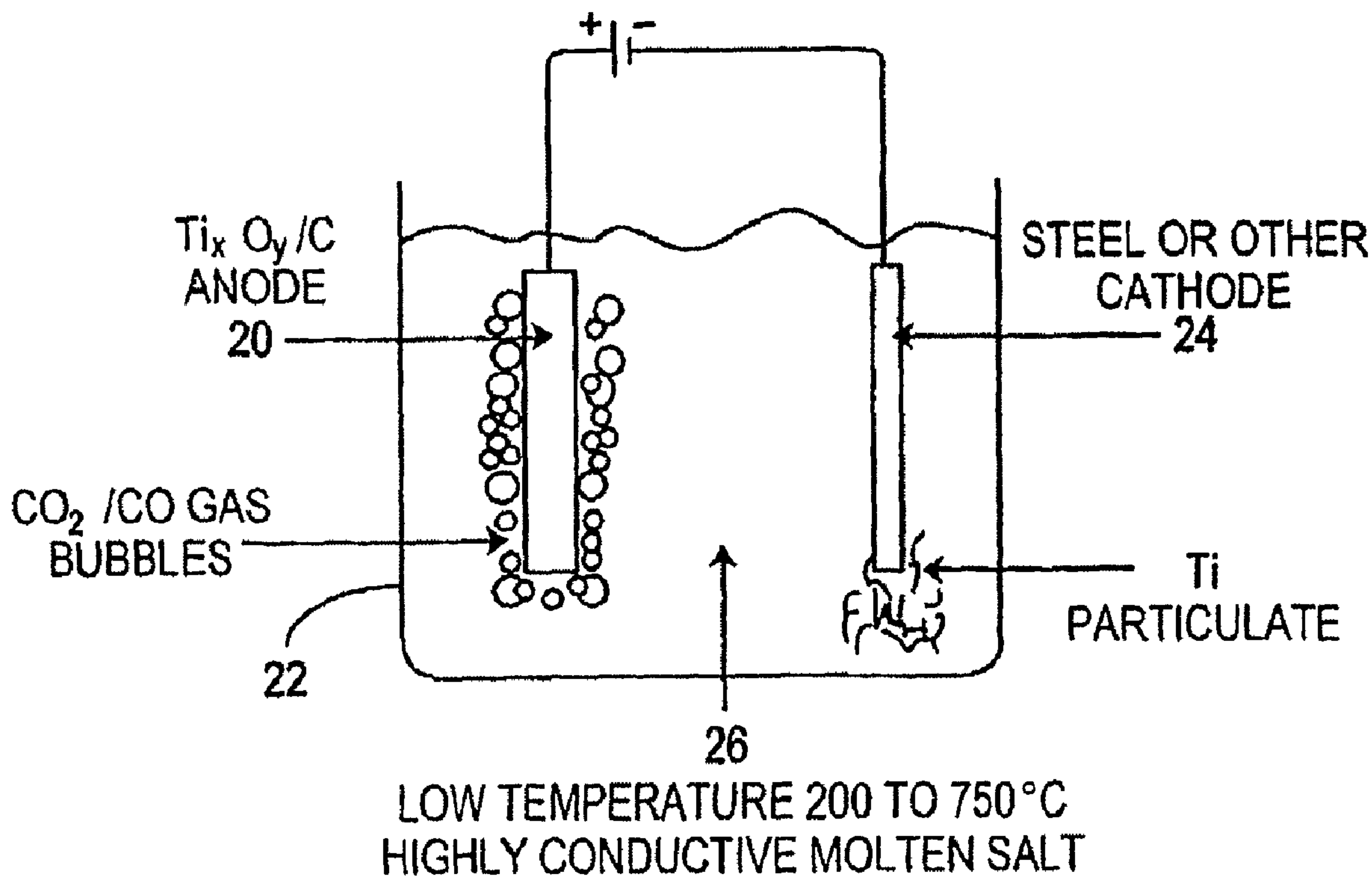




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 (72) **Inventeurs/Inventors:**  
 WITHERS, JAMES C., US;  
 LOUTFY, RAOUF O., US  
 (73) **Propriétaire/Owner:**  
 MATERIALS & ELECTROCHEMICAL RESEARCH  
 CORP., US  
 (74) **Agent:** OSLER, HOSKIN & HARCOURT LLP

(54) **Titre :** PROCÉDE THERMIQUE ET ELECTROCHIMIQUE DE PRODUCTION DE METAUX  
 (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.

Abstract

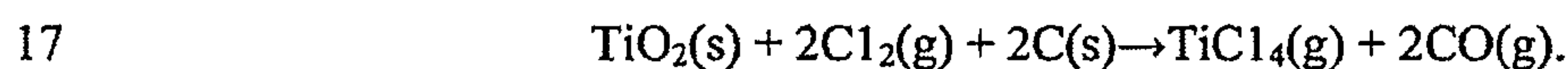
A system for purification of high value metals comprises an electrolytic cell in which an anode formed of a composite of a metal oxide of the metal of interest with carbon is electrochemically reduced in a molten salt electrolyte.

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) valence 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 (TiCl<sub>4</sub>) which is produced from the  
16 carbo-chlorination of a refined titanium dioxide (TiO<sub>2</sub>) according to the reaction:



18           In the Kroll process [2] TiCl<sub>4</sub> 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 MgCl<sub>2</sub> is removed by volatilization, under vacuum at  
23  $\approx 1000^\circ\text{C}$ . The MgCl<sub>2</sub> is then separated and recycled electrolytically to produce Mg  
24 as the reductant to further reduce the TiCl<sub>4</sub>. In the Hunter process [3,4] sodium is  
25 used as a reductant according to the reaction:



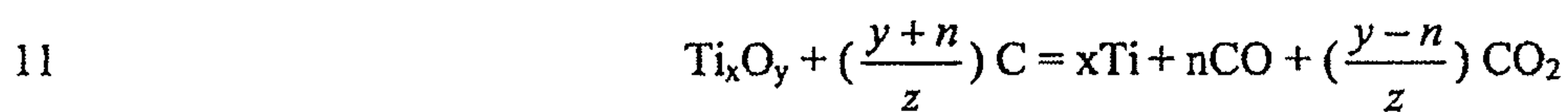
27           The titanium produced by either the Kroll or Hunter processes must not only be  
28 separated from the reductant halide by vacuum distillation and/or leaching in acidified  
29 solution to free the titanium sponge for further processing to useful titanium forms,  
30 but also require the 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  $\text{TiO}_2$  and  
7 plasma reduction of  $\text{TiCl}_4$ [18] without measurable success. Direct reduction of  $\text{TiO}_2$   
8 or  $\text{TiCl}_4$  using mechanochemical processing of ball milling with appropriate  
9 reductants of Mg or calcium hydride ( $\text{CaH}_2$ ) 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.

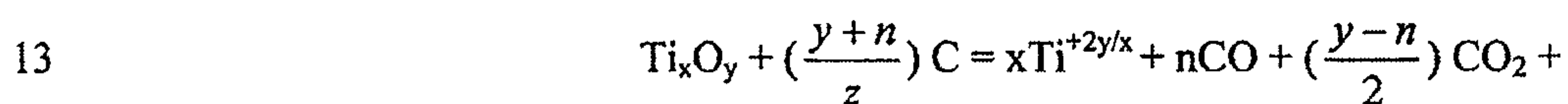
13           An electrolytic process has been reported [21] that utilizes  $\text{TiO}_2$  as a cathode  
14 and carbon or graphite as the anode in a calcium chloride electrolyte operated at  
15  $900^\circ\text{C}$ . By this process, calcium is deposited on the  $\text{TiO}_2$  cathode, which reduces the  
16  $\text{TiO}_2$  to titanium and calcium oxide. However, this process is limited by diffusion of  
17 calcium into the  $\text{TiO}_2$  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  $\text{TiO}_2$  cathode is not fully reduced which leaves contamination of  $\text{TiO}_2$  or  
20 reduced oxides such as  $\text{TiO}$ , 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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$ -C composite green electrode  
32 or billet. The  $\text{TiO}_2$ -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:



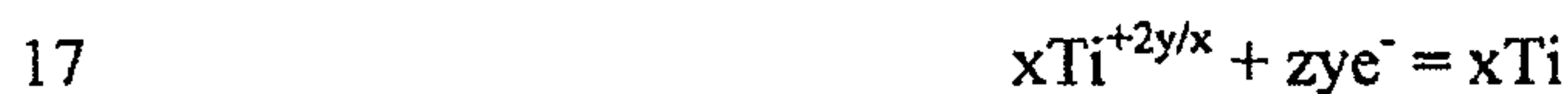
12 at the anode:



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;

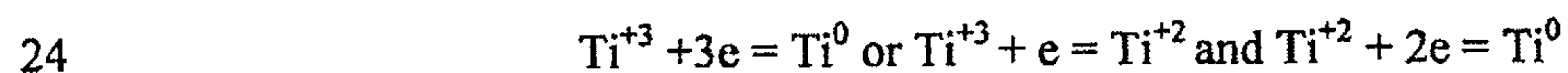
29 Fig. 4 is a perspective view showing details of an electrode in accordance with  
 30 the present invention;

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 ( $\text{TiO}_2$ ) has not been successful  
10 because  $\text{TiO}_2$  has little to no solubility in molten salt electrolytes which is also true of  
11 other titanium compounds. Titanium tetrachloride ( $\text{TiCl}_4$ ) 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  $\text{TiCl}_4$  could be  
15 reduced to lower valent ionic species of  $\text{Ti}^{+3}$  and  $\text{Ti}^{+2}$ , 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  $\text{TiCl}_4$  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  $\text{Ti}_x\text{O}_y$  in which a high valence metal such as  
30  $\text{Ti}^{+4}$ , 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  $\text{CO}_2$  and/or  $\text{CO}$  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  $\text{TiO}_2$  thermally is more economical  
5 than electrolytically reducing in a composite anode of  $\text{TiO}_2$ -carbon. If  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{Ti}_2\text{O}_3$  in  
10 which the titanium is in a +3 valence state can be produced over the temperature  
11 range of 1250-1700<sup>0</sup>C. Since the product is a solid  $\text{Ti}_2\text{O}_3$  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  $\text{TiO}_2$   
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 1700<sup>0</sup>C 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 1800<sup>0</sup>C is required to produce TiO free of TiC. At atmospheric  
23 pressure a reaction temperature above 2000<sup>0</sup>C 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  $\text{CO}_2$  and/or  $\text{CO}$ . 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 Al, WO  
13 02/083993 Al and WO03/002 785 Al, that  $\text{TiO}_2$  can serve as a cathode in a calcium  
14 chloride fused salt wherein the  $\text{TiO}_2$  is reduced to titanium metal with oxygen given  
15 off at the anode using an inert anode or  $\text{CO}_2/\text{CO}$  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  $\text{TiO}_2$ . Thus  
18 the reduced oxides of  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$  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 ( $\text{Al}_2\text{O}_3$ ) is soluble in molten  
22 cryolite ( $\text{NaAlF}_4$ ) which under electrolysis produces aluminum metal with  $\text{CO}_2/\text{CO}$   
23 being given off at a carbon anode, because there has not been identified a molten salt  
24 composition that will dissolve  $\text{TiO}_2$ . There is no known molten salt compound or  
25 combination of compounds that will dissolve  $\text{TiO}_2$ . However, there are molten salt  
26 compositions that will dissolve the reduced the suboxide  $\text{TiO}$  which is an ionic  
27 compound that is very electrically conductive. For example  $\text{TiO}$  is soluble in molten  
28 calcium chloride mixed alkali and alkaline earth chlorides as well as fluorides or  
29 mixed chlorides and fluorides. Thus  $\text{TiO}$  can be dissolved in  $\text{CaCl}_2$  or other salt  
30 mixture, and using a carbon/graphite anode electrolyzed to produce titanium at the  
31 cathode and  $\text{CO}_2/\text{CO}$  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 Ti<sub>2</sub>O<sub>3</sub>. 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 (CaF<sub>2</sub>) 1360°C, and  
12 barium fluoride BaF<sub>2</sub> 1280°C. It was found the titanium suboxides and particularly  
13 TiO is quite soluble in CaF<sub>2</sub> at temperatures above 1670°C. Thus titanium is readily  
14 electrowon from its suboxides dissolved in CaF<sub>2</sub> or other salts above 1670°C using a  
15 carbon/graphite anode that produces CO and CO<sub>2</sub> 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 TiO<sub>2</sub> to carbon of 7:1 to 4:1 using a ball mill mixer. The  
26 TiO<sub>2</sub> powder and carbon flakes were mixed dry, or optionally with a binder, in a ball  
27 mill mixer for 4-24 hours. The resulting TiO<sub>2</sub> 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  $\text{NaAlCl}_4$ , which melts as low as  $150^\circ\text{C}$ ,  
6 optionally containing fluoride additions such as an alkali fluoride and/or potassium  
7 titanium fluoride with the reduced state  $\text{Ti}_x\text{O}_y\text{-C}$  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  $300\text{-}900^\circ\text{C}$  range. For producing titanium preferred electrolytes include  $\text{NaCl}$  -  
11  $\text{CaCl}_2\text{-KCl}$  in a mole ratio of 50:50:20;  $\text{NaCl-LiCl-KCl}$  in a mole ratio of 20:60:40;  
12  $\text{AlCl}_3$  -  $\text{NaCl}$  -  $\text{NaF}$  in a mole ratio of 70:30:20  $\text{LiCl-KCl}$  eutectic with 20 wt%  $\text{NaF}$ ,  
13 eutectic of  $\text{LiF-KF}$ , 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  $\text{Ti}^{+3}$  and/or  $\text{Ti}^{+2}$  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  $\text{Ti}^{+3}$ , it is  
21 preferable to have only  $\text{Ti}^{+2}$  ions in solution which as they are reduced to the metal are  
22 replaced with other  $\text{Ti}^{+2}$  ions from the anode thus requiring  $\text{TiO}$  in the anode. Thus  
23 desirably the fused salt initially contains  $\text{Ti}^{+2}$  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  $\text{Ti-F}$  bond is stronger than the  $\text{Ti-Cl}$  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  $\text{TiF}_6^{-3}$   
33 and the  $\text{TiF}_6^{-2}$  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  $\text{Ti}^{+3}$  ions are released from the composite anode to produce the  $\text{TiF}_6^{-3}$   
 6  $^3$ . Thus titanium is directly reduced from the +3 valence to the metal. Because  
 7 titanium is multivalent it is also possible that  $\text{Ti}^{+3}$  is reduced to  $\text{Ti}^{+2}$  and then to the  
 8 metal  $\text{Ti}^0$ . 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/cm<sup>2</sup> range. The  
 22 most desirable cathode current densities are in the 0.1 to 2.0 amperes/cm<sup>2</sup> range, and  
 23 the preferred cathode current densities are in the 0.25 to 1 amperes/cm<sup>2</sup> 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/cm<sup>2</sup>.

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 electrolyte (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  $Al_2O_3$ -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/cm<sup>2</sup>. 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/cm<sup>2</sup> 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 TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>3</sub> 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/cm<sup>2</sup>, 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/cm<sup>2</sup>. 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 Y<sub>2</sub>O<sub>3</sub> 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 HfO<sub>2</sub> 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/cm<sup>2</sup>  
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  $1400^\circ\text{C}$  and then electrolyzed at a cathode current density of  $0.25 \text{ amps/cm}^2$  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%  $\text{TiO}_2$  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  $1200^\circ\text{C}$ . 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  $\text{AlCl}_3$  – 35  $\text{NaCl}$  mole %) -20 mole %  $\text{NaF}$  was  
16 utilized as the electrolyte at an operating temperature of  $190^\circ\text{C}$ . 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  $1 \text{ amps/cm}^2$ .

20 Example 11

21 Example 10 was repeated with a cathode current density of  $0.25 \text{ amps/cm}^2$ .  
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  $650^\circ\text{C}$  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 1450°C which produced the titanium suboxide of  $Ti_2O_3$  with no other suboxides or  
5 contaminates such as TiC. The  $Ti_2O_3$  was mixed with graphite flake, a binder of  
6 phenolic resin, and pressed into a block. The block was heated in the absence of air to  
7 1100°C which formed an anode. The resulting composite anode was used in a fused  
8 salt consisting of the eutectic of LiCl-KCl operated at 500°C. Electrolysis was  
9 conducted in trial one at 1 amp/cm<sup>2</sup> 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  $TiCl_4$  was bubbled onto the sponge which  
12 produced  $TiCl_2$  in the salt bath.  $TiCl_4$  continued until a concentration of 5%  $TiCl_2$  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  $TiCl_2$  was  
18 generated, and in trial one the electrolysis was performed at 40 amps/cm<sup>2</sup>. 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/cm<sup>2</sup> which produced titanium particles in  
21 approximately the same size as the 40 amps/cm<sup>2</sup> current density trial. In trial three  
22 electrolysis was also performed at 125 amps/cm<sup>2</sup> 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/cm<sup>2</sup> 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  $TiO_2$  and carbon were heated under a pressure of 0.01 residual argon  
29 atmosphere to 1850°C 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 1100°C which formed a composite anode. The resulting composite anode was placed  
32 in a salt mixture of 60NaCl-40MgCl<sub>2</sub> and 20 mole percent NaF based on the chloride  
33 salt mixture operated at 600°C. In trial one the electrolysis was performed at 0.15

1 amps/cm<sup>2</sup> 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 TiCl<sub>4</sub> was bubbled onto the sponge that produced TiCl<sub>2</sub> until the  
 4 concentration was 8% TiCl<sub>2</sub> in the salt. Electrolysis was performed at 0.15 amps/cm<sup>2</sup>  
 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-CaCl<sub>2</sub> operated at 650°C. Electrolysis was performed at 0.5  
 19 amps/cm<sup>2</sup> 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  $\text{TiO}_2$  was mixed with carbon and heated in a 90% nitrogen 10% hydrogen  
5 atmosphere to  $1600^\circ\text{C}$  which produced titanium nitride (TiN). The TiN was pressed  
6 and sintered at  $2000^\circ\text{C}$  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  $700^\circ\text{C}$ . Electrolysis was  
8 conducted at  $0.5 \text{ amps/cm}^2$  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  $\text{TiO}_2$  was mixed with carbon in a ratio of 1 to 1.5 over stoichiometry and  
12 heated in argon at  $1600^\circ\text{C}$  which produced titanium carbide (TiC). The TiC was  
13 pressed and sintered at  $2000^\circ\text{C}$ . The TiC was used as an anode in the same salt as in  
14 Example 17. During electrolysis at  $1 \text{ amp/cm}^2$  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  $\text{CO}_2/\text{CO}$  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  $\text{TiO}_2$  with stoichiometric carbon  
23 in a vacuum of 0.01 atmosphere at a temperature of  $1850^\circ\text{C}$ . The TiO was then  
24 pressed and practically sintered at  $1450^\circ\text{C}$  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  $900^\circ\text{C}$ . 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  $\text{CO}_2/\text{CO}$ .

29 Example 20

30 Example 19 was repeated using  $\text{Ti}_2\text{O}_3$  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  $750^\circ\text{C}$ . 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 CaCl<sub>2</sub> operated at 900<sup>0</sup>C showed a  
4 considerable solubility of the reduced suboxide of titanium TiO. In a salt bath  
5 operated at 900<sup>0</sup>C 5 wt % TiO was added and electrolysis conducted with a carbon  
6 anode. Titanium particularate was deposited on the cathode at a current density of 1  
7 amp/cm<sup>2</sup>. 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 particularate.

10 Example 23

11 A molten salt composition consisting of the CaCl<sub>2</sub>-NaCl eutectic containing  
12 20 mole % NaF was operated at 750<sup>0</sup>C 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/cm<sup>2</sup>. Titanium particularate was deposited on  
15 the cathode and CO<sub>2</sub> /CO was evolved from the carbon anode.

16 Example 24

17 TiO was produced as described in Example 15 and mixed with carbon  
18 particularate. 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 680<sup>0</sup>C.  
21 Electrolysis was performed at 1 amps/cm<sup>2</sup> which produced titanium particularate 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/cm<sup>2</sup> concurrent with  
27 hydrogen bubbling under the cathode. The deposit was titanium particularate 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/cm<sup>2</sup> 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 Ti<sub>2</sub>O<sub>3</sub> was then added at 10wt% of the melted CaF<sub>2</sub>. Electrolysis was conducted  
12 between a tungsten cathode and a platinum-iridium anode at a current density of 0.5  
13 amps/cm<sup>2</sup>. 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 CO<sub>2</sub>. 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

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A process for purification of rutile which comprises reacting rutile with carbon at an elevated temperature under an inert atmosphere.
2. The method of claim 1, wherein the temperature is in excess of 1200°C.
3. The method of claim 2, wherein the temperature is between 1200°C and 1850°C.
4. The method of any one of claims 1 to 3, further comprising the steps of forming said purified rutile into an electrode and employing the resulting electrode in electrolytic process to produce purified titanium.

1/4

FIG. 1

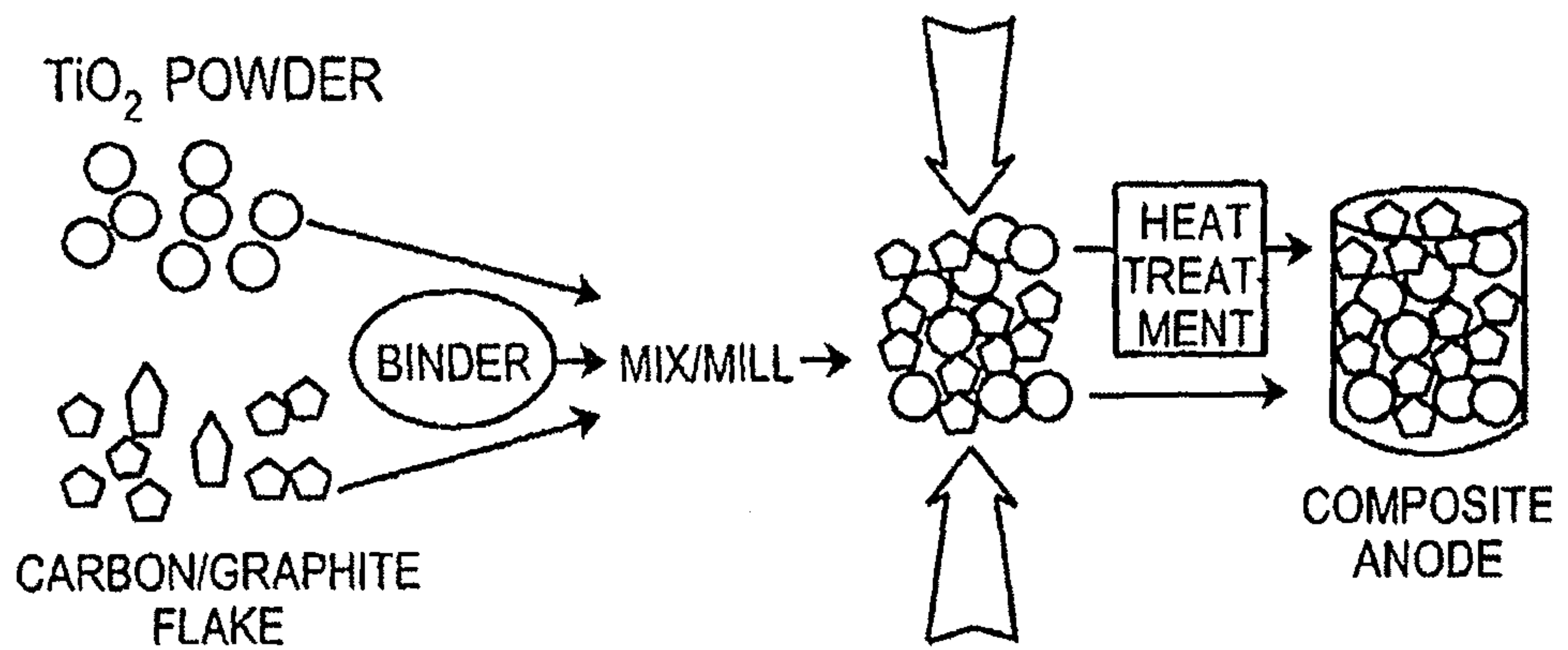


FIG. 2b

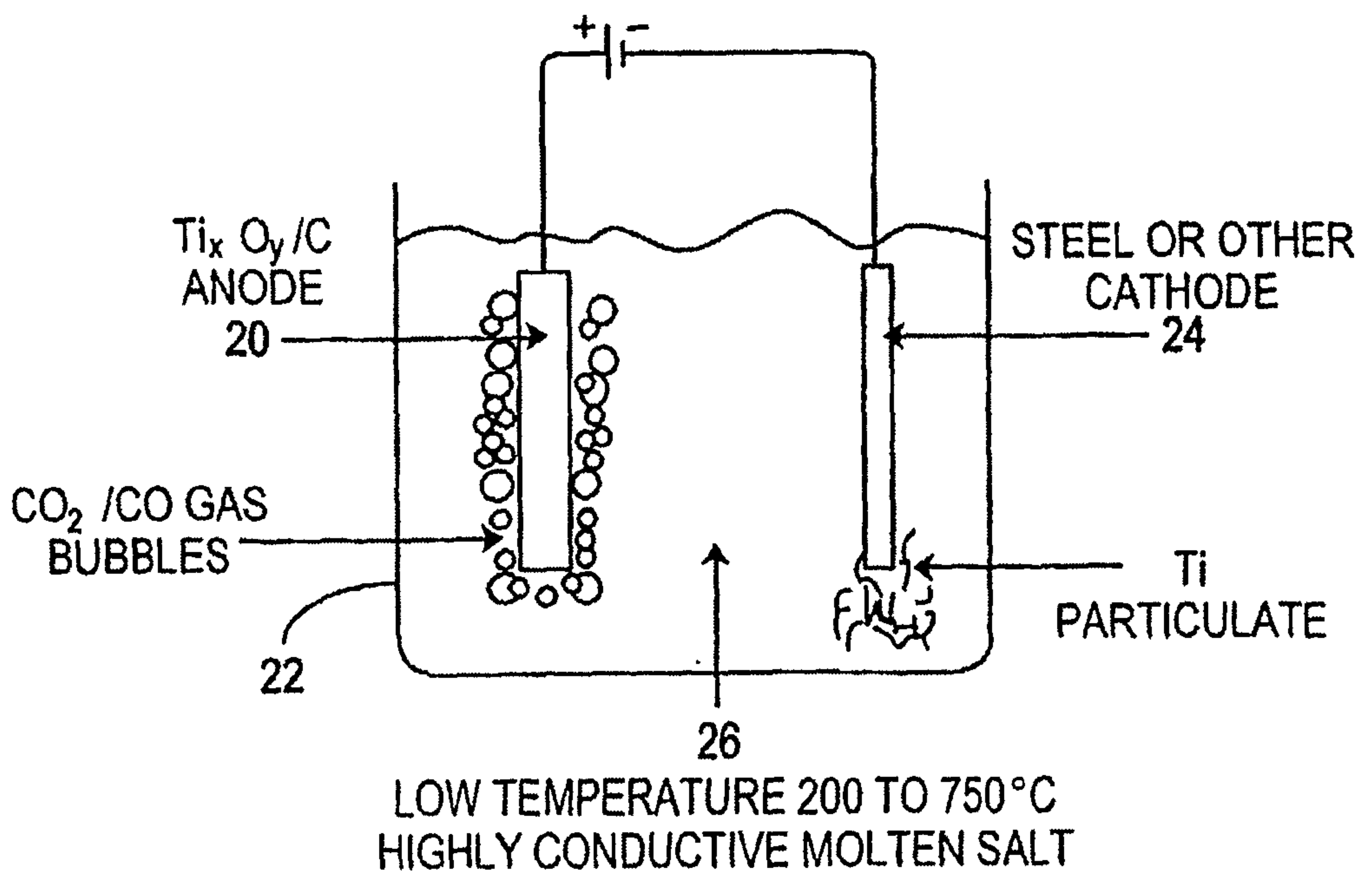
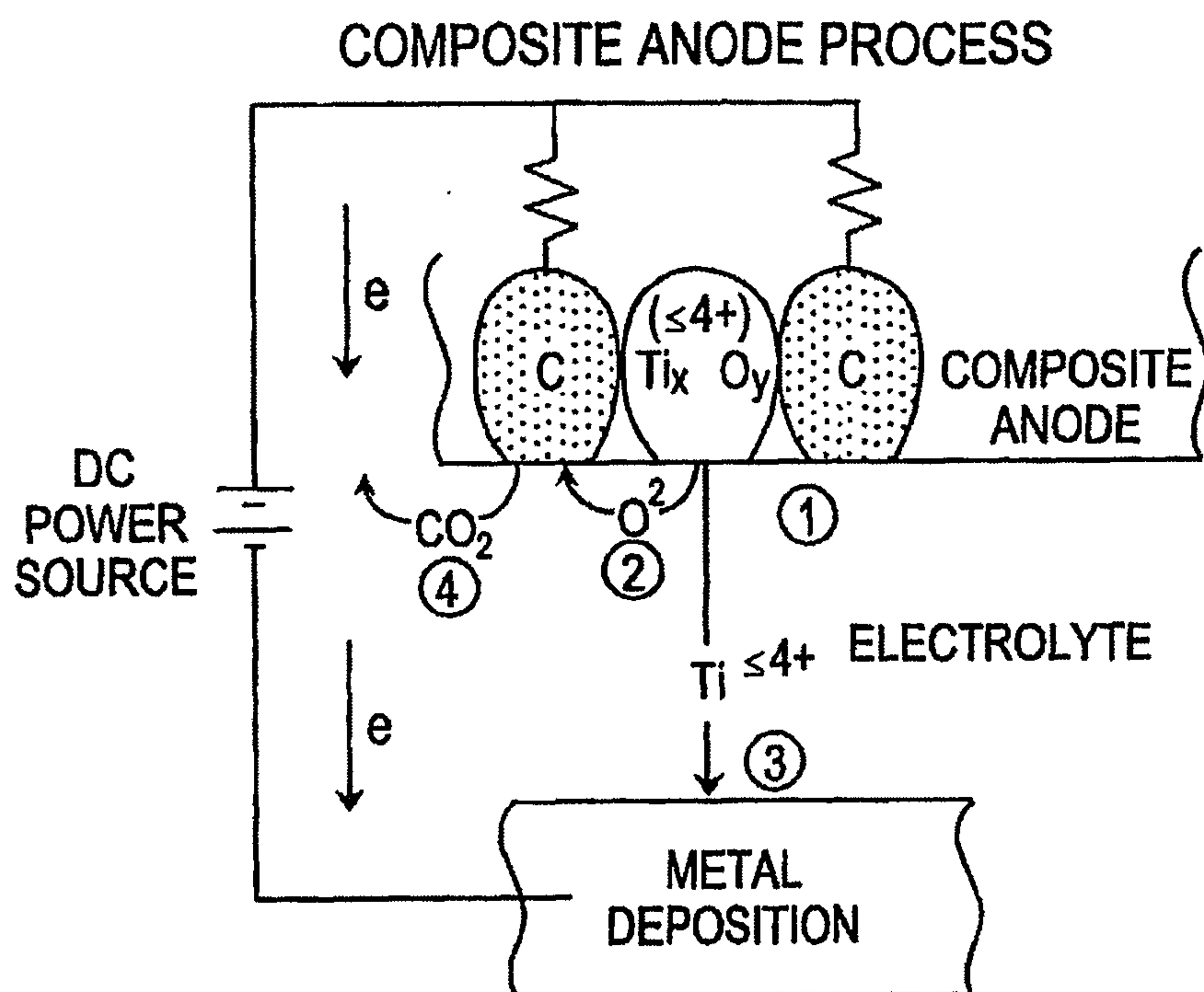


FIG. 2a



3/4

FIG. 3

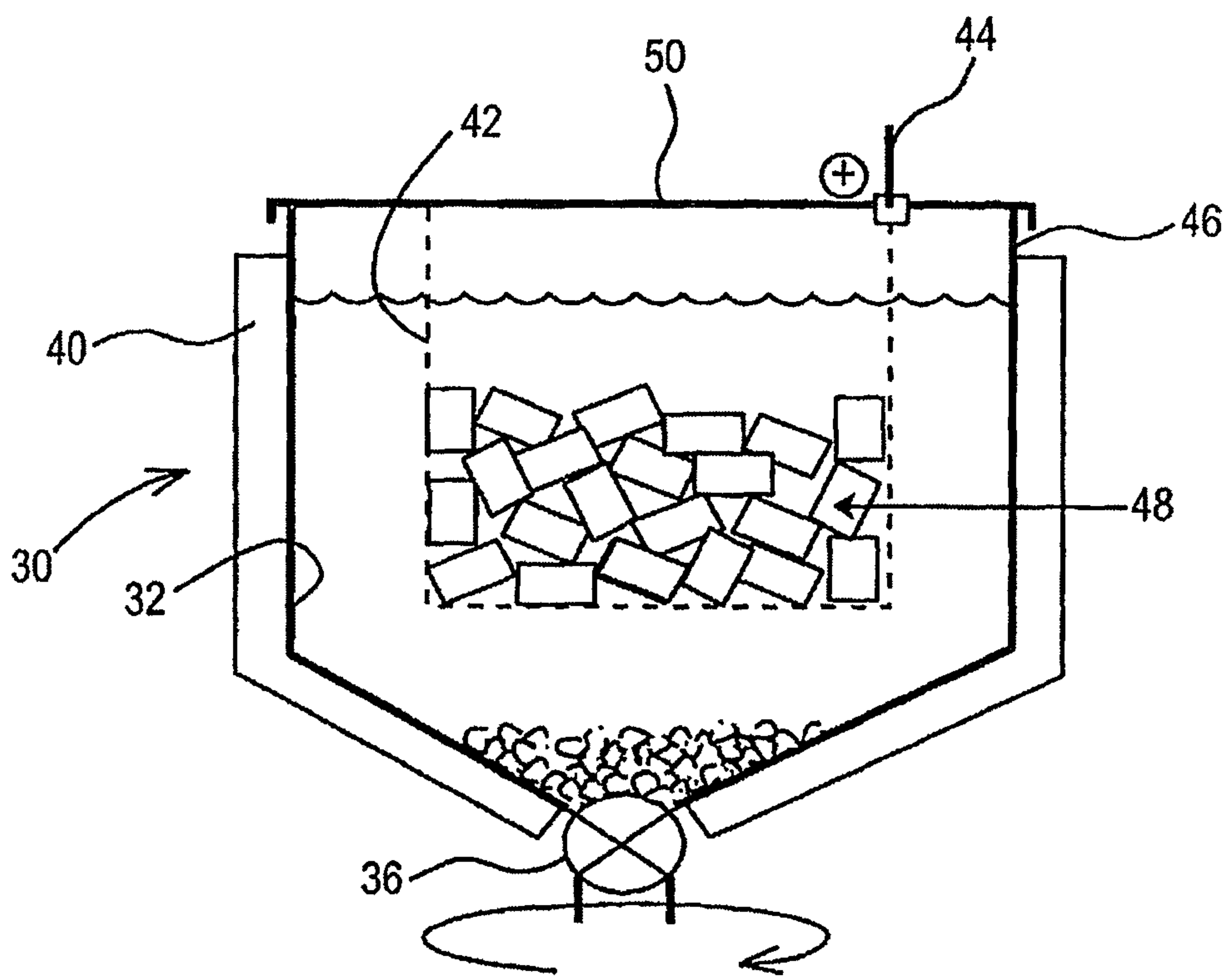


FIG. 4

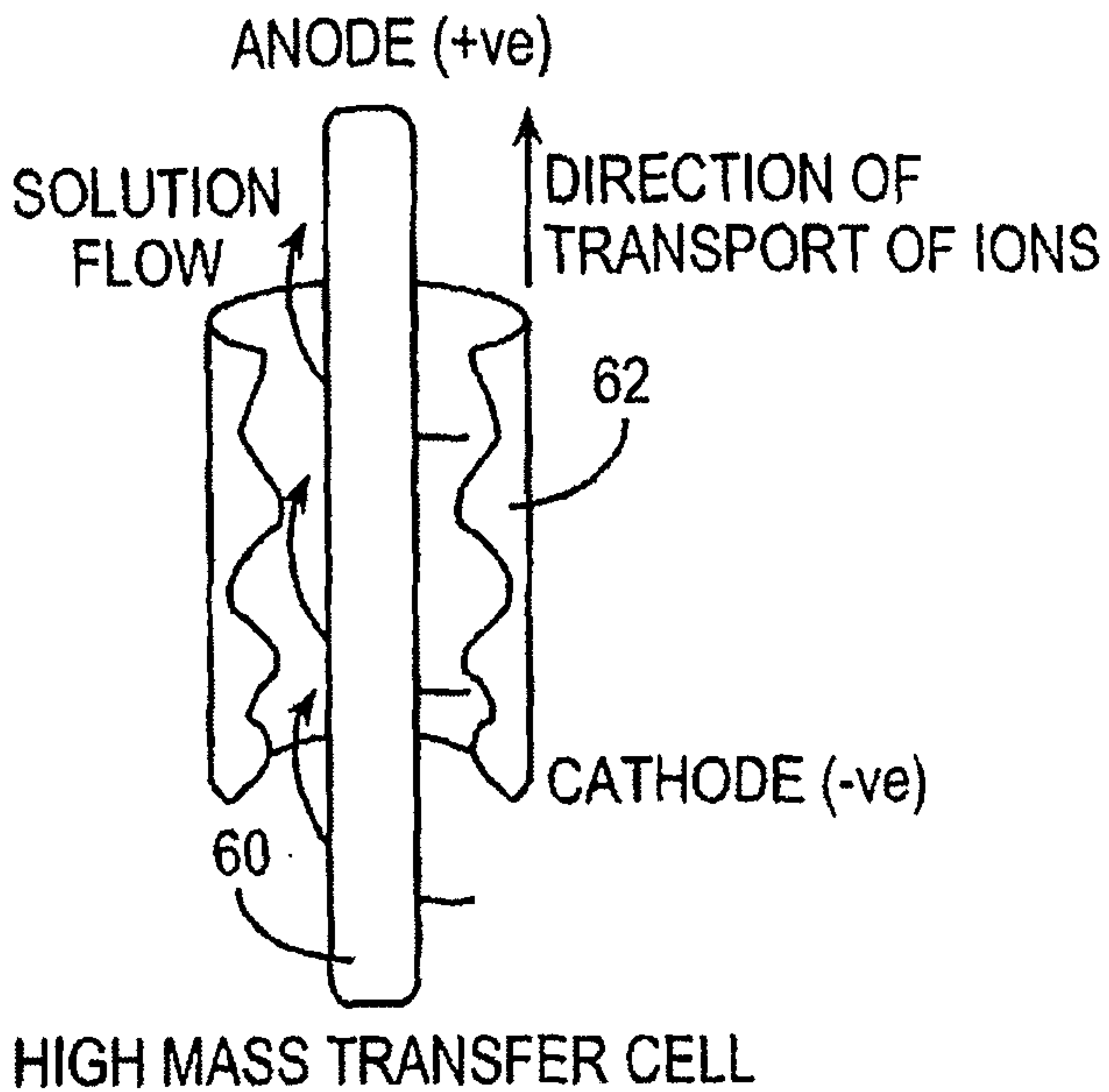
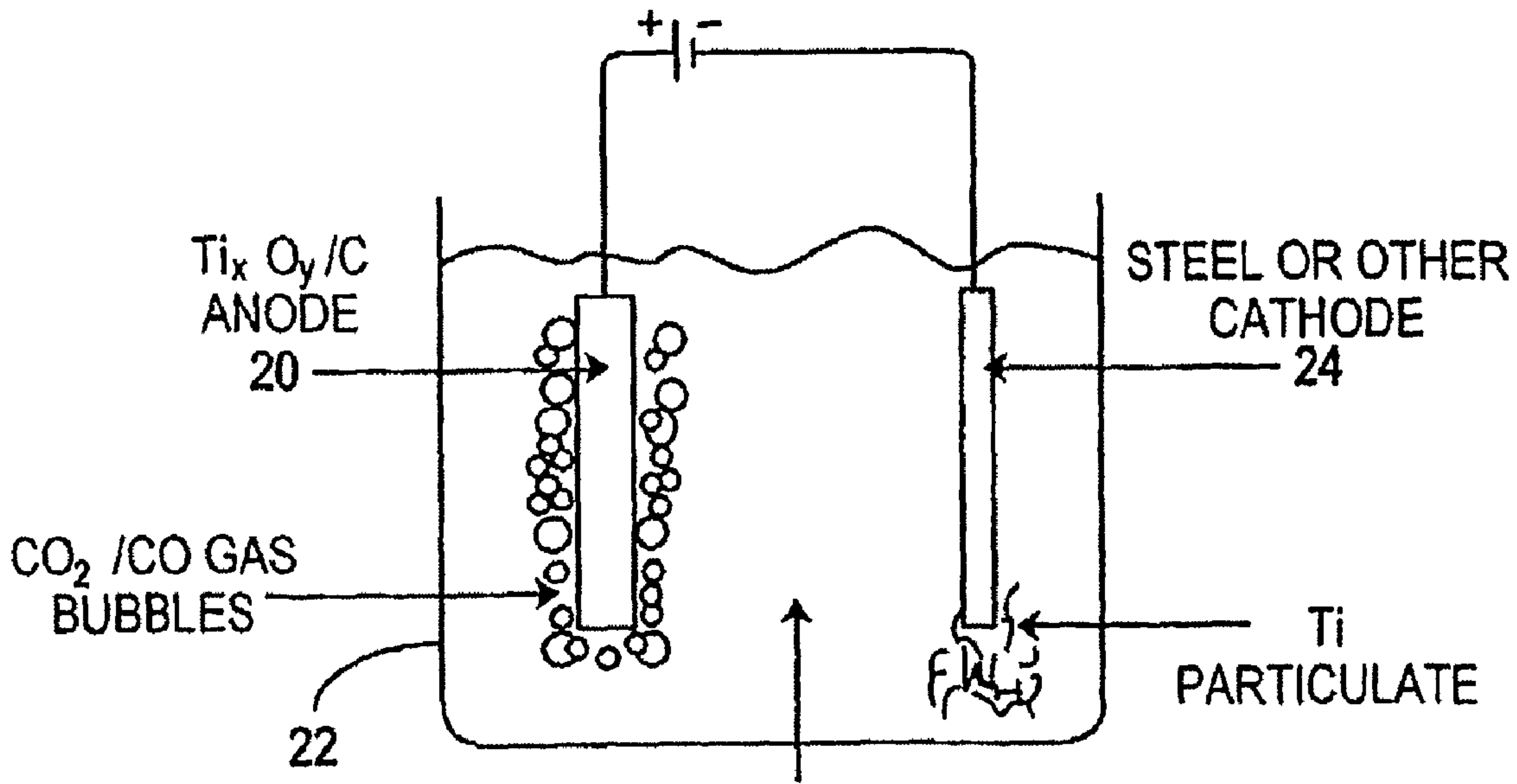


FIG. 5





LOW TEMPERATURE 200 TO 750°C  
HIGHLY CONDUCTIVE MOLTEN SALT