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 (72) Inventeurs/Inventors:
 WITHERS, JAMES C., US;
 LOUTFY, RAOUF O., US
 (73) Propriétaire/Owner:
 MATERIALS & ELECTROCHEMICAL RESEARCH
 CORP., US
 (74) Agent: OSLER, HOSKIN & HARCOURT LLP

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 (54) Title: THERMAL AND ELECTROCHEMICAL PROCESS FOR METAL PRODUCTION

(57) Abrégé/Abstract:

A system for purification of high value metals comprises an electrolytic cell in which an anode formed of a composite of a metal oxide of the metal of interest with carbon is electrochemically reduced in a molten salt electrolyte.



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- (71) Applicant (for all designated States except US): **MATERIALS & ELECTROCHEMICAL RESEARCH CORP.** [US/US]; 7960 South Kolb Road, Tucson, AZ 85706 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **WITHERS, James, C.** [US/US]; Materials & Electrochemical Research Corp., 7960 South Kolb Road, Tucson, AZ 85706 (US). **LOUTFY, Raouf, O.** [US/US]; Materials & Electrochemical Research Corp., 7960 South Kolb Road, Tucson, AZ 85706 (US).
- (74) Agents: **SOLOWAY, Norman, P.** et al.; Hayes Soloway P.C., 130 W. Cushing Street, Tucson, AZ 85701 (US).
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(54) Title: THERMAL AND ELECTROCHEMICAL PROCESS FOR METAL PRODUCTION

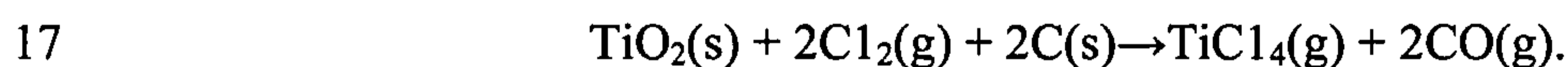
(57) Abstract: A system for purification of high value metals comprises an electrolytic cell in which an anode formed of a composite of a metal oxide of the metal of interest with carbon is electrochemically reduced in a molten salt electrolyte.

1 **THERMAL AND ELECTROCHEMICAL PROCESS**
2 **FOR METAL PRODUCTION**

3

4 The present invention relates to the production of metals. The invention has
5 particular utility in connection with the production of titanium and will be described
6 in connection with such utility, although other utilities are contemplated, e.g.,
7 production of other high value multi-valence and high (2 or more) valance metals, in
8 particular refractory metals such as chromium, hafnium, molybdenum, niobium,
9 tantalum, tungsten, vanadium and zirconium which are given as exemplary.

10 The properties of titanium have long been recognized as a light, strong, and
11 corrosion resistant metal, which has lead to many different approaches over the past
12 few decades to extract titanium from its ore. These methods were summarized by
13 Henrie [1]. Despite the many methods investigated to produce titanium, the only
14 methods currently utilized commercially are the Kroll and Hunter processes [2, 3].
15 These processes utilize titanium tetrachloride (TiCl₄) which is produced from the
16 carbo-chlorination of a refined titanium dioxide (TiO₂) according to the reaction:



18 In the Kroll process [2] TiCl₄ is reduced with molten magnesium at $\approx 800^\circ\text{C}$ in an
19 atmosphere of argon. This produces metallic titanium as a spongy mass according to
20 the reaction:



22 from which the excess Mg and MgCl₂ is removed by volatilization, under vacuum at
23 $\approx 1000^\circ\text{C}$. The MgCl₂ is then separated and recycled electrolytically to produce Mg
24 as the reductant to further reduce the TiCl₄. In the Hunter process [3,4] sodium is
25 used as a reductant according to the reaction:



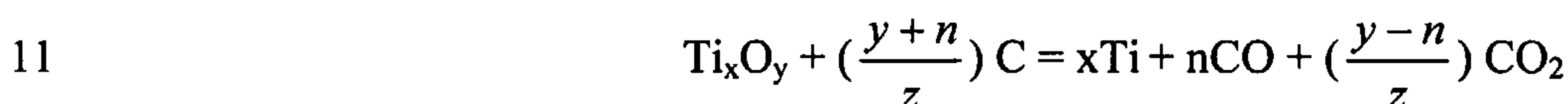
27 The titanium produced by either the Kroll or Hunter processes must not only be
28 separated from the reductant halide by vacuum distillation and/or leaching in acidified
29 solution to free the titanium sponge for further processing to useful titanium forms,
30 but also require the recycling of the reductant by electrolysis. Because of these
31 multiple steps the resultant titanium is quite expensive which limits its use to cost
32 insensitive applications.

1 The US Bureau of Mines performed extensive additional investigations [1,5-8]
2 to improve the Kroll and Hunter processes. Many other processes have been
3 investigated that include plasma techniques [9-13], molten chloride salt electrolytic
4 processes [14], molten fluoride methods [15], the Goldschmidt approach [16], and
5 alkali metal-calcium techniques [17]. Other processes investigated have included
6 aluminum, magnesium, carbothermic and carbo-nitrothermic reduction of TiO_2 and
7 plasma reduction of TiCl_4 [18] without measurable success. Direct reduction of TiO_2
8 or TiCl_4 using mechanochemical processing of ball milling with appropriate
9 reductants of Mg or calcium hydride (CaH_2) also have been investigated [19] without
10 measurable success. Kroll, who is considered as the father of the titanium industry
11 [20] predicted that titanium will be made competitively by fusion electrolysis but to
12 date, this has not been realized.

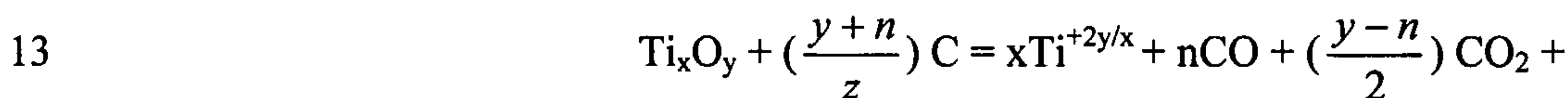
13 An electrolytic process has been reported [21] that utilizes TiO_2 as a cathode
14 and carbon or graphite as the anode in a calcium chloride electrolyte operated at
15 900°C . By this process, calcium is deposited on the TiO_2 cathode, which reduces the
16 TiO_2 to titanium and calcium oxide. However, this process is limited by diffusion of
17 calcium into the TiO_2 cathode and the build-up of calcium oxide in the cell, which
18 limits operating time to remove the calcium oxide or replacement of the electrolyte.
19 Also the TiO_2 cathode is not fully reduced which leaves contamination of TiO_2 or
20 reduced oxides such as TiO , mixed oxides such as calcium titanate as well as
21 titanium carbide being formed on the surface of the cathode thus also contaminating
22 the titanium. Thus, current TiO_2 cathode electrolytic processes are no more
23 commercially viable than the electrolytic processes before it.

24 The instant invention is a combination of a thermal and an electrochemical
25 process, which utilizes a carbon or composite anode containing a metal oxide of a
26 metal of interest, as a feed electrode. As used herein the term "carbon" is meant to
27 include carbon in any of its several crystalline forms including, for example, graphite.
28 For example, for producing purified titanium, the feed should comprise TiO_2 which
29 may be high purity, rutile, synthetic rutile, ilmenite or other source of titanium,
30 mixed with a source of carbon and pressed together with or without a binder that also
31 may be a source of carbon on pyrolysis to form a TiO_2 -C composite green electrode
32 or billet. The TiO_2 -C composite billet is then heated, in the absence of air to avoid
33 oxidation of the carbon component, to a temperature sufficient to reduce the plus four

1 valence of the titanium in the TiO_2 to a lower valence. The temperature of heating
 2 and time at temperature will determine the reduced oxide stoichiometry of the
 3 titanium oxide which may be expressed as Ti_xO_y where the ratio of y/x can be 0 to
 4 equal or less than 2 and y balances the valence charge of the titanium species. Some
 5 examples of reduced titanium oxide compounds include TiO , Ti_2O_3 , Ti_3O_5 , and Ti_4O_7
 6 and mixtures thereof. Sufficient residual carbon needs to remain after the thermal
 7 reduction step or can be added separately to stoichiometrically react with the reduced
 8 titanium oxide to electrochemically produce titanium at the cathode and CO_2 and/or
 9 CO at the anode. The reduced titanium state oxide composite anode overall general
 10 reactions are:



12 at the anode:



14 zye^-

15 where $2y/x$ is the oxide state of the titanium in the electrolyte,

16 at the cathode:



18 Further features and advantages of the present invention will be seen by the
 19 following detailed description, taken in conjunction with the accompanying drawings
 20 wherein:

21 Fig. 1 is a diagrammatic illustration schematically illustrating an
 22 electrochemical reaction according to the present invention;

23 Fig. 2a is a diagrammatic illustration of electrochemical process of the present
 24 invention;

25 Fig. 2b is a diagrammatic illustration of an electrochemical cell and process in
 26 accordance with the present invention;

27 Fig. 3 is a view similar to Fig. 2b providing further details of an
 28 electrochemical cell in accordance with the present invention;

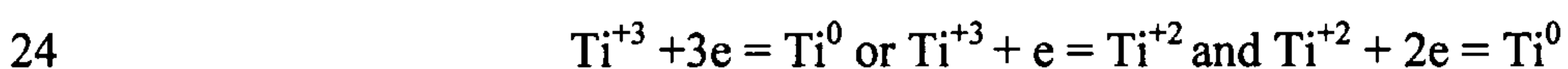
29 Fig. 4 is a perspective view showing details of an electrode in accordance with
 30 the present invention;

1 Fig. 5 is a graph illustrating surface resistivity of a titanium oxide carbon
2 anode over time.

3 The present invention employs a novel electrochemical system for producing
4 titanium and other metals by a combination of thermal and electrochemical processes
5 from a novel metal oxide-carbon composite anode. More particularly, the present
6 invention produces purified titanium or other metal powders by a
7 thermal/electroreduction composite anode process using a metal oxide-carbon anode in
8 a molten salt electrolyte.

9 Heretofore the electrolysis of titanium oxide (TiO_2) has not been successful
10 because TiO_2 has little to no solubility in molten salt electrolytes which is also true of
11 other titanium compounds. Titanium tetrachloride (TiCl_4) is a covalent compound
12 that has limited solubility in fused salts and does not readily form complexes with
13 other inorganic salts. It also is highly volatile and is quickly lost from most fused
14 salts. However, since titanium is multivalent, it has been shown that TiCl_4 could be
15 reduced to lower valent ionic species of Ti^{+3} and Ti^{+2} , which do show some solubility
16 in some molten salts. However, because of secondary reversibility reactions, which
17 lead to loss in current efficiency and poor quality of metal, heretofore no practical
18 process has evolved for electrowinning titanium from a TiCl_4 feed. Investigations of
19 separating the anolyte and catholyte to avoid alternating oxidation and reduction with
20 low current efficiency have not proven successful on a commercial scale.

21 Since titanium +3 (corresponding to y/x of 1.5) and titanium +2
22 (corresponding to y/x of 1.0) are ionic species, it should be possible to deposit
23 titanium at the cathode, i.e. according to the reactions:



25 from a molten salt electrolyte. However, such reactions have not been demonstrated
26 commercially since heretofore there has not been demonstrated an acceptable process
27 to continuously supply $\text{Ti}^{+2y/x}$ or lower valence ions where y/x is less than 2 to a
28 molten salt electrolyte. The present invention in one aspect provides a metal
29 oxide/carbon composite anode containing Ti_xO_y in which a high valence metal such as
30 Ti^{+4} , is thermally reduced to a valence less than +4, and is used to provide a
31 continuous supply of reduced titanium ions to a molten salt electrolyte. The oxygen
32 combines with the carbon in the anode to produce CO_2 and/or CO gas. Any excess
33 carbon in the anode floats to the top of the molten salt electrolyte where it periodically

1 can be skinned if necessary and does not interfere with the continuous electrolysis
2 process.

3 It is well established that thermal reduction is much more economical than
4 electrochemical reduction. Therefore reducing TiO_2 thermally is more economical
5 than electrolytically reducing in a composite anode of TiO_2 -carbon. If TiO_2 is heated
6 with carbon, carbo-thermic reduction will proceed based on the thermodynamic
7 prediction and kinetics of the reactants. For example it has been found when the
8 proper proportions of TiO_2 and carbon are heated to various temperatures, reduced
9 oxides are produced. An example reaction is $2\text{TiO}_2 + \text{C} = \text{Ti}_2\text{O}_3 + \text{CO}$. The Ti_2O_3 in
10 which the titanium is in a +3 valence state can be produced over the temperature
11 range of 1250-1700⁰C. Since the product is a solid Ti_2O_3 and gaseous CO if the
12 pressure is reduced the kinetics of the reactions is enhanced.

13 It is also possible to produce the suboxide TiO according to the reactions TiO_2
14 $+ \text{C} = \text{TiO} + \text{CO}$ or $\text{Ti}_2\text{O}_3 + \text{C} = 2\text{TiO} + \text{CO}$. Either reaction will be enhanced at reduced
15 pressure.

16 Titanium in TiO is in the +2 valence state. A competing reaction is $\text{TiO}_2 + 3\text{C} = \text{TiC}$
17 $+ 2\text{CO}$ or $\text{Ti}_2\text{O}_3 + 5\text{C} = 2\text{TiC} + 3\text{CO}$. When the suboxide is used as a feed for the
18 composite anode, the lowest valence is the most desirable. Thus it is desirable to
19 prevent TiC forming in which the titanium is in a +4 state. It has been found that TiO
20 can be produced at a reaction temperature above 1700⁰C if the pressure is reduced to
21 0.01 atmosphere or lower. If the pressure is as high as 0.1 atmosphere a reaction
22 temperature above 1800⁰C is required to produce TiO free of TiC. At atmospheric
23 pressure a reaction temperature above 2000⁰C is required to produce TiO free of TiC.

24 In addition to producing titanium from a composite anode consisting of a
25 reduced titanium oxide and a carbon source referred to as a composite anode it is also
26 possible to electrowin titanium from other titanium compounds that are not oxides.
27 These compounds include titanium nitride (TiN). Titanium nitride is a conductor and
28 does not require any conductive phase such as carbon with titanium suboxides. TiN
29 can be produced by reacting $\text{TiO}_2 + 2\text{C} + \text{N} = \text{TiN} + 2\text{CO}$. The TiN is pressed and
30 sintered in a nitrogen atmosphere to produce a solid of TiN. The TiN can then be
31 utilized as an anode in a fused salt to electrowin/deposit titanium at the cathode and
32 nitrogen gas will be evolved at the anode.

33 Another compound is titanium carbide (TiC). Titanium carbide is produced

1 by the reaction of $\text{TiO}_2 + 2\text{C} = \text{TiC} + 2\text{CO}$. The TiC is a conductor and when TiC
2 particles are pressed and sintered to a solid, the solid can serve as an anode. When
3 using TiC as the anode a separator or diaphragm should separate the cathode and
4 anode compartments. Titanium ions will be electrolytically dissolved from the anode
5 and reduced to titanium metal at the cathode. The released carbon will be in solid
6 form and must be accounted for in an overall materials balance. To account for the
7 carbon the anode can be depolarized with oxygen wherein the oxygen will react with
8 the carbon to form gaseous CO_2 and/or CO. Thus oxygen gas would be passed over
9 the anode to react with the carbon, but since titanium is so sensitive to oxygen the
10 cathode should be separated from the anode with a diaphragm to prevent the oxygen
11 from contacting the deposited titanium.

12 It is taught in WO09964638, US6,663,763B2, WO 02/066711 A1, WO
13 02/083993 A1 and WO03/002 785 A1, that TiO_2 can serve as a cathode in a calcium
14 chloride fused salt wherein the TiO_2 is reduced to titanium metal with oxygen given
15 off at the anode using an inert anode or CO_2/CO using a carbon/graphite anode. Those
16 teachings do not consider reduced or suboxides of titanium which require less
17 electrochemical energy to produce titanium metal than required to reduce TiO_2 . Thus
18 the reduced oxides of Ti_2O_3 or TiO can serve as cathodes and be electrochemically
19 reduced in molten calcium chloride or other molten salt electrolytes.

20 Heretofore, there has not been an electrochemical system to produce titanium
21 similar to electrowinning aluminum in which alumina (Al_2O_3) is soluble in molten
22 cryolite (NaAlF_4) which under electrolysis produces aluminum metal with CO_2/CO
23 being given off at a carbon anode, because there has not been identified a molten salt
24 composition that will dissolve TiO_2 . There is no known molten salt compound or
25 combination of compounds that will dissolve TiO_2 . However, there are molten salt
26 compositions that will dissolve the reduced the suboxide TiO which is an ionic
27 compound that is very electrically conductive. For example TiO is soluble in molten
28 calcium chloride mixed alkali and alkaline earth chlorides as well as fluorides or
29 mixed chlorides and fluorides. Thus TiO can be dissolved in CaCl_2 or other salt
30 mixture, and using a carbon/graphite anode electrolyzed to produce titanium at the
31 cathode and CO_2/CO at the anode or oxygen using an inert anode. Since titanium is
32 sensitive to oxygen a separator or diaphragm should be used between the anode and
33 cathode.

1 It is well know that the higher the temperature of a solvent the greater the
2 solubility of the solute. In this case the higher the molten salt temperature the greater
3 the solubility of a titanium suboxide such as TiO or Ti₂O₃. In the previous
4 discussions the operating salt temperatures are below that of the melting point of
5 titanium and thus titanium is deposited as a solid in a particulate morphology. As in
6 the case of electrowinning aluminum in which aluminum oxide is soluble in cryolite
7 at over 900°C, the aluminum is in a molten state and thus more easily separated from
8 the molten salt/cryolite. In order to achieve the same advantage with titanium, the
9 molten salt operating temperature should be above the melting point of titanium or
10 about 1670°C. Molten salts that have high melting temperatures that will not readily
11 vaporize at 1670°C or slightly above include calcium fluoride (CaF₂) 1360°C, and
12 barium fluoride BaF₂ 1280°C. It was found the titanium suboxides and particularly
13 TiO is quite soluble in CaF₂ at temperatures above 1670°C. Thus titanium is readily
14 electrowon from its suboxides dissolved in CaF₂ or other salts above 1670°C using a
15 carbon/graphite anode that produces CO and CO₂ on electrolysis or an oxygen stable
16 anode that produces oxygen on electrolysis. The titanium produced above 1670°C is
17 in a molten state and thus readily separatable from the molten salt whose density is
18 less than 3.0 g/cc at the operating temperature and titanium is approximately 4.0 g/cc
19 at the operating temperature thus causing the titanium to sink for easy separation.

20 Referring to Fig. 1, there is illustrated schematically the formation of a metal
21 oxide-carbon composite anode in accordance with the present invention. Titanium
22 oxide in a particle size of 0.001 - 1000 microns, preferably 0.01 - 500 microns, more
23 preferably 0.1 to 10 microns, is mixed with carbon flakes of average particle size
24 0.001 - 1000 microns, preferably 0.01 - 100 microns, more preferably 0.01 to 1
25 microns, in a weight ratio of TiO₂ to carbon of 7:1 to 4:1 using a ball mill mixer. The
26 TiO₂ powder and carbon flakes were mixed dry, or optionally with a binder, in a ball
27 mill mixer for 4-24 hours. The resulting TiO₂ powder/carbon flake mix was pressed
28 in a steel die to form a mechanically stable green electrode or billet. The billet was
29 then placed in an oven, and heated in the absence of air to 1000 to 2200°C, preferably
30 about 1100°C to 1800°C, for 0.1 to 100 hours, preferably about two hours, to form a
31 titanium suboxide/carbon composite electrode.

32 Referring to Figs. 2 and 2a, the titanium oxide/carbon composite electrode 20
33 made as above described is employed as an anode in an electrochemical cell 22 with a

1 conventional metallic, e.g., steel electrode 24, and an alkali metal molten salt
2 electrolyte 26.

3 The composition of the molten salt electrolyte 26 used in the cell 22 has an
4 effect on the titanium produced at the cathode. The electrolyte should comprise a
5 strong Lewis acid formulation such as NaAlCl_4 , which melts as low as 150°C ,
6 optionally containing fluoride additions such as an alkali fluoride and/or potassium
7 titanium fluoride with the reduced state Ti_xO_y -C anode. Other useful electrolyte
8 compositions include binary, tertiary, and quaternary alkali and alkaline earth
9 chlorides, fluorides and mixed chloride-fluorides with melting point temperatures in
10 the 300 - 900°C range. For producing titanium preferred electrolytes include NaCl -
11 CaCl_2 - KCl in a mole ratio of 50:50:20; NaCl - LiCl - KCl in a mole ratio of 20:60:40;
12 AlCl_3 - NaCl - NaF in a mole ratio of 70:30:20 LiCl - KCl eutectic with 20 wt% NaF ,
13 eutectic of LiF - KF , etc. Moreover, the polarizing strength of the cation will directly
14 affect the electroreduction of electrocrystallization to titanium. And, the small highly
15 ionic strength and steric effect of e.g., a lithium ion in the electrolyte enhances the
16 polarizing strength at the cathode and thus the electroreduction of titanium. Other
17 such highly ionic ions can aid in stabilizing the Ti^{+3} and/or Ti^{+2} ions in the molten salt
18 electrolyte as well as their electroreduction at the cathode.

19 To avoid disproportionation during the electrolysis between titanium in the
20 metallic state, that is electrowon titanium, and higher titanium ions such as Ti^{+3} , it is
21 preferable to have only Ti^{+2} ions in solution which as they are reduced to the metal are
22 replaced with other Ti^{+2} ions from the anode thus requiring TiO in the anode. Thus
23 desirably the fused salt initially contains Ti^{+2} ions which desirably is in the
24 concentration range of $\frac{1}{2}$ to 20%, more desirably in range of 1 to 10% and most
25 desirably in the range of 2 to 8%.

26 The anion also can have an influence on the steric and solvent effect of the
27 titanium species, which also influences the titanium deposit at the cathode. For
28 example, the Ti-F bond is stronger than the Ti-Cl bond, which brings about an
29 increase in the activity of the titanium ions in the molten salt electrolyte and
30 consequently the morphology of the titanium deposited at the cathode. The anion and
31 the titanium ion complex effects the number of crystallization centers available on the
32 cathode and thus the morphology of the titanium cathode deposit. The complex TiF_6^{-3}
33 and the TiF_6^{-2} anion is known and can be directly reduced to titanium. Mixed anions

1 are also known, such as $\text{TiF}_{6-N} \text{Cl}_N^{-3}$. A strong Lewis acid thus stabilizes and
2 increases the activity of the titanium ion. While not wishing to be bound by theory, it
3 is believed that the reactions proceed as follows:



5 and at the anode Ti^{+3} ions are released from the composite anode to produce the TiF_6^{-3} .
6 Thus titanium is directly reduced from the +3 valence to the metal. Because
7 titanium is multivalent it is also possible that Ti^{+3} is reduced to Ti^{+2} and then to the
8 metal Ti^0 . However, as stated above, if all titanium ions in solution are in the +2
9 valence then the reduction is $\text{Ti}^{+2} + 2e = \text{Ti}^0$.

10 Based on this analysis alkali fluorides may be regarded as stabilizing agents in
11 chloride molten salt electrolytes. Thus the ratio of F/Cl and/or Ti/F will have an
12 effect on the electroreduction of titanium. Indeed it has been demonstrated that all
13 chloride molten salt electrolytes produce small and/or dendritic deposits of titanium.
14 As fluorides are added to the molten salt electrolyte the morphology of the deposit
15 changes to larger and coherent particulate deposits. As the electrolyte changes to
16 primarily or all fluoride, the titanium deposits become flaky to a fully adherent film.
17 The major morphology change begins at a F/Cl ratio of approximately 0.1 and solid
18 films become possible at a ratio of approximately 1.0.

19 The morphology and size of the titanium deposit is also influenced by the
20 current density of the cathode. The higher the current density the smaller the particle
21 size. Typical cathode current densities are in the 0.05 to 5 amperes/cm² range. The
22 most desirable cathode current densities are in the 0.1 to 2.0 amperes/cm² range, and
23 the preferred cathode current densities are in the 0.25 to 1 amperes/cm² range,
24 depending on the morphology of the titanium desired at the cathode. It also has been
25 found that very high current densities can be used at the cathode under high mass flow
26 of the electrolyte and the use of the composite anode. By moving the electrolyte over
27 the cathode surface via gas bubbling or pumping at a fast rate it is possible to
28 electrolytically produce titanium particulate up to cathode current densities of 125
29 amps/cm².

30 It also has been found that pulsing the current affects the morphology, particle
31 size and cathodic efficiency. The current can be pulsed to on and off sequences in
32 various wave forms such as square, sinusoidal, etc. as well as periodically alternating
33 the polarity. It was found pulsing the current produced more coherent deposits and

1 larger particles as well as solid films on the cathode. It was also found periodically
2 reversing the polarity between two composite electrodes produced titanium within the
3 electrode. That is the Ti_xO_y in the electrode was reduced to titanium, which remained
4 as a solid agglomerate of titanium particles in the same form of the original composite
5 electrode.

6 A bench scale electrolytic cell for producing titanium in accordance with the
7 present invention is illustrated in Fig. 3. The cell 30 comprises a cylindrically shaped
8 steel walled vessel 32 having a funnel-shaped bottom closed by a valve 36. The
9 vessel walls 32 are wrapped in a resistance heater (not shown) which in turn is
10 covered by thermal insulation 40. A porous basket 42 formed of carbon fiber mesh is
11 suspended within container 30 and is connected via an anode connector 44 to the plus
12 side of the DC current source. Wall 32 of the steel vessel is connected via a
13 conductor 46 to the negative side of a DC current source. Basket 42 is loaded with
14 pellets or discs 48 of titanium suboxide - carbon flake anode material made as above
15 described. The cell is filled with a molten salt electrode (60:LiCl - 40KCl) the cell is
16 sealed with a top 50, swept with argon purge to remove air, and voltage of 3 applied
17 which resulted in precipitation of dendritic titanium sponge particles. The titanium
18 sponge particles were then removed via valve 36, separated from the electrolyte, and
19 found to have a purity of 99.9%.

20 It is possible to deposit other metals similarly. For example, by using a
21 composite anode which includes other metal oxides in addition to the Ti_xO_y , it is
22 possible to produce an alloy of titanium. For example, an alloy of Ti-Al-V can be
23 produced by mixing aluminum oxide, vanadium oxide and TiO_2 with carbon to form
24 the anode whereby to produce alloy particulate or solid films of Ti-Al-V. The E_0 and
25 current density should be adjusted to deposit precise composition alloy particles.
26 Other metals or alloys can be produced by incorporating other metal oxides in the
27 anode in accordance with the present invention.

28 From a practical commercial standpoint of producing titanium particulate in
29 which the particulate can be used directly in powdered metallurgical fabrication or
30 consolidated into billets for subsequent rolling into sheet, forging, etc. it is desirable
31 to produce the particulate at as low cost as possible. High mass transfer and high
32 current density that produces particle sizes that are desirable for commercial
33 applications can be achieved in a cell configuration such as shown in Figure 4.

1 In this case the anode container can be a porous carbon-carbon or other anodic
2 container in which Ti_xO_y -C anode segments 60 are placed, and the structural container
3 can be the cathode and/or a cathode 62 placed inside the structural container (not
4 shown). Preferably the container is insulated to maintain heat in the molten salt
5 electrolyte to achieve thermal neutrality with the IR/joule heating of the electrolyte at
6 high current densities. Also if desired the molten salt electrolyte could be pumped
7 through cyclone systems and filters to continuously collect the titanium particulate as
8 it is being produced. Commercial pumping systems are readily available to handle
9 pumping molten salt electrolytes such as used in the aluminum and mass soldering
10 industries to pump molten metals. Molten salt electrolytes that are desirable for high
11 mass transfer cell designs of which Figure 4 is just one example, include strong Lewis
12 acid compositions such as $NaAlCl_4$ and fluoride compositions, and fluoride or
13 chloride alkali and alkaline earth metal salts and mixtures thereof. Utilizing a high
14 mass transfer cell design in which the molten salt electrolyte is pumped over the
15 cathode surface, with high stirring rates and/or ultrasonics to agitate the molten salt
16 electrolyte or the cathode itself coupled with a reduced valence Ti_xO_y -C anode
17 permits production of titanium particulate at a relatively high rate and relatively low
18 cost. And current pulsing as well as periodic reversing the current can further
19 enhance the production of titanium particulates when coupled with a high mass
20 transfer rate cell as above described.

21 Heretofore aluminum and magnesium have been produced by a composite
22 anode process utilizing anodes of Al_2O_3 -C or MgO -C [23-26]. However, there is no
23 teaching a suggestion in any of the prior art that recognizes that high valence (4 or
24 more) or multi-valence metals could be produced by a composite anode process.
25 More importantly, it was not recognized that high value high valence or multi-valence
26 metals such as titanium, chromium, hafnium, molybdenum, niobium, tantalum,
27 tungsten, vanadium, and zirconium could be produced utilizing a composite anode, as
28 in the present invention. Neither was it recognized that a high valence metal oxide
29 could be thermally reduced to a lower valence state in a composite anode or that a
30 reduced valence state metal oxide-carbon anode could be used to produce particulate
31 metal by electroreduction.

32 In contrast to producing a molten metal aluminum (melting point approx. at
33 $660^\circ C$) and magnesium (melting point approx. at $650^\circ C$), the present invention

1 permits control of particle geometry and size, and grain size in the particle can be
2 controlled by the molten salt composition, its operating temperature and the cathode
3 current density. Moreover, the instant invention permits direct production of metals
4 in the powdered/particulate solid state, unlike the prior art processes which produced
5 molten aluminum [23, 25, 26] or magnesium [24].

6 In addition, the combination of thermal treatment to reduce the metal to a
7 lower valence state, the use of carbon in the anode to release a lower valence state
8 metal into the molten salt, and the selection of molten salt to stabilize the lower
9 valence state metal so as to produce a fully reduced metal at the cathode, is a unique
10 and advantageous feature of the current invention.

11 An alternative to reducing the titanium valence in the molten salt is to
12 depolarize the cathode using hydrogen which could not only prevent the re-oxidation
13 of the lower valence titanium at the anode and reduce the total cell voltage, but also
14 allow for the formation of titanium hydrides at the cathodes. Titanium hydride is
15 much more stable than titanium toward oxidation. The present invention thus permits
16 the production of very low oxygen titanium.

17 Moreover, the present invention overcomes a problem of poor electrical
18 conductivity of the metal oxide-carbon anode of my previous composite anode
19 process [23-26] which required the use of aluminum or magnesium metal conductors
20 through the composite anode to carry current and prevent high voltage drops due to
21 the poor electrical conductivity of the $\text{Al}_2\text{O}_3\text{-C}$ or MgO-C composite anodes. In the
22 instant invention, poor anode electrical conductivity is overcome by using highly
23 electrically conductive carbon flake as the major carbon source in the composite
24 anode. Small size composite anode pieces can also be utilized to reduce voltage drop
25 as illustrated in Figure 3 as contrasted to large size anodes which can result in high
26 resistivity and larger voltage drops that increase energy consumption. Examples of
27 low resistivity in a reduced valence state titanium oxide carbon anode is shown in
28 Figure 5. Further when the TiO_2 is reduced to TiO , the TiO is very electrically
29 conductive, more so than graphite. Thus anodes made with TiO are quite conductive
30 and in one iteration does not require pressing into a composite with graphite flake or
31 other carbon forms. The TiO is so conductive, it can be simply mixed with
32 carbon/graphite in a basket that serves as the anode with a conductor which can be the
33 basket or a graphite rod.

1 in Example 1 at a cathode current density of 1.0 amp/cm². Titanium powder was
2 produced at an efficiency of 90% in an average particle size of 10 microns.

3 Example 3

4 Example 2 was repeated with electrolysis at a cathode current density of 0.25
5 amps/cm² which produced an efficiency of 97% with a particle size of approximately
6 20 microns.

7 Example 4

8 A composite anode was produced using a mixture of TiO₂, Al₂O₃ and V₂O₃ in
9 an elemental ratio of Ti-6Al-4V. A stoichiometric ratio of graphite flake was mixed
10 with the oxides and a coal tar pitch binder was used. The molded composite anode
11 was heat treated to 1200°C in an inert atmosphere. The composite anode was placed
12 in the anode basket as described in Example 1 but a sheet of titanium was used as the
13 cathode. The electrolyte consisted of NaCl-LiCl-KCl eutectic with 20 mole % LiF.
14 Electrolysis was conducted at a cathode current density of 1.25 amps/cm², which
15 produced particles in a size primarily in the range of 10-80 microns. The harvested
16 particles were analyzed and found to contain a ratio of Ti-6Al-4V.

17 Example 5

18 A composite anode was prepared as described in Example 1 and heat treated
19 to 1150°C. The molten salt electrolyte consisted of KF-NaF-LiF eutectic operated at
20 650°C. The cathode was nickel metal with electrolysis conducted at a cathode current
21 density of 0.25 amps/cm². A coherent film of titanium 10 microns thick was
22 deposited on the nickel cathode.

23 Example 6

24 A composite anode was produced as described in Example 2 using Y₂O₃ and
25 graphite flake in stoichiometric ratio. The anode was electrolyzed as in Example 2,
26 which produced yttrium metal in a particle size of 10-30 microns.

27 Example 7

28 A composite anode was produced as described in Example 2 using
29 stoichiometric ratio of HfO₂ and carbon. Electrolysis of the anode in a molten salt
30 electrolyte, as in Example 4, at a cathode current density of 0.5 amperes/cm²
31 produced metal hafnium metal particulate having a particle size of 10 - 100 microns.

32

1 Example 8

2 A composite anode was produced by mixing a stoichiometric amount of
3 $\text{Cr}_2\text{O}_3\text{-C}$ and a pitch binder. The composite anode was heated in the absence of air to
4 1400°C and then electrolyzed at a cathode current density of 0.25 amps/cm^2 in a
5 molten salt electrolyte as in Example 4. A chromium particulate was produced having
6 a particle size of 5-40 microns.

7 Example 9

8 Rutile ore which contained approximately 95% TiO_2 was dried and mixed
9 with graphite flake and a resin binder to produce the oxide-carbon in stoichiometric
10 ratio. The mixture was compressed to 20,000 psi and heat treated in an inert
11 atmosphere to 1200°C . The anode was electrolyzed as in Example 4, which produced
12 a powder at the cathode containing primarily titanium, and small amounts of iron,
13 aluminum, niobium, vanadium and silicon having a particle size of 1 - 80 microns.

14 Example 10

15 A salt composition of (65 AlCl_3 – 35 NaCl mole %) -20 mole % NaF was
16 utilized as the electrolyte at an operating temperature of 190°C . A composite anode
17 was utilized as described in Example 1 with electrolysis conducted with a pulsed
18 current 3 seconds on and 1 second off. A crystalline titanium deposit of flake
19 morphology was produced at a cathode current density of 1 amps/cm^2 .

20 Example 11

21 Example 10 was repeated with a cathode current density of 0.25 amps/cm^2 .
22 The resulting titanium deposit was a solid film on the cathode. The pulse scheme was
23 then modified to 3 seconds on $\frac{1}{4}$ second off with periodic reverse polarity and then
24 repeating the cycle. The deposit was a solid film with a very fine grain
25 microstructure. Other shape form pulses provided similar results.

26 Example 12

27 Hydrogen was used at the cathode in an electrolytic cell similar to Example 10
28 with or without a pulsed current. Cell voltage was decreased by about 10 to 15%, and
29 titanium hydride powder formed in-situ in the cell instead of metallic titanium
30 powder. Washing the titanium hydride produced oxygen pick up of $\leq 200 \text{ ppm}$. The
31 resulting titanium hydride was then dehydrogenated by heating to about 650°C to
32 produce metallic titanium powder with $\leq 400 \text{ ppm}$ oxygen. This oxygen level is an
33 order of magnitude lower than titanium powder produced by any other process.

1 Example 13

2 Titanium oxide was mixed with a stoichiometric amount of carbon black and
3 heated under a reduced pressure of 0.01 atmosphere in argon to a temperature of
4 1450⁰C which produced the titanium suboxide of Ti₂O₃ with no other suboxides or
5 contaminates such as TiC. The Ti₂O₃ was mixed with graphite flake, a binder of
6 phenobic resin, and pressed into a block. The block was heated in the absence of air to
7 1100⁰C which formed an anode. The resulting composite anode was used in a fused
8 salt consisting of the eutectic of LiCl-KCl operated at 500⁰C. Electrolysis was
9 conducted in trial one at 1 amp/cm² on the cathode which produced titanium
10 particulate in a size of 1 to 10 microns. In a second trial a titanium sponge was
11 placed in the bottom of the fused salt and TiCl₄ was bubbled onto the sponge which
12 produced TiCl₂ in the salt bath. TiCl₄ continued until a concentration of 5% TiCl₂ was
13 generated. Electrolysis was then performed as in trial one and titanium particulate
14 with a size up to 400 microns was produced, thus showing with a titanium ion in
15 solution larger size titanium particulate was produced.

16 Example 14

17 An identical system as in Example 13 was created before and TiCl₂ was
18 generated, and in trial one the electrolysis was performed at 40 amps/cm². The
19 titanium particulate produced was in a size range of 20 to 100 microns. In trial two
20 electrolysis was performed at 125 amps/cm² which produced titanium particles in
21 approximately the same size as the 40 amps/cm² current density trial. In trial three
22 electrolysis was also performed at 125 amps/cm² with argon gas bubbling over the
23 cathode to create a large mass flow. The titanium particulate produced in the high
24 mass flow at 125 amps/cm² was in the size range of 40 to 200 microns. The titanium
25 suboxide-carbon composite anode provides the opportunity to operate at very high
26 cathode current densities and in a high mass flow regime.

27 Example 15

28 TiO₂ and carbon were heated under a pressure of 0.01 residual argon
29 atmosphere to 1850⁰C which produced TiO and CO. The TiO was mixed with
30 stoichiometric carbon and a binder and molded into a block which was heated to
31 1100⁰C which formed a composite anode. The resulting composite anode was placed
32 in a salt mixture of 60NaCl-40MgCl₂ and 20 mole percent NaF based on the chloride
33 salt mixture operated at 600⁰C. In trial one the electrolysis was performed at 0.15

1 amps/cm² and titanium particulate in the size range of 50 to 300 microns was
 2 produced. In trial two, a titanium sponge was placed in a small crucible immersed in
 3 the salt bath and TiCl₄ was bubbled onto the sponge that produced TiCl₂ until the
 4 concentration was 8% TiCl₂ in the salt. Electrolysis was performed at 0.15 amps/cm²
 5 which produced titanium particulate in the 200 to 500 micron size. The oxygen
 6 content was 380 parts per million.

7 Example 16

8 Rutile with a composition as follows, and the remainder titanium was
 9 processed as shown in the headings:

Impurities	Units	As received composition	After heating to 1700°C with carbon	Purity of Electrolytically produced titanium
Al	ppm	5300	4200	700
Ca	ppm	570	530	<100
Cr	ppm	300	150	100
Fe	ppm	4390	140	100
Mg	ppm	1470	1270	500
Si	ppm	12000	<100	<100
V	ppm	2290	2290	2000
Zr	ppm	360	250	300

10 With the remainder titanium

11 The rutile was mixed with carbon in a ratio of 1.1 to stoichiometry and heated to
 12 1700°C in argon at atmospheric pressure. The composition after heating is shown in
 13 the second column which shows the rutile was purified and particularly in the case of
 14 iron and silicon of which the latter is most undesirable as an impurity in titanium
 15 metal.

16 The purified rutile was mixed with carbon and resin and molded onto a block
 17 which was heat treated to 1250°C. The composite block was utilized as an anode in a
 18 salt bath of NaCl-CaCl₂ operated at 650°C. Electrolysis was performed at 0.5
 19 amps/cm² which produced particulate in the size range of 50-350 microns with a
 20 purity as shown in column five above. Aluminum and vanadium are desirable
 21 alloying elements for titanium and are used in most titanium alloys. Thus a relatively

1 pure titanium is produced from low cost domestic source rutile which can meet
2 virtually all market demands except the stringent aerospace requirements.

3 Example 17

4 TiO_2 was mixed with carbon and heated in a 90% nitrogen 10% hydrogen
5 atmosphere to 1600°C which produced titanium nitride (TiN). The TiN was pressed
6 and sintered at 2000°C in a nitrogen atmosphere. The TiN block was used as an anode
7 in a salt mixture of (NaCl-KCl) - 20 mole % NaF operated at 700°C . Electrolysis was
8 conducted at 0.5 amps/cm^2 which produced titanium particulate in the size range of
9 20 to 350 microns and nitrogen gas was given off at the anode.

10 Example 18

11 TiO_2 was mixed with carbon in a ratio of 1 to 1.5 over stoichiometry and
12 heated in argon at 1600°C which produced titanium carbide (TiC). The TiC was
13 pressed and sintered at 2000°C . The TiC was used as an anode in the same salt as in
14 Example 17. During electrolysis at 1 amp/cm^2 oxygen was bubbled under the TiC
15 anode in an amount equivalent to the current to produce titanium so that the oxygen
16 reacted with the freed carbon to produce CO_2/CO which is often referred to as
17 depolarizing the electrode. A diaphragm of porous alumina was placed between the
18 anode and cathode to prevent any oxygen from contacting the deposited titanium
19 particulate and oxidizing it. The particle size of titanium particulate produced was
20 in the size range of 20 to 200 microns.

21 Example 19

22 The suboxide TiO was produced by reacting TiO_2 with stoichiometric carbon
23 in a vacuum of 0.01 atmosphere at a temperature of 1850°C . The TiO was then
24 pressed and practically sintered at 1450°C to provide a porous body which served
25 as a cathode in a fused salt bath of calcium chloride containing 5% calcium oxide
26 operated at 900°C . A graphite anode was utilized and electrolysis performed at a
27 constant voltage of 3.0V for a period of 12 hours. The TiO was reduced to titanium
28 metal with oxygen being attracted to the anode to produce CO_2/CO .

29 Example 20

30 Example 19 was repeated using Ti_2O_3 as the starting material.

31 Example 21

32 Example 19 was repeated with the exception the electrolyte was the eutectic
33 of $\text{CaCl}_2\text{-NaCl}$ which was operated at 750°C . With the suboxide TiO, the lower

1 temperature salt bath can be used to reduce TiO to titanium metal.

2 Example 22

3 The molten salt bath electrolyte of CaCl₂ operated at 900⁰C showed a
4 considerable solubility of the reduced suboxide of titanium TiO. In a salt bath
5 operated at 900⁰C 5 wt % TiO was added and electrolysis conducted with a carbon
6 anode. Titanium particulate was deposited on the cathode at a current density of 1
7 amp/cm². In a second trial a porous alumina diaphragm was used around the anode to
8 prevent any oxygen from diffusing to the deposited titanium on the cathode and
9 contaminating the deposited titanium particulate.

10 Example 23

11 A molten salt composition consisting of the CaCl₂-NaCl eutectic containing
12 20 mole % NaF was operated at 750⁰C and 2 wt % TiO was added which became
13 soluble in the salt bath. A carbon anode was used and electrolysis performed at a
14 cathode current density of 0.25 amps/cm². Titanium particulate was deposited on
15 the cathode and CO₂ /CO was evolved from the carbon anode.

16 Example 24

17 TiO was produced as described in Example 15 and mixed with carbon
18 particulate. The mixture of TiO-C was placed in a porous carbon-carbon basket
19 which served as the anode electrical conductor. The anode basket containing TiO-C
20 was placed in a salt of LiCl-KCl eutectic containing 20 wt% NaF operated at 680⁰C.
21 Electrolysis was performed at 1 amps/cm² which produced titanium particulate in
22 the size range of 50-500 microns which demonstrated a physical mixture of TiO-C
23 can serve as an anode.

24 Example 25

25 An anode produced as described in Example 13 was utilized in the electrolyte
26 given in Example 13 with electrolysis conducted at 1 amps/cm² concurrent with
27 hydrogen bubbling under the cathode. The deposit was titanium particulate in the
28 size range of 50-800 microns. Heating the deposit showed hydrogen evolution as
29 detected in a mass spectrometer.

30 Example 26

31 A graphite crucible was set inside a steel cell with a cover and seal to provide
32 an inert atmosphere with an argon purge. A graphite rod with a reduced tip to serve
33 as a resistor was placed through a standard feed-through in the cell cover. Calcium

1 fluoride was placed in the graphite crucible. The graphite rod was heated resistively
2 between a connection to it and the steel cell which raised the temperature to 1700°C
3 which melted the calcium fluoride. TiO was then added at 5 wt%. Electrolysis was
4 conducted at 1 amps/cm² between a separate graphite anode and the crucible serving
5 as the cathode. After six hours of electrolysis the experiment was stopped and the
6 system cooled. Breaking the salt revealed beads of titanium that had been produced
7 in the molten salt.

8 Example 27

9 Example 26 was repeated with a graphite resistor heater located between two
10 graphite rods that melted the calcium fluoride and raised the temperature to 1710°C.
11 Ti₂O₃ was then added at 10wt% of the melted CaF₂. Electrolysis was conducted
12 between a tungsten cathode and a platinum-iridium anode at a current density of 0.5
13 amps/cm². During the electrolysis oxygen was given off at the anode which acted as a
14 non-consumable inert anode in contrast to graphite which forms CO and CO₂. After
15 five hours operation the experiment was stopped and the molten portion of the molten
16 salt cracked which revealed numerous beads of titanium metal.

17 The above embodiments and examples are given to illustrate the scope and
18 spirit of the instant invention. These embodiments and examples are within the
19 contemplation of the present invention. Therefore, the present invention should be
20 limited only by the appended claims.

21

What is claimed is:

1. A method for the production of titanium metal which comprises electrochemically dissolving, in a molten salt electrolyte, an anode formed of a titanium suboxide/carbon composite, and reducing the dissolved titanium suboxide, at a cathode, to titanium metal.
2. The method of claim 1, wherein said molten salt electrolyte comprises a strong Lewis acid.
3. The method of claim 2, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.
4. A method for the production of purified titanium from rutile ore which comprises electrowinning from an anode formed of a mixture of titanium suboxide/carbon composite in a molten salt electrolyte, and depositing purified titanium onto a cathode.
5. The method of claim 4, wherein the molten salt electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.
6. The method of claim 4, wherein titanium suboxide is mixed with carbon in a ratio of at least 1:1.5 over stoichiometry to produce TiC and CO₂/CO.

7. The method of claim 4, wherein the titanium suboxide is mixed with carbon in a ratio of at least 1:1 over stoichiometry to produce TiC and CO₂/CO.
8. A method for the production of purified titanium which comprises electrochemically dissolving an anode formed of a titanium suboxide/carbon composite in a molten salt electrolyte, and electrochemically reducing the dissolved titanium suboxide to purified titanium metal.
9. The method of claim 8, wherein the molten salt electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.
10. The method of claim 8, wherein titanium suboxide is mixed with carbon in a ratio of at least 1:1.5 over stoichiometry based on titanium to produce TiC and CO₂/CO.
11. The method of claim 8, wherein the titanium suboxide is mixed with carbon in a ratio of at least 1:1 over stoichiometry based on titanium to produce TiC and CO₂/CO.
12. The method of claim 8, wherein titanium suboxide-carbon composite anode is formed by heating a titanium oxide with carbon under an inert atmosphere.
13. The method according to any one of claims 8-12, wherein the anode comprises a composite of titanium suboxide and carbon, and including the step of adding a Ti²⁺ containing compound to the electrolyte.

14. A method for the direct production of titanium metal in a particulate state which comprises electrochemically dissolving an anode, formed of a titanium suboxide/carbon composite, in a molten salt electrolyte in an electrochemical cell, and electrochemically reducing the dissolved titanium suboxide to particulate titanium metal.
15. The method of claim 14, wherein said molten salt electrolyte comprises a strong Lewis acid.
16. The method of claim 15, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.
17. The method of claim 14, wherein the electrolyte includes a Ti^3 containing compound which is reduced in one step to titanium metal.
18. The method of claim 17, wherein the Ti^3 containing compound is added in a concentration of 1/2 to 20% by weight of the electrolyte.
19. The method of claim 18, wherein the Ti^3 containing compound is added in a concentration of 1 to 10% by weight of the electrolyte.
20. The method according to any one of claims 14-19, wherein the electrode is formed of a titanium oxide/carbon composite, and including the step of adding a Ti^2 containing compound to the electrolyte.

21. The method of claim 20, wherein the Ti^{2+} containing compound is added in a concentration of 1/2 to 20% by weight of the electrolyte.
22. The method of claim 21, wherein the Ti^{2+} containing compound is added in a concentration of 1 to 10% by weight of the electrolyte.
23. A method for the production of titanium metal which comprises electrochemically dissolving, in a molten salt electrolyte, an anode formed of a titanium oxide/carbon composite, wherein the molten salt electrolyte comprises a strong Lewis acid, and electrochemically reducing the dissolved titanium oxide to titanium metal at a cathode.
24. The method of claim 23, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.
25. A method for the direct production of titanium metal in a particulate state which comprises electrochemically dissolving an anode, formed of a titanium oxide/carbon composite, a molten salt electrolyte in an electrochemical cell, wherein the molten salt electrolyte comprises a strong Lewis acid, and electrochemically reducing the dissolved titanium oxide to titanium metal.
26. The method of claim 25, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

27. The method according to claim 25, wherein the electrode is formed of a titanium oxide/carbon composite, and including the step of adding a Ti^{2+} containing compound to the electrolyte.
28. The method of claim 27, wherein the Ti^{2+} containing compound is added in a concentration of 1/2 to 20% by weight of the electrolyte.
29. The method of claim 28, wherein the Ti^{2+} containing compound is added in a concentration of 1 to 10% by weight of the electrolyte.
30. The method of any one of claims 25-29, wherein the electrolyte includes Ti^{3+} containing compound which is reduced in one step to titanium metal.
31. The method of claim 30, wherein the Ti^{3+} containing compound is added in a concentration of 1/2 to 20% by weight of electrolyte.
32. The method of claim 31, wherein the Ti^{3+} containing compound is added in a concentration of 1 to 10% by weight of the electrolyte.
33. A method for the production of a metal alloy of interest which comprises electrochemically reducing an anode formed of a composite of two or more oxides of two or more metals of interest with carbon in a molten salt electrolyte, wherein sufficient carbon is present to stoichiometrically react with the reduced metal oxides to produce a substantially pure cathode and CO_2 and/or CO at the anode.
34. The method of claim 33, wherein the anode is formed of a carbon composite of two or more metal oxides selected from the group consisting of a titanium oxide-or titanium suboxide-carbon composite, a chromium oxide-carbon composite, a hafnium oxide-carbon composite, a molybdenum oxide-carbon composite, a niobium oxide-carbon composite, a

tantalum oxide-carbon composite, a tungsten oxide-carbon composite, a vanadium oxide-carbon composite and a zirconium oxide-carbon composite.

35. The method of claim 33, wherein said molten salt electrolyte comprises a strong Lewis acid.

36. The method of claim 35, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

37. The method of any one of claims 33-36, wherein an electric current is applied in a pulsed manner.

38. The method of any one of claims 33-36, wherein an electric current is in a pulsed, periodically reversed polarity.

39. A method for the direct production of a metal alloy of interest in a particulate state which comprises subjecting an anode, formed of a composite of oxides of two or more metals of interest with carbon, to electrolytic reduction in a cell containing a molten salt electrolyte, wherein sufficient carbon is present to stoichiometrically react with the reduced metal oxides to produce a substantially pure metal alloy of interest at the cathode, and CO₂ and/or CO at the anode.

40. The method of claim 39, wherein the anode is formed of a carbon composite of two or more metal oxides of interest selected from the group consisting of a titanium oxide-or titanium suboxide-carbon composite, a chromium oxide-carbon composite, a hafnium oxide-carbon composite, a molybdenum oxide-carbon composite, a niobium oxide-carbon

composite, a tantalum oxide-carbon composite, a tungsten oxide-carbon composite, a vanadium oxide-carbon composite, and a zirconium oxide-carbon composite.

41. The method of claim 39, wherein said molten salt electrolyte comprises a strong Lewis acid.

42. The method of claim 41, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

43. The method of any of claims 39-42, wherein an electric current is applied in a pulsed manner.

44. The method of any of claims 39-42, wherein an electric current is in a pulsed, periodically reversed polarity.

45. A method for the production of a metal of interest which comprises electrochemically reducing an anode formed of a composite of two or more oxides of the metal of interest with carbon in a molten salt electrolyte, wherein the carbon present stoichiometrically reacts with the reduced metal oxides to produce a substantially pure metal of interest at the cathode and CO₂ and/or CO at the anode, and wherein an electric current is applied in a pulsed manner.

46. The method of claim 45, wherein the anode is formed of a carbon composite of a metal oxide selected from the group consisting of a titanium oxide or titanium suboxide-carbon composite, a chromium oxide-carbon composite, a hafnium oxide-carbon composite, a molybdenum oxide-carbon composite, a niobium oxide-carbon composite, a tantalum

oxide-carbon composite, a tungsten oxide-carbon composite, a vanadium oxide-carbon composite, and a zirconium oxide-carbon composite.

47. The method of claim 45, wherein said molten salt electrolyte comprises a strong Lewis acid.

48. The method of claim 45, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

49. The method of any of claims 45-48, wherein an electric current is in a pulsed, periodically reversed polarity.

50. A method for the direct production of a metal of interest in a particulate state which comprises subjecting an anode, formed of a composite of two or more oxides of the metal of interest with carbon, to electrolytic reduction in a cell containing a molten salt electrolyte, wherein sufficient carbon is present to stoichiometrically react with the reduced metal oxides to produce a substantially pure metal of interest at the cathode and CO₂ and/or CO at the anode, and wherein an electric current is applied in a pulsed manner.

51. The method of claim 50, wherein the anode is formed of a carbon composite of a metal oxide selected from the group consisting of a titanium oxide or titanium suboxide-carbon composite.

52. The method of claim 50, wherein said molten salt electrolyte comprises a strong Lewis acid.

53. The method of any of claims 50-52, wherein the electrolyte is selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

54. An electrolytic cell for production of a metal of interest by electrowinning, said cell comprising in combination:

a molten salt electrolyte disposed in a cell, a DC current source;

a cathode and an anode in contact with said electrolyte, wherein said anode is a feed electrode formed of a composite of a partially reduced oxide of the metal of interest and carbon, wherein the anode is formed of a composite of a partially reduced oxide of the metal of interest with carbon selected from the group consisting of a titanium oxide-or titanium suboxide-carbon composite, a chromium oxide-carbon composite, a hafnium oxide-carbon composite, a molybdenum oxide-carbon composite, a niobium oxide-carbon composite, a tantalum oxide-carbon composite, a tungsten oxide-carbon composite, a vanadium oxide-carbon composite, and a zirconium oxide-carbon composite.

55. The cell of claim 54, wherein said source of electric current is connected to said cell via a current controller.

56. The cell of claim 54, wherein the anode comprises loose pieces of said metal oxide carbon composite contained within a porous basket.

57. The cell of claim 54, and further comprising a valved outlet adjacent a lower wall thereof.

58. The cell of any one of claims 54-57, further comprising a porous separator or diaphragm disposed between said anode and cathode for permitting passage therethrough of electrowon metal ion of interest free of oxygen.

59. The cell of claim 54, wherein the porous basket is connected to a plus side of the DC source.

60. The cell of claim 54, wherein the cathode has a current density in the range of 0.25 to 1.0 amperes/cm².

61. An electrolytic cell for production of a metal of interest, said cell comprising in combination:

a molten salt electrolyte disposed in a cell, said electrolyte comprising a strong Lewis acid selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride;

a DC current source; and

a cathode and an anode in contact with said electrolyte, wherein said anode is formed of a composite of an oxide of the metal of interest and carbon, wherein the anode is formed of a composite of an oxide of the metal of interest with carbon selected from the group consisting of a titanium oxide-or titanium suboxide-carbon composite, a chromium oxide-carbon composite, a hafnium oxide-carbon composite, a molybdenum oxide-carbon composite, a niobium oxide-carbon composite, a tantalum oxide-carbon composite, a tungsten oxide-carbon composite, a vanadium oxide-carbon composite, and a zirconium oxide-carbon composite, and wherein the anode is contained within a porous basket formed of an electrically conductive carbon fiber mesh material which is connected to a source of electric current; and

wherein the cathode has a current density of 40 to 125 amperes/cm².

62. The cell of claim 61, wherein said source of electric current is connected to said cell via a current controller.

63. The cell of claim 61, wherein the anode comprises loose pieces of said metal oxide carbon composite contained within said porous basket.

64. The cell of claim 61, and further comprising a valved outlet adjacent a lower wall thereof.

65. The cell of any one of claims 61-64, and further comprising a separator or diaphragm disposed between said anode and cathode.

66. The cell of claim 65, wherein the separator or diaphragm comprises porous alumina.

67. The cell of claim 61, wherein the porous basket is connected to a plus side of the DC source.

68. The cell of claim 61, wherein said electrolyte comprises a strong Lewis acid selected from the group consisting of an eutectic of sodium chloride, lithium chloride and potassium chloride, an eutectic of potassium fluoride, sodium fluoride and lithium fluoride, an eutectic of sodium chloride, calcium chloride and potassium chloride, an eutectic of sodium chloride, magnesium chloride and sodium fluoride, and an eutectic of sodium chloride, potassium chloride and sodium fluoride.

69. The cell of claim 61, wherein the anode is contained within a porous basket formed of an electrically conductive carbon fiber mesh material which is connected to a source of electric current.

70. The cell of claim 58, wherein the separator or diaphragm comprises porous alumina.

71. An electrolytic cell for production of a metal of interest by electrowinning, said cell comprising in combination:

a molten salt electrolyte disposed in a cell,

a DC current source;

a cathode and an anode in contact with said electrolyte, wherein said anode is a feed electrode formed of a carbide of the metal of interest;

a source of an oxygen gas in fluid connection with the anode such that the anode may be depolarized with the oxygen gas;

a diaphragm between the anode and the cathode to prevent the oxygen gas from contacting the reduced metal of interest on the cathode while allowing passage of metal ion from the anode to the cathode.

FIG. 1

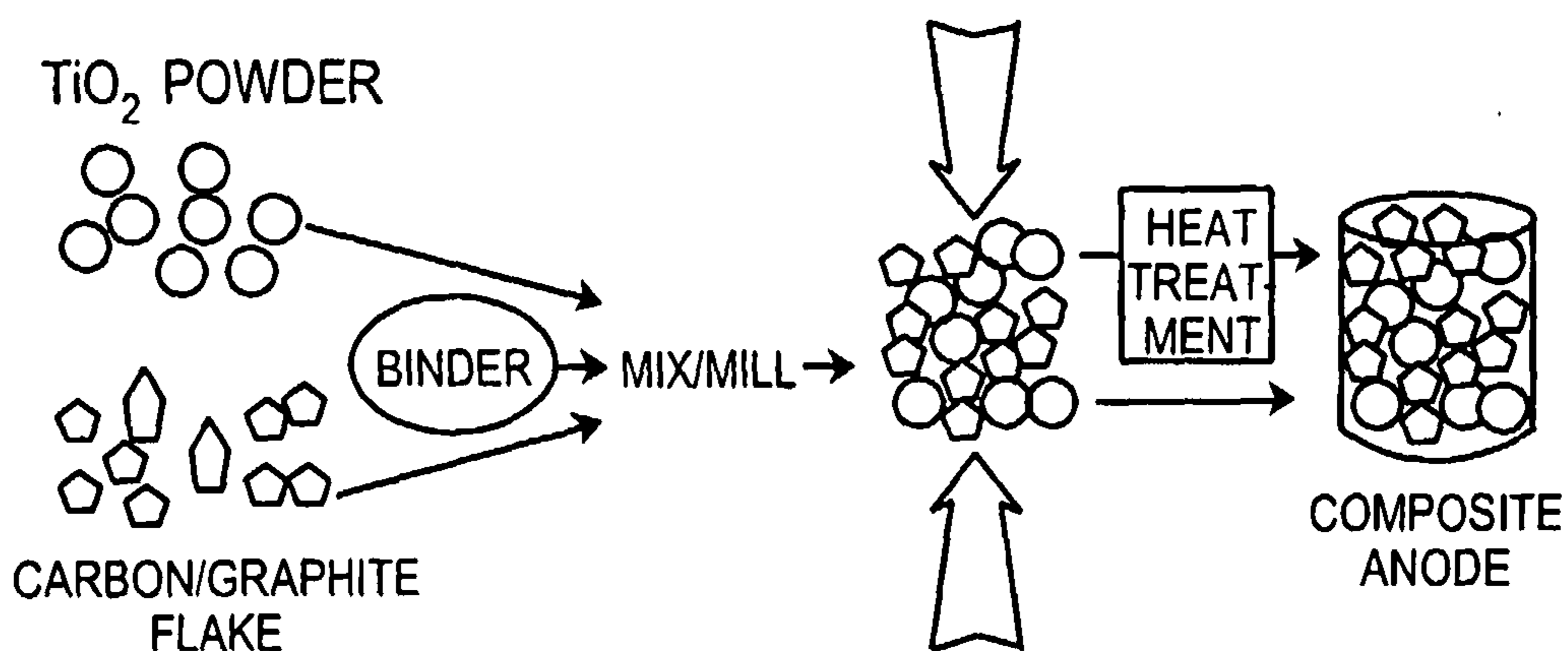
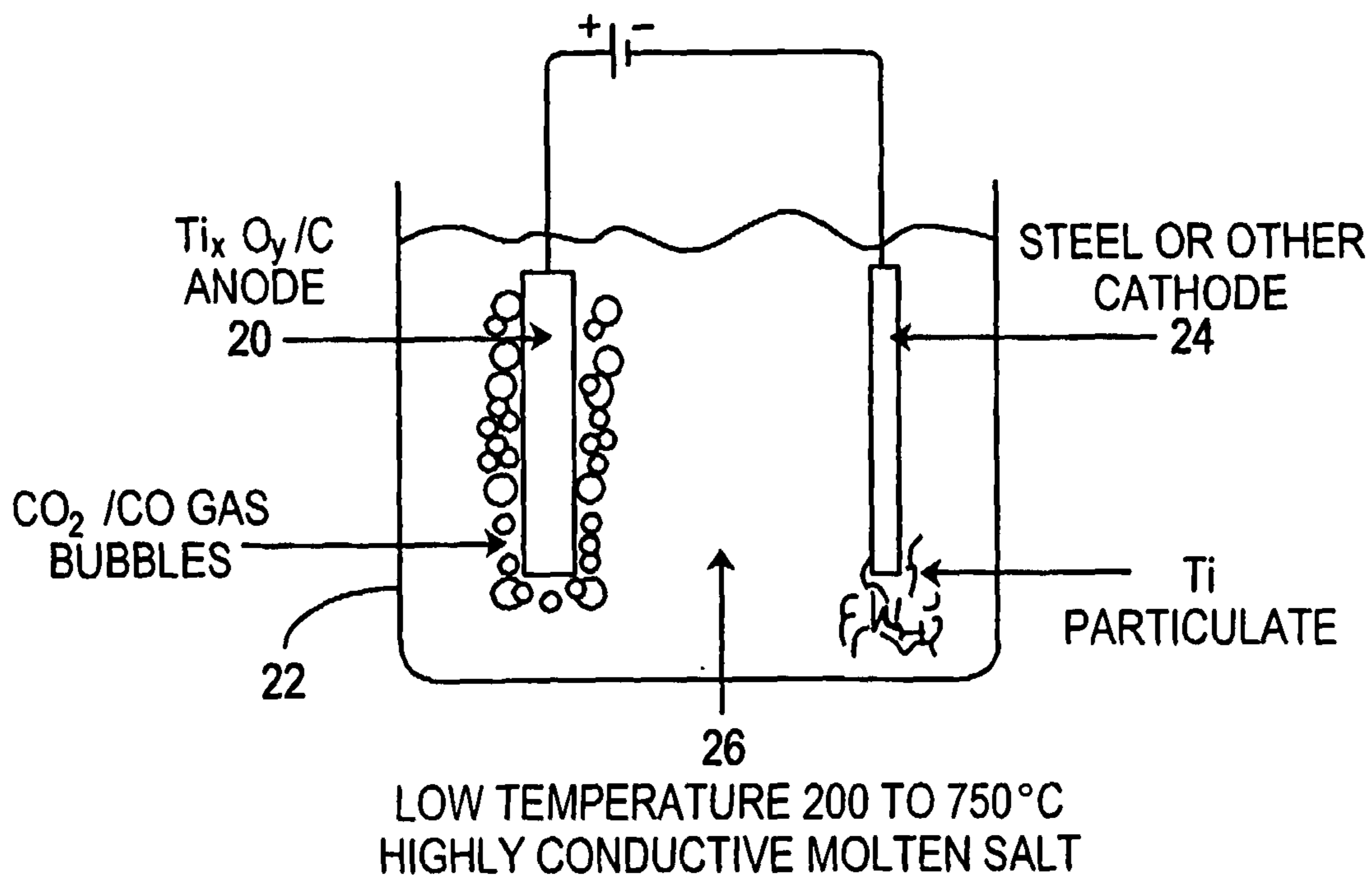
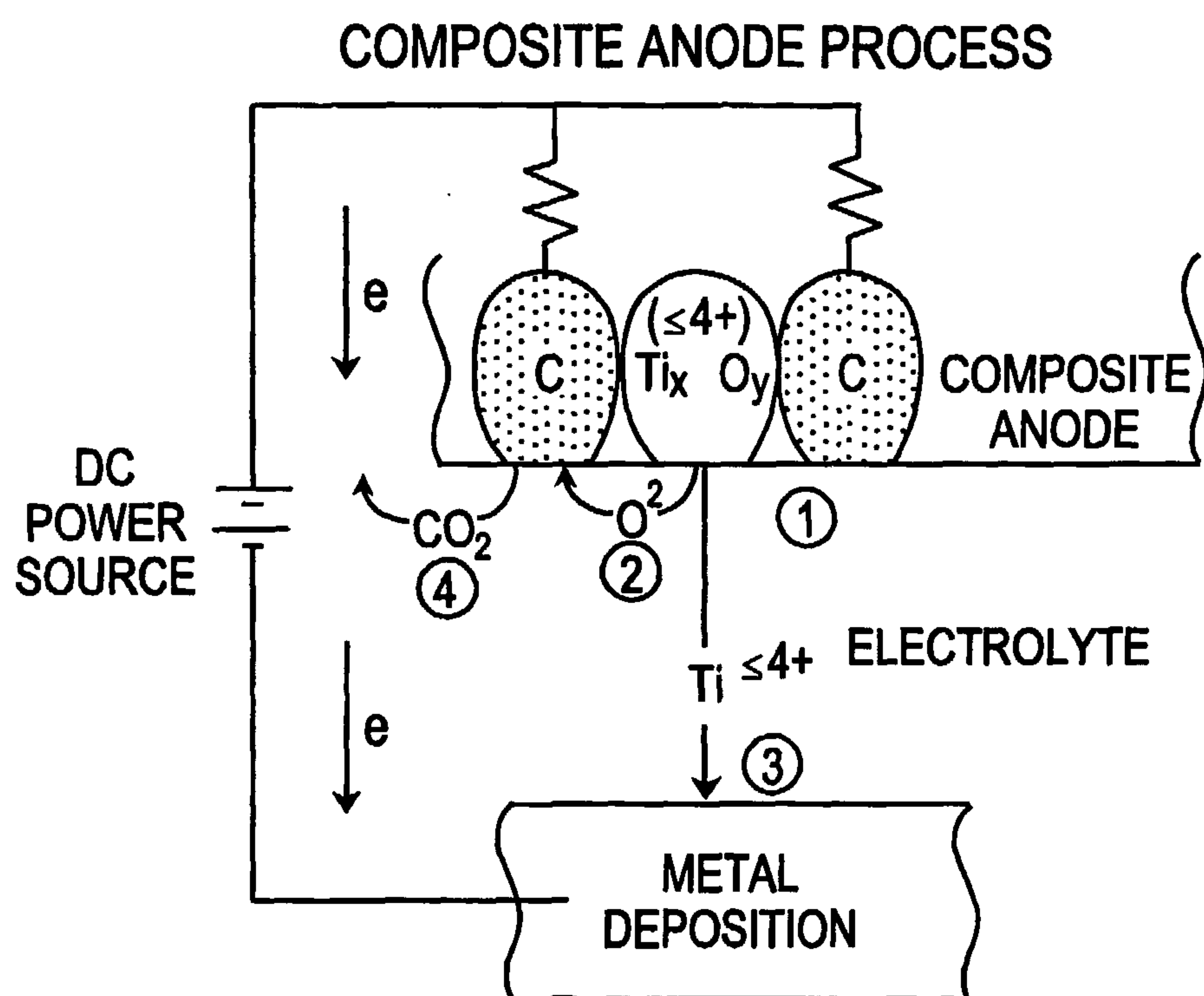


FIG. 2b



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FIG. 2a



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FIG. 3

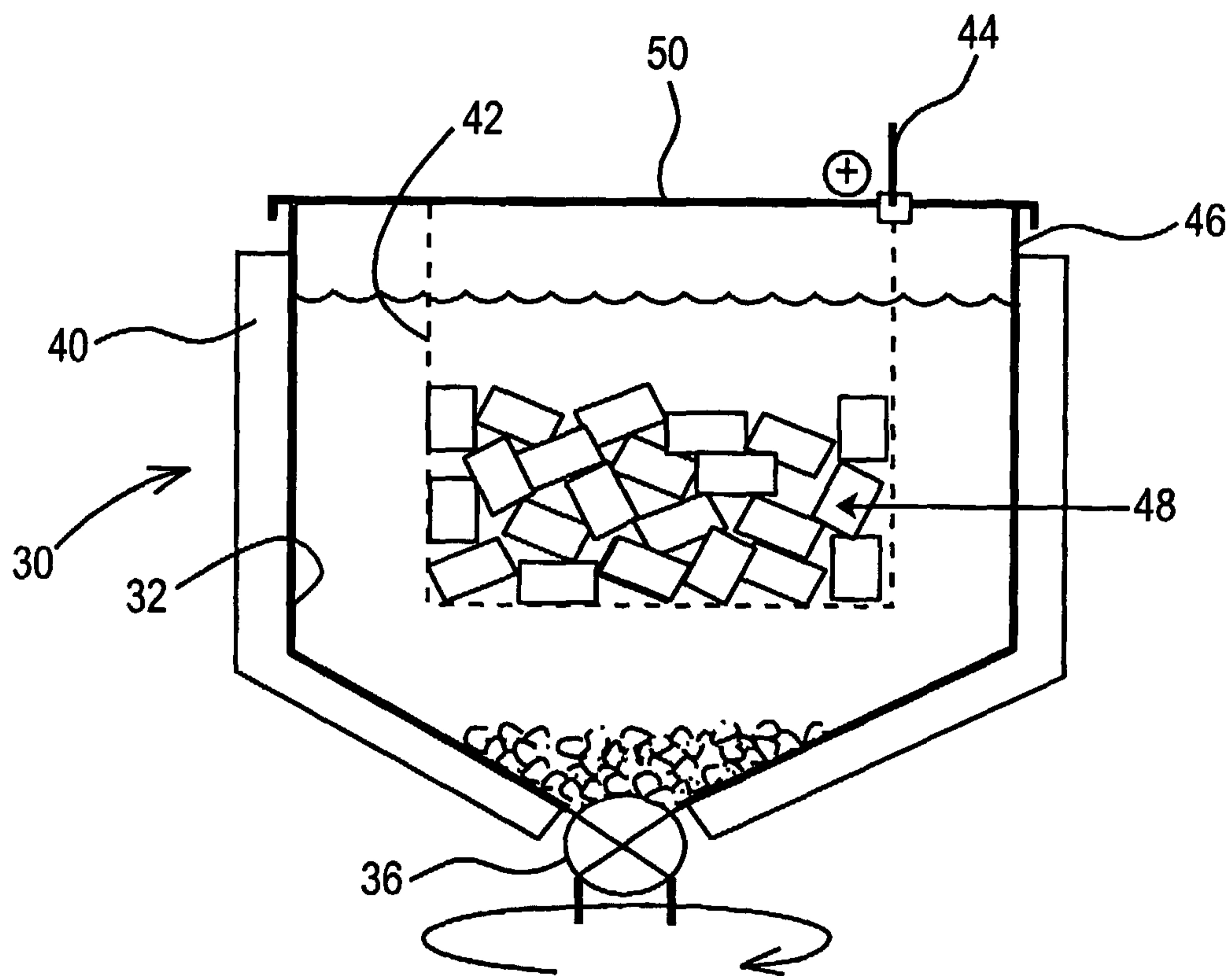


FIG. 4

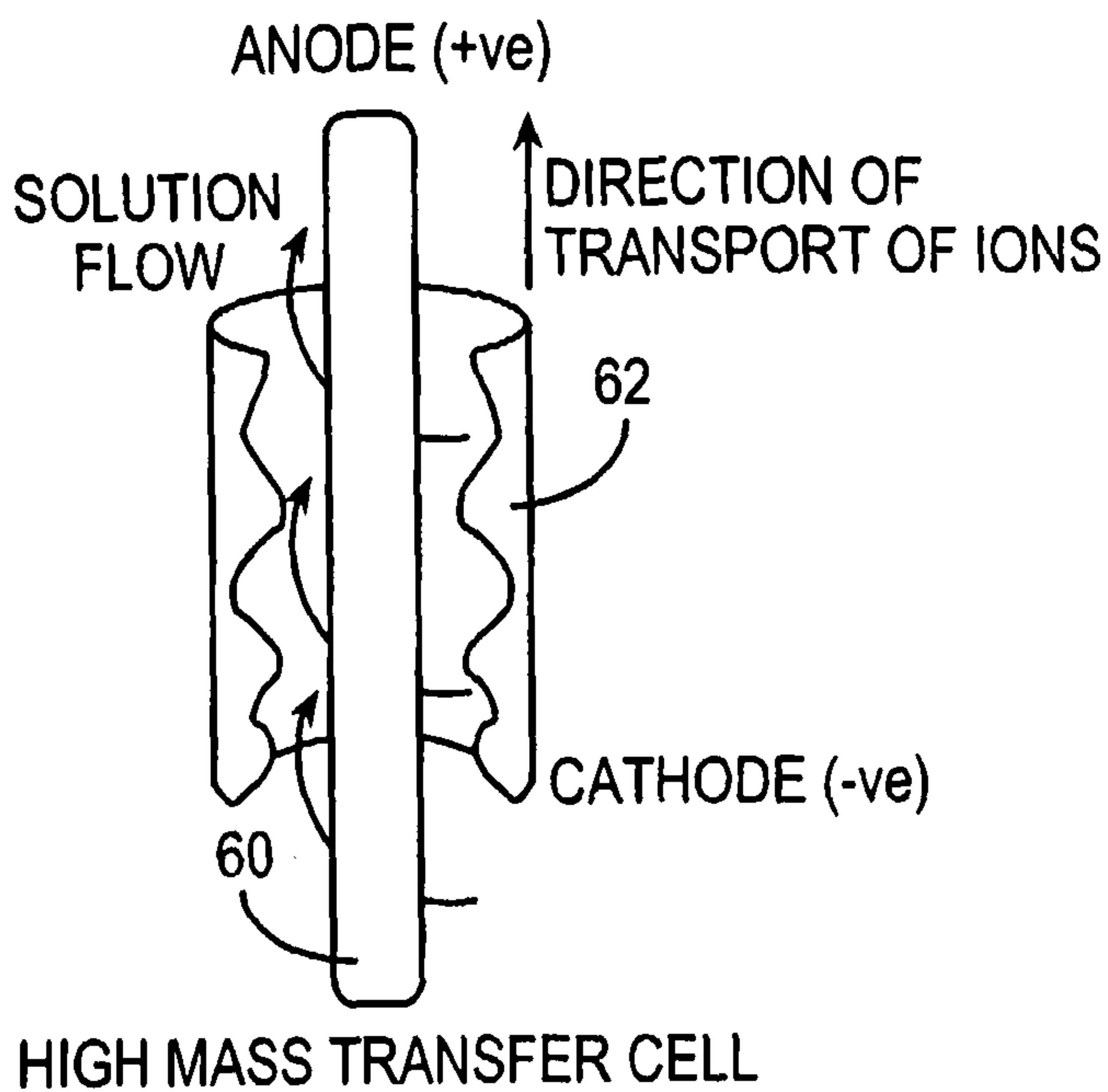


FIG. 5

