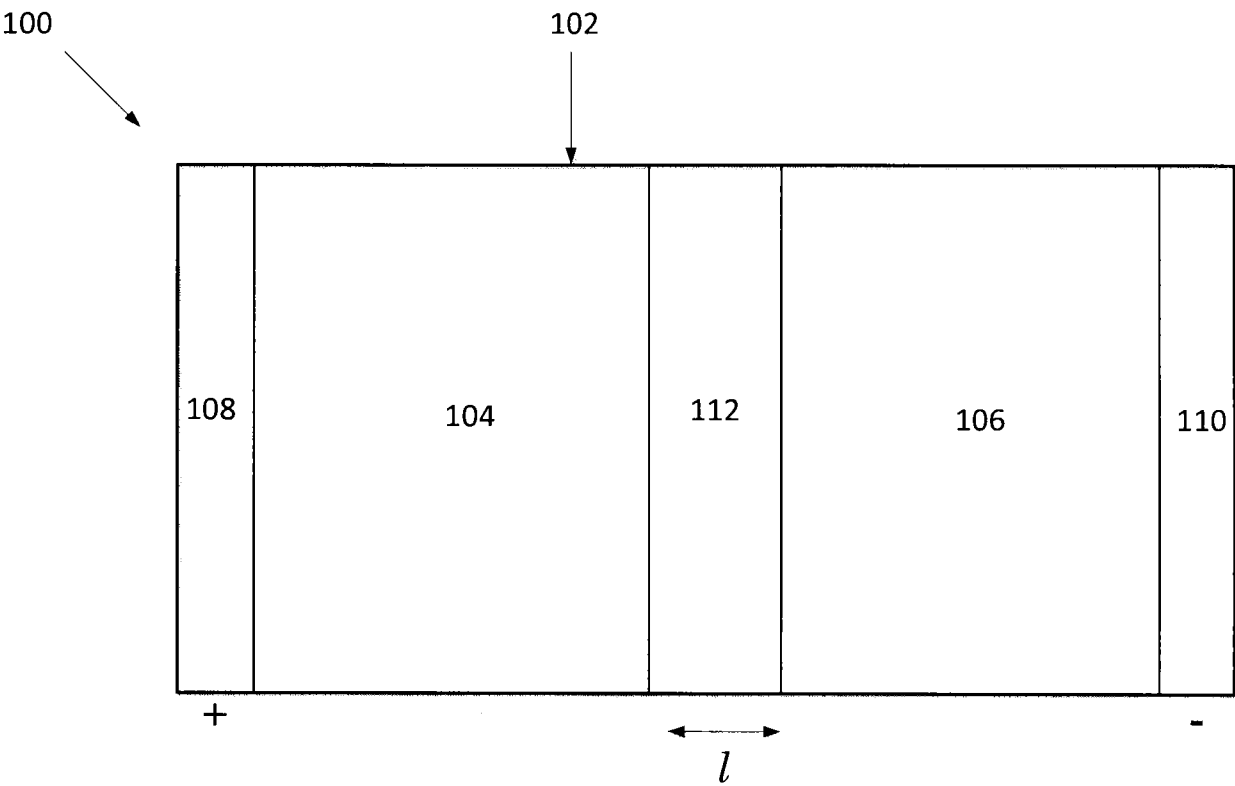


FIGURE 1

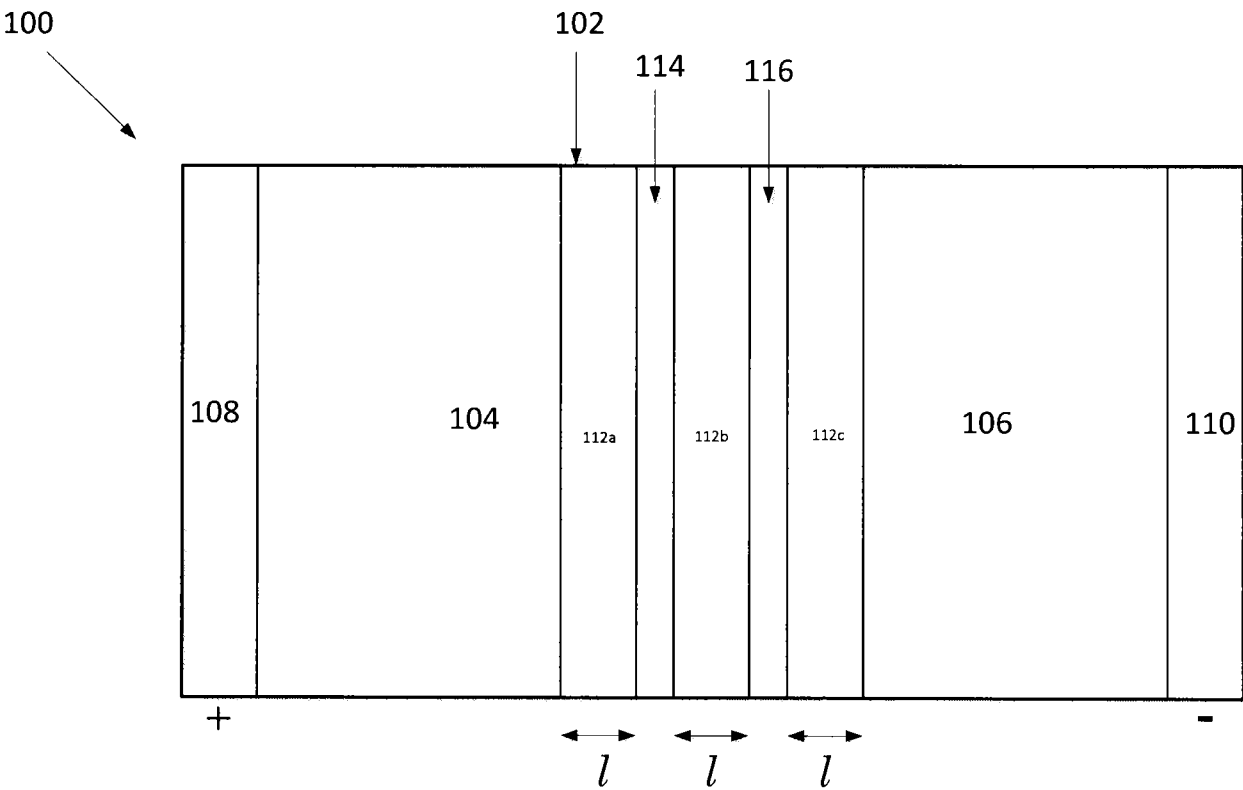


FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/047598

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25C7/04

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 116 801 A (JUCKNIESS PAUL R ET AL) 26 September 1978 (1978-09-26)	1-7, 11-22
Y	the whole document	8-10
X	US 4 118 291 A (JUCKNIESS PAUL R ET AL) 3 October 1978 (1978-10-03)	1-7, 11-22
Y	the whole document	8-10
X	US 3 764 493 A (NICKS L ET AL) 9 October 1973 (1973-10-09)	1,2,7,8, 11,14, 15,19, 21,22
Y	the whole document	8-10
X	US 3 098 802 A (BERNARD BEER HENRI) 23 July 1963 (1963-07-23)	1,7,8
Y	the whole document	8-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

1 October 2014

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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