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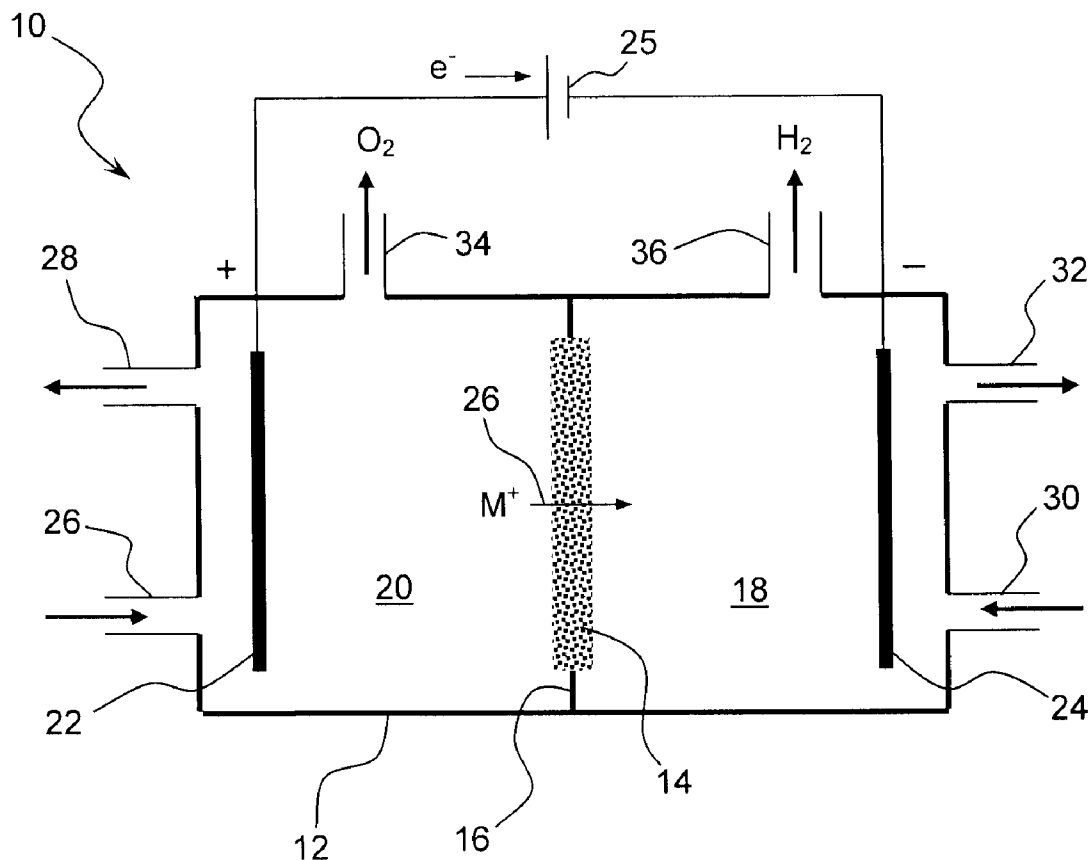
(19) **United States**(12) **Patent Application Publication**
Balagopal et al.(10) **Pub. No.: US 2008/0245671 A1**(43) **Pub. Date: Oct. 9, 2008**(54) **ELECTROCHEMICAL PROCESS TO
RECYCLE AQUEOUS ALKALI CHEMICALS
USING CERAMIC ION CONDUCTING SOLID
MEMBRANES****Related U.S. Application Data**

(60) Provisional application No. 60/909,735, filed on Apr. 3, 2007.

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(52) **U.S. Cl.** **205/510; 204/252**
(57) **ABSTRACT**

A method is provided to recycle and synthesize aqueous alkali chemicals from industrial and radioactively contaminated alkali salt based waste streams using a two-compartment electrolytic cell having an alkali cation-conductive ceramic membrane. The processes and apparatus provide the capability of recycling and synthesizing value added chemicals, including but not limited to, alkali hydroxides.

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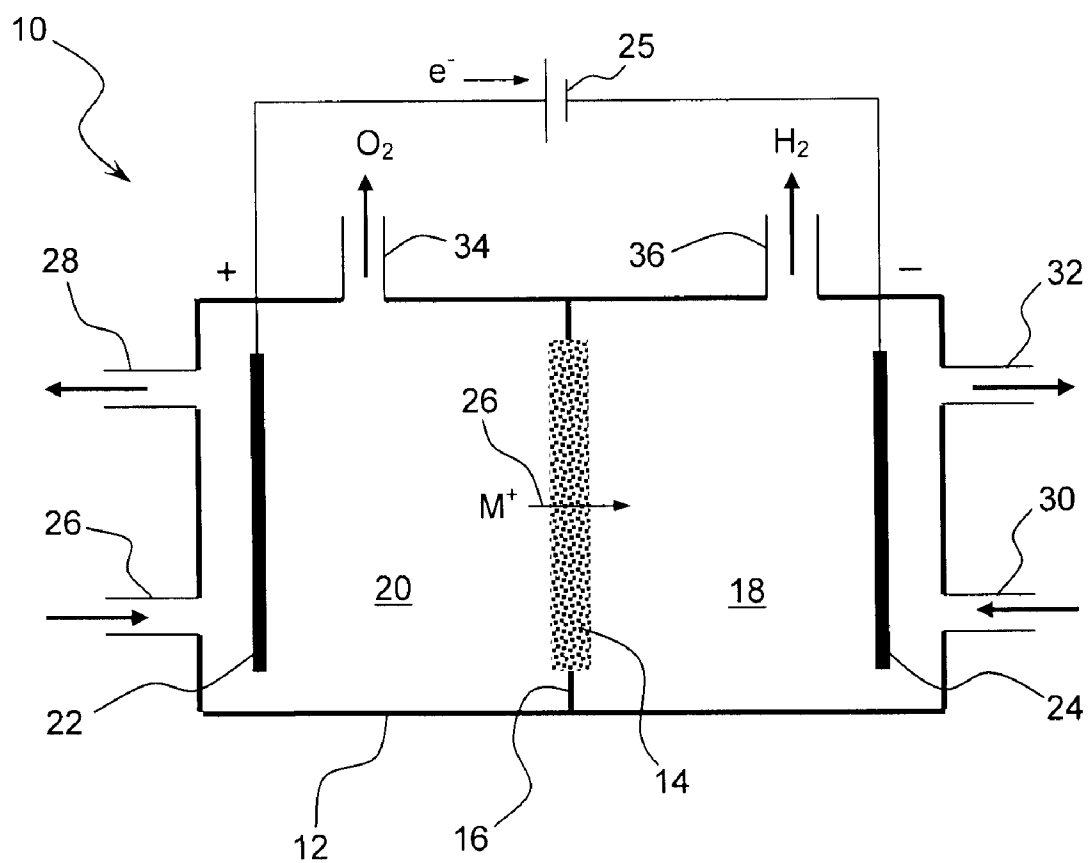


Fig. 1

Performance of NASD10 membrane in 3M NaNO₃ + 2M NaOH solution
@ 100 mA/cm²

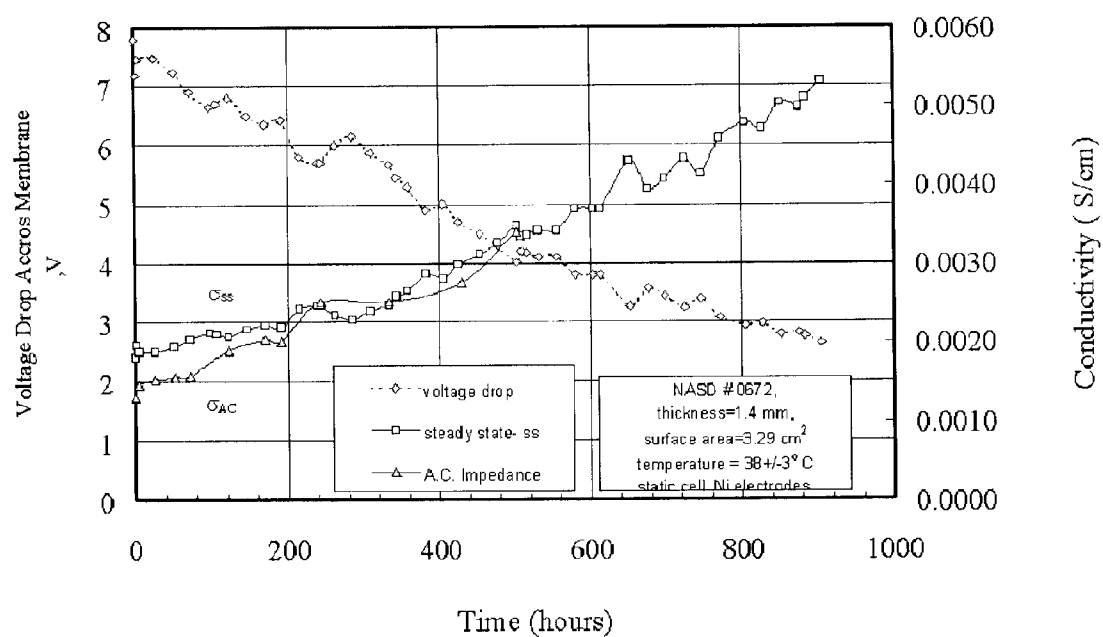


Fig. 2

NAS-D10 Electrochemical Performance
4.5 V, 40 °C, NaOH

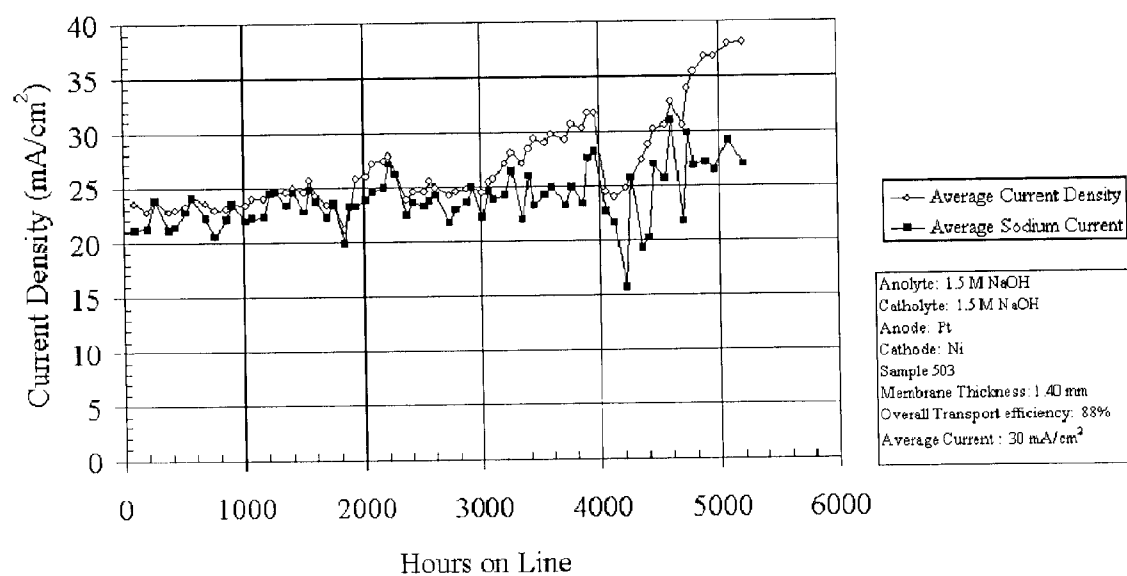


Fig. 3

NAS-E Electrochemical Performance 40 °C, 100 mA/cm², 1.5 M NaOH

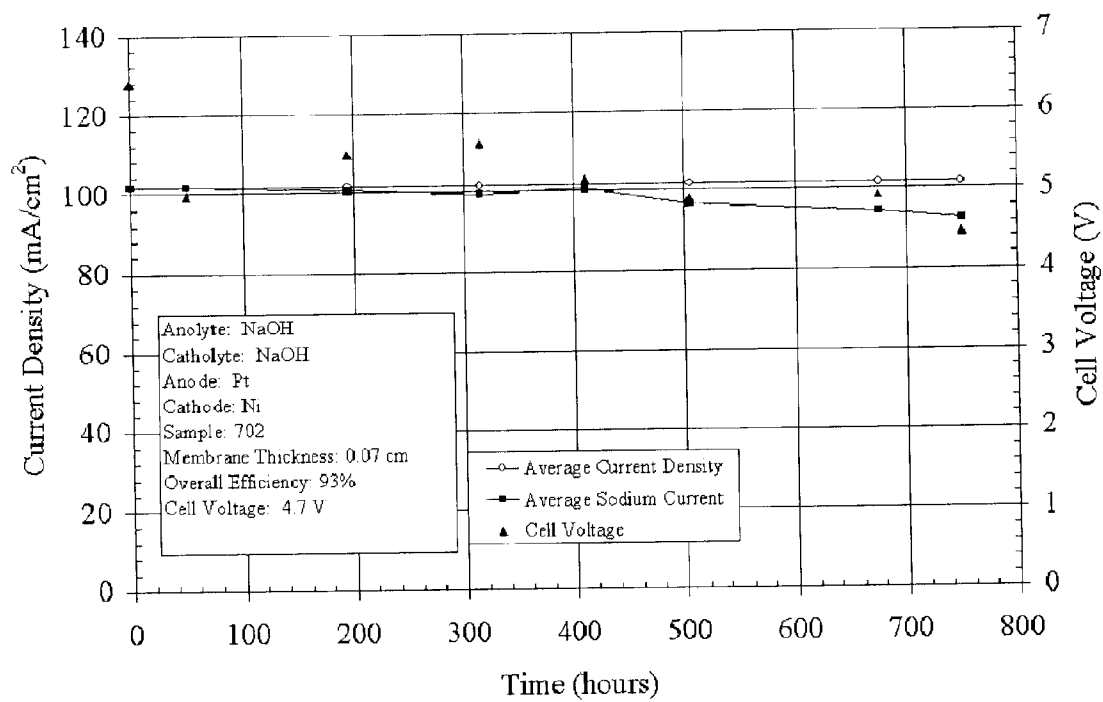


Fig. 4

NAS-G Electrochemical Performance 40 °C, NaOH

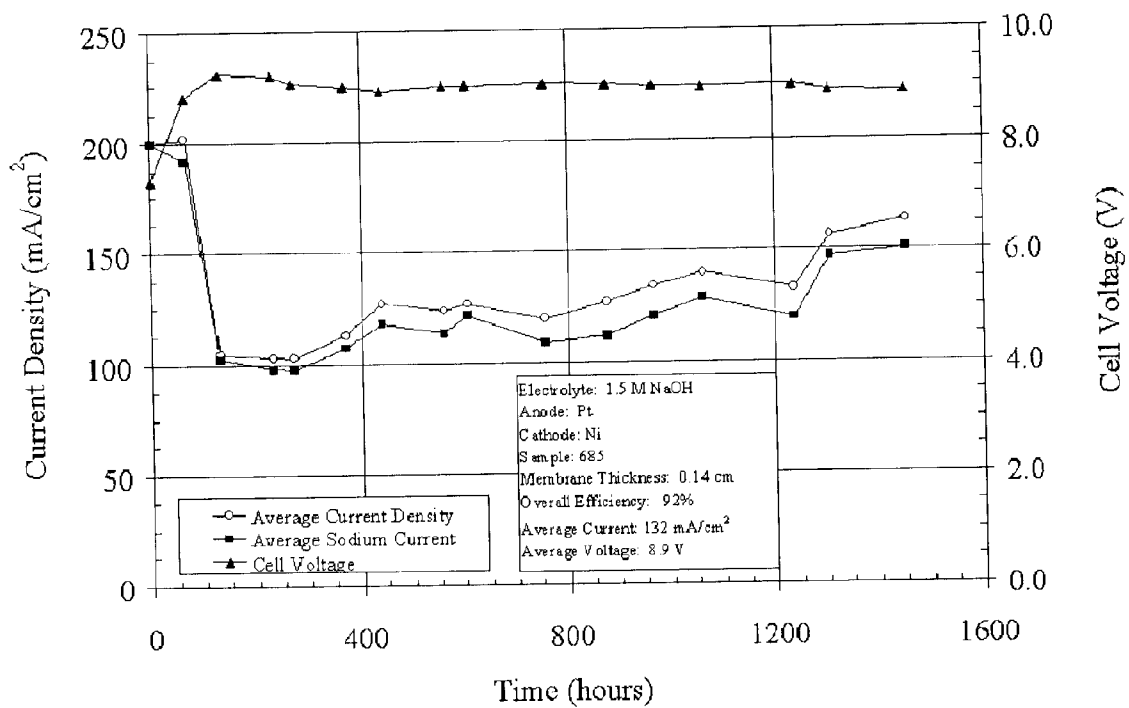


Fig. 5

NAS-G Electrochemical Performance
50 °C, SRS Simulant

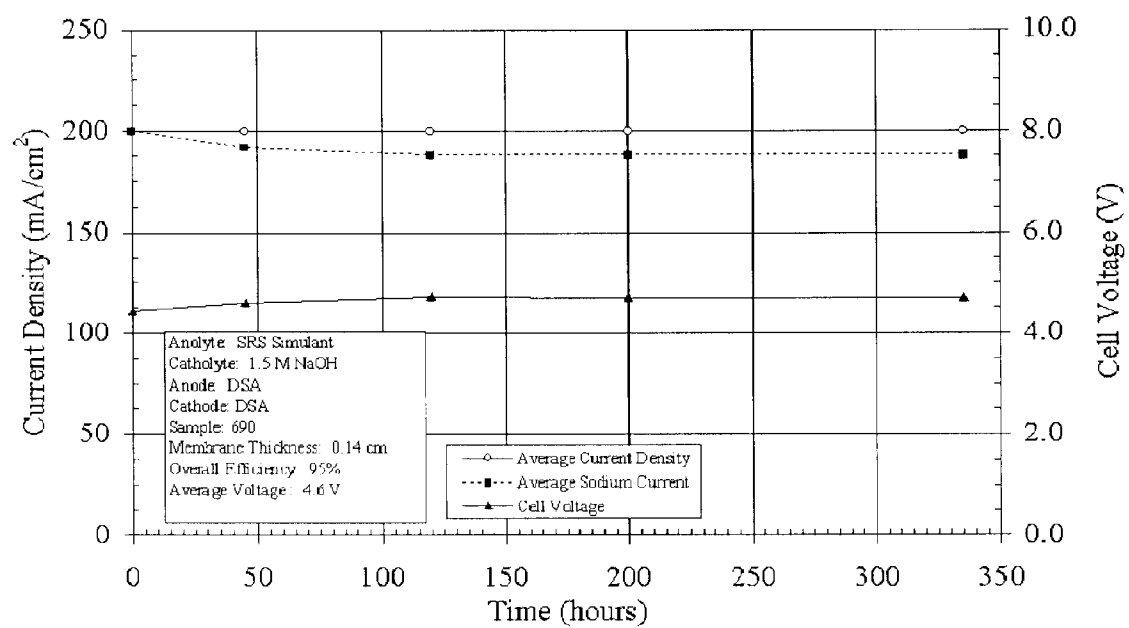


Fig. 6

NASG Electrochemical Performance at 50° C, 5 M Caustic

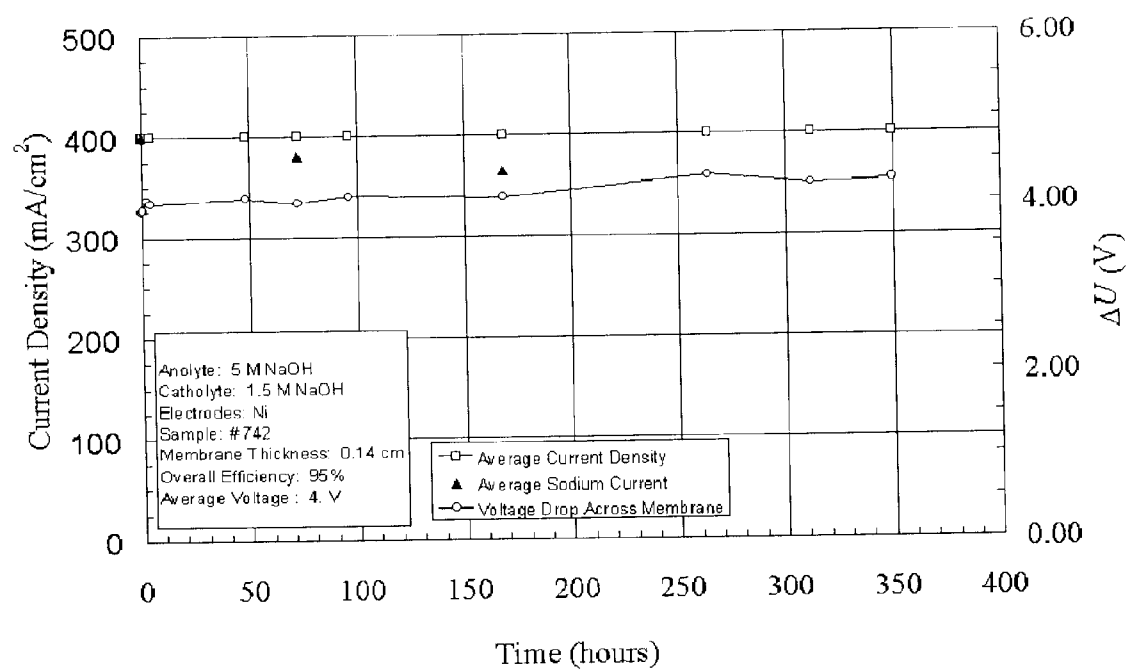


Fig. 7

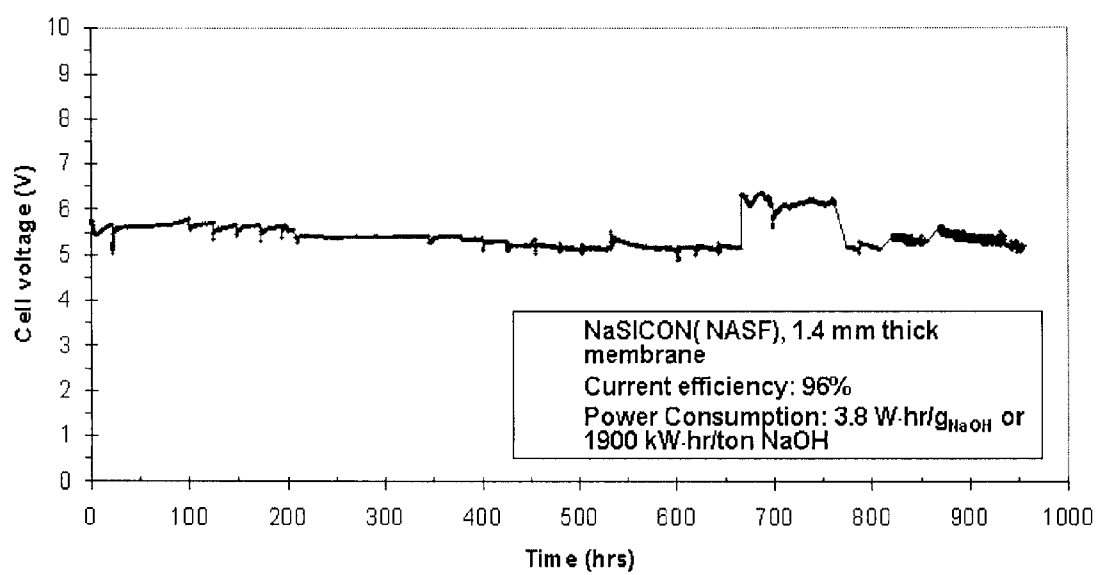


Fig. 8

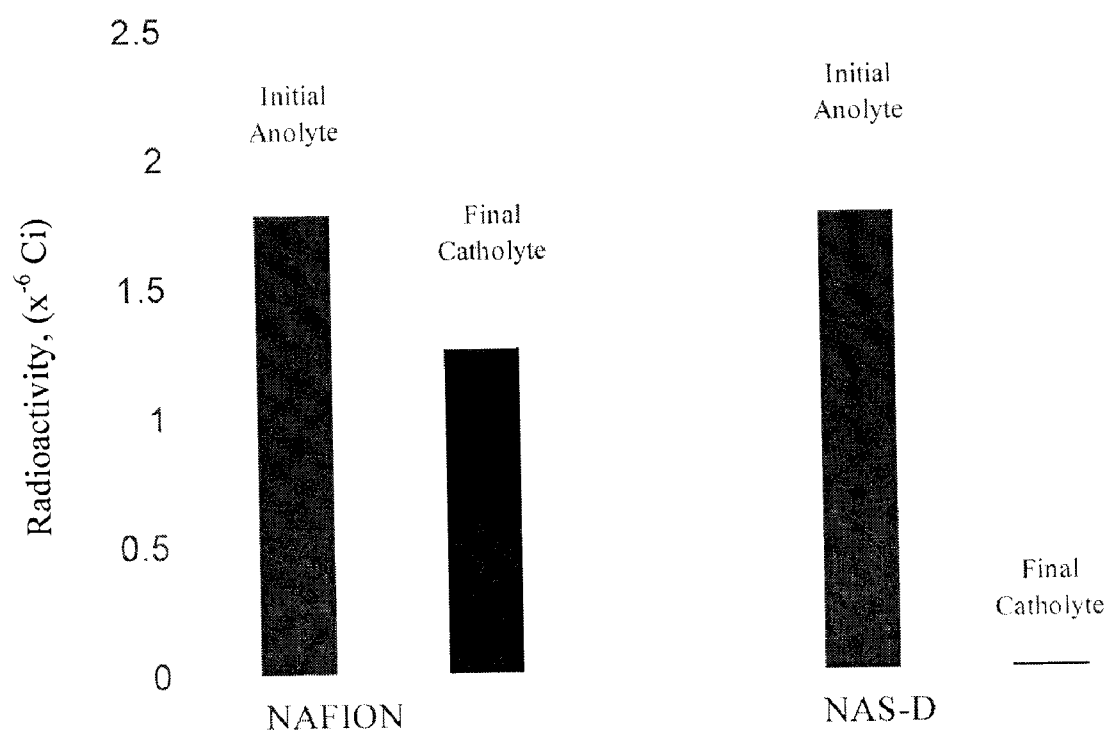


Fig. 9

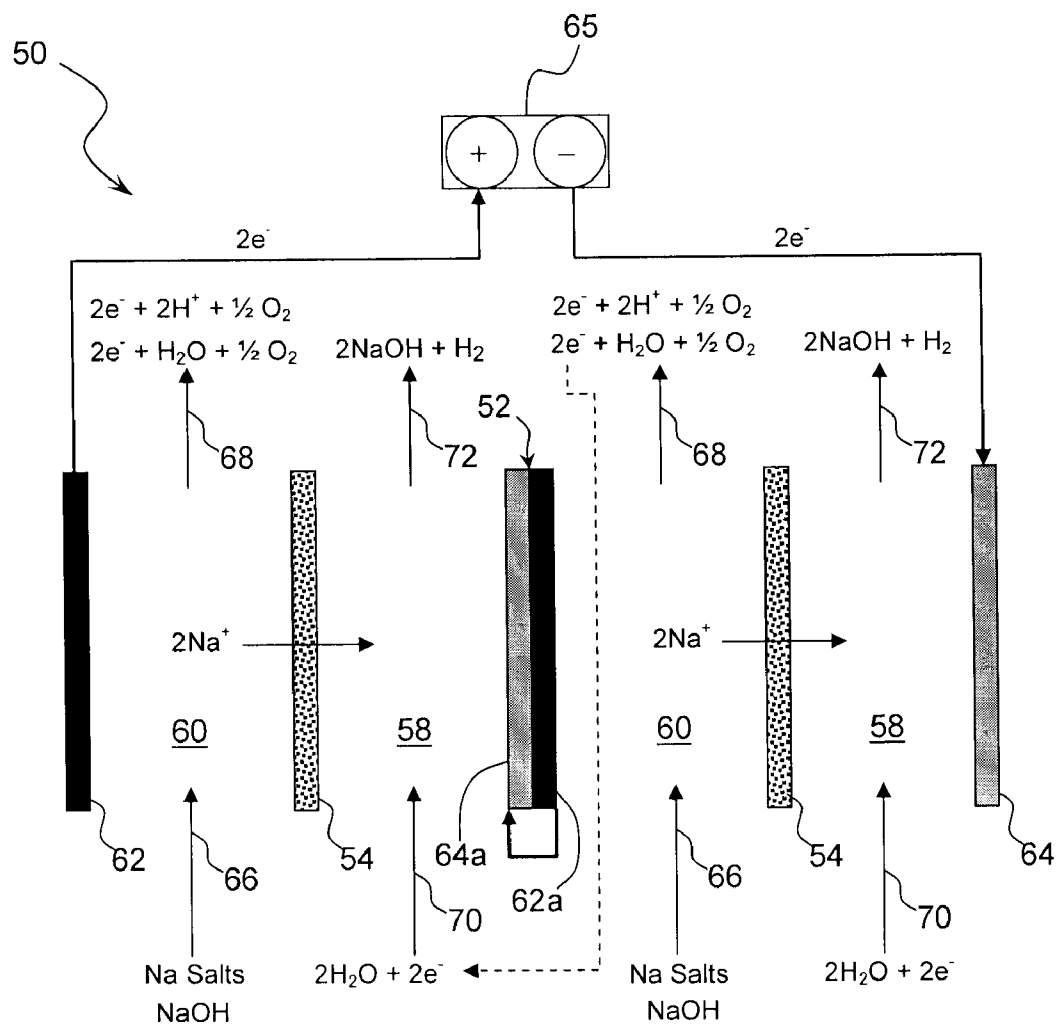


Fig. 10

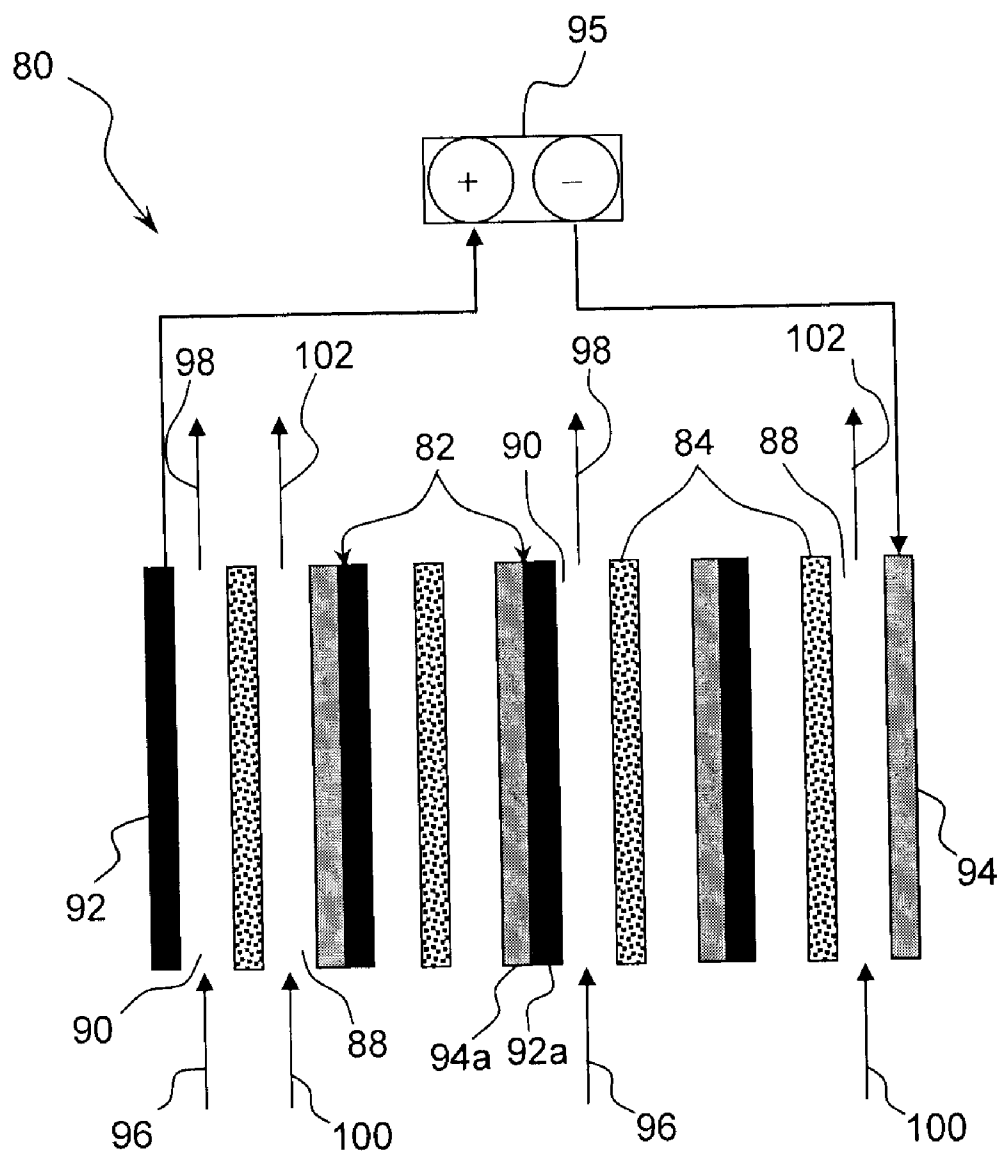


Fig. 11

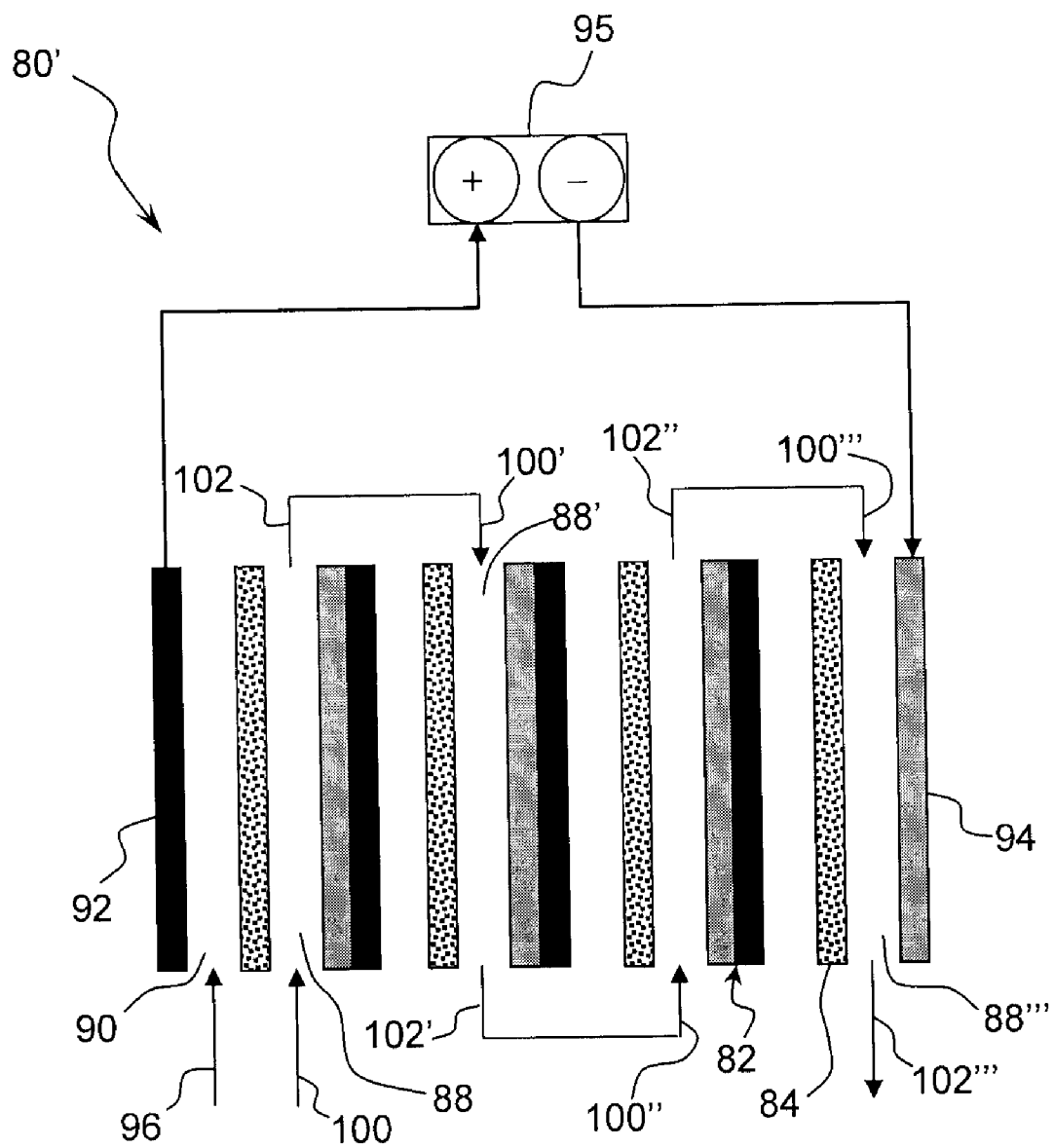


Fig. 12

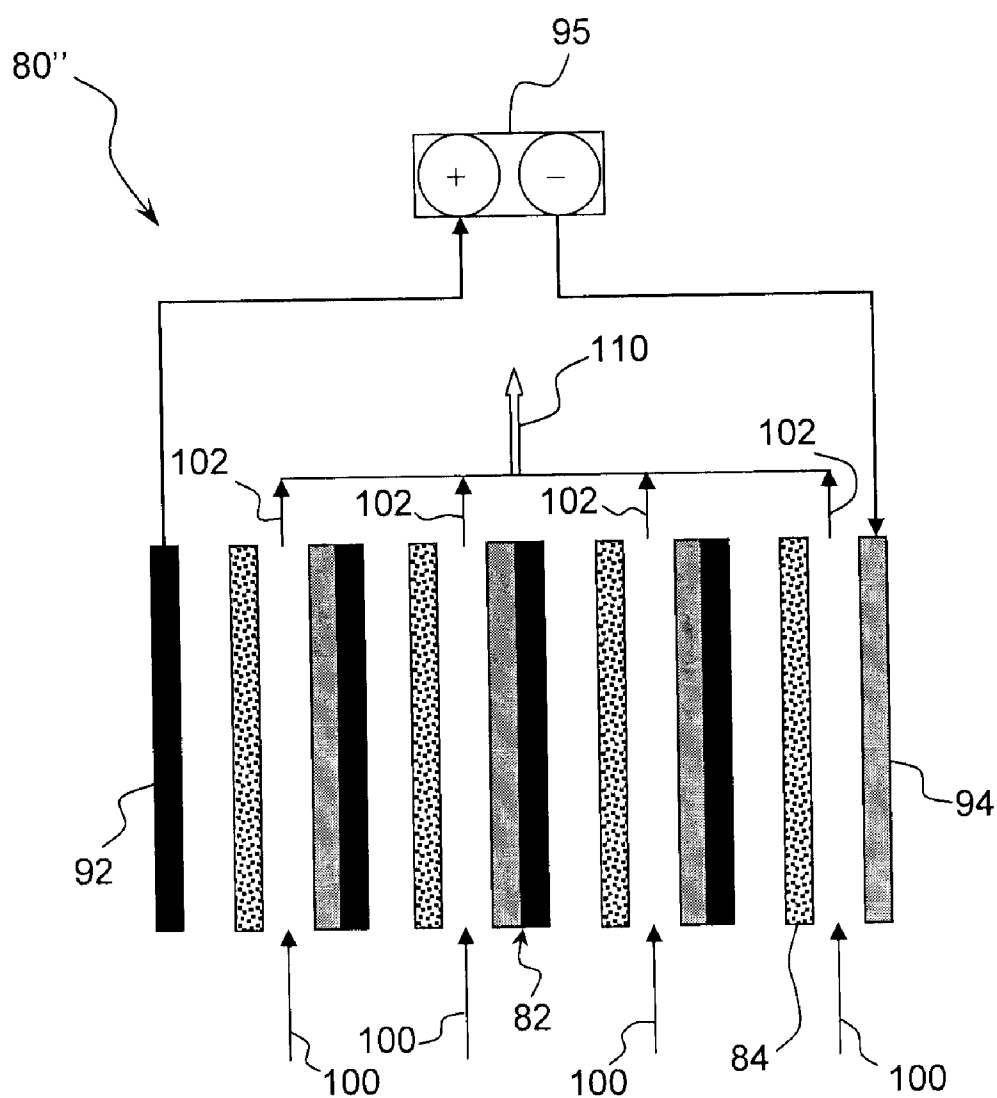


Fig. 13

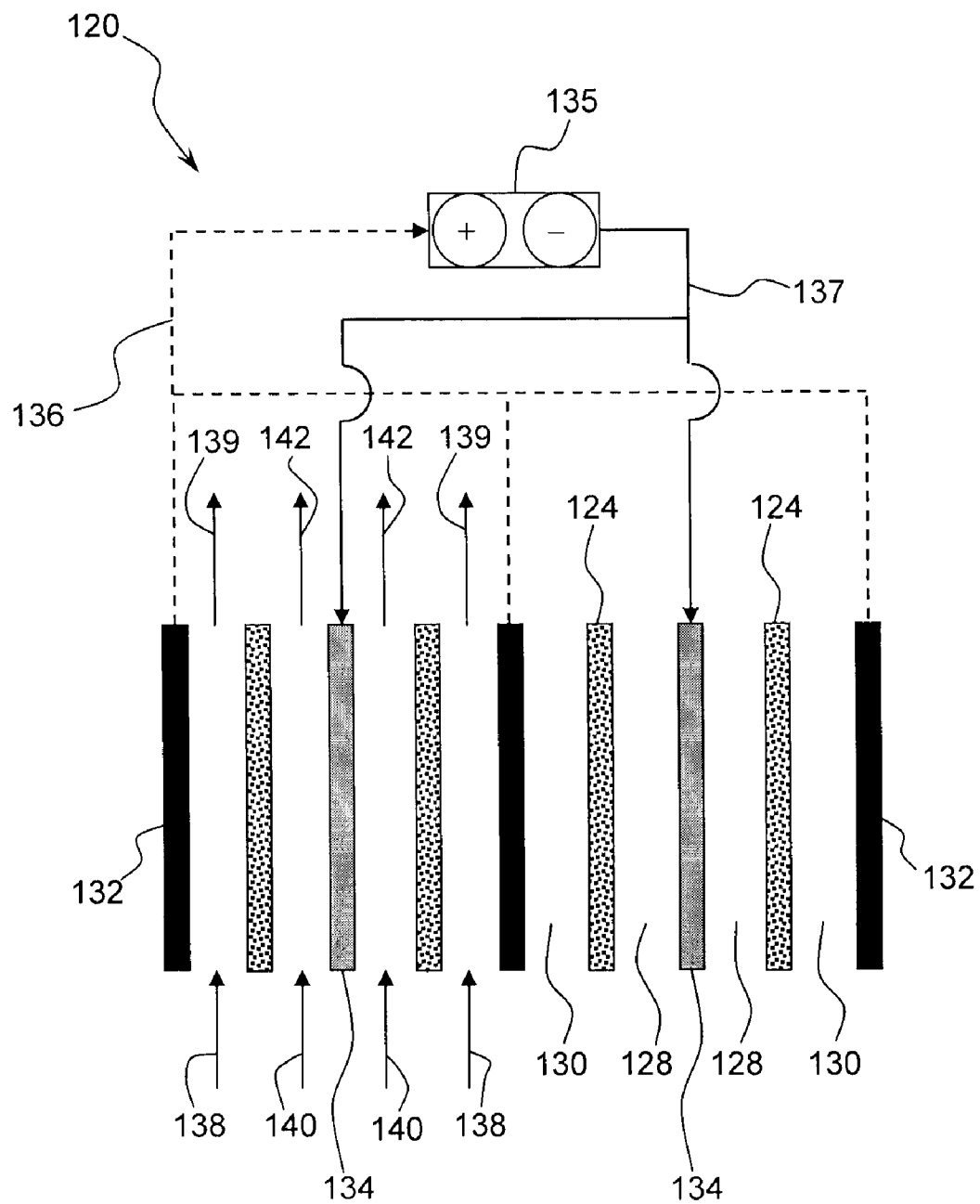


Fig. 14

ELECTROCHEMICAL PROCESS TO RECYCLE AQUEOUS ALKALI CHEMICALS USING CERAMIC ION CONDUCTING SOLID MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/909,735, filed Apr. 3, 2007, which application is incorporated by reference.

GOVERNMENT RIGHTS

[0002] This invention was made in part with government support under grant number DE-FG07-04ID14622 awarded by the United States Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] The present invention relates in general to a two-compartment electrolytic cell using an alkali cation-conductive ceramic membrane and to electrochemical processes performed in a two-compartment electrolytic cell using alkali cation-conductive ceramic membranes. More specifically, the invention relates to a two-compartment electrolytic cell, and a multi-compartment configuration of the electrolytic cell, and to a process to recycle and synthesize value added alkali chemicals from an aqueous or non-aqueous waste stream containing alkali cations and mixed monovalent and/or multivalent cations.

[0004] Many industrial processes produce aqueous and non-aqueous waste streams containing alkali metal salts in combination with other cations. Some processes, such as nuclear power plants, produce waste solutions that contain various cations, and in some cases radionuclides. Such waste solutions may include, but not limited to, Na, K, Cs, Ca, Sr, Ba, Al, etc. It would be an advancement in the art to selectively recover alkali metals (Li, Na, K) from the waste solution containing mixed cations while producing a useful alkali product.

BRIEF SUMMARY OF THE INVENTION

[0005] In accordance, there is provided a method of recycling and making alkali chemicals, acids and hydroxides, preferably from complex sodium or alkali salts, and a combination of alkali salt solutions. The method comprises feeding a salt solution, preferably into a catholyte compartment of an electrolytic cell, feeding an alkali metal salt solution or combination of salt solutions, into an anolyte compartment of the cell, and applying potential across the electrodes of the cell. The anolyte compartment and the catholyte compartment of the cell are separated by an alkali ion conductive ceramic membrane that, upon application of the electric current, selectively transports the specific alkali metal cations from the anolyte compartment to the catholyte compartment. The membrane is substantially impermeable to water, operates at a high current density, and/or operates at a low voltage. The alkali metal cations, following their transport across the membrane, react with the corresponding anions in the catholyte compartment of the cell.

[0006] In this process, salts are decomposed in an electrochemical cell and selected alkali ions are transferred across an alkali ion conducting solid electrolyte configured to selectively transport alkali ions. Oxidation and reduction are the

principal electrolysis reactions at the electrodes and depending on the nature of the salts other gas species evolve at the electrodes as product gases. The reduction of water at the cathode generates hydroxyl ions and hydrogen. As the sodium ions migrate through the membrane from the anolyte side of the cell to the catholyte side, they will combine with the hydroxyl ions produced by the reduction of water to form sodium hydroxide solution.

[0007] The separator is preferably an alkali ion conducting solid electrolyte configured to selectively transport alkali ions. It may be a specific alkali ion conductor. For example, the alkali ion conducting solid electrolyte may be a solid MeSICON (Metal Super Ion CONducting) material, where Me is Na, K, or Li. The alkali ion conducting solid electrolyte may comprise a material having the formula $\text{Me}_{1-x}\text{Zr}_x\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ where $0 \leq x \leq 3$, where Me is Na, K, or Li. Other alkali ion conducting solid electrolytes may comprise a material having the formula $\text{Me}_5\text{RESi}_4\text{O}_{12}$ where Me is Na, K, or Li, where RE is Y, Nd, Dy, or Sm, or any mixture thereof. The alkali ion conducting solid electrolyte may comprise a non-stoichiometric alkali-deficient material having the formula $(\text{Me}_5\text{RESi}_4\text{O}_{12})_{1-\delta}(\text{RE}_2\text{O}_3 \cdot 2\text{SiO}_2)_\delta$, where Me is Na, K, or Li, where RE is Nd, Dy, or Sm, or any mixture thereof and where δ is the measure of deviation from stoichiometry. The alkali ion conducting separator may be beta-alumina. In specific embodiments disclosed herein, the alkali ion conducting solid electrolyte is a NaSICON (Sodium Super Ionic CONductors) cation ceramic membrane.

[0008] Such processes and devices for conducting such processes are disclosed herein.

[0009] Other advantages and aspects of the present invention will become apparent upon reading the following description of the drawings and detailed description of the invention. These and other features and advantages of the present invention will become more fully apparent from the following figures, description, and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0010] In order that the manner in which the above-recited and other features and advantages of the invention are obtained will be readily understood, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof that are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

[0011] FIG. 1 is a schematic view of a two-compartment electrolytic cell comprising an alkali-cation conductive ceramic membrane according to the present invention.

[0012] FIG. 2 shows a graph of cell voltage as a function of time for Example 1.

[0013] FIG. 3 shows a graph of cell voltage as a function of time for Example 2.

[0014] FIG. 4 shows a graph of cell voltage as a function of time for Example 3.

[0015] FIG. 5 shows a graph of cell voltage and current density as a function of time for Example 4.

[0016] FIG. 6 shows a graph of cell voltage and current density as a function of time for Example 5.

[0017] FIG. 7 shows a graph of cell voltage and current density as a function of time for Example 6.

[0018] FIG. 8 shows a graph of cell voltage and current density as a function of time for Example 7.

[0019] FIG. 9 shows a graph of cell voltage and current density as a function of time for Example 8.

[0020] FIG. 10 shows a schematic view of a multi-compartment electrolytic cell comprising alkali-cation conductive ceramic membranes and a bipolar electrodes.

[0021] FIG. 11 shows a schematic view of a multi-compartment electrolytic cell arranged in series comprising alkali-cation conductive ceramic membranes and bipolar electrodes.

[0022] FIG. 12 shows a schematic representation of the multi-compartment electrolytic cell of FIG. 11 in which the alkali hydroxide produced in one catholyte compartment is introduced into a second catholyte compartment to increase the concentration of the alkali hydroxide produced within the second catholyte compartment.

[0023] FIG. 13 shows a schematic representation of the multi-compartment electrolytic cell of FIG. 11 in which the alkali hydroxide produced from several catholyte compartments are collected into a single catholyte outlet stream.

[0024] FIG. 14 shows a schematic view of a multi-compartment electrolytic cell arranged in parallel comprising alkali-cation conductive ceramic membranes.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The presently preferred embodiments of the present invention will be best understood by reference to the drawings, wherein like parts are designated by like numerals throughout. It will be readily understood that the components of the present invention, as generally described and illustrated in the figures herein, could be arranged and designed in a wide variety of different configurations. Thus, the following more detailed description of the embodiments of the electrolytic cell using alkali cation-conductive solid ceramic membranes of the present invention, and processes using the two-compartment and multi-compartment electrolytic cell as represented in FIGS. 1 through 14, is not intended to limit the scope of the invention, as claimed, but is merely representative of presently preferred embodiments of the invention.

[0026] The phrase “substantially impermeable to water,” when used in the instant application to refer to a membrane, means that a small amount of water may pass through the membrane, but that the amount that passes through is not of a quantity to diminish the usefulness of the present invention. The phrase “essentially impermeable to water,” as used herein in reference to a membrane, means that no water passes through the membrane, or that if water passes through the membrane, its passage is so limited so as to be undetectable by conventional means. The words “substantially” and “essentially” are used similarly as intensifiers in other places within this specification.

[0027] Referring to FIG. 1, there is provided a schematic representation of an electrolytic cell 10 that can be used in the methods for recycling alkali ions and producing alkali hydroxides according to the present invention described herein. In one embodiment, electrolytic cell 10 is used to make aqueous solutions of sodium hydroxide. The electrolytic cell 10 includes a container or shell 12, which may be corrosion resistant. An alkali-conducting ceramic membrane

14, which may be positioned in or supported by a scaffold or holder 16, together with the container 12 defines a catholyte compartment 18, and an anolyte compartment 20. The anolyte compartment 20 is configured with an anode 22 and the catholyte compartment 18 is configured with a cathode 24. An electric potential or voltage source 25 is provided to operate the electrolytic cell 10.

[0028] The container 12, and other parts of the cell 10, may be made of any suitable material, including metal, glass, plastics, composite, ceramic, other materials, or combinations of the foregoing. The material that forms any portion of the electrolytic cell 10 is preferably not reactive with or substantially degraded by the chemicals and conditions that it is exposed to as part of the process.

[0029] The electrolytic cell 10 further comprises an anolyte inlet 26 for introducing chemicals into the anolyte compartment 20 and an anolyte outlet 28 for removing or receiving anolyte solution from the anolyte compartment 20. The cell 10 also includes a catholyte inlet 30 for introducing chemicals into the catholyte compartment 18 and a catholyte outlet 32 for removing or receiving catholyte solution from the catholyte compartment 18. It will be appreciated by those of skill in the art that the cell configuration and relative positions of the inlets and outlets may vary while still practicing the teachings of the invention.

[0030] Because gases may be evolved from the cell during operation, venting means (34, 36) are provided to vent, treat and/or collect gases from the anolyte compartment 20 and/or catholyte compartment 18. The means may be a simple venting system such as openings, pores, holes, and the like. The venting means may also include without limitation, a collection tube, hose, or conduit in fluid communication with an airspace or gap above the fluid level in the anolyte and/or catholyte compartments. The gases which are evolved may be collected, vented to outside the electrolytic cell, sent through a scrubber or other treatment apparatus, or treated in any other suitable manner.

[0031] The anode 22 and cathode 24 materials may be good electrical conductors stable in the media to which they are exposed. Any suitable electrically and catalytically active material may be used, and the material may be solid, plated, perforated, expanded, or the like. In one embodiment, the anode 22 and cathode 24 material is a dimensionally stable anode (DSA) which is comprised of ruthenium oxide coated titanium (RuO_2/Ti). Suitable anodes 22 can also be formed from nickel, cobalt, nickel tungstate, nickel titanate, platinum and other noble anode metals, as solids plated on a substrate, such as platinum-plated titanium. Kovar (Ni-Co-Fe), stainless steel, lead, graphite, tungsten carbide and titanium diboride are also useful anode materials. Suitable cathodes 24 may be formed from metals such as nickel, cobalt, platinum, silver, Kovar and the like. The cathodes 24 may also be formed from alloys such as titanium carbide with small amounts of nickel. In one embodiment, the cathode is made of titanium carbide with less than about 3% nickel. Other embodiments include cathodes that include FeAl_3 , NiAl_3 , stainless steel, perovskite ceramics, and the like. Graphite is also a useful cathode material. In some embodiments, the electrodes are chosen to maximize cost efficiency effectiveness, by balancing electrical efficiency with low cost of electrodes.

[0032] The electrode material may be in any suitable form within the scope of the present invention, as would be understood by one of ordinary skill in the art. In some specific

embodiments, the form of the electrode materials may include at least one of the following: a solid, dense or porous solid-form, a dense or porous layer plated onto a substrate, a perforated form, an expanded form including a mesh, or any combination thereof.

[0033] In some embodiments of the present invention, the electrode materials may be composites of electrode materials with non-electrode materials, where non-electrode materials are poor electrical conductors under the conditions of use. A variety of insulative non-electrode materials are also known in the art, as would be understood by one of ordinary skill in the art. In some specific embodiments, the non-electrode materials may include at least one of the following: ceramic materials, polymers, and/or plastics. These non-electrode materials may also be selected to be stable in the media to which they are intended to be exposed.

[0034] In some embodiments, only electrolytic reactions occur in the cell and galvanic reactions are eliminated or greatly minimized. Accordingly, alkali ion conducting ceramic membranes **14** may include those which eliminate or minimize galvanic reactions and promote only electrolytic reactions. In one embodiment, the membrane **14** has high ionic conductivity with minimal or negligible electronic conductivity. The membrane may have high selectivity to preferred ionic species, such as lithium ions, sodium ions, or potassium ions. The membrane **14** may also physically separate the anolyte compartment from the catholyte compartment. This may be accomplished using a dense ceramic electrolyte.

[0035] The alkali ion conducting ceramic membrane **14** selectively transports a particular, desired alkali metal cation species from the anolyte to the catholyte side even in the presence of other cation species. The alkali ion conducting ceramic membrane **14** may also be impermeable to water and/or other undesired metal cations. In some specific embodiments, the ceramic membrane **14** has a current density from about 20 to about 200 mA/cm². In one embodiment, the current through the alkali ion conducting ceramic is predominantly ionic current.

[0036] In some specific embodiments, the alkali ion conducting ceramic membranes **14** are essentially impermeable to at least the water components of both the first or catholyte solution and second or anolyte solution. These alkali ion conducting ceramic solid electrolytes or ceramic membranes **14** may have low or even negligible electronic conductivity, which virtually eliminates any galvanic reactions from occurring when an applied potential or current is removed from the cell containing the membrane **14**. In another embodiment, these alkali ion conducting ceramic solid electrolyte or ceramic membranes **14** are selective to a specific alkali metal ion and hence a high transference number of preferred species, implying very low efficiency loss due to near zero electro-osmotic transport of water molecules.

[0037] A variety of alkali ion/alkali ion conducting ceramic materials are known in the art and would be suitable for constructing the alkali ion/alkali ion conducting solid electrolyte **14** of the present invention, as would be understood by one of ordinary skill in the art. In an embodiment within the scope of the present invention, the alkali ion conducting ceramic membrane **14** compositions comprising NaSICON (Sodium Super Ionic Conductors) materials are utilized for their characteristics of high ion-conductivity for sodium ions at low temperatures, selectivity for sodium ions, current efficiency and chemical stability in water, ionic solvents, and

corrosive alkali media under static and electrochemical conditions. Other similar alkali ion conducting ceramic membranes may be highly conductive for other alkali cations, such as lithium ions or potassium ions. Such alkali ion conducting ceramic membranes **14** may have one or more, or all, of the following desirable characteristics which make them suitable for aqueous and non-aqueous electrochemical applications. One characteristic is that, being dense, the ceramic membrane **14** is at least substantially impervious to water transport, and is not influenced by scaling or precipitation of divalent ions, trivalent ions, and tetravalent ions or dissolved solids present in the solutions. The ceramic membrane **14** may selectively transport sodium ions in the presence of other ions at a transfer efficiency that is in some instances above 90%. In some embodiments of the alkali cation-conductive ceramic materials of the present invention, the alkali cation-conductive ceramic materials may have a sodium ion conductivity ranging from about 1×10^{-4} S/cm to about 5×10^{-1} S/cm measured from ambient temperature to about 85° C. In yet another embodiment the ceramic membrane **14** provides resistance to fouling by precipitants, and/or electro-osmotic transport of water, which is common with organic or polymer membranes.

[0038] In some specific embodiments, the alkali cation-conductive ceramic membrane may include at least one of the following features and use characteristics, as would be understood by one of ordinary skill in the art: a solid form; a high alkali ion conductivity at temperatures below about 200° C.; low electronic conductivity; an alkali ion transfer efficiency (i.e. high transference number) greater than about 95%; a high selectivity for particular alkali cations (e.g. Na⁺) in relation to other alkali or non-alkali cations; stability in solutions of alkali ion containing salts and chemicals of weak or strong organic or inorganic acids; a density greater than about 95% of theoretical density value; substantially impermeable to water transport; resistant to acid, alkaline, caustic and/or corrosive chemicals.

[0039] As noted above, in some specific embodiments, the cation conducted by the alkali ion conducting ceramic membrane **14** is the sodium ion (Na⁺). In some specific embodiments, sodium-ion conducting ceramic membranes include alkali ion conducting ceramic membrane **14** compositions comprising NaSICON-type materials of general formula Na_{1-x}Zr₂Si_xP_{3-x}O₁₂ where $0 \leq x \leq 3$. The membrane **14** may include NaSICON materials of general formula Na₃RESi₄O₁₂ and non-stoichiometric sodium-deficient materials of general formula (Na₃RESi₄O₁₂)_{1-δ}(RE₂O₃·2SiO₂)_δ, where RE is Nd, Dy, or Sm, or any mixture thereof and where δ is the measure of deviation from stoichiometry, as disclosed in U.S. Pat. No. 5,580,430, and as explicitly incorporated herein by this reference in its entirety. Other analogs of NaSICON materials to transport alkali ions such as Li and K, to produce other alkali hydroxides are known to those of ordinary skill in the art, and their use is encompassed within the scope of this invention. These alkali ion conducting ceramic membranes comprising NaSICON materials or comprising analogs of NaSICON materials are particularly useful in electrolytic systems for simultaneous production of alkali hydroxides, by electrolysis of alkali (e.g., sodium) salt solutions. In specific methods, a solid sodium-ion conducting ceramic membrane **14** separates two compartments of a cell. The sodium ions transfer across the membrane **14** from the anolyte to the catholyte compartment under the influence of electrical potential to generate sodium hydroxides or mixture

of sodium salts or react to combine with other in-organic or organic compounds. Certain alkali ion conducting membranes do not allow transport of water there through, which makes the process more energy efficient. Furthermore, these ceramic membranes have low electronic conductivity, superior corrosion resistance, and high flux of specific alkali ions providing high ionic conductivity.

[0040] In some specific embodiments, the alkali ion conducting ceramic membrane **14** comprises NaSICON-type materials that may include at least one of the following: materials of general formula $M_{1+x}M'^xSi_xP_{3-x}O_{12}$ where $0 \leq x \leq 3$, where M is selected from the group consisting of Li, Na, K, or Ag, or mixture thereof, and where M' is selected from the group consisting of Zr, Ge, Ti, Sn, Y or Hf, or mixtures thereof, materials of general formula $Na_{1-x}L_zZr_{2-x}P_3O_{12}$ where $0 \leq z \leq 2.0$, and where L is selected from the group consisting of Cr, Yb, Er, Dy, Sc, Fe, In, or Y, or mixtures or combinations thereof; materials of general formula $M''_5RESi_4O_{12}$, where M'' may be Li, Na, K or Ag, or any mixture or combination thereof, and where RE is Y or any rare earth element.

[0041] In some specific embodiments, the NaSICON-type materials may include at least one of the following: non-stoichiometric materials, zirconium-deficient (or sodium rich) materials of general formula $Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$ where $1.55 \leq x \leq 3$. In some specific embodiments, the alkali ion conducting ceramic membrane **14** compositions comprising NaSICON-type materials may include at least one of the following: non-stoichiometric materials, sodium-deficient materials of general formula $Na_{1+x}(A_yZr_{2-y})(Si_xP_{3-x})O_{12-\delta}$ where A is selected from the group consisting of Yb, Er, Dy, Sc, In, or Y, or mixtures or combinations thereof, $1.8 \leq x \leq 2.6$, $0 \leq y \leq 0.2$, $x < z$, and δ is selected to maintain charge neutrality. In some specific embodiments, the NaSICON-type materials may include sodium-deficient materials of formula $Na_{3.7}Zr_2Si_{2.3}P_{0.7}O_{12-\delta}$.

[0042] Other exemplary NaSICON-type materials are described by H. Y-P. Hong in "Crystal structures and crystal chemistry in the system $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ", Materials Research Bulletin, Vol. 11, pp. 173-182, 1976; J. B. Goodenough et al., in "Fast Na^+ -ion transport skeleton structures", Materials Research Bulletin, Vol. 11, pp. 203-220, 1976; J. J. Bentzen et al., in "The preparation and characterization of dense, highly conductive $Na_5GdSi_4O_{12}$ nasicon (NGS)", Materials Research Bulletin, Vol. 15, pp. 1737-1745, 1980; C. Delmas et al., in "Crystal chemistry of the $Na_{1+x}Zr_{2-x}L_x(PO_4)_3$ (L=Cr, In, Yb) solid solutions", Materials Research Bulletin, Vol. 16, pp. 285-290, 1981; V. von Alpen et al., in "Compositional dependence of the electrochemical and structural parameters in the NASICON system $(Na_{1+x}Si_xZr_{2-x}P_{3-x}O_{12})$ ", Solid State Ionics, Vol. 3/4, pp. 215-218, 1981; S. Fujitsu et al., in "Conduction paths in sintered ionic conductive material $Na_{1+x}Y_xZr_{2-x}(PO_4)_3$ ", Materials Research Bulletin, Vol. 16, pp. 1299-1309, 1981; Y. Saito et al., in "Ionic conductivity of NASICON-type conductors $Na_{1.5}M_{0.5}Zr_{1.5}(PO_4)_3$ (M: Al^{3+} , Ga^{3+} , Cr^{3+} , Sc^{3+} , Fe^{3+} , In^{3+} , Yb^{3+} , Y^{3+})", Solid State Ionics, Vol. 58, pp. 327-331, 1992; J. Alamo in "Chemistry and properties of solids with the [NZP] skeleton", Solid State Ionics, Vol. 63-65, pp. 547-561, 1993; K. Shimazu in "Electrical conductivity and Ti^{4+} ion substitution range in NASICON system", Solid State Ionics, Vol. 79, pp. 106-110, 1995; Y. Miyajima in "Ionic conductivity of NASICON-type $Na_{1-x}M_xZr_{2-x}P_3O_{12}$ (M: Yb, Er, Dy)", Solid State Ionics, Vol. 84,

pp. 61-64, 1996. These references are incorporated in their entirety herein by this reference.

[0043] While the alkali ion conducting ceramic materials disclosed herein encompass or include many formulations of NaSICON materials, this disclosure concentrates on an examination of ceramic membranes comprising NaSICON materials for the sake of simplicity. The focused discussion of NaSICON materials as one example of materials is not, however, intended to limit the scope of the invention. For example, the materials disclosed herein as being highly conductive and having high selectivity include those alkali super ion conducting materials that are capable of transporting or conducting any alkali cation, such as sodium (Na), lithium (Li), potassium (K), ions for producing alkali hydroxides.

[0044] The alkali ion conducting ceramic membranes comprising NaSICON materials may be used or produced for use in the processes and apparatus of the present invention in any suitable form, as would be understood by one of ordinary skill in the art. In some specific embodiments, the form of the alkali ion conducting ceramic membranes may include at least one of the following: monolithic flat plate geometries, supported structures in flat plate geometries, monolithic tubular geometries, supported structures in tubular geometries, monolithic honeycomb geometries, or supported structures in honeycomb geometries. In another embodiment, the membrane **14** may be a supported membrane **14** known to those of skill in the art. Supported structures or membranes may comprise dense layers of ion-conducting ceramic solid electrolyte supported on porous supports. A variety of forms for the supported membranes are known in the art and would be suitable for providing the supported membranes for alkali ion conducting ceramic membranes with supported structures, including, but not limited to: ceramic layers sintered to below full density with resultant continuous open porosity, slotted-form layers, perforated-form layers, expanded-form layers including a mesh, or combinations thereof. In some embodiments, the porosity of the porous supports is substantially continuous open-porosity so that the liquid solutions on either side of the alkali ion conducting ceramic membrane **14** may be in intimate contact with a large area of the dense-layers of alkali ion conducting ceramic solid electrolytes, and in some, the continuous open-porosity ranges from about 30 volume % to about 90 volume %. In some embodiments of the present invention, the porous supports for the supported structures may be present on one side of the dense layer of alkali ion conducting ceramic solid electrolyte. In some embodiments of the present invention, the porous supports for the supported structures may be present on both sides of the dense layer of alkali ion conducting ceramic solid electrolyte.

[0045] A variety of materials for the porous supports or supported membranes are known in the art and would be suitable for providing the porous supports for alkali ion conducting ceramic membranes with supported-structures, including: electrode materials, NaSICON-type materials, β' -alumina, β'' -alumina, other ion-conducting ceramic solid electrolyte materials, and non-conductive materials such as plastics, polymers, organics or ceramic materials, metals, and metal alloys. The thickness of the dense layer of alkali ion conducting ceramic solid electrolyte material in monolithic structures is generally from about 0.3 mm to about 5 mm, and in some instances from about 0.5 mm to about 1.5 mm. The thickness of the dense layer of alkali ion conducting ceramic solid electrolyte material in supported-structures is generally from about 25 μ m to about 2 mm, and often from about 0.5

mm to about 1.5 mm. Layers as thin as about 25 μm to about 0.5 mm are readily producible, as would be understood by one of ordinary skill in the art. In some specific embodiments, the alkali ion conducting ceramic membranes are structurally supported by the cathode, which is porous. This may dictate characteristics of both the form of the alkali ion conducting ceramic membranes, and/or of the cathode and/or anode. In some specific embodiments, the porous substrate has similar thermal expansion and good bonding with the alkali ion conducting ceramic membrane **14** as well as good mechanical strength. One of ordinary skill in the art would understand that the number and configuration of the layers used to construct the alkali ion conducting ceramic membrane **14** as supported-structures could be widely varied within the scope of the invention.

[0046] In some embodiments of the alkali ion conducting ceramic membranes of the present invention, the alkali ion conducting ceramic membranes may be composites of alkali ion conducting ceramic solid electrolyte materials with non-conductive materials, where the non-conductive materials are poor ionic and electronic electrical conductors under the conditions of use. A variety of insulative non-conductive materials are also known in the art, as would be understood by one of ordinary skill in the art. In some specific embodiments, the non-conductive materials may include at least one of the following: ceramic materials, polymers, and/or plastics that are substantially stable in the media to which they are exposed.

[0047] Layered alkali ion conducting ceramic-polymer composite membranes are also particularly suitable for use as alkali ion conducting ceramic membranes in the present invention. Layered alkali ion conducting ceramic-polymer composite membranes generally comprise ion-selective polymers layered on alkali ion conducting ceramic solid electrolyte materials. In some specific embodiments, the alkali ion conducting ceramic solid electrolyte materials of the layered alkali ion conducting ceramic-polymer composite membranes may include at least one of the following: NaSICON-type materials or beta-alumina. Ion-selective polymer materials have the disadvantage of having poor selectivity to sodium ions, yet they demonstrate the advantage of high chemical stability.

[0048] In some specific embodiments, the alkali ion conducting ceramic membrane **14** may comprise two or more co-joined layers of different alkali ion conducting ceramic membrane **14** materials. Such co-joined alkali ion conducting ceramic membrane **14** layers could include NaSICON materials joined to other alkali ion conducting ceramic materials, such as, but not limited to, beta-alumina. Such co-joined layers could be joined to each other using a method such as, but not limited to, thermal spraying, plasma spraying, co-firing, joining following sintering, etc. Other suitable joining methods are known by one of ordinary skill in the art and are included herein.

[0049] The alkali ion conducting ceramic solid electrolyte materials disclosed herein are particularly suitable for use in the electrolysis of alkali metal based salt solutions because they have high ion-conductivity for alkali metal cations at low temperatures, high selectivity for alkali metal cations, good current efficiency and stability in water and corrosive media under static and electrochemical conditions. Comparatively, beta alumina is a ceramic material with high ion conductivity

at temperatures above 300° C., but has low conductivity at temperatures below 100° C., making it less practical for applications below 100° C.

[0050] Sodium ion conductivity in NaSICON structures has an Arrhenius dependency on temperature, generally increases as a function of temperature. The sodium ion conductivity of ceramic membranes comprising NaSICON materials ranges from about 1×10^{-4} S/cm to about 1×10^{-1} S/cm from room temperature to 85° C.

[0051] Alkali ion conducting ceramic membranes comprising NaSICON materials, especially of the type described herein, have low or negligible electronic conductivity, and as such aid in virtually eliminating the occurrence of any galvanic reactions when the applied potential or current is removed. Certain NaSICON analogs according to the present invention have very mobile cations, including, but not limited to lithium, sodium, and potassium ions, that provide high ionic conductivity, low electronic conductivity and comparatively high corrosion resistance.

[0052] The sodium-ion conducting ceramic materials referred herein for use in electrolytic cells can be used successfully in the formation of sodium hydroxides from the electrolysis of aqueous sodium salt solutions, including, but not limited to, such solutions as sodium carbonate, sodium nitrate, sodium phosphate, sodium hypochlorite, sodium chloride, sodium perchlorate, and sodium organic salts.

[0053] One alkali ion conducting ceramic solid electrolyte or alkali ion conducting ceramic membrane **14** is an electronic insulator and an excellent ionic conductor. The $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (where $0 \leq x \leq 3$) composition is the best known member of a large family of sodium-ion conducting ceramic solid electrolyte materials that have been extensively studied. The structure has hexagonal arrangement and remains stable through a wide variation in atomic parameters as well in the number of extra occupancies or vacancies.

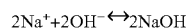
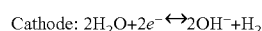
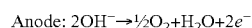
[0054] One of ordinary skill in the art would understand that a number of ceramic powder processing methods are known for processing of the alkali ion conducting ceramic solid electrolyte materials such as high temperature solid-state reaction processes, co-precipitation processes, hydrothermal processes, or sol-gel processes. In some embodiments of the present invention it may be advantageous to synthesize the alkali ion conducting ceramic solid electrolyte materials by high temperature solid-state reaction processes. Specifically, ceramic the processing of $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (where $0 \leq x \leq 3$) and $\text{Na}_5\text{RESi}_4\text{O}_{12}$ NaSICON compositions (where RE is either Yttrium or a rare earth element) may proceed as follows. Alkali ion conducting ceramic membranes may be systematically synthesized by solid-state oxide mixing techniques. A mixture of the starting precursors may be mixed in methanol in polyethylene jars, and the mixed precursor oxides are dried at 60° C. to evolve the solvent. The dried powder or material may be calcined at 800° C., to form the required composition, followed by wet ball milled with zirconium oxide media (or another media known to one of ordinary skill in the art) to achieve the prerequisite particle size distribution. One of ordinary skill in the art would understand that a number of polymers are known for processing with ceramic powders such as those set forth above as prerequisite for preparing a green-form, and that a number of conventional ceramic fabrication processing methods are known for processing ceramic membranes such as those set forth above in a green-form. Green-form membranes at 0.60 to 2.5 inch diameter sizes may be pressed by compaction in a

die and punch assembly and then sintered in air at temperatures between 1100° C. and 1200° C. to make dense alkali ion conducting ceramic membranes. XRD analysis of the alkali ion conducting ceramic membranes may be performed to identify the NaSICON composition crystal structure and phase purity. Stoichiometric and non-stoichiometric compositions of the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_2$ type formula (where $0 \leq x \leq 3$) are one type of alkali ion conducting ceramic membrane **14** produced in this manner. Non-stoichiometric in this instance means un-equivalent substitution of Zr, Si, and/or P in the formula. The stability or resistance to corrosive media of the alkali ion conducting ceramic membrane **14** materials described herein may be enhanced by chemistry variation

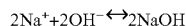
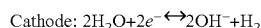
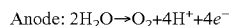
[0055] The alkali ion conducting ceramic membrane **14** may have flat plate geometry, tubular geometry, or supported geometry. The solid membrane **14** may be sandwiched between two pockets, made of a chemically-resistant HDPE, PPE, PPR plastics and sealed, by compression loading using a suitable gasket or o-ring, such as an EPDM (ethylene propylene diene monomer) rubber gaskets or o-ring.

[0056] The NaSICON materials or modified NaSICON materials referred herein are useful, for example, as sodium-ion conducting ceramic membranes in electrolytic cells. In one embodiment, the method for the production of sodium hydroxide solution comprises introducing a lower concentration solution of sodium hydroxide solution into a catholyte compartment of an electrolytic cell, introducing an aqueous solution comprising one or more sodium salts (examples of stream chemistry presented in Tables 1 and 2) into an anolyte compartment of the electrolytic cell, wherein the anolyte compartment and the catholyte compartment of the electrolytic cell are separated by a ceramic membrane **14** comprising NaSICON, applying electric potential across the electrodes in the electrolytic cell to selectively transport sodium ions from the anolyte compartment to the catholyte compartment where the sodium ions react with the hydroxyl ions to form sodium hydroxide at higher concentration in the catholyte compartment of the electrolytic cell, and wherein the composition of the solution of sodium hydroxide solution in the catholyte compartment of the electrolytic cell comprises between at least about 2% by weight sodium hydroxide and at most about 50% by weight sodium hydroxide. In a further embodiment, the method comprises separation of the anolyte compartment and the catholyte compartment of the electrolytic cell by a ceramic membrane **14** comprising NaSICON, and a composition of the solution of sodium hydroxide in the catholyte compartment of the electrolytic cell comprising between at least about 1% by weight sodium hydroxide and at most about 30% by weight sodium hydroxide. In a further embodiment, the method comprises separation of the anolyte compartment and the catholyte compartment of the electrolytic cell by a ceramic membrane **14** comprising NaSICON, and a composition of the solution of sodium hydroxide solution in the catholyte compartment of the electrolytic cell comprising between at least about 0.1% by weight sodium hydroxide and at most about 20% by weight sodium hydroxide.

[0057] An example of an overall electrolytic reaction, using sodium hydroxide as the source of sodium ion, is as follows:



[0058] An example of an overall electrolytic reaction, using sodium salts in an aqueous waste stream as the source of sodium ion, is as follows:



[0059] The reactions described above are electrolytic reactions, taking place under an induced current wherein electrons are introduced or are removed to cause the reactions. The reactions proceed only so long as a current is flowing through the cell. Contrary to electrolytic reactions, galvanic reactions may occur when an applied potential to the cell is removed, which tends to reduce the efficiency of the electrolytic cell. In one embodiment, only electrolytic reactions occur in the cell and galvanic reactions are eliminated or greatly minimized.

[0060] In some specific embodiments, the alkali cation-conductive ceramic membrane may comprise two or more co-joined layers of different alkali cation-conductive ceramic materials. Such co-joined alkali cation-conductive ceramic membrane layers could include NaSICON-type materials joined to other ceramics, such as, but not limited to, beta-alumina. Such layers could be joined to each other using a method such as, but not limited to, co-firing, joining following sintering, etc. Other suitable joining methods are known by one of ordinary skill in the art and are included herein.

[0061] The alkali cation-conductive ceramic membranes may be used or produced for use in the processes and apparatus of the present invention in any suitable form, as would be understood by one of ordinary skill in the art. In some specific embodiments, the form of the alkali cation-conductive ceramic membranes may include at least one of the following: monolithic flat plate geometries, supported structures in flat plate geometries, monolithic tubular geometries, supported structures in tubular geometries, monolithic honeycomb geometries, or supported structures in honeycomb geometries. Supported structures may comprise dense layers of alkali cation-conductive ceramic materials supported on porous supports. A variety of forms for the porous supports are known in the art and would be suitable for providing the porous supports for alkali cation-conductive ceramic membranes with supported structures, including: ceramic layers sintered to below full density with resultant continuous open porosity, slotted-form layers, perforated-form layers, expanded-form layers including a mesh, or combinations thereof. In some embodiments, the porosity of the porous supports is substantially continuous open-porosity so that the liquid solutions on either side of the alkali cation-conductive ceramic membrane may be in intimate contact with a large area of the dense-layers of alkali cation-conductive ceramic materials, and in some, the continuous open-porosity ranges from about 30 volume % to about 90 volume %. In some embodiments of the present invention, the porous supports for the supported structures may be present on one side of the dense layer of alkali cation-conductive ceramic material. In some embodiments of the present invention, the porous supports for the supported structures may be present on both sides of the dense layer of alkali cation-conductive ceramic material.

[0062] A variety of materials for the porous supports are known in the art and would be suitable for providing the porous supports for alkali cation-conductive ceramic mem-

branes with supported-structures, including: electrode materials, NaSICON-type materials, β^I -alumina, β^{II} -alumina, other cation-conductive materials, and non-conductive materials such as plastics or ceramic materials, metals, and metal alloys. The thickness of the dense layer of alkali cation-conductive ceramic material in monolithic structures is generally from about 0.3 mm to about 5 mm, and in some instances from about 0.5 mm to about 1.5 mm. The thickness of the dense layer of alkali cation-conductive ceramic material in supported-structures is generally from about 25 μ m to about 2 mm, and often from about 0.5 mm to about 1.5 mm. Layers as thin as about 25 μ m to about 0.5 mm are readily producible, as would be understood by one of ordinary skill in the art. In some specific embodiments, the alkali cation-conductive ceramic membranes are structurally supported by the cathode, which is porous. This may dictate characteristics of both the form of the membranes, and/or of the cathode and/or anode. In some specific embodiments, the porous substrate must have similar thermal expansion and good bonding with the alkali cation-conductive ceramic membrane as well as good mechanical strength. One of ordinary skill in the art would understand that the number and configuration of the layers used to construct the alkali cation-conductive ceramic membrane as supported-structures could be widely varied within the scope of the invention.

[0063] In some embodiments of the alkali cation-conductive ceramic membranes of the present invention, the alkali cation-conductive ceramic membranes may be composites of alkali cation-conductive ceramic materials with non-conductive materials, where the non-conductive materials are poor ionic and electronic electrical conductors under the conditions of use. A variety of insulative non-conductive materials are also known in the art, as would be understood by one of ordinary skill in the art. In some specific embodiments, the non-conductive materials may include at least one of the following: ceramic materials, polymers, and/or plastics that are substantially stable in the media to which they are exposed.

[0064] It not necessary for the cathode to contact the alkali cation-conductive ceramic membrane in the processes or apparatus of the present invention. Both the catholyte and anolyte are ion-conductive so that from an electrical standpoint the electrodes may be remote from the membranes. In such an event, a thin-film dense alkali cation-conductive ceramic membrane may be deposited on a porous substrate which does not have to be an electrode,

[0065] One of ordinary skill in the art would understand that a number of ceramic powder processing methods are known for processing of the alkali cation-conductive ceramic materials such as high temperature solid-state reaction processes, co-precipitation processes, hydrothermal processes, or sol-gel processes. In some embodiments of the present invention it may be advantageous to synthesize the alkali cation-conductive ceramic materials by high temperature solid-state reaction processes. Specifically, for NaSICON-type materials, a mixture of starting precursors such as simple oxides and/or carbonates of the individual components may be mixed at the desired proportions in methanol in polyethylene vessels, and dried at approximately 60° C. to evolve the solvent; the dried mixture of starting precursors may be calcined in the range of from about 800° C. to about 1200° C. dependent on the composition, followed by milling of the calcined powder with media such as stabilized-zirconia or alumina or another media known to one of ordinary skill in

the art to achieve the prerequisite particle size distribution. To achieve the prerequisite particle size distribution, the calcined powder may be milled using a technique such as vibratory milling, attrition milling, jet milling, ball milling, or another technique known to one of ordinary skill in the art, using media (as appropriate) such as stabilized-zirconia or alumina or another media known to one of ordinary skill in the art.

[0066] One of ordinary skill in the art would understand that a number of conventional ceramic fabrication processing methods are known for processing ceramic membranes such as those set forth above in a green-form. Such methods include, but are not limited to, tape casting, calendaring, embossing, punching, laser-cutting, solvent bonding, lamination, heat lamination, extrusion, co-extrusion, centrifugal casting, slip casting, gel casting, die casting, pressing, isostatic pressing, hot isostatic pressing, uniaxial pressing, and sol gel processing. The resulting green form ceramic membrane may then be sintered to form an alkali cation-conductive ceramic membrane using a technique known to one of ordinary skill in the art, such as conventional thermal processing in air, or controlled atmospheres to minimize loss of individual components of the alkali cation-conductive ceramic membranes. In some embodiments of the present invention it may be advantageous to fabricate the ceramic membrane in a green form by die-pressing, optionally followed by isostatic pressing. In other embodiments of the present invention it may potentially be advantageous to fabricate the ceramic membrane as a multi-channel device in a green form using a combination of techniques such as tape casting, punching, laser-cutting, solvent bonding, heat lamination, or other techniques known to one of ordinary skill in the art. Specifically, for NaSICON-type materials, a ceramic membrane in a green-form may be green-formed by pressing in a die, followed by isostatic pressing and then sintering in air in the range of from about 925° C. to about 1300° C. for up to about 8 hours to make sintered alkali cation-conductive ceramic membrane structures with dense layers of alkali cation-conductive ceramic materials. Standard x-ray diffraction analysis techniques may be performed to identify the crystal structure and phase purity of the alkali cation-conductive ceramic materials in the sintered ceramic membrane.

[0067] In some specific embodiments, alkali cation-conductive ceramic membranes for use in the processes and apparatus of the present invention may be fabricated by a vapor deposition method onto a porous support, including at least one of the following methods: physical vapor deposition, chemical vapor deposition, sputtering, thermal spraying, or plasma spraying. The thickness of the alkali cation-conductive ceramic membrane formed by a vapor deposition method onto a porous support is generally from about 1 μ m to about 100 μ m, but may be varied as is known to one of ordinary skill in the art.

[0068] In one embodiment of the processes and apparatus of the present invention, the electrolytic cell 10 may be operated in a continuous mode. In a continuous mode, the cell is initially filled with anolyte solution and catholyte solution and then, during operation, additional solutions are fed into the cell and products, by-products, and/or diluted solutions are removed from the cell without ceasing operation of the cell. The feeding of the anolyte solution and catholyte solution may be done continuously or it may be done intermittently, meaning that the flow of a given solution is initiated or stopped according to the need for the solution and/or to maintain desired concentrations of solutions in the cell compartment.

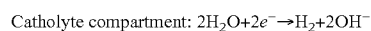
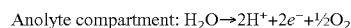
ments, without emptying any one individual compartment or any combination of the two compartments. Similarly, the removal of solutions from the anolyte compartment and the catholyte compartment may also be continuous or intermittent. Control of the addition and/or removal of solutions from the cell may be done by any suitable means. Such means include manual operation, such as by one or more human operators, and automated operation, such as by using sensors, electronic valves, laboratory robots, etc. operating under computer or analog control. In automated operation, a valve or stopcock may be opened or closed according to a signal received from a computer or electronic controller on the basis of a timer, the output of a sensor, or other means. Examples of automated systems are well known in the art. Some combination of manual and automated operation may also be used. Alternatively, the amount of each solution that is to be added or removed per unit time to maintain a steady state may be experimentally determined for a given cell, and the flow of solutions into and out of the system set accordingly to achieve the steady state flow conditions.

[0069] In another embodiment, the electrolytic cell **10** is operated in batch mode. In batch mode, the anolyte solution and catholyte solution are fed initially into the cell and then the cell is operated until the desired concentration of product is produced in the anolyte and catholyte. The cell is then emptied, the products collected, and the cell refilled to start the process again. Alternatively, combinations of continuous mode and batch mode production may be used. Also, in either mode, the feeding of solutions may be done using a pre-prepared solution or using components that form the solution in situ.

[0070] It should be noted that both continuous and batch mode have dynamic flow of solutions. In one embodiment of continuous mode operation, the anolyte solution is added to the anolyte chamber so that the sodium concentration is maintained at a certain concentration or concentration range during operation of the electrolytic cell **10**. In one embodiment of batch mode operation, a certain quantity of sodium ions are transferred through the alkali cation-conductive ceramic membrane to the catholyte chamber and are not replenished, with the cell operation is stopped when the sodium concentration in the anolyte-chamber reduces to a certain amount or when the appropriate product concentration is reached in the catholyte.

[0071] Several examples are provided below which discuss the construction, use, and testing of specific embodiments of the present invention. These embodiments are exemplary in nature and should not be construed to limit the scope of the invention in any way.

[0072] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane **14** is used to split an aqueous solution of sodium salts based complex chemistry. The alkali cation-conductive ceramic material **14** may be NaSICON-type material. The alkali ions transport across the alkali cation-conductive ceramic membrane to the catholyte compartment **18**. The gaseous product is oxygen in the anolyte compartment **20** venting at **34**, and hydrogen in the catholyte compartment **18** venting at **36**. Reactions are as follows:



[0073] The anolyte compartment **20** is greater than about pH 7 and below about pH 14, and whereas the catholyte

compartment **18** is greater than about pH 7. The process can be operated between about ambient temperature and about 125° C. The anolyte inlet **26** is an aqueous feed of sodium based salts such as sodium hydroxide, sodium sulfate and other alkali and transition metal impurities. The catholyte inlet **30** is an aqueous solution of sodium hydroxide. The catholyte outlet **32** is an aqueous solution of sodium hydroxide, at a higher concentration than the catholyte inlet **30**.

[0074] The radioactively-contaminated aqueous (nuclear) waste stream typically comprises significant amounts of sodium nitrate, sodium nitrite, sodium hydroxide, sodium carbonate, sodium hydroxide, sodium chloride, sodium chlorate, sodium oxalate, sodium fluoride and salts of potassium, cesium, and strontium, calcium, aluminum, and host of radionuclide elements (Cs, Sr). The inlet stream of radioactively-contaminated aqueous (nuclear) waste comprising sodium hydroxide, strontium nitrate, sodium chloride, sodium fluoride, sodium hydrogen phosphate, sodium carbonate, sodium oxalate, sodium sulfate, sodium nitrite, sodium nitrate, potassium nitrate, potassium hydroxide, cesium nitrate, calcium nitrate, cesium nitrate, barium nitrate, silicon dioxide, and aluminum nitrate, iron oxide, iron nitrate, chromium oxide, and a list of other elements in the periodic table.

EXAMPLE 1

[0075] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic membrane **14** (NASD10 membrane-1.4 mm thick) was assembled. Platinum and nickel were used as anode and cathode. The alkali cation-conductive ceramic membrane material **14** is $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ composition. The electrolytic cell was operated in batch mode in 3 molar NaNO_3 +2 Molar NaOH solutions with fresh solution periodically replacing the sodium replenished anolyte. The cell was operated at 100 mA/cm² current density at 38° C. for 900 hours. The membrane transported approximately 63 moles of sodium from the anolyte to the catholyte chamber. The voltage across the membrane was between 3 and 6.5 volts. The gaseous products in oxygen in the anolyte compartment **20** venting at **34**, and hydrogen in the catholyte compartment **18** venting at **36**.

EXAMPLE 2

[0076] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic membrane **14** was assembled. The alkali cation-conductive ceramic membrane material **14** is $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ composition (coded: NAS-D10). Platinum and nickel were used as anode and cathode. The electrolytic cell was operated in batch mode in NaOH solution, with fresh solution periodically replacing the replenished anolyte. The cell was continuously operated at 4.5 V and 40° C. for 5000 hours. FIG. 3 shows the test result, where the sodium ionic current is compared to the total current. The sodium transport efficiency achieved is very high (>90%) and remains constant up to 3000 hours, and drops below 90% between 3000-5000 hours of testing. The transport efficiency was measured periodically when a fresh batch of anolyte was introduced. Though the membrane was operated at a relatively small current density of 25 mA/cm², it is evident from this test that the sodium transport efficiency is very high and steady at 90%, and most importantly, that the NASD10 membrane was structurally stable during the entire duration of the test. The gaseous products are oxygen in the

anolyte compartment **20** venting at **34**, and hydrogen in the catholyte compartment **18** venting at **36**

EXAMPLE 3

[0077] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material **14** with four NASE (2 inch diameter) membranes were assembled in the scaffold fitted into an Electrocell MP cell configuration. The alkali cation-conductive ceramic material **14** is $\text{Na}_{3.2}\text{Zr}_2\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ composition (coded: NAS-E). Platinum and nickel were used as anode and cathode. The stack was checked by pressuring the anolyte inlet with DI water and looked for leak in the catholyte compartment. The leak checked scaffold was assembled into the Electrocell MP, and secured in the testing jig. The plumbing connection was made between the inlets and outlets of the Electrocell MP cell and the individual holding tanks, and similarly electrical connection was made between the electrodes, power supply and the data acquisition system.

[0078] The 20 liter holding tanks were half filled with 1.5 molar sodium based aqueous electrolytes, and heated to just above 40° C. and allowed to equilibrate. The pumps were turned on to circulate the electrolyte in the cell manifold and checked for leaks before the power supply was turned on. The flow rate was maintained at 1.6 gpm. The stack was operated in constant current mode at 100 mA/cm² current density. The gaseous products are oxygen in the anolyte compartment **20** venting at **34**, and hydrogen in the catholyte compartment **18** venting at **36**. The cell voltage remained steady during the entire duration of the test (FIG. 4). The sodium transport efficiency after every 150 hours of testing was between 90 and 96%.

EXAMPLE 4

[0079] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane **14** to synthesize sodium hydroxide and an acid from transition-metal based sodium salts containing by-product industrial stream. The alkali cation-conductive ceramic material **14** is $\text{Na}_{3.3}\text{Zr}_2\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{12}$ composition (coded: NAS-G). Platinum and nickel were used as anode and cathode.

[0080] The electrolytic cell was operated using 1.5 M aqueous NaOH anolyte and catholyte. The purpose of this test was to validate the influence of various cations and anions present in the anolyte on electrochemical performance of the ceramic membrane. This test was operated at 50° C., and current density in the 100 to 150 mA/cm² range. The results are shown in FIG. 5 in which the sodium current density is compared to total current efficiency. High sodium current efficiency (90%) was observed again which remained constant during the 300 hours of testing. The total applied voltage in this test was high (8.5 to 9 volts). The steady state conductivity of the NASG membrane during the test, based on the voltage measurement across the membrane, was 2×10^{-2} S/cm. The sodium mass balance of anolyte and the catholyte in this experiment did not show any loss of sodium

EXAMPLE 5

[0081] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane **14** to synthesize sodium hydroxide from transition-metal based sodium salts containing by-product industrial

stream was assembled. The alkali cation-conductive ceramic material **14** is $\text{Na}_{3.3}\text{Zr}_2\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{12}$ composition (coded: NAS-G). Platinum and nickel were used as anode and cathode.

[0082] The electrolytic cell was operated using 1.5 M NaOH catholyte. The composition of the anolyte was prepared to simulate the radioactively contaminated salt waste stream at Savannah River Site, a DOE facility. The composition of this anolyte feed (Simulant Chemistry 1) is shown in Table 1.

TABLE 1

Anolyte Simulant Chemistry 1	
	wt %
H ₂ O	55.540%
NaOH	8.252%
Sr(NO ₃) ₂	0.018%
NaCl	0.092%
NaF	0.066%
Na ₂ HPO ₄	0.096%
Na ₂ C ₂ O ₄	0.011%
Na ₂ CO ₃	1.330%
Na ₂ SO ₄	1.562%
NaNO ₂	3.256%
NaNO ₃	6.734%
KNO ₃	0.056%
Ca(NO ₃) ₂ •4H ₂ O	0.018%
CsNO ₃	0.002%
SiO ₂	0.020%
Al(NO ₃) ₃ •9H ₂ O	22.947%

[0083] The purpose of this test was to validate the influence of various cations and anions present in the anolyte on the electrochemical performance of the ceramic membrane. This test was operated at 50° C., and constant current density of 200 mA/cm². The results are shown in FIG. 6. High sodium current efficiency (90%) was observed again which remained constant during the 300 hours of testing. The total average voltage across the membrane was 4.75 volts because of the cell design where the electrodes were positioned far away from the membrane. During the course of this test, Al(OH)₃ precipitated in the anolyte when the pH of the solution dropped below 12. This however did not influence the performance of membrane. Sodium ions are selectively transported from anolyte membrane across the membrane in the presence of other +1, +2, +3, +4 and +5 valence cations and anions such as NO₃⁻, CO₃²⁻, SO₄²⁻, NO₂⁻, Cl⁻, F⁻, PO₄³⁻, and HPO₄²⁻ ions in the anolyte stream. The overall sodium transport efficiency dropped from 94% to 90% in this test. The voltage across the membrane peaked at the 200 hours mark since we allowed the test to run at lower sodium concentration in the anolyte (<0.5 moles). It is typical in such a situation for the total cell resistance to increase dominated by the electrolyte-membrane interface.

EXAMPLE 6

[0084] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane **14** was assembled. The alkali cation-conductive ceramic material **14** is a NaSICON composition (coded: NAS-G). Platinum and nickel were used as anode and cathode.

[0085] The electrolytic cell was operated using 5 M aqueous NaOH anolyte and 1.5 M aqueous NaOH catholyte. The purpose of this test was to validate the influence of various

cations and anions present in the anolyte on the electrochemical performance of the ceramic membrane. This test was operated at 50° C., and constant current density of 400 mA/cm². The results are shown in FIG. 7. High sodium current efficiency (92%) was observed again which remained constant during the 350 hours of testing. The voltage drop across the membrane voltage was maintained at a steady 4.75 volts.

EXAMPLE 7

[0086] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane 14 to synthesize sodium hydroxide from transition-metal based sodium salts containing by-product industrial stream. The alkali cation-conductive ceramic material 14 is NaSICON composition (coded: NAS-F). Platinum and nickel were used as anode and cathode. The electrolytic cell was operated using the anolyte Simulant Chemistry 2 and 1.5 M NaOH catholyte. The composition of this anolyte feed was prepared to simulate the radioactively contaminated salt waste stream at Hanford (PNNL), a DOE facility. Simulant Chemistry 2 is shown in Table 2.

TABLE 2

Anolyte Simulant Chemistry 2	
	wt %
H ₂ O	68.0460%
NaOH	8.5777%
Sr(NO ₃) ₂	0.0021%
NaCl	0.1056%
NaF	0.0513%
Na ₂ HPO ₄	0.0989%
Na ₂ C ₂ O ₄	0.1569%
Na ₂ CO ₃	1.3832%
Na ₂ SO ₄	1.6212%
NaNO ₂	3.3748%
NaNO ₃	6.9556%
KNO ₃	0.1237%
Ca(NO ₃) ₂ •4H ₂ O	0.0004%
CsNO ₃	0.0016%
Ba(NO ₃) ₂	0.0021%
SiO ₂	0.0186%
Al(NO ₃) ₃ •7H ₂ O	9.4793%

[0087] This test was operated at 50° C. and constant current density of 100 mA/cm² for a period of 950 hours. Based on the results shown in FIG. 8, the energy estimates based on the test results is 1900 kWh/ton of NaOH production by the ceramic material membrane based electrolytic cell.

EXAMPLE 8

[0088] A two-compartment electrolytic cell as described in FIG. 1, based on an alkali cation-conductive ceramic material membrane 14 is Na₃Zr₂Si₂PO₁₂ composition (coded: NAS-D10). Platinum and nickel were used as anode and cathode. The electrolytic cell was operated in batch mode in radioactively contaminated waste. The cell was operated at 25 mA/cm² at ambient temperature. FIG. 9 compares the test results of a ceramic alkali ion conducting membrane (coded NASD) with a polymer Nafion membrane based cell. The results presented in FIG. 9 shows the ceramic NASD membrane transfers almost zero amount of radionuclide, such as Cs or Sr, through the membrane. Only sodium ions were

selectively transported across the ceramic alkali ion conducting membrane from the anode compartment (20) into the cathode compartment (18), while the Nafion polymer membrane cell transfers about 60% of the radioactive species present in the anolyte feed (26) from the anode compartment (20) into the cathode compartment (18) across the Nafion membrane.

[0089] Hydrogen produced in the catholyte compartment 18 may be utilized by a fuel cell to generate additional power, the hydrogen can be vented or flared.

[0090] The two-compartment electrolytic cell shown in FIG. 1 may be configured in multi-compartment embodiments. FIG. 10 shows a schematic representation of an electrolytic cell 50 comprising two, two-compartment electrolytic cells arranged in series, separated by a bipolar electrode 52. Each two compartment cell in the electrolytic cell 50 includes an alkali cation-conductive ceramic material membrane 54 used to split an aqueous solution of sodium salts. The alkali cation-conductive ceramic material 54 may be NaSICON-type material. The alkali cation-conductive ceramic material 54 separates a catholyte compartment 58 from an anolyte compartment 60. The sodium ions transport across the alkali cation-conductive ceramic membranes 54 from the anolyte compartment 60 to the catholyte compartment 58. The gaseous product is oxygen in the anolyte compartment 60, and hydrogen in the catholyte compartment 58. The anolyte compartment 60 is configured with an anode 62 and the catholyte compartment 58 is configured with a cathode 64. The bipolar electrode 52 includes the dual properties of an anode 62a and a cathode 64a. An electric potential or voltage source 65 is provided to operate the electrolytic cell 50.

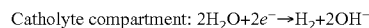
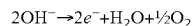
[0091] The electrolytic cell 50 further comprises an anolyte inlet 66 for introducing chemicals into the anolyte compartment 60 and an anolyte outlet 68 for removing or receiving anolyte solution from the anolyte compartment 60. The cell 50 also includes a catholyte inlet 70 for introducing chemicals into the catholyte compartment 58 and a catholyte outlet 72 for removing or receiving catholyte solution from the catholyte compartment 58.

[0092] The parts of the electrolytic cell 50 may be made of any suitable material, including metal, glass, plastics, composite, ceramic, other materials, or combinations of the foregoing. The material that forms any portion of the electrolytic cell 50 is preferably not reactive with or substantially degraded by the chemicals and conditions that it is exposed to as part of the process.

[0093] The bipolar electrode 52 may be fabricated from a variety of materials known in the art, including but not limited to, Kovar alloy (approximately 54% iron, 29% nickel, 17% cobalt), nickel, ruthenium oxide coated on titanium substrate (RuO₂/Ti) dimensionally stable anode (DSA), platinum, platinum coated on titanium substrate, stainless steel, HASTEALLOY® nickel based alloy, INCOLOY® Alloy 800 (iron, nickel, and chromium alloy), and carbon steel.

[0094] The operation of the electrolytic cell 50 is similar to that of cell 10, discussed above. There are several potential reactions in the anolyte compartment depending upon the composition of the anolyte inlet stream 66. The anolyte inlet stream may be an aqueous feed of sodium based salts which may include sodium hydroxide and sodium sulfate and other alkali and transition metal impurities.

[0095] The electrolysis reactions may be as follows:



[0096] The process can be operated between about ambient temperature and about 100° C. The catholyte inlet 70 includes water. It may also include an aqueous solution of sodium hydroxide. The catholyte outlet 72 comprises an aqueous solution of sodium hydroxide, at a higher concentration than the catholyte inlet 70.

[0097] The electrolytic cell 50 shown in FIG. 10 may be expanded to include additional two compartment cells separated by bipolar electrodes. FIG. 11 shows a schematic representation of an electrolytic cell 80 comprising four electrolytic cells stacked in series, separated by three bipolar membranes 82.

[0098] Each two compartment cell in the electrolytic cell 80 includes an alkali cation-conductive ceramic material membrane 84 used to split an aqueous solution of sodium salts. The alkali cation-conductive ceramic material 84 may be NaSICON-type material, as disclosed herein. The alkali cation-conductive ceramic material 84 separates a catholyte compartment 88 from an anolyte compartment 90. The anolyte compartment 90 is configured with an anode 92 and the catholyte compartment 88 is configured with a cathode 94. The bipolar electrode 82 includes the dual properties of an anode 92a and a cathode 94a. An electric potential or voltage source 95 is provided to operate the electrolytic cell 80.

[0099] The electrolytic cell 80 further comprises an anolyte inlet 96 for introducing chemicals into the anolyte compartment 90 and an anolyte outlet 98 for removing or receiving anolyte solution from the anolyte compartment 90. The cell 80 also includes a catholyte inlet 100 for introducing chemicals into the catholyte compartment 88 and a catholyte outlet 102 for removing or receiving catholyte solution from the catholyte compartment 88.

[0100] FIG. 12 shows a schematic representation of electrolytic cell 80', which is based upon the general structure of the electrolytic cell 80 illustrated in FIG. 11. The electrolytic cell 80' is designed to produce alkali hydroxide, such as sodium hydroxide, in the catholyte solution produced in the catholyte compartment. The catholyte solution from one catholyte compartment is introduced into a second catholyte compartment to increase the concentration of the alkali hydroxide within the second catholyte compartment. As shown, the catholyte outlet 102 from catholyte compartment 88 becomes the catholyte inlet 100' for the catholyte compartment 88'. This can be repeated in successive catholyte compartments to produce a catholyte outlet solution having increased alkali hydroxide concentration. FIG. 12 shows one possible configuration of this concept wherein catholyte outlet 102' becomes the catholyte inlet 100'', catholyte outlet 102'' becomes the catholyte inlet 100''' for catholyte compartment 88'', and catholyte outlet 102''' contains the final catholyte solution with high concentration of alkali hydroxide.

[0101] FIG. 13 shows a schematic representation of electrolytic cell 80'', which is based upon the general structure of the electrolytic cell 80 illustrated in FIG. 11. The electrolytic cell 80'' is designed to produce alkali hydroxide, such as sodium hydroxide, in the catholyte solution produced in the catholyte compartment. The catholyte solution containing

alkali metal hydroxide, may be simultaneously received from a plurality of catholyte compartments in the electrolytic cell. As shown in FIG. 13, the catholyte outlet 102 from several catholyte compartments 88 is collected into a single catholyte outlet stream 110.

[0102] FIG. 14 shows a schematic representation of a multi-compartment electrolytic cell 120 comprising four two-compartment electrolytic cells stacked in a parallel configuration. Each two compartment cell in the electrolytic cell 120 includes an alkali cation-conductive ceramic material membrane 124 used to split an aqueous solution of sodium salts. The alkali cation-conductive ceramic material 124 may be NaSICON-type material, as disclosed herein. The alkali cation-conductive ceramic material 124 separates a catholyte compartment 128 from an anolyte compartment 130. The anolyte compartment 130 is configured with an anode 132 and the catholyte compartment 128 is configured with a cathode 134. An electric potential or voltage source 135 is provided to operate the electrolytic cell 120. An anode lead wire 136 electrically connects the voltage source to each anode 132. A cathode lead wire 137 electrically connects the voltage source to each cathode 134.

[0103] The electrolytic cell 120 further comprises an anolyte inlet 138 for introducing chemicals into the anolyte compartment 130 and an anolyte outlet 139 for removing or receiving anolyte solution from the anolyte compartment 130. The cell 120 also includes a catholyte inlet 140 for introducing chemicals into the catholyte compartment 128 and a catholyte outlet 142 for removing or receiving catholyte solution from the catholyte compartment 128. The electrolytic cell 120 operates in a manner similar to the other electrolytic cell embodiments disclosed herein. While not shown in FIG. 14, it will be appreciated that the catholyte outlet 102 from several catholyte compartments 88 may be collected into a single catholyte outlet stream as shown in FIG. 13.

[0104] Benefits and applications from two compartment electrolytic cell, either alone or combined in a multi-compartment embodiment include, but are not limited to:

[0105] 1. The two compartment electrolytic cell provides the opportunity to separate and recycle complex industrial alkali (sodium) based salt feed containing impurities of other alkali, transitional and salts form main groups to make up to 50% concentrated sodium hydroxide in the catholyte in the cell configuration.

[0106] 2. Alkali (or sodium elements) ions can be removed up to ppm levels from any incoming industrial aqueous byproduct feed chemistries which makes the process most attractive, efficient, and economical for industrial salt splitting, separation and recycling applications.

[0107] 3. An energy efficient approach for electro-synthesis of value added chemicals from alkali salts with and without the presence of impurities to make for example, pure sodium hydroxide stream and reduce or consolidate the volume of the feed anolyte.

[0108] While specific embodiments of the present invention have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

1. A method for producing an alkali metal hydroxide, comprising:
providing an electrolytic cell comprising at least one membrane comprising ceramic material configured to selec-

tively transport the alkali metal ions, the membrane positioned between an anolyte compartment configured with an anode and a catholyte compartment configured with a cathode;

introducing a first solution comprising an alkali metal hydroxide solution into the catholyte compartment of the electrolytic cell such that said first solution is in communication with the membrane and the cathode;

introducing a second solution comprising at least one alkali metal salt and one or more monovalent, divalent, or multivalent metal salts into the anolyte compartment of the electrolytic cell such that said second solution is in communication with the membrane and the anode; and applying an electric potential to the electrolytic cell such that alkali metal ions pass through the membrane and are available to undertake a chemical reaction with hydroxyl ions in the catholyte compartment to form alkali metal hydroxide.

2. The method of claim 1, wherein introducing a first solution into the catholyte compartment and introducing a second solution into the anolyte compartment comprise a continuous operation.

3. The method of claim 1, wherein introducing a first solution into the catholyte compartment and introducing a second solution into the anolyte compartment comprise a batch operation.

4. The method of claim 1, wherein the alkali metal comprises sodium.

5. The method of claim 4, wherein introducing a first solution into the catholyte compartment comprises introducing sodium hydroxide as an aqueous solution wherein the concentration of sodium hydroxide is between about 1% by weight and about 50% by weight of the solution.

6. The method of claim 5, further comprising maintaining the concentration of sodium hydroxide in the catholyte compartment between about 10% and about 20% by weight.

7. The method of claim 4, further comprising maintaining the concentration of the sodium salt in the anolyte compartment between about 1% and about 50% by weight of the second solution.

8. The method of claim 7, further comprising maintaining the concentration of sodium in the anolyte compartment between about 5% and about 20% by weight.

9. The method of claim 4, wherein the ceramic membrane comprises a NaSICON material.

10. The method of claim 4, wherein the ceramic membrane comprises a NaSICON material having the formula $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ where $0 \leq x \leq 3$.

11. The method of claim 4, wherein the ceramic membrane comprises a NaSICON material having the formula, $\text{M}_{1-x}\text{M}'_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ where $0 \leq x \leq 3$, where M is selected from the group consisting of Li, Cs, Na, K, or Ag, or mixture thereof, and where M' is selected from the group consisting of Zr, Ge, Y, Ti, Sn, Y or Hf, or mixtures thereof.

12. The method of claim 4, wherein the ceramic membrane comprises a NaSICON material having the formula $\text{Na}_5\text{RESi}_4\text{O}_{12}$ where RE is Y, Nd, Dy, or Sm, or any mixture thereof.

13. The method of claim 4, wherein the ceramic membrane comprises a non-stoichiometric sodium-deficient NaSICON material having the formula $(\text{Na}_5\text{RESi}_4\text{O}_{12})_{1-\delta}(\text{RE}_2\text{O}_3 \cdot 2\text{SiO}_2)_\delta$, where RE is Nd, Dy, or Sm, or any mixture thereof and where δ is the measure of deviation from stoichiometry.

14. The method of claim 4, wherein the second solution introduced into the anolyte compartment comprises a sodium salt selected from the group consisting of: sodium hydroxide, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate, sodium chlorate, sodium phosphate, sodium perchlorate, sodium nitrite, sodium fluoride, sodium oxalate, sodium organic salts and any combination thereof.

15. The method of claim 1, wherein the second solution comprises one or more monovalent, divalent, or multivalent metal salts selected from Na, K, Cs, Ca, Sr, Ba, Al, and mixtures thereof.

16. The method of claim 1, wherein the second solution comprises one or more non-alkali, radioactive metal salts and wherein the alkali metal hydroxide formed in the catholyte compartment is substantially non-radioactive.

17. The method of claim 1, wherein the membrane operates at a current density of between about 20 mA/cm² and about 200 mA/cm².

18. The method of claim 1, wherein the sodium-ion conducting ceramic membrane operates at a current density greater than 100 mA/cm².

19. The method of claim 1, wherein the electrolytic cell comprises a plurality of membranes, each configured to selectively transport sodium ions, and at least one bipolar electrode positioned between a pair of said membranes such that the electrolytic cell comprises a plurality of anolyte compartments and a plurality of catholyte compartments.

20. The method of claim 19, wherein alkali metal hydroxide solution is simultaneously received from the plurality of catholyte compartments.

21. The method of claim 20, wherein sodium hydroxide is received from a first catholyte compartment and introduced into a second catholyte compartment to increase the concentration of the sodium hydroxide in a sodium hydroxide solution in successive catholyte compartments.

22. The method of claim 1, wherein the ceramic membrane comprises a material having the formula $\text{Na}_{1+z}\text{L}_z\text{Zr}_{2-z}\text{P}_3\text{O}_{12}$ where $0 \leq z \leq 2.0$, and where L is selected from the group consisting of Cr, Yb, Er, Dy, Sc, Fe, In, or Y, or mixtures thereof;

23. The method of claim 1, wherein the ceramic membrane comprises a material having the formula $\text{M}^{II}_5\text{RESi}_4\text{O}_{12}$, where M^{II} may be Li, Na, K or Ag, or mixtures thereof, and where RE is Y or any rare earth element.

24. An electrolytic cell for producing sodium hydroxide, comprising:

an anolyte compartment configured with an anode, said anolyte compartment comprising an anolyte solution comprising at least one sodium salt and one or more monovalent, divalent, or multivalent metal salts selected from K, Cs, Ca, Sr, Ba, Al, and mixtures thereof such that said anolyte solution is in communication with the anode;

a catholyte compartment configured with a cathode; said catholyte compartment comprising a catholyte solution comprising a sodium hydroxide solution such that said catholyte solution is in communication with the cathode; at least one membrane comprising a ceramic NaSICON material configured to selectively transport sodium ions, the membrane positioned between the anolyte compartment and the catholyte compartment, wherein said anolyte solution is in communication with the membrane and said catholyte solution is in communication with the membrane; and

a source of electric potential connected to the anode and the cathode such that sodium ions from the anolyte compartment pass through the membrane and are available to undertake a chemical reaction with hydroxyl ions in the catholyte compartment to form sodium hydroxide.

25. The electrolytic cell of claim **24**, wherein the ceramic membrane comprises a NaSICON material having the formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ where $0 \leq x \leq 3$.

26. The electrolytic cell of claim **24**, wherein the ceramic membrane comprises a NaSICON material having the formula, $\text{M}_{1+x}\text{M}'_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ where $0 \leq x \leq 3$, where M is selected from the group consisting of Li, Cs, Na, K, or Ag, or mixture thereof, and where M' is selected from the group consisting of Zr, Ge, Y, Ti, Sn, or Hf, or mixtures thereof.

27. The electrolytic cell of claim **24**, wherein the ceramic membrane comprises a NaSICON material having the formula $\text{Na}_5\text{RESi}_4\text{O}_{12}$ where RE is Y, Nd, Dy, or Sm, or any mixture thereof.

28. The electrolytic cell of claim **24**, wherein the ceramic membrane comprises a non-stoichiometric sodium-deficient NaSICON material having the formula $(\text{Na}_5\text{RESi}_4\text{O}_{12})_{1-\delta}(\text{RE}_2\text{O}_3 \cdot 2\text{SiO}_2)_\delta$, where RE is Nd, Dy, or Sm, or any mixture thereof and where δ is the measure of deviation from stoichiometry.

29. The electrolytic cell of claim **24**, wherein the membrane operates at a current density of between about 20 mA/cm² and about 200 mA/cm².

30. The electrolytic cell of claim **24**, wherein the membrane comprises a monolithic flat plate, a monolithic tube, a monolithic honeycomb, or supported structures of the foregoing.

31. The electrolytic cell of claim **24**, wherein the sodium-ion conducting ceramic membrane comprises a layered sodium-ion conducting ceramic-polymer composite membrane, comprising sodium ion-conducting polymers layered on sodium ion-conducting ceramic solid electrolyte materials.

32. The electrolytic cell of claim **24**, wherein the sodium ion conducting ceramic membrane comprises a plurality of co-joined layers of two or more different sodium ion conducting ceramic materials.

33. The electrolytic cell of claim **24**, wherein the anolyte solution comprises one or more non-sodium, radioactive metal salts and wherein the sodium hydroxide formed in the catholyte compartment is substantially non-radioactive.

34. The method of claim **24**, wherein the ceramic membrane comprises a material having the formula $\text{Na}_{1+L}\text{Zr}_{2-z}\text{P}_3\text{O}_{12}$ where $0 \leq z \leq 2.0$, and where L is selected from the group consisting of Cr, Yb, Er, Dy, Sc, Fe, In, or Y, or mixtures thereof;

35. The method of claim **24**, wherein the ceramic membrane comprises a material having the formula $\text{M}''_5\text{RESi}_4\text{O}_{12}$, where M'' may be Li, Na, K or Ag, or mixtures thereof, and where RE is Y or any rare earth element.

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