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(54) **PRODUCING LITHIUM**

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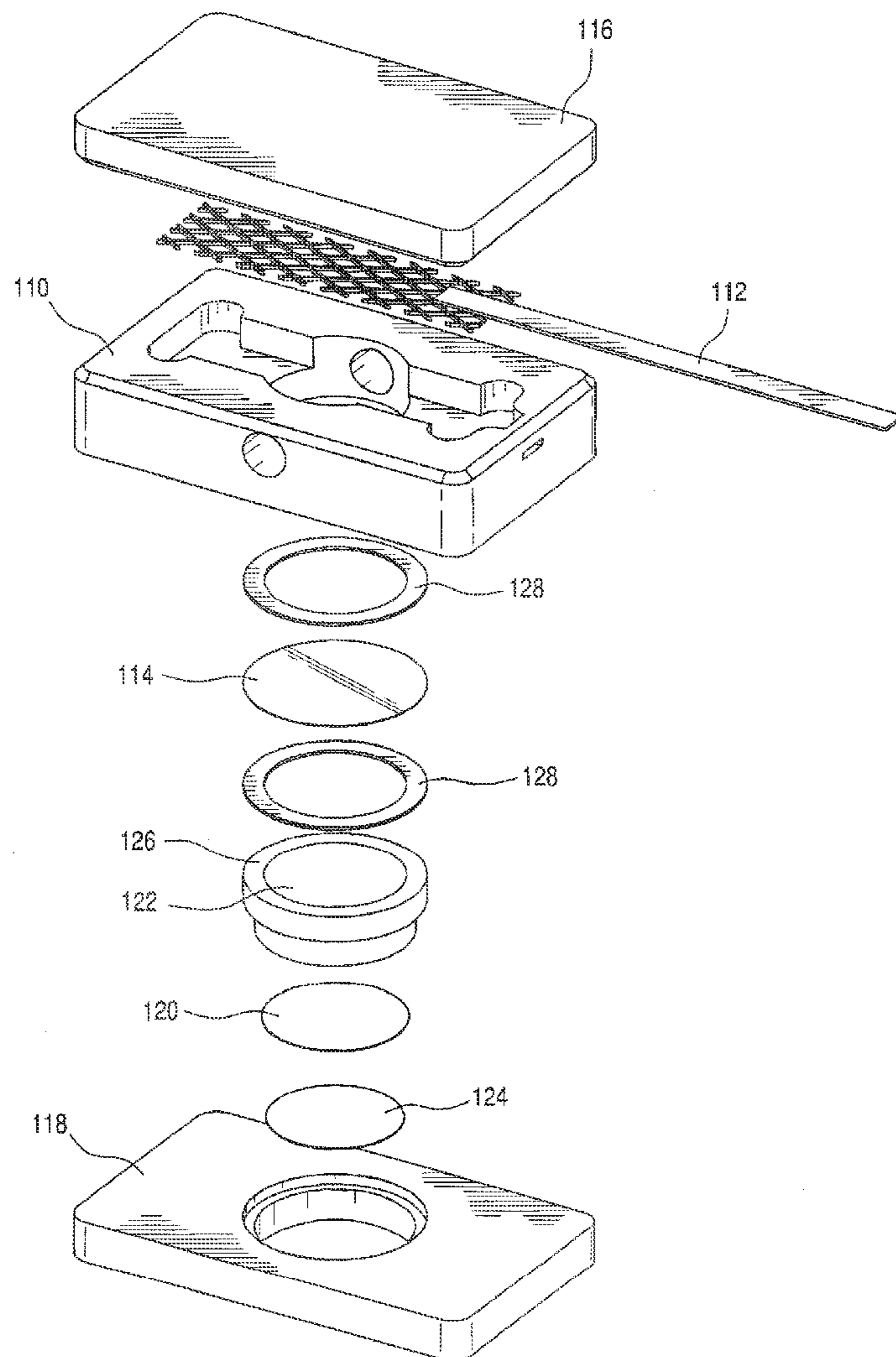
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(57) **ABSTRACT**

A electrolytic process for continuous production of lithium metal from lithium carbonate or other lithium salts by use of an aqueous acid electrolyte and a lithium producing cell structure which includes: a cell body with a cathode within the cell body; an electrolyte aqueous solution within the cell body, the solution containing lithium ion and an anion; and a composite layer intercalated between the cathode and the electrolyte aqueous solution, the composite layer comprising a lithium ion conductive glass ceramic (LI-GC) and a lithium ion conductive barrier film (LI-BF) that isolates cathode-forming lithium from the electrolyte aqueous solution.



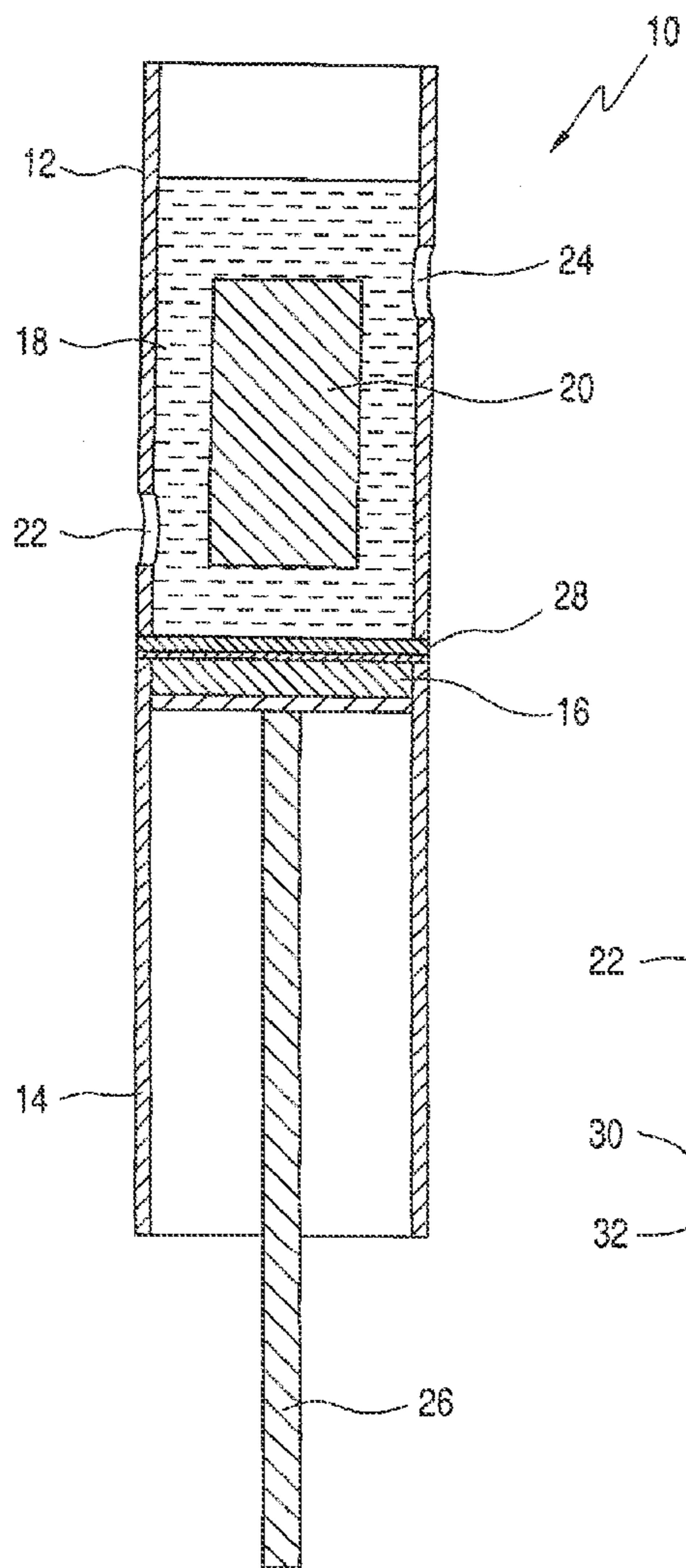


FIG. 1

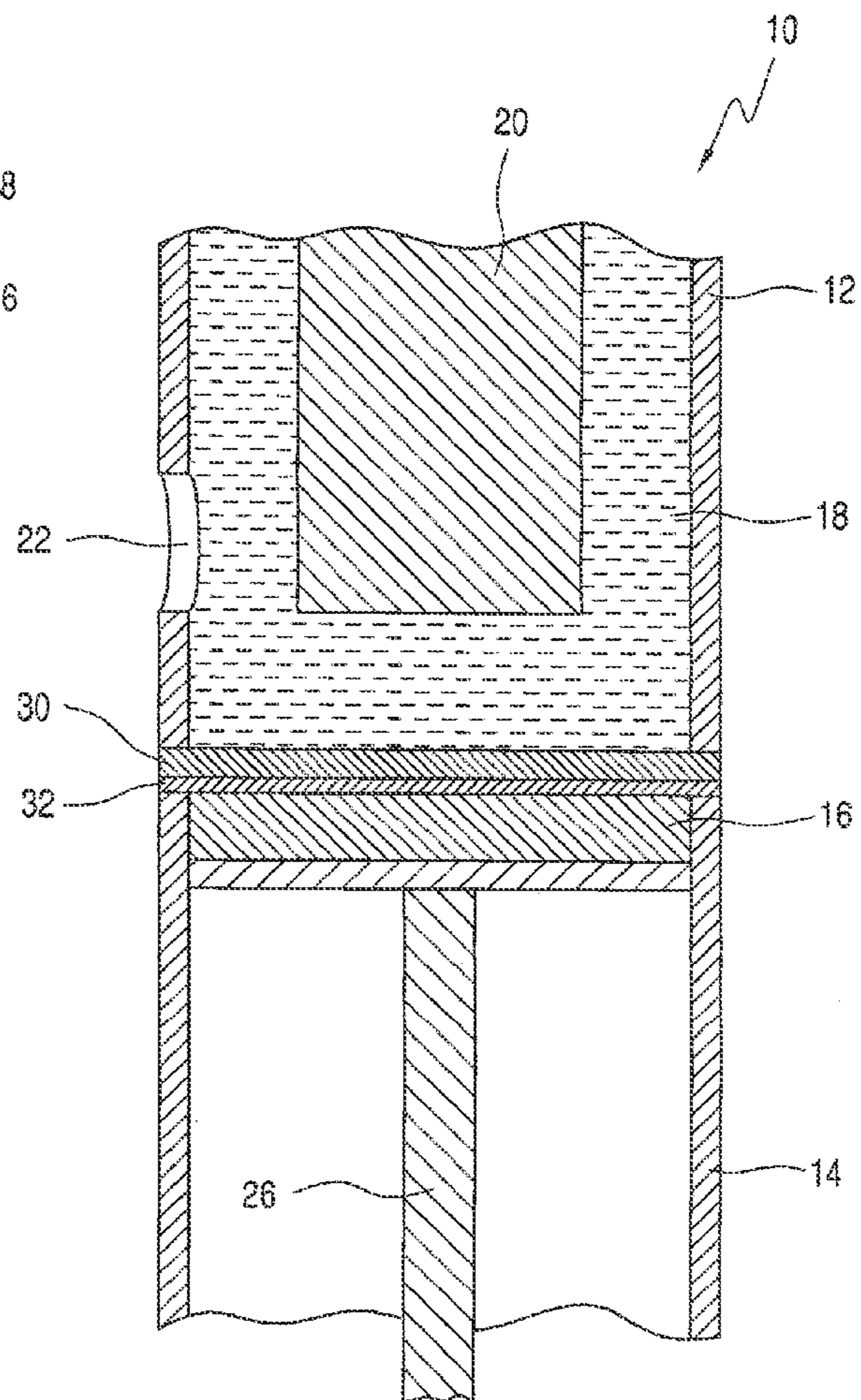


FIG. 2

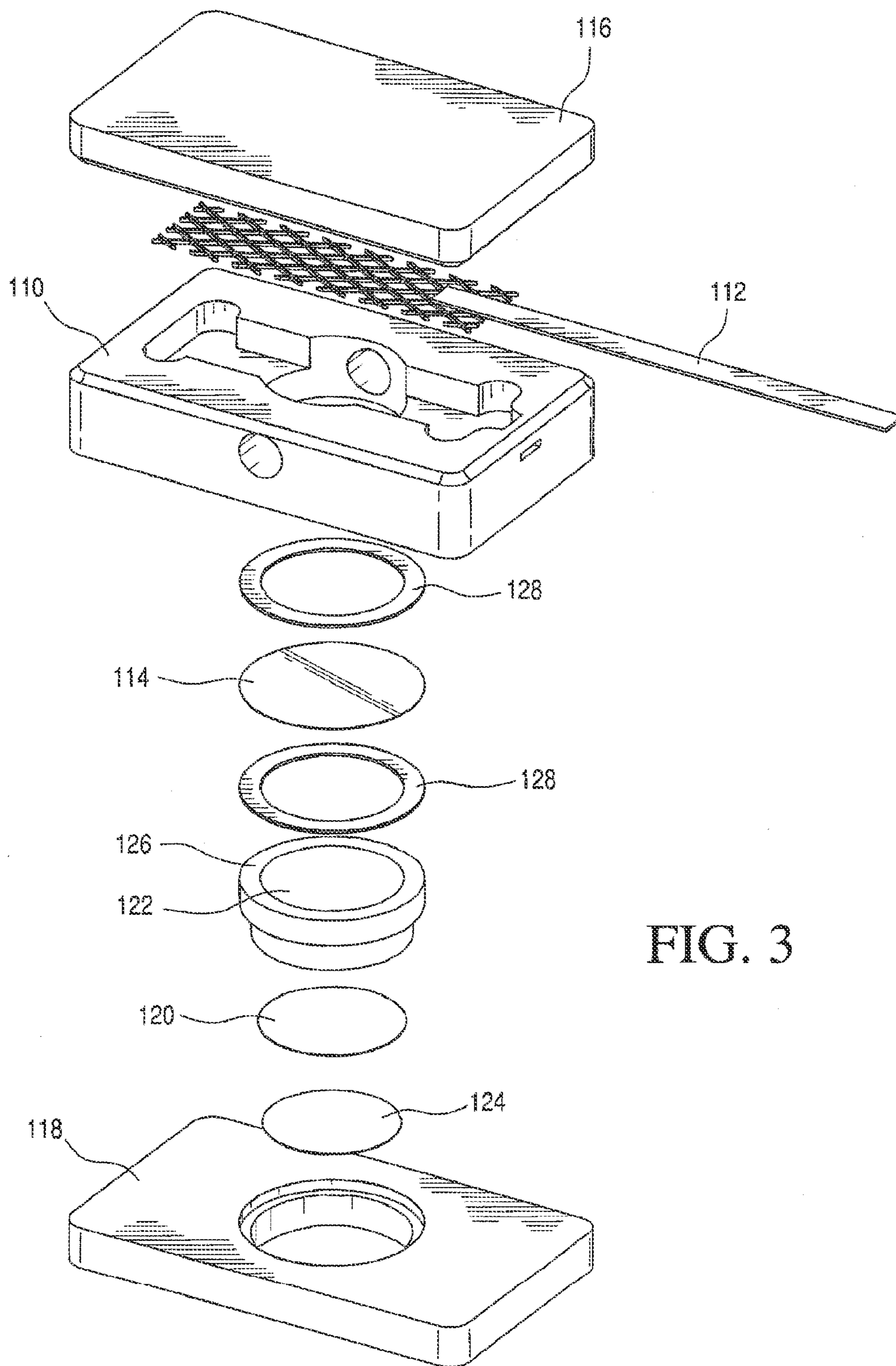


FIG. 3



## PRODUCING LITHIUM

**[0001]** This application claims the benefit of provisional application Ser. No. 61/844,482, filed Jul. 10, 2013, the disclosure of which is incorporated into this specification by reference in its entirety.

### BACKGROUND OF THE INVENTION

**[0002]** The invention is a continuous process for obtaining lithium metal and a cell for carrying out the process.

**[0003]** Lithium is a soft, silver-white metal belonging to the alkali metal group of chemical elements. It is the lightest metal and the least dense solid element. Lithium is highly reactive and flammable. Because of its high reactivity, it does not occur freely in nature, and instead, only appears in compositions, usually ionic in nature. Like the other alkali metals, lithium has a single valence electron that is easily given up to form a cation. Because of this, it is a good conductor of heat and electricity as well as a highly reactive element. Because of its reactivity, lithium is usually stored under cover of a hydrocarbon, often mineral oil. In moist air, lithium rapidly tarnishes to form a black coating of lithium hydroxide (LiOH and LiOH.H<sub>2</sub>O).

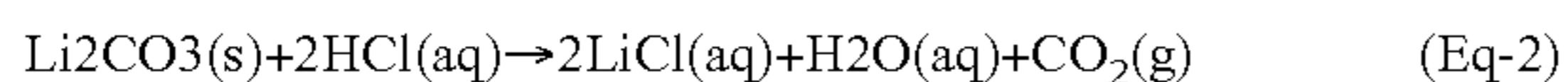
**[0004]** Uses of lithium compounds include lithium oxide as a flux for processing silica to glazes of low coefficients of thermal expansion, lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), as a component in ovenware and with lithium hydroxide, which is a strong base that can be heated with a fat to produce a lithium stearate soap. Lithium soap can be used to thicken oils and in the manufacture of lubricating greases. Metallic lithium can be used as a flux for welding or soldering to promote fusing of metals to eliminate oxide formation by absorbing impurities. Its fusing quality is important as a flux for producing ceramics, enamels and glass. Metallic lithium is used to manufacture primary lithium batteries.

**[0005]** Lithium carbonate is a common form of lithium produced from spodumene or lithium containing brine. Lithium metal can be extracted from lithium carbonate in phases:

Conversion of lithium carbonate into lithium chloride.

Electrolysis of lithium chloride.

**[0006]** To convert lithium carbonate to lithium chloride the lithium carbonate is heated and mixed with hydrochloric acid (typically 31% HCL) in an agitated reactor:



**[0007]** The formed carbon dioxide is vented from the reactant solution. A small amount of barium chloride can be added to precipitate any sulfate. After filtering, the solution is evaporated to a saleable 40% LiCl liquid product. Potassium chloride can be added to provide a dry lithium chloride-potassium chloride (45% LiCl; 55% KCl) of decreased melting point (614° C. to approximate 420° C.). Then the lithium chloride-potassium chloride (45% LiCl; 55% KCl) in a molten pure and dry state can be utilized to produce lithium metal in a steel reaction cell.

**[0008]** One steel cell has exterior ceramic insulation and a steel rod on the bottom as a cathode. The anode is constructed of graphite, which slowly sloughs-off during processing. The cell can be heated by gas firing between ceramic insulation and a cell's interior steel wall. Lithium metal accumulates at the surface of the cell wall and is then poured into ingots. Chloride gas generated by reaction is routed away. Typically, the electrolysis process is operated with a cell voltage of

6.7~7.5V, the typical cell current can be in the range of 30~60 kA. The processing consumes 30~35 kWh of electricity energy and 6.2~6.4 kg LiCl to produce one kilogram lithium metal with 20~40% energy efficiency.



**[0009]** A low temperature technology involves electrolysis of brine to form chlorine at an anode and sodium hydroxide or potassium hydroxide via a series of cathode reactions. The formation of either of these hydroxides can involve the reduction of an alkali cation, e.g. Li<sup>+</sup> to metal at a liquid mercury cathode, followed by reaction of the formed mercury amalgam with water. The process operates near room temperature with a lower voltage than required for the molten salt system.

**[0010]** Amendola et al. U.S. Pat. No. 8,715,482 provides a system and process that obviates a mercury electrode. The liquid metal alloy electrode system of U.S. Pat. No. 8,715,482 includes: an electrolytic cell comprising a liquid metal cathode and an aqueous solution wherein the aqueous solution containing lithium ion and at least an anion selected from sulfate, trifluoromethane sulfonate, fluorosulfonate, trifluoroborate, trifluoroacetate, trifluorosilicate and kinetically hindered acid anions and wherein the lithium ion is produced from lithium carbonate. A heating system maintains temperature of the cell and liquid metal circulating systems higher than the melting point of the liquid metal cathode but lower than the boiling point of the aqueous solution. The reduced lithium from the electrolytic cell is extracted from the liquid metal cathode using a suitable extraction solution and a distillation system for isolating the lithium metal. This system is solid at room temperature and is less toxic than previous systems.

**[0011]** Putter et al. U.S. Pat. No. 6,770,187 discloses another process that overcomes some of the high energy consumption and high temperature requirement of prior art processes. The Putter et al process enables recycling of alkali metals from aqueous alkali metal waste, in particular lithium from aqueous lithium waste. Putter et al provides an electrolysis cell comprising an anode compartment which comprises an aqueous solution of at least one alkali metal salt, a cathode compartment and an ion conducting solid composite that separates the anode compartment and the cathode compartment from one another, wherein that part of the surface of the solid electrolyte composite that is in contact with the anode compartment and/or that part of the surface of the solid electrolyte that is in contact with the cathode compartment has/have at least one further ion-conducting layer. The electrolyte used in U.S. Pat. No. 6,770,187 is water or water with organic solvent.

**[0012]** Previous lithium producing system have involved substantial capital and operating costs. There is a need for a direct and improved electrolysis process that requires reduced capital and operating costs in a system that effectively provides direct production of lithium metal. Additionally, Potter et al. points out that “[a]lkali metal ion conductors of this type are frequently not resistant to water and/or to alkali metals, and the experiment therefore leads to damage of the alkali metal ion conductors after only a short period. This damage can comprise either mechanical failure of the ion conductor or loss of its conductivity. A further aim of the



current invention therefore is to keep the ion conductors stable over a prolonged working life.

**[0013]** There is a need for a process that does not have the disadvantages described above (high energy consumption, high temperature, etc.). A further object is to provide an electrolysis cell suitable for carrying out this process.

#### BRIEF DESCRIPTION OF THE INVENTION

**[0014]** The invention provides an electrolysis cell and process characterized by a selective permeable barrier composite that provides for direct recovery of lithium metal. The cell and process are reasonably energy consuming and the lithium ion conducting composite layer is stable even in a highly corrosive anode compartment acid environment. In an embodiment, the invention is a lithium producing cell structure, comprising: a cell body with an anode and cathode within the cell body; an electrolyte aqueous solution within the cell body, the solution containing lithium ion; and a composite layer intercalated between the cathode and the electrolyte aqueous solution, the composite layer comprising a substantially impervious, lithium ion conductive composite layer (Li-GC) such as a glass ceramic and an active lithium ion conducting separation layer (Li-BF) that isolates cathode-forming lithium from the Li-GC.

**[0015]** In an embodiment, the invention is a process for producing lithium, comprising: providing a lithium ion source (lithium carbonate) and at least an acid in an aqueous solvent wherein lithium anion is dissolved in the solvent to form a lithium feed solution; providing an anode in contact with the solution; providing a cathode suitable for electrolysis of lithium; providing an ionizing electric current to the electrolysis cell thereby producing lithium metal at the cathode; and providing a composite layer transecting an axis of the cell body, the composite layer, comprising a lithium ion glass ceramic and lithium ion conductive barrier film that isolates cathode-forming lithium from the anion-containing solution as lithium metal is formed.

#### BRIEF DESCRIPTION OF THE DRAWING

**[0016]** FIG. 1 of the drawings is a schematic elevation view of a lithium producing cell structure;

**[0017]** FIG. 2 is a schematic detail of the cell structure of FIG. 1; and

**[0018]** FIG. 3 is a schematic exploded detail of a cell of this application.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0019]** Because of lithium's high electrochemical potential, it is an important component of electrolyte and electrodes in batteries. A typical lithium-ion battery can generate approximately 3 volts, compared with 2.1 volts for lead-acid or 1.5 volts for zinc-carbon cells. Because of its low atomic mass, it also has a high charge- and power-to-weight ratio. Lithium-ion batteries are high energy-density rechargeable batteries. Other rechargeable battery types include the lithium-ion polymer battery, lithium iron phosphate battery, and the nanowire battery.

**[0020]** This invention is for the production of lithium metal from lithium carbonate feed stock (or other lithium salt such as lithium chloride which dissociates in an acid electrolyte and releases the non-lithium portion of the feed stock as gas). My process can continuously process lithium carbonate into lithium metal. This is done by using a sulfuric acid electrolyte

to disassociate lithium carbonate, placing the lithium ions into solution for processing and venting off the carbonate portion without it entering into solution.

**[0021]** The use of sulfuric acid for lithium carbonate processing is important: Lithium carbonate is essentially insoluble in water and organic solvents. Lithium cannot be efficiently extracted from lithium carbonate salt using an aqueous electrolyte with or without organic solvent. Use of a sulfuric acid solution provides much higher solubility of lithium carbonate into solution allowing efficient production of lithium metal from lithium carbonate. By disassociating the lithium carbonate and only placing the lithium ions into solution, the electrolyte solution remains stable and does not build up a concentration of the non-lithium ion portion of the feed stock. Lithium carbonate can be continuously fed into a tank outside of the electrolysis cell, venting off the CO<sub>2</sub> gas released by the sulfuric acid electrolyte. The acid electrolyte does not need to be disposed of or replenished, lithium carbonate can be continuously added to a feed tank, venting off CO<sub>2</sub> and harvesting lithium metal from a cathode. This can be continuously operated or conducted as a batch process.

**[0022]** The invention provides a cathode separated from lithium ion rich solution by a selectively permeable barrier composite (LIC-GC-BF). The composite comprises a lithium ion conductive glass ceramic layer (LI-GC) and a lithium ion conductive barrier film (LI-BF). The LIC-GC-BF composite allows for direct production of lithium metal from solution and direct deposition of lithium metal onto a clean cathode, without need for an additional extraction process. The inventive system can include: an electrolyte feed system that provides a lithium ion rich electrolyte to the electrolysis cell; an electrolytic cell to move lithium metal from a water-based lithium ion solution through the LIC-GC-BF composite; and a method to package lithium metal. The invention can be part of a continuous lithium metal production process or as a batch process.

**[0023]** Features of the invention will become apparent from the drawings and following detailed discussion, which by way of example without limitation describe preferred embodiments of the invention.

**[0024]** The FIGS. 1 and 2 illustrate a production process of the invention wherein lithium-rich electrolyte flows through an extraction cell. When potential is applied to the system, lithium metal builds up on a moving cathode below an intercalated composite layer. FIG. 1 of the drawings is a schematic elevation view of lithium producing cell structure and FIG. 2 is a schematic detail of the cell structure of FIG. 1. In FIG. 1, and FIG. 2, the electrolytic cell 10 according to an embodiment of the invention, includes an upper section 12 and lower section 14. The cell 10 is characterized by a movable cathode 16 that transects a cross-section of the cell. The cathode 16 transposes an axis of cell 10, advancing as an electrolysis reaction takes place in electrolyte 18 above the cathode 16, through the LIC-GC-BF composite layer. Anode 20 is provided to the cell upper section 12. The cell section 12 above the cathode 10 is loaded with electrolyte 18 via inlet 22, electrolysis proceeds and spent electrolyte is discharged via outlet 24. The cathode 16 is in contact with the electrolyte 18 through a composite layer 28 intercalated between the cathode 16 and electrolyte 18. The composite layer 28 comprises a lithium ion conductive glass ceramic layer (LI-GC) 30 adjacent the electrolyte 18 and a lithium ion conductive barrier film (LI-BF) 32 interposed between the ceramic layer 30 and cathode 18. The barrier layer 32 and glass ceramic layer



**30** composite **28** isolates forming lithium at cathode **16** from electrolyte **18**. Shaft **26** advances the cathode **16** and composite **28** as lithium metal is formed and deposited through the composite layer **28** onto the advancing cathode **16**. The Lithium metal produced at the solid cathode **16** can be drawn off as a pure metallic phase.

**[0025]** Suitable feed to the cell includes water-soluble lithium salts including but not limited to  $\text{Li}_2\text{CO}_3$  and  $\text{LiCl}$ . To improve solubility, the lithium salt is dissolved in hydrated acid and used as electrolyte in the electrolytic cell. Lithium Carbonate ( $\text{Li}_2\text{CO}_3$ ) was used as feed stock for initial trials.

**[0026]** Some suitable cell components in the present invention are described in US20130004852, which is incorporated into this disclosure in its entirety by reference.

**[0027]** Suitable electrolyte **18** components include water-soluble lithium salts including but not limited to  $\text{Li}_2\text{CO}_3$  and  $\text{LiCl}$ . To improve solubility the lithium salt can be dissolved in hydrated acid to be used as electrolyte. Lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) is the most readily available lithium salt, being relatively inexpensive and is a preferred lithium source. Cathode **16** is characterized by the intercalated composite (Li-GC/Li-BF) **28** meaning the composite **28** is inserted or interposed between the cathode **16** and electrolyte **18**. The cathode **16** can be characterized as “transpositioning” meaning the cathode advances along an axis of the cell **10** to transpire produced lithium through the composite **28** and to isolate cathode-deposited lithium. The cathode comprises a suitable material that is non-reactive with lithium metal and the composite layer. The Li-GC/Li-BF composite layer is a stationary barrier between the anode compartment and the lithium metal forming on the cathode. The cathode moves to accommodate the continuously thickening layer of lithium metal on the cathode.

**[0028]** Composite layer (Li-GC/Li-BF) **28** includes lithium ion conductive glass ceramic layer (LI-GC) **30** and lithium ion conductive barrier film (LI-BF) **32**. The substantially impervious layer (LI-GC) **30** can be an active metal ion conducting glass or glass-ceramic (e.g., a lithium ion conductive glass-ceramic that has high active metal ion conductivity and stability to aggressive electrolytes that vigorously react with lithium metal. Suitable materials are substantially impervious, ionically conductive and chemically compatible with aqueous electrolytes or other electrolyte (catholyte) and/or cathode materials that would otherwise adversely react with lithium metal. Such glass or glass-ceramic materials are substantially gap-free, non-swelling and are inherently ionically conductive. That is, they do not depend on the presence of a liquid electrolyte or other agent for their ionically conductive properties. They also have high ionic conductivity, at least  $10^{-7}$  S/cm, generally at least  $10^{-6}$  S/cm, for example at least  $10^{-5}$  S/cm to  $10^{-4}$  S/cm, and as high as  $10^{-3}$  S/cm or higher so that the overall ionic conductivity of the multi-layer protective structure is at least  $10^{-7}$  S/cm and as high as  $10^{-3}$  S/cm or higher. The thickness of the layer is preferably about 0.1 to 1000 microns, or, where the ionic conductivity of the layer is about  $10^{-7}$  S/cm, about 0.25 to 1 micron, or, where the ionic conductivity of the layer is between about  $10^{-4}$  to  $10^{-3}$  S/cm, about 10 to 1000 microns, preferably between 1 and 500 microns, and more preferably between 50 and 250 microns, for example, about 150 microns.

**[0029]** Examples of glass ceramic layer (LI-GC) **30** include glassy or amorphous metal ion conductors, such as a phosphorus-based glass, oxide-based glass, phosphorus-oxynitride-based glass, sulfur-based glass, oxide/sulfide based

glass, selenide based glass, gallium based glass, germanium-based glass or boracite glass (such as are described D. P. Button et al., Solid State Ionics, Vols. 9-10, Part 1, 585-592 (December 1983); ceramic active metal ion conductors, such as lithium beta-alumina, sodium beta-alumina, Li superionic conductor (LISICON), Na superionic conductor (NASICON), and the like; or glass ceramic active metal ion conductors. Specific examples include LiPON,  $\text{Li}_3\text{PO}_4\cdot\text{Li}_2\text{S}\cdot\text{SiS}_2$ ,  $\text{Li}_2\text{S}\cdot\text{GeS}_2\cdot\text{Ga}_2\text{S}_3$ ,  $\text{Li}_2\text{O}$ .

**[0030]** Suitable glass-ceramic materials (LI-GC) include a lithium ion conductive glass-ceramic having the following composition in mol percent:  $\text{P}_2\text{O}_5$  26-55%;  $\text{SiO}_2$  0-15%;  $\text{GeO}_2+\text{TiO}_2$  25-50%; in which  $\text{GeO}_2$  0-50%;  $\text{TiO}_2$  0-50%;  $\text{ZrO}_2$  0-10%;  $\text{M}_2\text{O}_3$  0-10%;  $\text{Al}_2\text{O}_3$  0-15%;  $\text{Ga}_2\text{O}_3$  0-15%;  $\text{Li}_2\text{O}$  3-25% and containing a predominant crystalline phase comprising  $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$  where  $X \leq 0.8$  and  $0 \leq Y \leq 1.0$  and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb, and/or  $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_3\text{P}_3\text{O}_{12}$  where  $0 < X \leq 0.4$  and  $0 < Y \leq 0.6$ , and where Q is Al or Ga. Other examples include  $11\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$ ,  $(\text{Na}, \text{Li})_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$  ( $0.6 \leq x \leq 0.9$ ) and crystallographically related structures,  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ,  $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_4$ ,  $\text{Na}_5\text{ZrP}_3\text{O}_{12}$ ,  $\text{Na}_5\text{TiP}_3\text{O}_{12}$ ,  $\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ ,  $\text{Na}_4\text{NbP}_3\text{O}_{12}$ ,  $\text{Li}_5\text{ZrP}_3\text{O}_{12}$ ,  $\text{Li}_5\text{TiP}_3\text{O}_{12}$ ,  $\text{Li}_5\text{Fe}_2\text{P}_3\text{O}_{12}$  and  $\text{Li}_4\text{NbP}_3\text{O}_{12}$  and combinations thereof, optionally sintered or melted. Suitable ceramic ion active metal ion conductors are described, for example, in U.S. Pat. No. 4,985,317 to Adachi et al., incorporated by reference herein in its entirety.

**[0031]** Suitable LI-GC material includes a product from Ohara, Inc. (Kanagawa, JP), trademarked LIC-GC™, LISICON,  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2$  (LATP). Suitable material with similarly high lithium metal ion conductivity and environmental/chemical resistance are manufactured by Ohara and others. See for example, Inda, DN20100113243, now U.S. Pat. No. 8,476,174, incorporated herein in their entirety by reference. U.S. Pat. No. 8,476,174 discloses a glass-ceramic comprising at least crystallines having a having a  $\text{LiTi}_2\text{P}_3\text{O}_{12}$  structure, the crystallines satisfying  $1 < I_{4113}/I_{4104} \leq 2$ , wherein  $I_{4104}$  is the peak intensity assigned to the plane index 104 ( $2\theta=20$  to  $21^\circ$ ), and  $I_{4113}$  is the peak intensity assigned to the plane index 113 ( $2\theta=24$  to  $25^\circ$ ) as determined by X-ray diffractometry.

**[0032]** The lithium ion conductive barrier film **32** (LI-BF) is a lithium metal ion conductive film or coating with high lithium metal ion conductivity, typically The lithium ion conductive barrier film **32** (LI-BF) is a lithium metal ion conductive film or coating with high lithium metal ion conductivity, typically 1.0 mS/cm to 100 mS/cm. A high lithium ion transference number ( $t_+$ ) is preferred. Low  $t_+\text{Li}^+$  electrolytes will hinder performance by allowing ion concentration gradients within the cell, leading to high internal resistances that may limit cell lifetime and limit reduction rates. Transference numbers between  $t_+=0.70$  and  $t_+=1.0$  are preferred. The lithium ion conductive barrier film is non-reactive to both lithium metal and the LI-GC material.

**[0033]** The LI-BF film **32** includes an active metal composite, where “active metals” are lithium, sodium, magnesium, calcium, and aluminum used as the active material of batteries. Suitable LI-BF material includes a composite reaction product of active metal with  $\text{Cu}_3\text{N}$ , active metal nitrides, active metal phosphides, active metal halides, active metal phosphorus sulfide glass and active metal phosphorous oxynitride glass ( $\text{Cu}_3\text{N}$ ,  $\text{L}_3\text{N}$ ,  $\text{Li}_3\text{P}$ , LiI, LiF, LiBr, LiCl and



LiPON). The LI-BF material must also protect against dendrites forming on the cathode from coming in contact with the LI-GC material. This may be accomplished by creating physical distance between the cathode and LI-GC and/or providing a physical barrier that the dendrites do not penetrate easily. One preferred LI-BF film is a physical organogel electrolyte produced by in situ thermo-irreversible gelation and single ion-predominant conduction as described by Kim et al. in *Scientific Reports* at [http://www.nature.com/srep/2013/130529/srep01917/fig\\_tab/srep01917\\_F1.html](http://www.nature.com/srep/2013/130529/srep01917/fig_tab/srep01917_F1.html). (article number: 1917 doi:10.1038/srep01917). This electrolyte has  $t_+ = 0.84$  and conductivity of 8.63 mS/cm at room temperature. This organogel electrolyte can be set up in a porous membrane to provide additional structure and resistance to dendrite penetration. Typical porous membrane thickness is 1  $\mu\text{m}$  to 500  $\mu\text{m}$ , for example 20  $\mu\text{m}$ . Acceptable porous membrane includes HIPORE polyolefin flat-film membrane by Asahi Kasei E-materials Corporation.

**[0034]** The invention produces lithium metal that can be used as part of a continuous lithium metal production process. In particular, the present process can utilize inexpensive lithium carbonate or an equivalent source of lithium ions. The process can be used to produce lithium metal directly from the acid solution used to leech lithium metal out of spodumene ore or other natural lithium sources.

**[0035]** Features of the invention are apparent from the drawings and following detailed discussion, which by way of example without limitation describe one preferred embodiments of the invention.

#### EXAMPLE

**[0036]** The cell used is shown schematically in FIG. 3. The cell **110** includes cell cover **116**, retainer **118**, Pt anode **112**, cathode **124** and a LI-GC conductive glass **114** with lithium ion conductive barrier film **120** incorporated into a porous polyolefin flat-film membrane **122**. The supported LI-GC-BF multilayer is intercalated between cathode **124** and a lithium ion-rich electrolyte **18** (in FIGS. 1 and 2). The cell further comprises supporting Teflon® sleeve structure **126** with gaskets **128**. One gasket seals between the LI-GC and the housing to prevent leakage of the electrolyte from the anode compartment into the cathode compartment. The other gasket allows for even compression of the LI-GC by the Teflon Sleeve to prevent breakage of the LI-GC plate.

**[0037]** The cell **110** includes anode **112** that is a platinized titanium anode, 1"×4" rhodium and palladium jewelry plating). The cathode is a palladium cathode disk fabricated in-house, 1.4 inch round. The LI-GC **114** material is LICGC® G71-3 N33: DIA 2 IN×150  $\mu\text{m}$  Tape cast, 150  $\mu\text{m}$  thick, 2 inch round from Ohara Corporation, 23141 Arroyo Vista, Rancho Santa Margarita, Calif. 92688.

**[0038]** The lithium ion conducting gel electrolyte **120** is fabricated from: a PVA-CN polymer supplied by the Ulsan National Institute of Science and Technology in Ulsan South Korea, Dr. Hyun-Kon Song, UNIST/82.52.217.2512/echem.kr., procured from Alfa Aesar, stock number H61502; LiPF<sub>6</sub> (Lithium hexafluorophosphate), 98%,; EMC (ethyl methyl carbonate), 99%, from Sigma Aldrich, product Number 754935; EC (ethylene carbonate), anhydrous, from Sigma Aldrich, product number 676802 and a porous membrane, ND420 polyolefin flat-film membrane from Asahi Corp.

**[0039]** The LI-BF bather layer **120** is fabricated in an argon purged glove bag. The glove bag is loaded with all materials,

precision scale, syringes, and other cell components then filled and evacuated 4 times before the start of the electrolyte fabrication process.

**[0040]** The organogel electrolyte is mixed up as follows: 4.0 ml of EMC is liquified by heating to about 140° F., and placed in a vial. 2.0 ml of the EMC is then added to the vial 0.133 g (2% wt) PVA-CN polymer is added to the vial and the is agitated for 1 hour to dissolve the PVA-CN. Then 0.133 g (2% wt) FEC is added as SEI-forming additive 0.972 g (1M) LiPF<sub>6</sub> is then added and mixed to complete the organogel electrolyte mixture. The electrolysis cell is then assembled inside the glove bag. With the LI-GC and gaskets in place, the anode and cathode compartments are sealed from each other. The organogel electrolyte mixture is used to wet the cathode side of the LI-GC, the HIPORE membrane is placed on the cathode side of the LI-GC and wetted again with organogel electrolyte mixture. The cathode disk is then placed on top of the organogel mixture. The cell is placed in a Mylar® bag and sealed while still under argon purge. The sealed Mylar® bag with assembled cell is then placed in an oven at 60 C for 24 hours to gel the electrolyte.

**[0041]** The electrolysis cell **10** is removed from the oven and placed in the argon purged glove bag, and allowed to cool to room temperature. Clear polypro tape is used to seal the empty space above the cathode disc and secure the electrode wire. The electrolysis cell **10** is now ready for use, is removed from the glove bag, and is connected to the electrolyte circulating system.

**[0042]** An electrolyte **18** is prepared with 120 g of lithium carbonated in 200 ml of deionized water and 500 ml of 20% wt sulfuric acid. The sulfuric acid is slowly added to the lithium carbonate suspension and mixed well. Undissolved lithium carbonate is allowed to settle. A supernatant is collected from the stock solution, an 18% wt lithium stock solution. The 18% wt lithium solution has a measured pH of 9. Solution pH is lowered by addition of 20% wt sulfuric acid. Again, the sulfuric acid is added slowly to minimize foaming. The 18% wt lithium stock solution is adjusted to pH 4.5. Preferred PH is between PH3.0 and PH4.5, most preferred is between PH3.0 and PH4.0, but process can be run at PH7.0 or below. PH above 7.0 will result in carbonate in solution.

**[0043]** The electrolyte mixture is then poured into the circulating system. The circulating pump is primed and solution circulated for 30 minutes to check for leaks.

**[0044]** The lithium ion-rich electrolyte **18** flows through the top half of cell **110** over the LI-GC-BF multilayer **114/120** and past anode **112**. When potential is applied to the system, lithium metal builds up on the moving cathode below the LI-GC-BF multilayer **114/120** system.

**[0045]** A Gamry Reference 3000 Potentiostat/Galvanostat/ZRA is attached to the cell **10**. At voltages of 3-6 volts there is no significant activity. When voltage is raised to 10V the system responds. Amperage draw increases when voltage is raised to 11 vdc. No gassing on the anode side of the cell was noted at 11 vdc. The Gamry Reference 3000 would not go above 11 vdc. Since no gassing occurred at 11 vdc the reduction rate could most likely be much higher if voltage were increased. An even higher voltage and reduction rate are preferable if achieved with negligible oxygen production at the anode. PH of the electrolyte at time zero is 4.46. PH of the solution decreases to 4.29 after 35 minutes, and is 4.05 at the end of the experiment. The lowering PH indicates lithium ion removal from the electrolyte solution.



**[0046]** An amperage draw of 20 mA is noted at the start of the experiment. The amperage draw slowly increased to 60 mA after 30 minutes. Amperage holds fairly steady at this value for another 30 minutes. Experiment timer and graph are paused for 30 minutes to extend experiment (voltage held at 11 vdc). After approximately 65 minutes of run time a large amperage spike and sudden vigorous gassing is noted on the anode side of the cell This is indicative of LiCGC **114/120** membrane failure.

**[0047]** Rapid gassing and bright white flame is observed when the cell **10** is opened and cathode **16** side is exposed to electrolyte leaking through the LI-GC **114/120**, evidencing that the cell produces lithium metal by electrolysis of lithium ions in a sulfuric acid aqueous solution, through a LI-GC-BF **114/120** membrane system.

**[0048]** While preferred embodiments of the invention have been described, the present invention is capable of variation and modification and therefore should not be limited to the precise details of the Examples. The invention includes changes and alterations that fall within the purview of the following claims.

What is claimed is:

1. A lithium producing cell structure, comprising:  
a cell body with a cathode within the cell body;  
a sulfuric acid solution within the cell body, the solution containing lithium ion and an anion; and  
a composite layer intercalated between the cathode and the electrolyte aqueous solution, the composite layer comprising a lithium ion conductive glass ceramic (LI-GC) and a lithium ion conductive barrier film (LI-BF) that isolates cathode-forming lithium from the electrolyte aqueous solution.
2. The lithium producing cell of claim **1**, wherein the composite layer is characterized by high lithium metal ion conductivity and is nonreactive to both lithium metal and the LI-GC material.
3. The lithium producing cell of claim **1**, wherein the lithium ion conductive barrier film of the composite layer comprises a physical organogel electrolyte.
4. The lithium producing cell of claim **1**, wherein the lithium ion conductive barrier film of the composite layer comprises an organogel product of an in situ thermo-irreversible gelation and single ion-predominant conduction.
5. The lithium producing cell of claim **1**, wherein the composite layer comprises a lithium ion conductive glass ceramic and a lithium ion conductive barrier film.
6. The lithium producing cell of claim **1**, wherein the substantially impervious ionically conductive polymeric separator layer comprises a glass-ceramic active metal ion conductor.
7. The lithium producing cell of claim **1**, wherein the lithium ion conductive glass ceramic (LI-GC) is an ion conductive glass-ceramic having the following composition in mol percent:  $P_2O_5$  26-55%;  $SiO_2$  0-15%;  $GeO_2+TiO_2$  25-50%; in which  $GeO_2$  0-50%;  $TiO_2$  0-50%;  $ZrO_2$  0-10%;  $M_2O_3$  0-10%;  $Al_2O_3$  0-15%;  $Ga_2O_3$  0-15%;  $Li_2O$  3-25% and containing a predominant crystalline phase comprising  $Li_{1+x}(M, Al, Ga)_x(Ge_{1-y}Ti_y)_{2-x}(PO_4)_3$  where  $X \leq 0.8$  and  $0 \leq Y \leq 1$  and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb, and/or  $Li_{1+x+y}Q_xTi_{2-x}Si_3P_3-yO_{12}$  where  $0 < X \leq 0.4$  and  $0 < Y \leq 0.6$ , and where Q is Al or Ga.

8. The lithium producing cell of claim **1**, wherein the composite layer has an ionic conductivity of at least  $10^{-4}$  S/cm.

9. The lithium producing cell of claim **1**, wherein the cathode comprises a catholyte selected from the group consisting of non-aqueous electrolyte

10. The lithium producing cell of claim **1**, wherein the cathode further comprises electrochemically active material selected from the group consisting of solid, liquid and gaseous oxidizers.

11. The lithium producing cell of claim **1**, wherein the catholyte comprises an ionic liquid.

12. The lithium producing cell of claim **1**, wherein the composite layer comprises a substantially impervious protective ceramic composite layer and the lithium ion conductive barrier film.

13. The lithium producing cell of claim **1**, wherein cathode is movable along an axis of the cell.

14. A process for producing lithium, comprising:

providing a lithium ion source in a sulfuric acid solvent wherein lithium anion is dissolved in the solvent to form a lithium feed solution;

providing an anode in contact with the solution;

providing a cathode suitable for electrolysis of lithium, wherein the cathode in contact with the solution through a composite ion-conducting barrier forms an electrolysis cell;

providing an ionizing electric current to the electrolysis cell thereby producing lithium metal at the cathode; and  
providing a composite layer transecting an axis of the cell body, the composite layer, comprising a lithium ion glass ceramic and lithium, ion conductive barrier film that isolates cathode-forming lithium from the anion-containing solution as lithium metal is formed.

15. The process for producing lithium of claim **14**, wherein the composite layer is characterized by high lithium metal ion conductivity and is nonreactive to both lithium metal and the LI-GC material

16. The process for producing lithium of claim **14**, wherein the cathode is drivable along a cell axis away from anode as lithium metal is deposited on the cathode.

17. The process for producing lithium of claim **14**, wherein, the cell is postured with upper moving cathode and lower cell containing electrolyte to drive the cathode away from the composite ion conducting layer as lithium metal is deposited on the cathode.

18. The lithium producing cell of claim **14**, wherein the lithium ion conductive barrier film of the composite layer comprises a physical organogel electrolyte.

19. The lithium producing cell of claim **14**, wherein the lithium ion conductive barrier film of the composite layer comprises an organogel product of an in situ thermo-irreversible gelation and single ion-predominant conduction.

20. The process of claim **14** where the lithium ion source is lithium carbonate

21. The process of claim **14** where the lithium ion source is another lithium salt which dissociates in an acid solvent placing the lithium ions into solution and releasing the non-lithium portion of the salt as a gas.

22. The process of claim **14** where the acid is other than sulfuric acid but dissociates the lithium source in the same manner, placing lithium ions into solution while releasing the non-lithium portion of the source as a gas.

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