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(54) **Title:** LITHIUM TRITIDE (LiT) ELECTROLYSIS CELL FOR REMOVING TRITIUM FROM LITHIUM METAL

(57) **Abstract:** Lithium hydroxide (LiOH) can be used as solvent for extracting lithium tritide from molten lithium metal, such as that found in a lithium blanket of a nuclear fusion reactor. Use of LiOH avoids the problems of generation of acids, particularly of HF, by the prior art process. Electrochemical cells for electrolyzing LiT are provided with suitably high anode and cathode areas or suitably long flow paths, which have been found to be required for superior operation.



LITHIUM TRITIDE (LiT) ELECTROLYSIS CELL FOR REMOVING TRITIUM FROM LITHIUM METAL

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application claims the benefit of U.S. provisional application serial number 61/643,066 filed May 4, 2012 and the benefit of U.S. provisional application serial number 61/643,119 filed May 4, 2012. Both of these applications are hereby incorporated by reference.

10 GOVERNMENT RIGHTS

[0002] This invention was made with government support under DE-AC52-07NA27344 awarded by the Department of Energy. The government has certain rights in the invention.

15 INTRODUCTION

[0003] Tritium is an important radioisotope used in a broad range of applications, ranging from emergency exit lighting to nuclear weapons. In the future, tritium will serve as the primary fuel for fusion reactors, which will eventually supply much of the energy required by civilization.

[0004] Fusion reactors now on the drawing table, including LLNL's LIFE reactor, require liquid lithium blankets for cooling and breeding tritium fuel. The tritium fuel must be continuously removed from the blanket so that it can be returned to the reactor for burning, via target manufacturing in the case of LIFE. The baseline process for accomplishing this in the LIFE reactor is the well-known Maroni process which uses high-temperature molten mixed alkali metal halide salts (LiCl:LiF:LiBr at 530°C) as an extraction solvent. With the generation of hydrogen isotopes, liquid and gaseous acids such as HCl, HF and HBr (and the deuterium and tritium analogs) form in the salt phase, making these solvents very corrosive, with other problems due to volatility. The separation of the molten lithium and molten chloride salt phases requires numerous high-temperature (530°C) high-speed centrifugal separators, with bearings and seals exposed to the highly corrosive

fluids. Following extraction of lithium tritide from the molten lithium, the tritide anion must undergo electrochemical oxidation in a high-temperature electrochemical cell to form tritium gas, which can then be separated by stripping in stream of inert gas such as xenon or helium. The volatility of TCl, TF and TBr, and other halides of hydrogen isotopes complicate this separation. Alternatives are needed.

SUMMARY

[0005] It has now been determined that other molten lithium compounds, including lithium hydroxide (LiOH) and lithium carbonate (Li₂CO₃) can be used as the solvent for extracting lithium tritide from the molten lithium metal, such as that found in a lithium blanket of a nuclear fusion reactor. Use of LiOH or lithium carbonate avoids the problems of generation of acids, particularly of HF, by the prior art process.

[0006] Theoretical considerations and empirical observations have also led to improvements to electrochemical cells that can be used to carry out electrolysis of lithium tritide dissolved in molten lithium salts, including the lithium halides of the prior art. In particular, the cells need long flow paths to operate most efficiently. Accordingly, electrochemical cells are provided having suitably high anode and cathode areas or suitably long flow paths, which have been found to be required for superior operation. Various teachings provide configurations of cathode and anode, as well as materials requirements.

[0007] In a non-limiting embodiment, a method of removing and recovering tritium from a solution of LiT in molten lithium metal includes the steps of extracting LiT from the molten lithium into a solvent comprising one or more lithium salts and then subjecting the solvent containing LiT to electrolysis in a electrochemical cell operating at a voltage sufficient to reduce lithium ion to lithium metal and to oxidize tritide ion to tritium gas. The cell comprises a spaced apart cathode and anode defining a flow path, and a porous conductive material disposed in the flow path and coupled to the cathode or anode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a flow chart of a LiOH extraction process.

[0009] Figure 2 shows electrochemical reactions of a prior art process.

[0010] Figure 3 show electrochemical reactions of a LiOH process.

[0011] Figure 4 is a schematic of a high temperature electrochemical flow cell.

[0012] Figure 5 shows the dependence of electrolysis efficiency on flow path length.

[0013] Figure 6 is a schematic of an electrochemical cell with a serpentine flow path.

[0014] Figure 7 is a schematic of an electrochemical cell with porous material coupled to the electrodes.

DESCRIPTION

[0015] In one embodiment, LiOH or lithium carbonate is provided for use as a solvent for LiT extraction from molten lithium metal.

[0016] A method of removing LiT from a lithium blanket to recover tritium for reuse involves transferring molten lithium containing LiT from the lithium blanket to a separator; extracting a fraction of the LiT from the molten lithium into a solvent phase by contacting the molten lithium phase in an extraction column of the separator with a solvent phase comprising molten lithium hydroxide or molten lithium carbonate; separating the phases after contacting; recovering the solvent phase containing a fraction of the LiT present in the molten lithium before contact; and subjecting the solvent phase containing LiT to an electrochemical process to recover tritium for reuse.

[0017] In various embodiments, the separator is a centrifugal separator or a non-centrifugal contactor. In an exemplary embodiment, the molten lithium transferred from the lithium blanket has a concentration of 0.1 to 10 ppm LiT. Typical is to transfer the molten lithium to the separator at a rate of 5-10 kg/sec. The electrochemical processes comprises operating an electrochemical cell at a temperature above 450°C (the approximate melting point of LiOH) and below 650°C (the melting point of LiT).

[0018] In another embodiment, a special electrochemical cell and method is provided for use with any LiT solvent, including but not limited to LiF, LiF-LiCl-LiBr, LiOH, and lithium carbonate. The cell is made of materials that withstand the high temperature conditions, such as platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys, and is characterized by high surface area electrodes. To illustrate, a method of removing and

recovering tritium from a solution of LiT in molten lithium metal involves the steps of extracting LiT from the molten lithium into a solvent comprising one or more lithium salts and then subjecting the solvent containing LiT to electrolysis in an electrochemical cell operating at a voltage sufficient to reduce lithium ion to lithium metal and to oxidize tritide ion to tritium gas. The cell has a spaced apart cathode and anode defining a flow path, and a porous conductive material disposed in the flow path and coupled to the cathode or anode. Coupling the porous material increases the effective surface area of the electrodes and provides efficient conversion despite what would otherwise be too short of a flow path. Examples of solvent include lithium halides (LiF, LiCl, LiBr), lithium hydroxide (LiOH) and lithium carbonate (Li₂CO₃).

[0019] In various embodiments, the porous conductive material is selected from reticulated vitreous carbon (RVC) foam, monolithic resorcinol-formaldehyde (RF) based carbon aerogel, or an appropriate conductive metal foam. An example of the latter is metal foam made from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys. The porous conductive material can also be made by coating a porous substrate with an appropriate corrosion-resistant metal coating, which includes, but is not limited to, platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys. Electrodes of ferrous and nickel-based steels can also be used, but are more prone to corrosive attack.

[0020] In a variation, the flow path contains a first porous conductive material coupled to the cathode, a second porous conductive material coupled to the anode, and a separator disposed between the first and second porous conductive materials. The separator prevents shorting between the high surface area electrodes and also prevents convective mixing of electrolyte from the anode compartment (anolyte) with that in the cathode compartment (catholyte). In various embodiments, the cathode or anode is coated with a metal selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys.. Especially when the solvent is a lithium halide, the cathode, anode, or porous conductive material can be coated with a composition selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and

refractory-metal alloys.. Electrodes of ferrous and nickel-based steels can also be used, but are more prone to corrosive attack.

[0021] A method of operating an electrochemical cell according to any of the embodiments described herein comprises applying a voltage sufficient to reduce lithium ion to lithium metal and oxidize tritide anion to gaseous tritium.

[0022] In another embodiment, an electrochemical cell has interdigitated electrodes to provide a long flow path. The cell has an array of parallel cathodes, and an array of parallel anodes. When combined, the cathodes and anodes define a serpentine flow path, with one anode and one cathode defining the walls of each channel, and with molten lithium salt electrolyte in the flow path. The electrolyte comprises a solution of LiT in a molten lithium salt, such as LiF, LiCl, LiBr, LiOH, or lithium carbonate. Optionally, the cathode or anode are coated with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys, , which is especially effective when the electrolyte comprises a halide. The cell is operated by applying a voltage sufficient to reduce lithium ion to lithium metal at the cathode and oxidize tritide ion to tritium gas at the anode.

[0023] A method of removing and recovering tritium from a solution of LiT in molten lithium metal involves extracting LiT from the molten lithium into a solvent comprising one or more lithium salts and subjecting the solvent containing LiT to electrolysis in a electrochemical cell operating at a voltage sufficient to reduce lithium ion to lithium metal and to oxidize tritide ion to tritium gas, wherein the cell as described above comprises a cathode and anode defining a serpentine flow path.

Extraction of Tritium using LiOH as Solvent

[0024] An alternative electrolytic process for the conversion of lithium tritide to tritium gas and metallic lithium based upon the use of benign lithium hydroxide electrolyte (LiOH) which is an extremely attractive alternative to the very volatile and corrosive lithium halide electrolyte. Figure 1 shows the process flow chart for halide-free alternative to Maroni tritium separation process. Molten lithium hydroxide is used to extract lithium tritide from the lithium blanket, or buffer in a centrifugal (or non-centrifugal) contactor. The lithium hydroxide with the dissolved

lithium tritide solute then flows through an electrochemical cell, where the lithium tritide is converted to lithium metal, which is deposited on the cathode, and tritium gas, which forms during the anodic oxidation of tritide anion. Figure 2 shows pertinent electrochemistry for halide-free alternative to Maroni tritium separation process, showing reactions involved in the conventional process for comparison. Specifically, the mixed molten halide salt used in the conventional process can be converted to bromine, fluorine and chlorine gas as the potential at the anode is increased. In the presence of a concentrated halide salt, the steel anode will also undergo corrosion, with the dissolution of iron and chromium ions, as shown. The oxidation-reduction potentials for conducting these reactions in aqueous solution at standard conditions are known, and are given to provide some insight into the relative potential levels where these reactions occur. Since the electrolyte temperature and concentrations of the various ions are different in the molten salt case, the actual oxidation-reduction potentials will be different.

[0025] The electrode reactions for the electrolysis cell are expected to occur within the thermochemical limits of the lithium hydroxide electrolyte. Figure 3 shows pertinent electrochemistry for halide-free alternative to Maroni tritium separation process, showing possible electrode reactions only. Figure 4 shows schematic representation of the high-temperature electrochemical flow cell for the halide-free alternative to Maroni tritium separation process. The design of this electrochemical cell required knowledge of the operative mass transport mechanisms in the electrochemical cell. The rate of mass transfer in this electrochemical cell has contributions from diffusion, convection, and electromigration:

[0026]

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \nabla C_i = z_i F \nabla \cdot (\mu_i C_i \nabla \phi) + \nabla \cdot (D_i \nabla C_i) + R_i$$

The electromigration term requires knowledge of the potential distribution and simultaneous solution of:

$$\nabla^2 \phi = -\frac{F}{\epsilon} \sum_i z_i C_i$$

Substantial simplifications are possible for steady state conditions and strong supporting electrolyte.

[0027] The design of the required electrochemical cell assumes that the electrochemical reaction for conversion of lithium tritide to lithium metal and tritium gas is diffusion limited. Therefore, the limiting current density at any point along the length of the cell (i_L) is dependent upon the local solute concentration and mass transfer coefficient, which in turn is dependent upon the thickness of the mass transport boundary layer. This boundary layer (δ) is reflected in the Sherwood number (Sh), which can be estimated from dimensionless correlations involving the Reynolds and Schmidt numbers (Re and Sc).

[0028]
$$k_p^0 = \frac{D_{AB}}{D} x Sh$$

$$Sh = 0.023 Sc^{0.33} Re^{0.80}$$

[0029]
$$\frac{k_p^0}{D_{AB}} = 0.023 \left(\frac{\mu}{\rho D_{AB}} \right)^{0.33} \left(\frac{D \mu_0 \rho}{\mu} \right)^{0.80}$$

[0030] The differential mass balance for lithium tritide solute along the length of the cell can be formulated in terms of a simple ordinary differential equation, whose solution shows that the solute concentration and the corresponding limiting current density decreases with increasing path length (x) in the cell. Integration of the expression for the limiting current density over the entire length of the cell yields the following expression for the total cell current(I), where n is the number of electrons transferred in the reaction, F is Faraday's constant, FW is the formula weight of the solute, k_p^0 is the mass transfer coefficient calculated from the flow-rate dependent Sherwood number, a is the width of the anode or cathode

compartment in the electrochemical cell, and G is the volumetric flow rate of anolyte or catholyte through the respective compartment.

5 [0031]
$$I = \frac{nF}{FW} \rho C_0 G \left[1 - \exp \left[-k_p^0 \frac{a}{G} x \right] \right]$$

[0032] The average current density over the length of the cell (L) is calculated by dividing the total current (I) by the area ($A = a \times L$).

10

[0033]
$$\langle i_L \rangle = \frac{I}{a \times L} = \frac{nF}{FW} \frac{\rho C_0 G}{a \times L} \left[1 - \exp \left[-k_p^0 \frac{a}{G} x \right] \right]$$

[0034] If the total current required for conversion of the solute to lithium metal and tritium gas is first calculated with Faraday's law, the average current density, which depends upon the wetted perimeters of the electrode compartment, the lengths of the electrode, the electrolyte flow rate through the electrode compartment, and temperature-dependent properties of the flowing electrolyte, the required electrode area can be calculated as follows:

20 [0035]
$$Area = \frac{I_{required}}{\langle i_L \rangle}$$

[0036] Figure 5 shows the results of modeling mass transport in electrochemical flow cell showing a need for long path length for conversion of lithium tritide to plated lithium metal and tritium gas. This curve was calculated based upon
25 aforementioned design equations.

[0037] Calculations thus show that an electrochemical cell for electrolyzing LiT to lithium metal and tritium gas in the presence of molten lithium salts requires a longer cell path than heretofore appreciated. One solution is shown in
30 Figure 6, which schematically shows a cell where the required long channel length for conversion of lithium tritide to lithium metal and dissolve tritium gas is achieved in a compact cell with long serpentine flow path. The anode and cathode are

interdigitated, providing a long and serpentine flow path, and subjecting the LiT to high voltage gradients between the anode and cathode. In various embodiments, the anode or cathode can be coated with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys. When the solvent includes the corrosive halides, it has been found desirable to coat cell components with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys... In another embodiment, the electrodes are made of oxide dispersion strengthened (ODS) ferritic-martensitic steels, optionally clad with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), or other noble-metal and refractory-metal alloys...

[0038] Figure 7 shows a slightly different cell design where large electrode area and enhanced mass transfer are achieved with porous electrodes in a divided cell. The idea is to provide a larger electrode surface area to make up for the short flow path through any conveniently sized electrochemical cell. The solution is to couple a conductive foam to the current collectors of the respective electrodes. In various embodiments, the porous conductive material is selected from reticulated vitreous carbon (RVC) foam, monolithic resorcinol-formaldehyde (RF) based carbon aerogel, or an appropriate conductive metal foam. An example of the latter is metal foam made from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), or other noble-metal and refractory-metal alloys. The porous conductive material can also be made by coating a porous substrate with an appropriate corrosion-resistant metal coating, which includes, but is not limited to, platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys. Electrodes of ferrous and nickel-based steels can also be used, but are more prone to corrosive attack. Together, the foam material and collector need to be stable at the temperature of use and in the presence of any corrosive materials resulting from the process.

[0039] The porous material lies in the flow path between the electrodes. In a variation, there is a porous conductive material coupled to each of the electrodes, and a separator is disposed in the flow path between the two porous materials. The separator is an insulating, ion conducting material that

is porous, but does permit convective mixing across the separator. Examples include ceramic separators.

[0040] In various embodiments, the methods described herein are used in processes to recover and recycle tritium (as lithium tritide or LiT) from a lithium blanket that is being used as coolant for a nuclear fusion engine. The fusion process emits neutrons that react with molten lithium metal in the blanket to produce, among other products, lithium tritide. Periodically, the blanket needs to be cleaned or purified of the LiT, which would otherwise continue to build up. The method of clean up involves removing the built up LiT from the molten lithium by extracting it into a solvent containing one or more molten lithium salts. In the prior art, extraction involved use of a centrifugal separator with moving parts to mix and separate the phases.

[0041] A non-centrifugal contactor is now available to carry out the extraction and separation of phases using no moving parts. It is the subject of an international application filed on May 6, 2013 by Lawrence Livermore National Laboratory entitled "Non-centrifugal Contactor for Molten-Salt Tritium-Extraction Process," the disclosure of which is useful for background reference and is hereby incorporated by reference.

[0042] Briefly, the non-centrifugal contactor has an extraction column that is fluidically coupled to separator that operates with no moving parts under a cyclonic (or hydrocyclonic) regime. Mixing or contacting of the phase occurs in the extraction column, and mixing is enhanced through the use of distributor plates that turn one or both phases into small drops of higher surface area, by the use of ultrasonic energy, by electromagnetic pulsing of the lithium metal of the molten lithium, and so on.

[0043] In various embodiments, methods for use of the non-centrifugal contactor involve 1) increasing interfacial area during contacting of the two phases in the extraction column; 2) increasing turbulence in the reactor to increase the mass transfer coefficient during contacting; 3) sizing the extraction column to provide adequate residence time for the extraction to occur during contacting of the two phases; and 4) consolidating and separating the lithium and salt phases after the contacting. Advantageously, the separator has no moving parts.

[0044] Methods of using the non-centrifugal contactor involve feeding the lighter phase (the one containing lithium metal and dissolved LiT) to the extraction column at a rate 1-20 kg/sec. Where a method involves more than 1 feed of the lighter phase, the rate of 1-20 kg/sec is divided between the first and second feeds. In other embodiments, the rate is 5-10 kg/sec, or about 7 kg/sec. In this and other embodiments, the concentrations of LiT in the feeds to the extraction column are typically on the order of 0.1 to 10 ppm, 0.3 to 3 ppm, or 0.5 to 2 ppm.

[0045] In various embodiments of methods described herein, the extraction column has a volume size to achieve a suitable residence time for the extraction. In a non-limiting example, the extraction column has a volume of 5 to 20 m³. Thus in various embodiments, the lighter phase containing lithium metal and lithium tritide is fed at a rate of 1-20 kg/sec, the concentration of LiT in the lighter phase is 0.1 to 10 ppm, extraction column has a volume of 5 to 20 m³. In certain embodiments, the lighter phase is fed at a rate of about 7 kg/sec, the concentration of LiT in the lighter phase at the inlet to the extraction column is about 1 ppm, and the reactor has a volume of about 15 m³.

[0046] The output of the contactor is then input to the electrochemical cells described herein.

EXAMPLES

[0047] Further non-limiting description of embodiments of the current teachings are given in the following examples.

[0048] Example 1 - LiOH as solvent for LiT extraction from molten lithium metal

1. A method of removing LiT from a lithium blanket to recover tritium for reuse, the method comprising

transferring molten lithium containing LiT from the lithium blanket to a separator;

extracting a fraction of the LiT from the molten lithium into a solvent phase by contacting the molten lithium phase in an extraction column of the separator with a solvent phase comprising molten lithium hydroxide or molten lithium carbonate;

separating the phases after contacting;

recovering the solvent phase containing a fraction of the LiT present in the molten lithium before contact; and

subjecting the solvent phase containing LiT to an electrochemical process to recover tritium for reuse.

2. The method according to embodiment 1, wherein the separator is a centrifugal
5 separator.

3. The method according to embodiment 1, wherein the separator is a non-centrifugal contactor.

10 4. The method according to embodiment 1, wherein the molten lithium transferred from the lithium blanket has a concentration of 0.1 to 10 ppm LiT.

5. The method according to embodiment 4, comprising transferring molten lithium to the separator at a rate of 5-10 kg/sec.

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6. The method according to embodiment 1, wherein the electrochemical processes comprises operating an electrochemical cell at a temperature above 450°C and below 650°C.

20 7. The method according to embodiment 1, wherein the solvent phase comprises lithium hydroxide.

8. The method according to embodiment 1, wherein the solvent phase comprises lithium carbonate.

25

[0049] Example 2 – use of cell with any solvent, and with high surface area electrodes

9. A method of removing and recovering tritium from a solution of LiT in molten
30 lithium metal, comprising
extracting LiT from the molten lithium into a solvent comprising one or more
lithium salts and

subjecting the solvent containing LiT to electrolysis in a electrochemical cell
operating at a voltage sufficient to reduce lithium ion to lithium metal and
to oxidize tritide ion to tritium gas,

wherein the cell comprises a spaced apart cathode and anode defining a flow path, and a
5 porous conductive material disposed in the flow path and coupled to the cathode or
anode.

10. The method according to embodiment 9, wherein the solvent comprises LiF,
LiCl, or LiBr.

10

11. The method according to embodiment 9, wherein the solvent comprises LiOH.

12. The method according to embodiment 9, wherein the solvent comprises lithium
carbonate.

15 13. The method according to embodiment 9, wherein the porous conductive material
comprises a reticulated vitreous carbon foam, a carbon aerogel, or a metal foam.

14. The method according to embodiment 13, wherein the porous conductive
material comprises a metal foam made from tantalum or tantalum-tungsten alloys.

20

15. The method according to embodiment 9, wherein the porous conductive material
comprises a metal coating.

16. The method according to embodiment 15, wherein the coating comprises a
25 material selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-
2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...

17. The method according to embodiment 9, wherein the flow path contains a first
porous conductive material coupled to the cathode, a second porous conductive material
30 coupled to the anode, and a separator disposed between the first and second porous
conductive materials.

18. The method according to embodiment 9, wherein the cathode or anode is coated with a metal comprising a material selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...

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19. The method according to embodiment 10, wherein the cathode, anode, or porous conductive material is coated with a composition selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...

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[0050] Example 3 – Electrochemical cell for lithium salt electrolyte and having high surface area electrodes

20. An electrochemical cell, comprising a spaced apart cathode and anode defining a flow path, a porous conductive material disposed in the flow path and coupled to the cathode or anode, and an electrolyte in the flow path, wherein the electrolyte comprising a solution of LiT in a molten lithium salt.

21. The cell according to embodiment 20, wherein the electrolyte comprises LiF, LiCl, or LiBr.

22. The cell according to embodiment 20, wherein the electrolyte comprises LiOH.

23. The cell according to embodiment 20, wherein the electrolyte comprises lithium carbonate.

24. The cell according to embodiment 20, wherein the porous conductive material comprises a reticulated vitreous carbon foam, a carbon aerogel, or a metal foam.

25. The cell according to embodiment 24, wherein the porous conductive material comprises a metal foam made from tantalum or tantalum-tungsten alloys.

26. The cell according to embodiment 20, wherein the porous conductive material comprises a metal coating.

27. The cell according to embodiment 26, wherein the coating comprises Pt, Ru, Ta,
5 or a Ta-W alloy.

28. The cell according to embodiment 20, wherein the flow path contains a first porous conductive material coupled to the cathode, a second porous conductive material coupled to the anode, and a separator disposed between the first and second porous
10 conductive materials, wherein the separator is ion conducting and prevents convective mixing of electrolyte across the separator.

29. The cell according to embodiment 20, wherein the cathode or anode is coated with a metal selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...
15

30. The cell according to embodiment 21, wherein the cathode, anode, or porous conductive material is coated with a composition selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...
20

31. A method of operating an electrochemical cell according to any of embodiments 20-30, comprising applying a voltage sufficient to reduce lithium ion to lithium metal and oxidize tritide ion to tritium gas.
25

[0051] Example 4 – Electrochemical cell with interdigitated electrodes to provide a long flow path.

32. An electrochemical cell, comprising a cathode and anode defining a serpentine flow path and an electrolyte in the flow path, wherein the electrolyte comprises a
30 solution of LiT in a molten lithium salt.

33. The cell according to embodiment 32, wherein the molten lithium salt comprises LiF, LiCl, or LiBr.

34. The cell of embodiment 33, wherein the cathode or anode are coated with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), or other noble-metal and refractory-metal alloys...

35. The cell according to embodiment 32, wherein the molten lithium salt comprises LiOH.

36. The cell according to embodiment 32, wherein the molten lithium salt comprises lithium carbonate.

37. A method of operating an electrochemical cell according to any of embodiments 32-36, comprising applying a voltage sufficient to reduce lithium ion to lithium metal and oxidize tritide ion to tritium gas.

[0052] Example 5 – use of cell with any solvent – long flow path

38. A method of removing and recovering tritium from a solution of LiT in molten lithium metal, comprising

extracting LiT from the molten lithium into a solvent comprising one or more lithium salts and

subjecting the solvent containing LiT to electrolysis in a electrochemical cell

operating at a voltage sufficient to reduce lithium ion to lithium metal and to oxidize tritide ion to tritium gas,

wherein the cell comprises a cathode and anode defining a serpentine flow path.

39. The method according to embodiment 38, wherein the molten lithium salt comprises LiF, LiCl, or LiBr.

40. The method of embodiment 39, wherein the cathode or anode are coated with platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), or other noble-metal and refractory-metal alloys...
41. The method according to embodiment 38, wherein the molten lithium salt
5 comprises LiOH.
42. The method according to embodiment 38, wherein the molten lithium salt comprises lithium carbonate.

We claim:

1. A method of removing LiT from a lithium blanket to recover tritium for reuse,
5 the method comprising
transferring molten lithium containing LiT from the lithium blanket to a
separator;
extracting a fraction of the LiT from the molten lithium into a solvent phase by
contacting the molten lithium phase in an extraction column of the separator
10 with a solvent phase comprising molten lithium hydroxide or molten lithium
carbonate;
separating the phases after contacting;
recovering the solvent phase containing a fraction of the LiT present in the
molten lithium before contact; and
15 subjecting the solvent phase containing LiT to an electrochemical process to
recover tritium for reuse.
2. The method according to claim 1, wherein the separator is a centrifugal separator.
3. The method according to claim 1, wherein the separator is a non-centrifugal
20 contactor.
4. The method according to claim 1, wherein the molten lithium transferred from
the lithium blanket has a concentration of 0.1 to 10 ppm LiT.
- 25 5. The method according to claim 4, comprising transferring molten lithium to the
separator at a rate of 5-10 kg/sec.
6. The method according to claim 1, wherein the electrochemical processes
comprises operating an electrochemical cell at a temperature above 450°C and below
30 650°C.
7. The method according to claim 1, wherein the solvent phase comprises lithium
hydroxide.

8. The method according to claim 1, wherein the solvent phase comprises lithium carbonate.

5

9. A method of removing and recovering tritium from a solution of LiT in molten lithium metal, comprising

extracting LiT from the molten lithium into a solvent comprising one or more lithium salts and

10

subjecting the solvent containing LiT to electrolysis in a electrochemical cell operating at a voltage sufficient to reduce lithium ion to lithium metal and to oxidize tritide ion to tritium gas,

wherein the cell comprises a spaced apart cathode and anode defining a flow path, and a porous conductive material disposed in the flow path and coupled to the cathode or anode.

15

10. The method according to claim 9, wherein the solvent comprises LiF, LiCl, or LiBr.

20

11. The method according to claim 9, wherein the solvent comprises LiOH.

12. The method according to claim 9, wherein the solvent comprises lithium carbonate.

25

13. The method according to claim 9, wherein the porous conductive material comprises a reticulated vitreous carbon foam, a carbon aerogel, or a metal foam.

14. The method according to claim 13, wherein the porous conductive material comprises a metal foam made from tantalum or tantalum-tungsten alloys.

30

15. The method according to claim 9, wherein the porous conductive material comprises a metal coating.

16. The method according to claim 15, wherein the coating comprises Pt, Ru, Ta, or a Ta-W alloy.
- 5 17. The method according to claim 9, wherein the flow path contains a first porous conductive material coupled to the cathode, a second porous conductive material coupled to the anode, and a separator disposed between the first and second porous conductive materials.
- 10 18. The method according to claim 9, wherein the cathode or anode is coated with a metal comprising a noble metal, Pt, Ru, Ta, or Ta-W alloy.
19. The method according to claim 10, wherein the cathode, anode, or porous conductive material is coated with a composition selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...
- 15 20. An electrochemical cell, comprising a spaced apart cathode and anode defining a flow path, a porous conductive material disposed in the flow path and coupled to the cathode or anode, and an electrolyte in the flow path, wherein the electrolyte comprising a solution of LiT in a molten lithium salt.
- 20 21. The cell according to claim 20, wherein the electrolyte comprises LiF, LiCl, or LiBr.
- 25 22. The cell according to claim 20, wherein the electrolyte comprises LiOH.
23. The cell according to claim 20, wherein the electrolyte comprises lithium carbonate.
- 30 24. The cell according to claim 20, wherein the porous conductive material comprises a reticulated vitreous carbon foam, a carbon aerogel, or a metal foam.

25. The cell according to claim 24, wherein the porous conductive material comprises a metal foam made from tantalum or tantalum-tungsten alloys.

5 26. The cell according to claim 20, wherein the porous conductive material comprises a metal coating.

27. The cell according to claim 26, wherein the coating comprises a material selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-2.5W, and Ta-
10 10W), and other noble-metal and refractory-metal alloys...

28. The cell according to claim 20, wherein the flow path contains a first porous conductive material coupled to the cathode, a second porous conductive material coupled to the anode, and a separator disposed between the first and second porous conductive
15 materials, wherein the separator is ion conducting and prevents convective mixing of electrolyte across the separator.

29. The cell according to claim 20, wherein the cathode or anode is coated with a metal selected from platinum alloys, tantalum and tantalum-tungsten alloys (Ta, Ta-
20 2.5W, and Ta-10W), and other noble-metal and refractory-metal alloys...

30. The cell according to claim 21, wherein the cathode, anode, or porous conductive material is coated with a composition selected from Ta, Ta-2.5W alloy, and Ta-10W alloy.
25

31. A method of operating an electrochemical cell according to any of claims 20-30, comprising applying a voltage sufficient to reduce lithium ion to lithium metal and oxidize tritide ion to tritium gas.
30

32. An electrochemical cell, comprising a cathode and anode defining a serpentine flow path and an electrolyte in the flow path, wherein the electrolyte comprises a solution of LiT in a molten lithium salt.
- 5 33. The cell according to claim 32, wherein the molten lithium salt comprises LiF, LiCl, or LiBr.
34. The cell of claim 33, wherein the cathode or anode are coated with a material selected from platinum alloys, tantalum, tantalum-tungsten alloys, Ta, Ta-2.5W, Ta-
10 10W, and other noble-metal and refractory-metal alloys.
35. The cell according to claim 32, wherein the molten lithium salt comprises LiOH.
36. The cell according to claim 32, wherein the molten lithium salt comprises lithium
15 carbonate.
37. A method of operating an electrochemical cell according to any of claims 32-36, comprising applying a voltage sufficient to reduce lithium ion to lithium metal and oxidize tritide ion to tritium gas.
20
38. A method of removing and recovering tritium from a solution of LiT in molten lithium metal, comprising
extracting LiT from the molten lithium into a solvent comprising one or more
lithium salts and
25 subjecting the solvent containing LiT to electrolysis in a electrochemical cell
operating at a voltage sufficient to reduce lithium ion to lithium metal and
to oxidize tritide ion to tritium gas,
wherein the cell comprises a cathode and anode defining a serpentine flow path.
- 30 39. The method according to claim 38, wherein the molten lithium salt comprises LiF, LiCl, or LiBr.

40. The method of claim 39, wherein the cathode or anode are coated with Ta, Ta-2.5W alloy, or Ta-10W alloy.
41. The method according to claim 38, wherein the molten lithium salt comprises
5 LiOH.
42. The method according to claim 38, wherein the molten lithium salt comprises lithium carbonate.

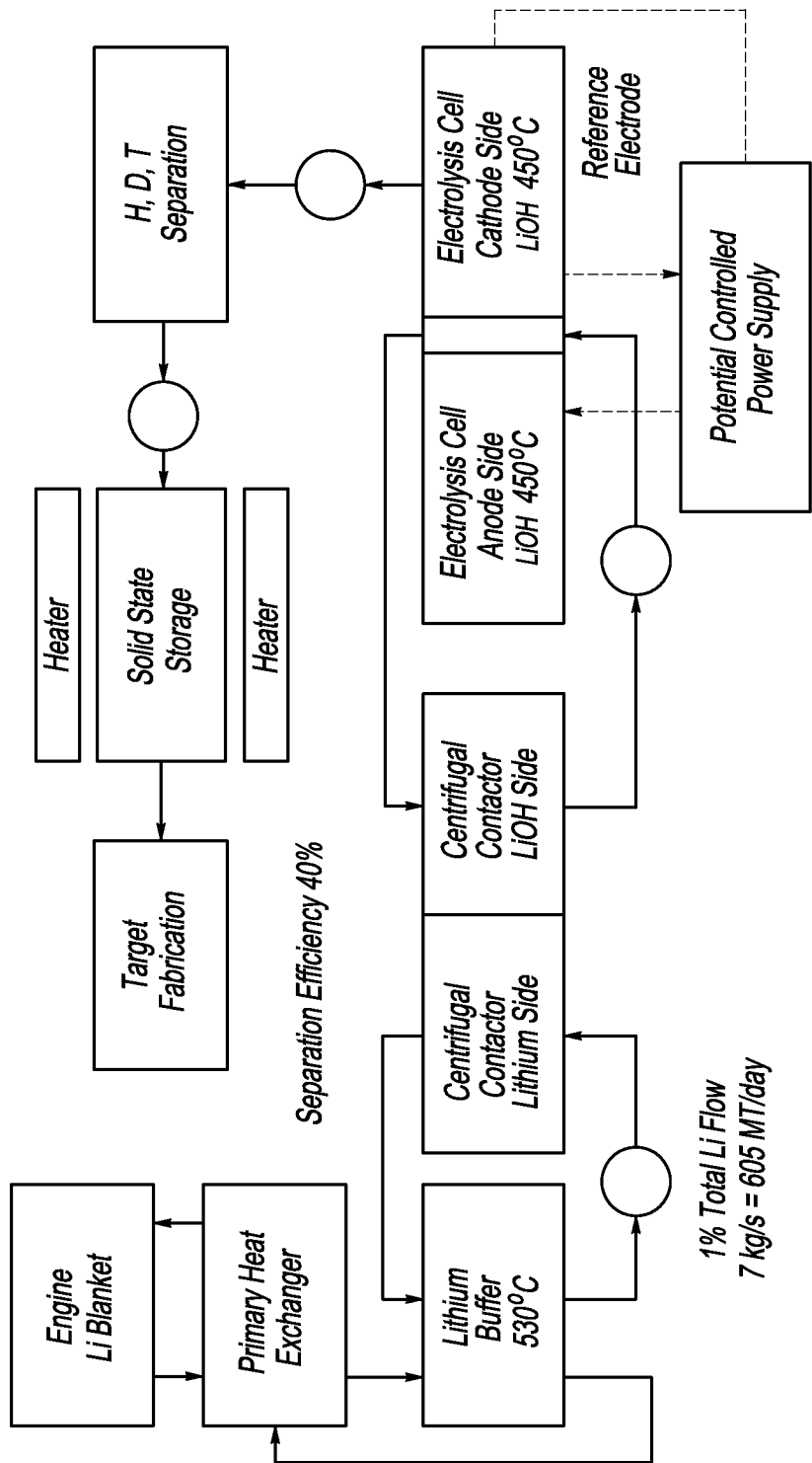


FIG - 1

FIG - 2

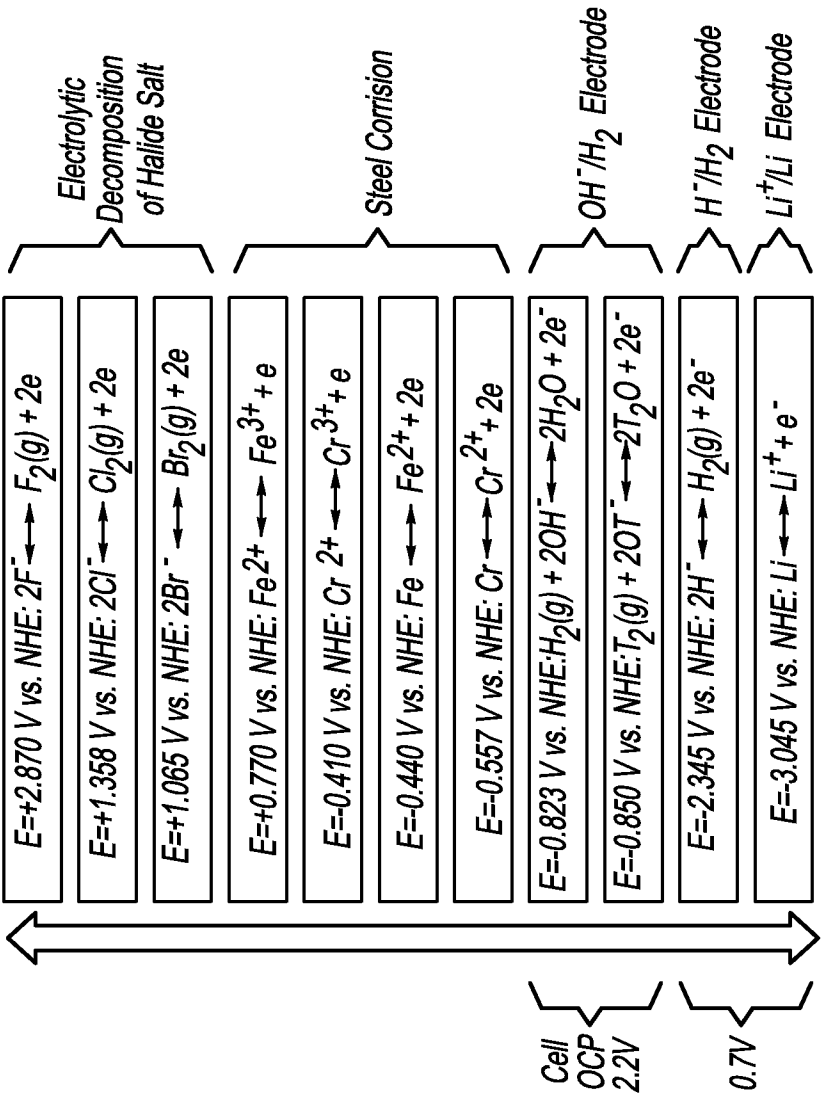
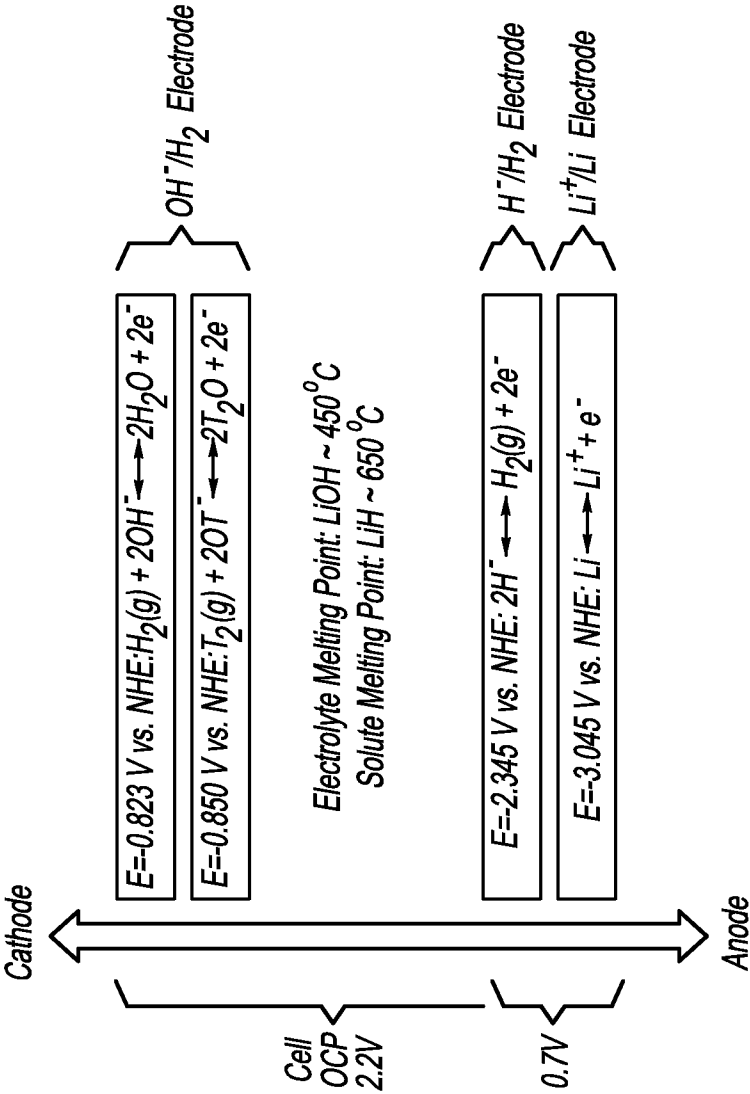
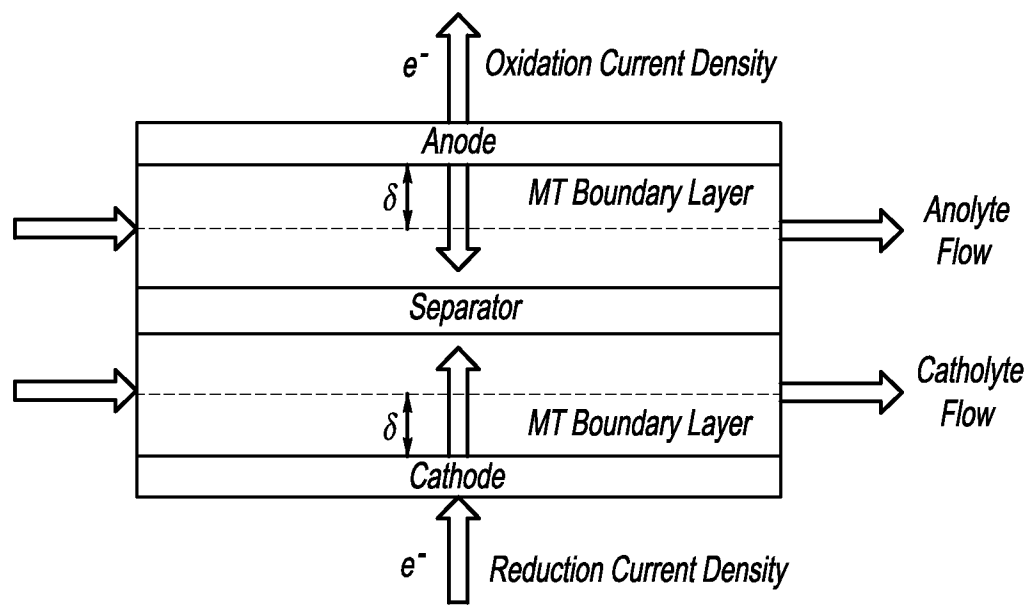


FIG - 3



FIG - 4

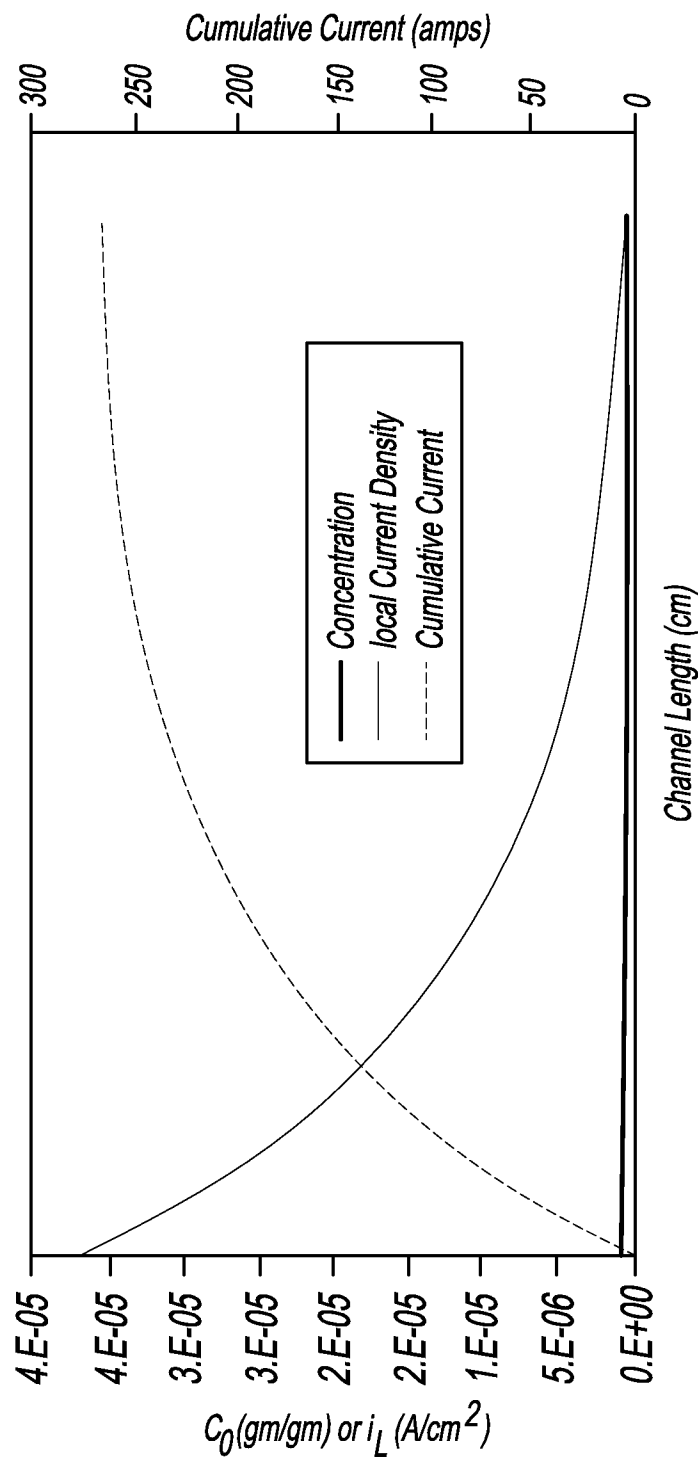


FIG - 5

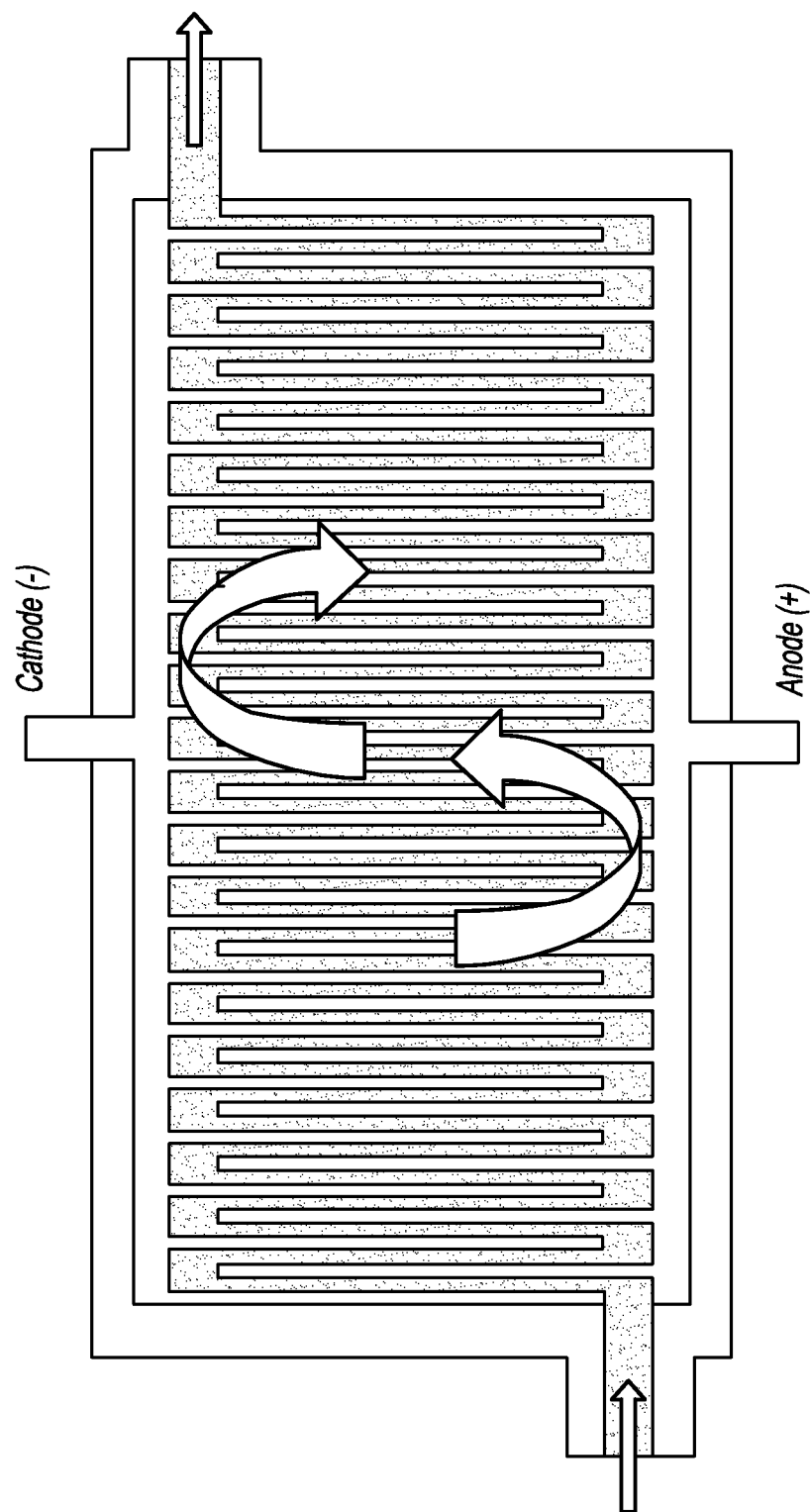


FIG - 6

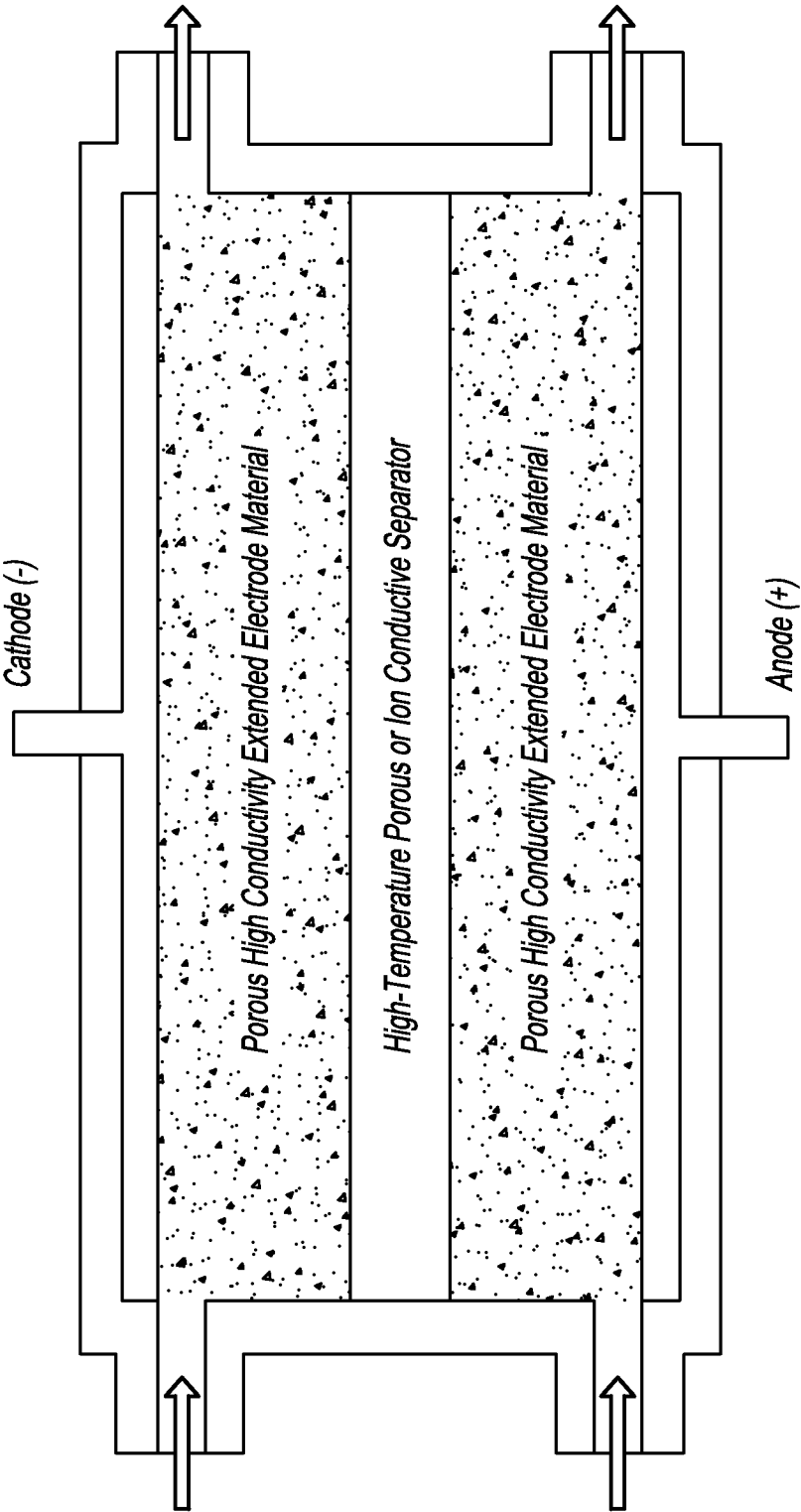


FIG - 7