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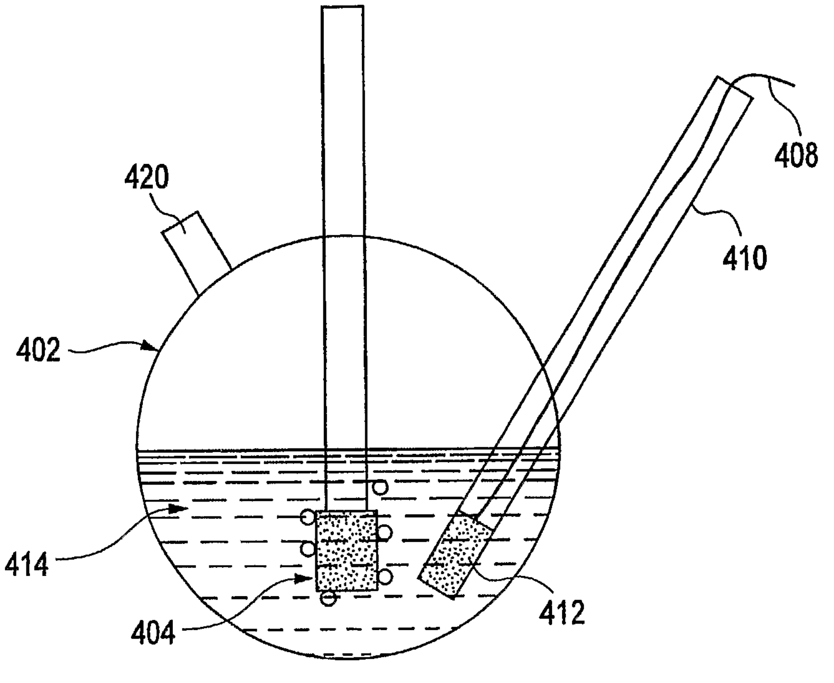

(57) Abstract: An electrochemical process and apparatus for preparing metal hydride compounds from metal salts under a hydrogen atmosphere are disclosed. The electrochemical process may be integrated with chemical reaction of a boron compound to produce borohydride compounds. A metal salt and a borate are charged to the cathode of an electrolytic cell wherein the borate reacts with the hydride, to produce the borohydride compound.

METHODS AND APPARTUS FOR SYNTHESIS OF METAL HYDRIDES

[0000] This application claims the benefit of U.S. Provisional Application Serial Nos. 60/622,789 filed on October 29, 2004, and 60/662,555 filed on March 17, 2005, the entire disclosures of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention was made with Government support under Cooperative Agreement No. DE-FC36-04GO14008 awarded by the Department of Energy. The Government has certain rights in this invention.

FIELD OF THE INVENTION

[0002] The present invention relates to the electrochemical reduction of active metal salt compounds with applications in active metal hydride and active metal borohydride production.

BACKGROUND OF THE INVENTION

[0003] Sodium borohydride is a very versatile chemical and is used in organic synthesis, waste water treatment, and pulp and paper bleaching. The high hydrogen content of this compound also makes it a good candidate for being a hydrogen carrier, and it could play a major role as an enabler of a hydrogen economy if the cost of producing this chemical can be reduced.

[0004] Today, sodium borohydride is produced by the so-called Schlesinger process, which is a multi-step synthetic process, wherein sodium borohydride is produced from the reaction of sodium hydride and trimethyl borate in mineral oil. As none of the reagents are soluble in mineral oil, it is necessary to ensure high dispersions and the reaction must proceed at elevated temperatures, typically around 250 °C. In addition, mineral oil evaporates and can contribute to VOC emissions.

[0005] U.S. Patent No. 3,734,842, U.S. Patent No. 4,904,357, and U.S. Patent No. 4,931,154, the disclosures of which are incorporated by reference herein in their entirety, refer to electrochemical synthesis of sodium borohydride from aqueous sodium metaborate solution. Such processes involve conversion of sodium metaborate and water to form sodium borohydride and oxygen in an electrical cell, as shown in the following half-cell reactions:

Cathode: $B(OH)_4^- + 4\ H_2O + 8\ e^- \rightarrow BH_4^- + 8\ OH^-$ (1a)

Anode: $8\ OH^- \rightarrow 4\ H_2O + 2\ O_2 + 8\ e$ (1b)

[0006] However, none of these processes has been implemented in commercial practice.

BRIEF SUMMARY OF THE INVENTION

[0007] The invention is directed to electrochemical processes and apparatus for preparing metal hydride compounds from active metal salts.

[0008] In accordance with one aspect of the present invention, molten active metal salts are electrolyzed under a hydrogen atmosphere to produce active metal hydrides.

[0009] In accordance with another aspect of the present invention, active metal salts are electrolyzed in ionic liquids under a hydrogen atmosphere to produce active metal hydrides.

[0010] In accordance with another aspect of the present invention, the electrochemical process is integrated with a chemical reaction of a boron compound to produce boron hydride compounds.

[0011] In another aspect of the present invention, the electrochemical process is integrated with an *in situ* chemical reaction of an oxidized boron compound to produce boron hydride compounds.

[0012] In another aspect of the present invention, oxidized boron compounds are reduced by reaction with active metal hydrides in a liquid salt to produce boron hydride compounds.

[0013] These and other features and advantages of the invention will become apparent from the following detailed description that is provided in connection with the accompanying drawings and illustrated exemplary embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 is a schematic view of an electrolytic cell in accordance with one embodiment of the invention, where hydrogen-containing gas is passed into the cathode compartment for synthesis of an active metal hydride from molten active metal salt;

[0015] Figure 2 is a schematic diagram for producing borohydride anions according to an exemplary process of the present invention;

[0016] Figure 3 is a schematic diagram for producing borohydride anions according to another exemplary process of the present invention; and

[0017] Figure 4 is a view of an exemplary electrolytic cell suitable for use in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In accordance with an exemplary embodiment of the present invention, a metal salt or a mixture of metal salts are converted into a metal hydride via electrolysis in the presence of hydrogen. Without being limited by theory, it is thought that an electrochemical reduction of the metal salt yields metal at the cathode, and the metal formed then reacts chemically with hydrogen to give metal hydride. The overall reaction is shown in Equation (2) wherein X represents a halide anion (the reaction product of the anion will depend on the anion, X, chosen),

$$MX_n + {}^n/_2\, H_2 \rightarrow MH_n + {}^n/_2\, X_2 \qquad (2)$$

where M is preferably selected from the group of metals and semimetals wherein the potential of the reaction between the metal, M, and oxygen to make a metal oxide is greater than about 1.6 volts, where the potential is defined as the negative of the free energy of reaction (ΔG, measured in joules per mole of metal) at standard conditions, wherein temperature is 298.15 K (25 °C) and pressure is 101.325 kPa (1 atm), divided by the number of moles of electrons transferred per mole of metal (n), divided by Faraday's constant (F) (Faraday's constant = 96485 coulombs/mole of electron), or Potential = $-\Delta G/nF$; X is chosen from the group of anions comprising halides, tosylate, sulfate and sulfate derivatives, trifluoromethanesulfonate and other sulfonates, nitrate, phosphates, hexafluorophosphate, and other phosphate derivatives, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, tris(trifuoromethylsulfonyl)methide and other methides, and bis(trifluoromethylsufonyl)imide and other imides; and n is the valence of the metal, preferably an integer from 1 to 4. Metals and semimetals falling under this definition are herein referred to as "active metals."

[0019] Active metals, include, but are not limited to, the alkali metals, the alkaline earth metals, transition metals from Groups 3, 4, 12, and the lanthanide family. The active metals form cations that include, but are not limited to, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Ti^{3+}, Ti^{4+}, Zn^{2+}, Al^{3+}, Si^{4+}, Y^{3+}, Y^+, Zr^{2+}, Zr^{3+}, Zr^{4+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, and lanthanides in the +3 oxidation state. M is preferably chosen from the group of alkali metals, and more preferably is lithium, sodium, potassium, and cesium; and X is preferably chloride or bromide.

[0020] An exemplary two-compartment electrolysis cell 100 employed in the process of the present invention is illustrated in Figure 1. The cell 100 comprises an anode compartment 104, anode 102, cathode compartment 112, cathode 108, separator 106 which separates the anode and cathode compartments but allows ionic transport, and an optional gas inlet means 110 to supply a gas comprising hydrogen to the cathode compartment. The anodes and cathodes may comprise any suitable electrode material.

[0021] Separator 106 may preferably comprise a material such as glass, polymer, or ceramic that allows ionic transport between the cathodic and anionic compartments, but restricts reaction between the active metal produced at the cathode and the product produced at the anode. Porous separators such as porous glass, porous metal, porous plastics, and porous ceramics are suitable separators. Paper, polymer, polymer membranes, and perfluoronated ion-conducting polymer membranes, are also suitable separators. Nonlimiting examples of polymer separators include polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer, perfluorosulfonated ionomers, polyamides, nylon polymers, and polyethylene. Optionally, cationic conducting ceramics may be employed as the separator. Nonlimiting examples of ceramic separators include lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, lithium analogs of NaSICON ceramics, LiSICONs, and lithium ion conductors with perovskite structure, sodium-β-aluminum oxide, sodium-β″-aluminum oxide, sodium-β/β″-aluminum oxide, NaSICON ceramics, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, potassium-β/β″-aluminum oxide, and potassium analogs of NaSICON ceramics.

[0022] In a preferred embodiment of the method of the present invention, one or more active metal salts of formula MX_n are charged to the cathode chamber 112 to prepare a metal hydride. The cell is preferably maintained at temperatures from about 70 °C to about 500 °C, so that the one or more active metal salts are in a liquid molten state. The active metal salts can be used neat, i.e., without solvent, or a solvent may be included.

[0023] Alternatively, the one or more active metal salts can be dissolved in an ionic liquid. Ionic liquids are defined herein as salts with a melting point between about -100 °C and about 200 °C, and preferably containing at least 1 carbon atom in the cation. Typical ionic liquid cations include, but are not limited to, mono-, di-, tri-, and tetra substituted ammonium; mono-, di-, tri-, and tetra substituted phosphonium, *N*-alkylpyridinium, 1,3-disubstituted pyridiniums, 1,4-disubstituted pyridiniums, 1,3-disubstituted imidazolium, 1,2,3-trisubstituted imidazolium, 1,1 disubstituted pyrrolidiums, trialkylsulfonium, and trialkyloxonium cations. The anion in an ionic liquid can be any anion. Some typical anions are halides, but other representative and non-limiting examples include the group of common complex ions such as tosylate, sulfate and sulfate derivatives, trifluoromethanesulfonate and other sulfonates, nitrate, phosphates, hexafluorophosphate, and other phosphate derivatives, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, tris(trifuoromethylsulfonyl)methide and other methides, and bis(trifluoromethylsufonyl)imide and other imides. Preferably, neither the cation nor the anion of the ionic liquid is easily reducible by strong hydrides. It is not necessary that the liquid salt be a liquid at room temperature, but only that at least a portion of the salt be liquid at the reaction temperature.

[0024] Hydrogen is preferably supplied to the cathode chamber as a gas stream via a gas inlet means. Suitable gas inlet means for supplying a hydrogen or hydrogen-containing gas stream include a pipe, a sparger, a hose, or a hydrogen gas diffusion material. Alternatively, hydrogen can be absorbed in a metal or metal alloy which can be released as the temperature increases. Such metals or alloys can be impregnated with hydrogen and used as the cathode. Preferably, a gas stream comprising hydrogen bubbles through or otherwise agitates the catholyte.

[0025] Upon the application of an electric potential, preferably from about 1.0 to about 10.0 V, preferably from about 1.0 V to about 5.0 V, the active metal ions are reduced at the cathode to the metal or semimetal as shown in Equation (3), and the anion is oxidized at the anode as shown in Equation (4a) for a monovalent anion such as a halide:

$$\text{Cathode}: \quad 2\,M^{y+} + y\,e^- \rightarrow M \qquad (3)$$

$$\text{Anode}: \quad y\,X^- \rightarrow {}^{y}/_{2}\,X_2 + y\,e^- \qquad (4a)$$

[0026] The active metal reacts with the hydrogen gas to form an active metal hydride compound as shown in Equation (5):

$$M + {}^{y}/_{2}\,H_2 \rightarrow MH_y \qquad (5)$$

[0027] In Equations (3), (4), and (5), y is an integer from 1 to 4 and typically depends on the preferred (i.e. the most stable) oxidation state of the active metal when it combines with oxygen to make the active metal oxide. Some exceptions are known, such as titanium, which preferentially forms a TiH_2 hydride, rather than TiH_3 or TiH_4.

[0028] Hydrogen may be supplied to the anode as well as to the cathode to convert the anion oxidation product to a desirable or valuable reaction product as shown in Equations (4b) and (4c) wherein X is a halide, and halogen is converted to HX. Electrochemically oxidizing H_2 at the anode in preference to X^- will generally result in a lower cell potential than the comparable electrochemical system that generates X_2 depicted in Equation (4a).

$$\text{Anode:} \quad \tfrac{1}{2} H_2 \rightarrow H^+ + e^- \quad (4b)$$

$$X^- + H^+ \rightarrow HX + e^- \quad (4c)$$

[0029] In another aspect of the present invention, the electrochemical-chemical process for obtaining metal hydrides according to the present invention can be incorporated into a process for producing boron hydride compounds. In this embodiment, oxidized boron compounds are reduced by a hydride carrier in a liquid salt to produce a boron hydride compound. The hydride carrier may be, for example, derived from the electrochemical reduction of active metal salts as described, wherein a molten active metal salt or mixture of molten active metal salts, either neat or in an ionic liquid, is converted into an active metal hydride via electrolysis under an atmosphere of hydrogen. The process of the present invention provides a ready "one-pot" means to reduce boron compounds such as boron-oxygen compounds and boron halide compounds, to boron hydride compounds including borohydride anions (BH_4^-).

[0030] To produce a boron hydride compound, at least one active metal salt is charged to the cathode compartment of an electrolytic cell and an electric potential from about 1.0 V to about 10.0 V and preferably from about 1.0 V to about 5.0 V is applied to form the active metal as described above.

[0031] After the active metal has reacted with hydrogen gas to produce the active hydride, the applied potential may be removed and the cell maintained at a temperature such that the metal hydride is at least partially dissolved in a liquid salt. Thus, for neat metal salt systems, the cell is maintained at temperatures above the melting point of the active metal salt or mixture of active metal salts. For systems wherein the metal salt was dissolved in an ionic liquid, the cell is maintained at a temperature that allows the solvent to be liquid.

[0032] As shown schematically in Figure 2, an oxidized boron species is introduced to the liquid salt containing the active metal hydride. The oxidized boron compound is selected from the group of boron oxygen and boron halide compounds. The boron-oxygen compound, collectively referred to as a "borate" in this application, is preferably selected from the group comprising trialkyl borates of formula $B(OR)_3$, where R is a straight-, branched-chain, or cyclic alkyl group containing from 1 to 6, preferably from 1 to 4, carbon atoms; boric oxide, B_2O_3; boric acid, $B(OH)_3$; and the group of alkali metal borate salts represented by the formula $zM_2O{\cdot}xB_2O_3{\cdot}yH_2O$, wherein z is ½ to 5; x is 0.1 to 5, y is 0 to 10; and M is an alkali metal ion such as sodium, potassium, or lithium. The boron halide compounds can be chosen from the group of compounds represented by formula BX_3, where X is a halide, preferably chloride or bromide.

[0033] The oxidized boron compound reacts with the active hydride. Equation (6a) illustrates the formation of borohydride from a trialkyl borate and an active metal hydride such as MH:

$$4\ MH + B(OR)_3 \rightarrow MBH_4 + 3\ MOR \quad (6a)$$

[0034] The stoichiometry of the reduction reaction can be adjusted as shown in Equations (6b) to (6d) to ensure the generation of a borohydride compound from various active metal hydrides and other oxidized boron compounds:

$$4\ MH_2 + 2\ B(OR)_3 \rightarrow M(BH_4)_2 + 3\ M(OR)_2 \quad (6b)$$
$$4\ MH_3 + 3\ B(OR)_3 \rightarrow M(BH_4)_3 + 3\ M(OR)_3 \quad (6c)$$
$$4\ MH_4 + 4\ B(OR)_3 \rightarrow M(BH_4)_4 + 3\ M(OR)_4 \quad (6d)$$

[0035] Higher boron hydride compounds, such as diborane and triborohydride compounds, can be prepared by varying the stoichiometric ratio between the hydride and the oxidized boron compound, as illustrated in Equation (6e) for the formation of the diborane ion from a trialkyl borate:

$$6\ MH + 2\ B(OR)_3 \rightarrow 6\ M^+ + {}^-B_2H_6 + 6\ (OR)^- \quad (6e)$$

[0036] The use of triborohydride compounds for hydrogen storage and related methods for their preparation are described in co-pending U.S. Patent Application Serial No. 10/741,192, entitled "Triborohydride Salts as Hydrogen Storage Materials and Preparation Thereof," filed December 19, 2003, the disclosure of which is incorporated by reference herein in its entirety.

[0037] Figure 3 schematically illustrates the process wherein the oxidized boron compound is charged to the cathode compartment of an electrolytic cell along with at least one active metal salt. For a neat reaction, the metal salt may be used as the "solvent" for the oxidized boron compound by heating the cell at temperatures from about 70 °C to about 500 °C so that the one or more active metal salts are in a liquid molten state. Alternatively, the metal salt and oxidized boron compound may be dissolved in an ionic liquid.

[0038] The oxidized boron compound/alkali metal salt mixture is subjected to a potential from about 1.0 V to about 5.0 V to form the active metal as described above. The oxidized boron compound reacts with the active hydride as it is produced, to form a boron hydride. In this case, the reactions illustrated in Equations (6a) - (6d) occur continuously as the metal hydride is formed.

[0039] Alkali metal borates, B_2O_3, and trialkyl borates such as $B(OR)_3$, may be reacted with alkali metal hydrides to obtain borohydride compounds in suspension. For example, at 275 °C, NaH and $B(OCH)_3$ react in mineral oil to form $NaBH_4$, and $NaOCH_3$. The present invention can achieve this reaction in a liquid salt, a solvent system that supports ionic conduction, and therefore electrochemical synthesis, wherein the reactants and products are in a dissolved state. The liquid salts include molten active metal salts and ionic liquids.

[0040] As an example of the process of this exemplary embodiment of the present invention, borohydride anions are obtained from a molten mixture of lithium bromide, potassium bromide, and cesium bromide under a hydrogen atmosphere by the electrolytic process of the present invention, where boric oxide is added to the melt before the application of a potential. Without being limited to any one particular theory, it is believed that electrolysis reduces the metal ions in the melt to the corresponding metals, which then react with hydrogen to make the metal hydrides. One or more of the metal hydrides then react with the boric oxide to make borohydride anions. A borohydride compound may then be isolated by suitable separation and extraction steps.

[0041] For the particular case where the oxidized boron compound is sodium metaborate, $NaBO_2$, it is preferable that the active metal hydride be lithium hydride. Lithium hydride can be formed *in situ* according to the teachings herein by the electrolytic reduction of lithium bromide, either as a liquid molten salt or dissolved in an ionic liquid, under a hydrogen atmosphere to form lithium hydride.

[0042] Hydrogen may be supplied to the anode as well as the cathode to convert the anion oxidation product and to lower cell potential according to the teachings herein.

[0043] In another embodiment of the invention, oxidized boron compounds are converted to boron hydride compounds via reaction with metal hydrides dissolved in liquid salts, wherein the metal hydrides may be, for example, commercially available products and/or not otherwise derived from the electrochemical reduction of active metal salts as taught herein. The metal hydrides should preferably be at least sparingly soluble in the liquid salt solvent. The liquid salt may be a molten metal salt, or a mixture of molten metal salts, or an ionic liquid.

[0044] The metal hydrides may be selected from, for example, the group of alkali metal hydrides, alkaline earth metal hydrides, aluminum hydrides including alane (AlH_3), and zinc hydride. A suitable metal hydride is chosen based on the standard reduction potential of the metal. Any metal wherein the standard reduction potential for the reaction of that metal with oxygen to yield the most thermodynamically stable metal oxide is more than about 1.6 V could be employed in this reaction.

[0045] The following examples further describe and demonstrate features of the present invention. The examples are given solely for illustration and are not to be construed as a limitation of the present invention.

Example 1

[0046] A schematic illustration of the reactions taking place in the process is provided in Figure 2. The working electrode (cathode) is a nickel wire. The counter electrode (anode) is a platinum mesh inside a glass sparging tube. The interior of the glass sparger comprises the anode chamber, and the region external to the sparging tube comprises the cathode chamber.

[0047] A mixture consisting of about 39.2 g LiBr, 18.1 g KBr, and 42.8 g of CsBr was charged to cathode compartment and was electrolyzed at about 5 V for about 5 hours under a hydrogen atmosphere to produce lithium metal at the cathode and bromine at the anode. The tube impeded mixing of the bromine that formed at the anode with the melt external to the tube, and thus slowed the back-reaction of lithium and bromine to lithium bromide. The tube also facilitated removal of gaseous bromine from the reactor under a stream of flowing nitrogen. The reaction flask containing the melt was maintained in a constant temperature bath at about 300°C.

[0048] After about 5 hours, 587 mAh of current passed through the cell. The nickel cathode and the sparging tube containing the anode were both removed from the melt, and a cold-water condenser was attached to the reaction flask. About 1.25 mL of tri-n-butyl borate was injected directly into the melt using a syringe. The reaction was allowed to proceed for about 15 minutes, and the reaction flask was removed from the constant temperature bath and allowed to cool. The melt solidified as it cooled. The cool, solid melt was dissolved in 0.5 M NaOH aqueous solution. A 50 mL sample of the solution was titrated using the iodate assay for borohydride as put forth in the *Sodium Borohydride Digest* by Rohm and Haas Company. The titration indicated that 3.15 x 10^{-4} mol BH_4^- was formed, a yield of 5.7% based on the 587 mAh of charge that passed through the cell. Boron NMR of the aqueous solution confirmed the presence of borohydride anion (chemical Shift = -40.85 ppm, Splitting = 80.6 Hz).

Example 2

[0049] Using the procedure described in Example 1, a melt consisting of about 39.2 g LiBr, 18.1 g KBr, and 42.8 g of CsBr was electrolyzed under an argon atmosphere at about 3 V for 34 minutes. The potential, at 3 V, was too low to reduce the cations in the melt to metal, and instead reduced the Ni surface of the cathode and generated bromine at the anode. The reactor 400 was assembled as shown in Figure 4. The reaction flask 402 containing the melt in cathode compartment 414 was maintained in a constant temperature bath at about 275 °C. The working electrode (cathode) was a nickel frit 404 connected to an inlet 406 through which a gas was passed (the gas could exit the reactor via outlet 420). The counter electrode 408 (anode) was a platinum mesh inside a glass sparging tube 410 with a glass frit separator 412. After 34 minutes, argon flowing through the cathode frit was replaced by flowing hydrogen. Argon continued to flow over the anode to remove bromine. The current was not interrupted as the gas changed. No changes were observed in the current. After 74 minutes, about 0.2 grams of B_2O_3 was added to the melt in chamber 414. No appreciable changes in the current were observed after being allowed to run an additional 126 minutes.

[0050] The electrolysis was reset to run for about 20 hours at about 5 V. After 20 hours, 1975 mAh of current passed through the cell. The nickel frit cathode and the sparging tube containing the anode were both removed from the melt. The reaction flask was removed from the constant temperature bath and allowed to cool. The melt solidified as it cooled, and the melt was dissolved in 0.5 M NaOH aqueous solution. A 50 mL sample of the solution was titrated using the iodate method for borohydride. The titration indicated that 2.34×10^{-4} mol BH_4^- anion was formed, a yield of 1.3% based on the 1975 mAh of charge that passed through the cell. Boron NMR of the aqueous solution confirmed the presence of borohydride anion.

Example 3

[0051] A melt consisting of about 9.8 g LiBr, 4.5 g KBr, and 10.7 g of CsBr under a nitrogen atmosphere was heated to about 250 °C. To this melt, 1.6 grams of B_2O_3 was added. With stirring, 0.27 g of LiH was added to the melt. After adding LiH, the temperature bath was turned off, but stirring was continued until melt solidified. After dissolving the cooled melt in 100 mL of 0.5 M NaOH, a 50 mL sample of the solution was titrated using the iodate method for borohydride. The titration indicated that 5.3×10^{-3} mol BH_4^- was formed, a yield of 62% based on the 0.27 grams of LiH added to the reactor. Boron NMR of the aqueous solution confirmed the presence of the borohydride anion.

Example 4

[0052] A mixture of about 39.2 g of LiBr, 18.1 g of KBr, and 42.8 g of CsBr, and 0.5 g of B_2O_3 were added to a 3-neck flask. The solids were heated to about 300 °C, a temperature at which this mixture is molten. A nickel metal sparging tube was inserted into the solution of molten alkali bromides, and H_2 gas passed through the sparger and bubbled through the solution. This tube comprised the cathode. H_2 gas was allowed to escape from the cell through one of the necks of the flask. A glass tube terminating in a porous glass sparger was also inserted into the solution. Platinum wire and platinum gauze were inside the tube, and the platinum comprised the anode. The porous glass of the sparging tube acted as a separator between the anode compartment (inside the glass tube) and the cathode compartment (outside the tube). The application of about 5 V of potential led to the passage of 1448 mAh of charge over 20 hours.

[0053] The net reaction at the cathode was the generation of alkali metal and boron-hydride compounds. At the anode Br_2 gas was evolved. A stream of Ar gas helped carry the Br_2 gas out of the anode compartment.

[0054] After about 20 hours, the potential was removed, and the cathode sparger and the anode tube were withdrawn from the molten solution and the solution was allowed to cool to room temperature and solidify. The resulting solid was dissolved in about 100 mL of 0.5 M aqueous NaOH solution. A small aliquot of solution was submitted to ^{11}B-NMR analysis, which showed the presence of borohydride (BH_4^-) anions in solution. Another sample of the same aqueous solution was titrated, determining the yield of boron-hydride anions to be 4%, with respect to the number of mAh of current passed through the cell.

Example 5

[0055] Using the process described in Example 4, about 39.2 g of LiBr, 18.1 g of KBr, and 42.8 g of CsBr, and 1 g of B_2O_3 were added to a 3-neck flask. The solids were heated to about 300 °C, a temperature at which this mixture is molten. A nickel metal sparging tube was inserted into the solution of molten alkali bromides, and H_2 gas passed through the sparger and bubbled through the solution. This tube is the cell cathode. H_2 gas was allowed to escape from the cell through one of the necks of the flask. A glass tube terminating in a porous glass sparger was also inserted into the solution. Platinum wire and platinum gauze were inside the tube, and the platinum comprised the anode. The porous glass of the sparging tube acted as a separator between the anode compartment (inside the glass tube) and the cathode compartment (outside the tube). The application of about 5 V of potential led to the passage of 1000 mAh of charge over about 6 hours.

[0056] After the 6 hour period, the potential applied across the anode and cathode was removed. The cathode sparger and the anode tube were withdrawn from the molten solution and the solution was allowed to cool to room temperature and solidify. The resulting solid was dissolved in about 100 mL of 0.5 M aqueous NaOH solution. A small aliquot of solution was submitted to ^{11}B-NMR analysis, which showed the presence of both BH_4- (borohydride) and B_3H_8- (triborohydride) anions in solution. Another sample of the same aqueous solution was titrated, determining the yield of boron hydride anions to be 8.3%, with respect to the number of mAh of current passed through the cell.

Example 6

[0057] Tetra-n-butylammonium bromide was heated to about about 120 °C, and about 1.5 mL of tri-n-butyl borate ($B(O\text{-}Bu)_3$) followed by about 0.5 grams of sodium hydride was added to the hot ionic liquid. The starting materials are only sparingly soluble in the melt and fast stirring was necessary to ensure adequate dispersion. After addition of the sodium hydride was complete, the melt was cooled to room temperature and dissolved in the minimum amount of aqueous 0.5 M NaOH. The presence of borohydride in the aqueous solution was verified by NMR spectroscopy.

[0058] The above description and drawings illustrate preferred embodiments that achieve the objects, features and advantages of the present invention. It is not intended that the present invention be limited to the illustrated embodiments.

Any modification of the present invention that comes within the spirit and scope of the following claims should be considered part of the present invention.

CLAIMS

What is claimed as new and desired to be protected by Letters Patent:

1. A process for preparing a metal hydride compound, comprising:

providing an electrolytic cell containing anode and cathode compartments separated by a separator which is permeable to ions;

supplying at least one metal salt in molten form to the cathode compartment;

applying an electric potential to the cell; and

providing hydrogen to the cathode compartment.

2. The process of claim 1, wherein the metal salt has the formula MX_n, wherein M is an active metal cation selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Ti^{3+}, Ti^{4+}, Zn^{2+}, Al^{3+}, Si^{4+}, Y^{3+}, Y^+, Zr^{2+}, Zr^{3+}, Zr^{4+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, and lanthanides in the +3 oxidation state; X is an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides; and n is the valence of the active metal cation.

3. The process of claim 2, wherein M is selected from the group consisting of Li^+, Na^+, K^+ and Cs^+; and X is chloride or bromide.

4. The process of claim 1, wherein the separator comprises a material selected from the group consisting of lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, sodium-β-aluminum oxide, sodium-β″-aluminum

oxide, sodium-β/β″-aluminum oxide, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, and potassium-β/β″-aluminum oxide.

5. The process of claim 1, wherein the separator is a NaSICON membrane.

6. The process of claim 1, wherein the separator is a LiSICON membrane.

7. The process of claim 1, wherein the separator comprises a material selected from the group consisting of porous glass, porous metals, porous ceramics, porous plastics, paper polymers, fluorinated polymers, ion-conducting polymers, and fluorinated ion-conducting polymers.

8. The process of claim 1, wherein the electrical potential is from about 1 to about 10 volts.

9. The process of claim 7, wherein the electrical potential is from about 1 to about 5 volts.

10. The process of claim 1, further comprising passing hydrogen or a hydrogen containing gas to the cathode compartment through a gas inlet means.

11. The process of claim 1, further comprising bubbling hydrogen gas through the cathode compartment to agitate the catholyte.

12. The process of claim 1, further comprising providing hydrogen to the cathode compartment from hydrogen absorbed in a metal.

13. The process of claim 1, further comprising providing hydrogen to the anode compartment and electrooxidizing hydrogen at the anode.

14. A process for producing a metal hydride compound, comprising:

providing an electrolytic cell containing anode and cathode compartments separated by a separator which is permeable to ions;

supplying at least one metal salt to the cathode compartment, wherein the metal salt is at least partially dissolved in an ionic liquid;

applying an electric potential to the cell; and

providing hydrogen to the cathode compartment.

15. The process of claim 14, wherein the metal salt has the formula MX_n, wherein M is an active metal cation selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Ti^{3+}, Ti^{4+}, Zn^{2+}, Al^{3+}, Si^{4+}, Y^{3+}, Y^+, Zr^{2+}, Zr^{3+}, Zr^{4+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, and lanthanides in the +3 oxidation state; X is an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides; and n is the valence of the active metal cation.

16. The process of claim 15, wherein M is selected from the group consisting of Li^+, Na^+, K^+ and Cs^+; and X is chloride or bromide.

17. The process of claim 14, wherein the separator comprises a material selected from the group consisting of lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, sodium-β-aluminum oxide, sodium-β″-aluminum oxide, sodium-β/β″-aluminum oxide, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, and potassium-β/β″-aluminum oxide.

18. The process of claim 14, wherein the separator is a NaSICON membrane.

19. The process of claim 14, wherein the separator is a LiSICON membrane.

20. The process of claim 14, wherein the separator comprises a material selected from the group consisting of porous glass, porous metals, porous ceramics, porous plastics, paper polymers, fluorinated polymers, ion-conducting polymers, and fluorinated ion-conducting polymers.

21. The process of claim 14, wherein the electrical potential is from about 1 to about 10 volts.

22. The process of claim 21, wherein the electrical potential is from about 1 to about 5 volts.

23. The process of claim 14, further comprising passing hydrogen or a hydrogen containing gas to the cathode compartment through a gas inlet means.

24. The process of claim 14, further comprising bubbling hydrogen the cathode compartment to agitate the catholyte.

25. The process of claim 14, further comprising providing hydrogen to the cathode compartment from hydrogen absorbed in a metal.

26. The process of claim 14, further comprising providing hydrogen to the anode compartment and electrooxidizing hydrogen at the anode.

27. The process of claim 14, wherein the ionic liquid is a salt comprising a cation containing at least one carbon atom and having a melting point between about -100 °C to about 200 °C.

28. The process of claim 14, wherein the ionic liquid comprises a cation selected from the group consisting of mono-, di-, tri-, and tetra substituted ammonium; mono-, di-, tri-, and tetra substituted phosphonium, N-alkylpyridinium, 1,3-disubstituted pyridiniums, 1,4-disubstituted pyridiniums, 1,3-disubstituted imidazolium, 1,2,3-trisubstituted imidazolium, 1,1 disubstituted pyrrolidiums, trialkylsulfonium, and trialkyloxonium cations.

29. The process of claim 14, wherein the ionic liquid comprises an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides.

30. A process for producing a boron hydride compound, comprising:

providing an electrolytic cell containing anode and cathode compartments separated by a separator which is permeable to ions;

supplying at least one metal salt in molten form to the cathode compartment;

applying an electric potential to the cell;

providing hydrogen to the cathode compartment; and

providing a boron compound to the cathode compartment.

31. The process of claim 30, wherein the metal salt has the formula MX_n, wherein M is an active metal cation selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Ti^{3+}, Ti^{4+}, Zn^{2+}, Al^{3+}, Si^{4+}, Y^{3+}, Y^+, Zr^{2+}, Zr^{3+}, Zr^{4+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, and lanthanides in the +3 oxidation state; X is an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides; and n is the valence of the active metal cation.

32. The process of claim 31, wherein M is selected from the group consisting of Li^+, Na^+, K^+ and Cs^+; and X is chloride or bromide.

33. The process of claim 30, wherein the separator comprises a material selected from the group consisting of lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, sodium-β-aluminum oxide, sodium-β″-aluminum oxide, sodium-β/β″-aluminum oxide, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, and potassium-β/β″-aluminum oxide.

34. The process of claim 30, wherein the separator comprises a material selected from the group consisting of NaSICON and LiSICON membranes.

35. The process of claim 30, wherein the separator comprises a material selected from the group consisting of porous glass, porous metals, porous ceramics, and porous plastics.

36. The process of claim 30, wherein the electrical potential is from about 1 to about 10 volts.

37. The process of claim 36, wherein the electrical potential is from about 1 to about 5 volts.

38. The process of claim 30, further comprising passing hydrogen or a hydrogen containing gas to the cathode compartment through a gas inlet means.

39. The process of claim 30, further comprising bubbling hydrogen the cathode compartment to agitate the catholyte.

40. The process of claim 30, further comprising providing hydrogen to the cathode compartment from hydrogen absorbed in a metal.

41. The process of claim 30, wherein the boron compound is an oxidized boron compound.

42. The process of claim 41, wherein the oxidized boron compound is sodium metaborate and the metal halide is lithium bromide.

43. The process of claim 30, further comprising maintaining the cell at a temperature of about 70 to about 500 °C.

44. The process of claim 30, further comprising providing hydrogen to the anode compartment and electrooxidizing hydrogen at the anode.

45. The process of claim 30, wherein the electric potential is removed before providing the boron compound.

46. The process of claim 30, wherein the boron compound is provided before applying the electric potential.

47. The process of claim 30, further comprising separating the boron hydride compound.

48. The process of claim 30, wherein the boron compound is a boron halide.

49. The process of claim 30, wherein the boron compound is an alkyl borate.

50. The process of claim 30, wherein the boron compound is a borate.

51. The process of claim 30, wherein the boron compound is selected from the group consisting of boric oxide and boric acid.

52. The process of claim 30, wherein the boron compound is an alkali metal borate salt.

53. A process for producing a boron hydride compound, comprising:

providing an electrolytic cell containing anode and cathode compartments separated by a separator which is permeable to ions;

supplying at least one metal salt to the cathode compartment, wherein the metal salt is at least partially dissolved in an ionic liquid;

applying an electric potential to the cell;

providing hydrogen to the cathode compartment; and

providing a boron compound to the cathode compartment.

54. The process of claim 53, wherein the metal salt has the formula MX_n, wherein M is an active metal cation selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Ti^{3+}, Ti^{4+}, Zn^{2+}, Al^{3+}, Si^{4+}, Y^{3+}, Y^+, Zr^{2+}, Zr^{3+}, Zr^{4+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, and lanthanides in the +3 oxidation state; X is an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides; and n is the valence of the active metal cation.

55. The process of claim 54, wherein M is selected from the group consisting of Li^+, Na^+, K^+ and Cs^+; and X is chloride or bromide.

56. The process of claim 53, wherein the separator comprises a material selected from the group consisting of lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, sodium-β-aluminum oxide, sodium-β″-aluminum oxide, sodium-β/β″-aluminum oxide, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, and potassium-β/β″-aluminum oxide.

57. The process of claim 53, wherein the separator comprises a material selected from the group consisting of NaSICON and LiSICON membranes.

58. The process of claim 53, wherein the separator comprises a material selected from the group consisting of porous glass, porous metals, porous ceramics,

porous plastics, paper polymers, fluorinated polymers, ion-conducting polymers, and fluorinated ion-conducting polymers.

59. The process of claim 53, wherein the electrical potential is from about 1 to about 10 volts.

60. The process of claim 53, wherein the electrical potential is from about 1 to about 5 volts.

61. The process of claim 53, further comprising passing hydrogen or a hydrogen containing gas to the cathode compartment through a gas inlet means.

62. The process of claim 53, further comprising bubbling hydrogen the cathode compartment to agitate the catholyte.

63. The process of claim 53, further comprising providing hydrogen to the cathode compartment from hydrogen absorbed in a metal.

64. The process of claim 53, wherein the ionic liquid is a salt comprising a cation containing at least one carbon atom and having a melting point between about -100 °C to about 200 °C.

65. The process of claim 53, wherein the ionic liquid comprises a cation selected from the group consisting of mono-, di-, tri-, and tetra substituted ammonium;

mono-, di-, tri-, and tetra substituted phosphonium, N-alkylpyridinium, 1,3-disubstituted pyridiniums, 1,4-disubstituted pyridiniums, 1,3-disubstituted imidazolium, 1,2,3-trisubstituted imidazolium, 1,1 disubstituted pyrrolidiums, trialkylsulfonium, and trialkyloxonium cations.

66. The process of claim 53, wherein the ionic liquid comprises an anion selected from the group consisting of halides, tosylate, sulfate, sulfonates, nitrate, phosphates, hexafluorophosphate, phosphates, phosphinates, dicyanamide, tetrafluoroborate, acetate, trifluoroacetate, borohydride, benzoate, tetrachloroaluminate, thiocyanate, thiosalicylate, methides, and imides.

67. The process of claim 53, wherein the boron compound is a boron-oxygen compound.

68. The process of claim 53, wherein the boron compound is an alkyl borate.

69. The process of claim 53, wherein the boron compound is a borate.

70. The process of claim 53, wherein the boron compound is selected from the group consisting of boric oxide and boric acid.

71. The process of claim 53, wherein the boron compound is an alkali metal borate salt.

72. The process of claim 53, wherein the boron compound is sodium metaborate and the metal halide is lithium bromide.

73. The process of claim 53, further comprising maintaining the cell at a temperature of about 70 to about 500 °C.

74. The process of claim 53, further comprising providing hydrogen to the anode compartment and electrooxidizing hydrogen at the anode.

75. The process of claim 53, wherein the electric potential is removed before providing the boron compound.

76. The process of claim 53, wherein the boron compound is provided before applying the electric potential.

77. The process of claim 53, further comprising separating the boron hydride compound.

78. A process for producing borohydride anions comprising dissolving a metal hydride and a boron compound in at least one liquid salt.

79. The process of claim 78, wherein the metal hydride is selected from the group consisting of alkali metal hydrides, alkaline earth metal hydrides, aluminum hydrides and zinc hydrides.

80. The process of claim 78, wherein the metal hydride comprises a metal characterized in that the standard reduction potential for the reaction of the metal with oxygen is at least about 1.6 V.

81. The process of claim 78, wherein the metal hydride is formed by the steps of:

supplying at least one active metal salt in molten form to a cathode compartment of an electrolytic cell containing anode and cathode compartments separated by a separator which is permeable to ions;

applying an electric potential to said cell to reduce the metal compound at the cathode; and

passing hydrogen or a hydrogen containing gas in the cathode compartment while the compound is reduced at the cathode.

82. The process of claim 78, wherein the metal hydride is formed *in situ*.

83. The process of claim 78, wherein the boron compound is an oxidized boron compound.

84. The process of claim 78, wherein the liquid salt is a molten active metal salt.

85. The process of claim 78, wherein the liquid salt is a mixture of molten active metal salts.

86. The process of claim 78, wherein the liquid salt is an ionic liquid.

87. The process of claim 78, wherein the liquid salt is a mixture of at least one molten active metal salt and at least one ionic liquid.

88. An apparatus for reducing boron compounds to produce boron hydride compounds, comprising:

an anode compartment containing on anode;

a cathode compartment containing a cathode;

a separator between the anode and cathode compartments, wherein the separator is permeable to ions;

at least one inlet for charging metal salt and boron compounds to the cathode compartment; and

a means for supplying hydrogen to the cathode compartment.

89. The apparatus of claim 88, wherein the apparatus is configured to maintain the cathode compartment at a temperature of about 70 °C to about 500 °C.

90. The apparatus of claim 88, wherein the separator comprises a material selected from the group consisting of lithium-β-aluminum oxide, lithium-β″-aluminum oxide, lithium-β/β″-aluminum oxide, sodium-β-aluminum oxide, sodium-β″-aluminum

oxide, sodium-β/β″-aluminum oxide, potassium-β-aluminum oxide, potassium-β″-aluminum oxide, and potassium-β/β″-aluminum oxide.

91. The apparatus of claim 88, wherein the separator is a NaSICON membrane.

92. The apparatus of claim 88, wherein the separator is a LiSICON membrane.

93. The apparatus of claim 88, wherein the separator comprises a material selected from the group consisting of porous glass, porous metals, porous ceramics, porous plastics, paper polymers, fluorinated polymers, ion-conducting polymers, and fluorinated ion-conducting polymers.

94. The apparatus of claim 88, further comprising a means for bubbling hydrogen gas through the cathode compartment to agitate the catholyte.

95. The apparatus of claim 88, wherein the cathode compartment contains hydrogen absorbed in a metal adapted to release hydrogen when heated.

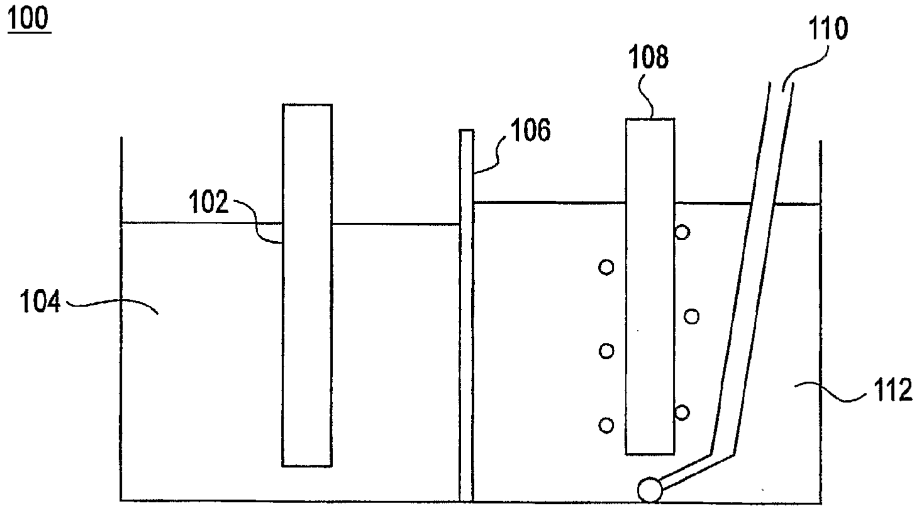

FIG. 1

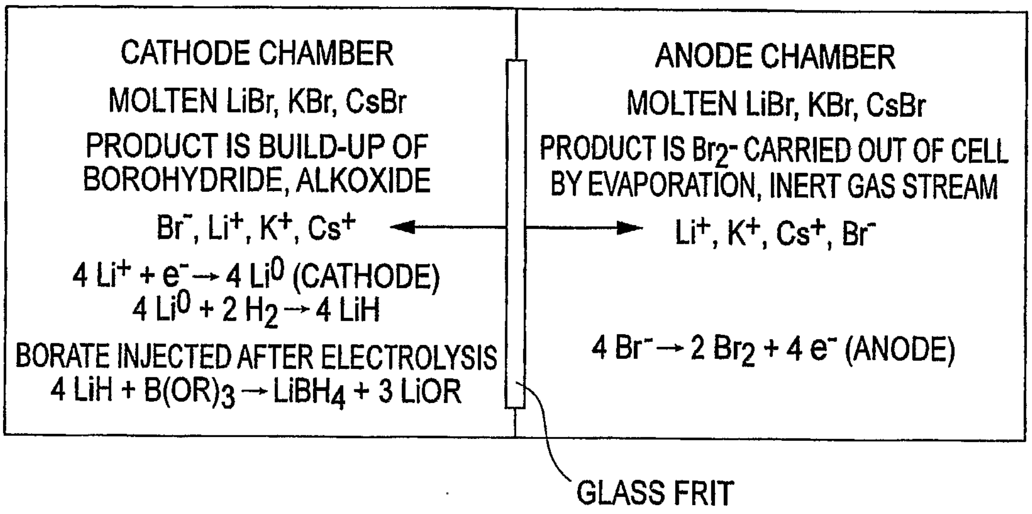
CATHODE CHAMBER
MOLTEN LiBr, KBr, CsBr
PRODUCT IS BUILD-UP OF BOROHYDRIDE, ALKOXIDE
Br^-, Li^+, K^+, Cs^+
$4\ Li^+ + e^- \rightarrow 4\ Li^0$ (CATHODE)
$4\ Li^0 + 2\ H_2 \rightarrow 4\ LiH$
BORATE INJECTED AFTER ELECTROLYSIS
$4\ LiH + B(OR)_3 \rightarrow LiBH_4 + 3\ LiOR$
ANODE CHAMBER
MOLTEN LiBr, KBr, CsBr
PRODUCT IS Br_2- CARRIED OUT OF CELL BY EVAPORATION, INERT GAS STREAM
Li^+, K^+, Cs^+, Br^-
$4\ Br^- \rightarrow 2\ Br_2 + 4\ e^-$ (ANODE)
GLASS FRIT

FIG. 2

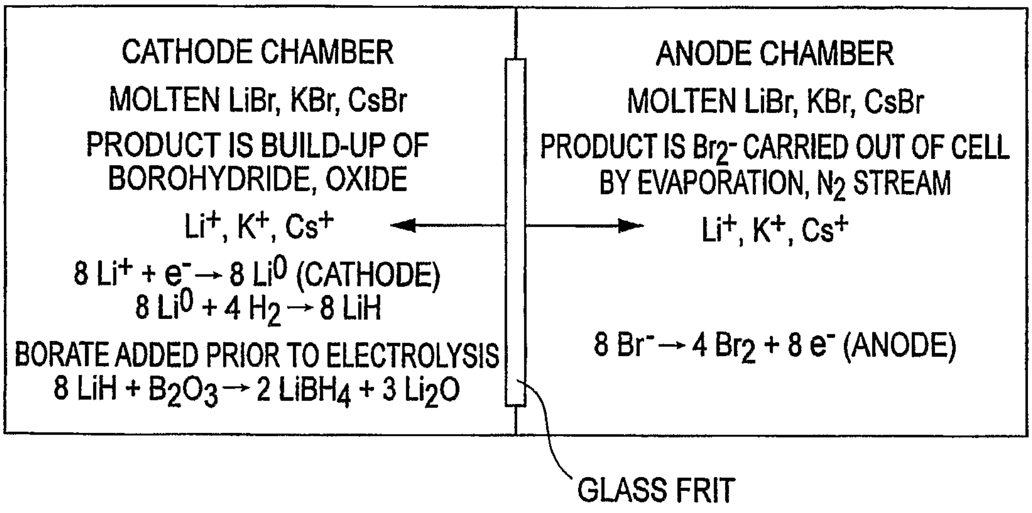
CATHODE CHAMBER
MOLTEN LiBr, KBr, CsBr
PRODUCT IS BUILD-UP OF BOROHYDRIDE, OXIDE
Li^+, K^+, Cs^+
$8\ Li^+ + e^- \rightarrow 8\ Li^0$ (CATHODE)
$8\ Li^0 + 4\ H_2 \rightarrow 8\ LiH$
BORATE ADDED PRIOR TO ELECTROLYSIS
$8\ LiH + B_2O_3 \rightarrow 2\ LiBH_4 + 3\ Li_2O$
ANODE CHAMBER
MOLTEN LiBr, KBr, CsBr
PRODUCT IS Br_2- CARRIED OUT OF CELL BY EVAPORATION, N_2 STREAM
Li^+, K^+, Cs^+
$8\ Br^- \rightarrow 4\ Br_2 + 8\ e^-$ (ANODE)
GLASS FRIT

FIG. 3

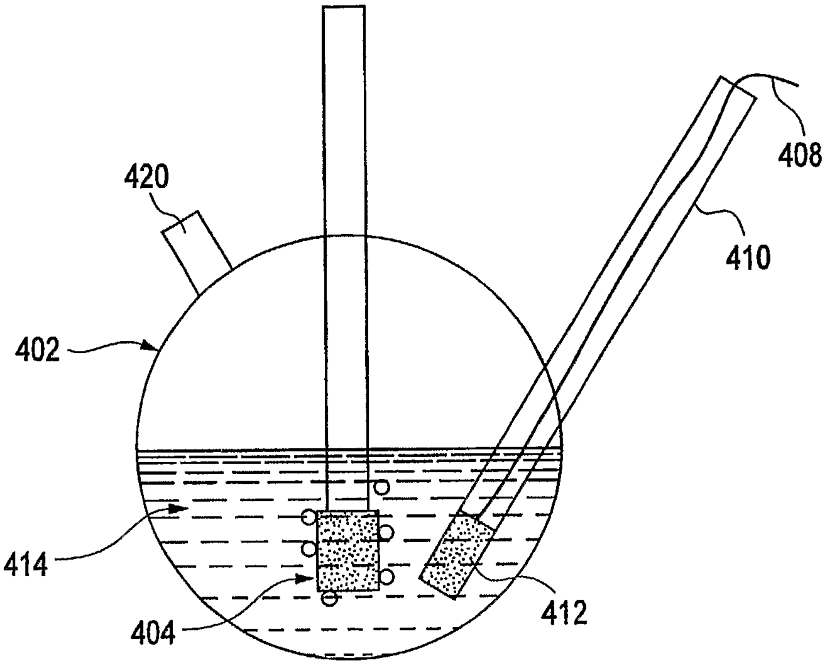

FIG. 4