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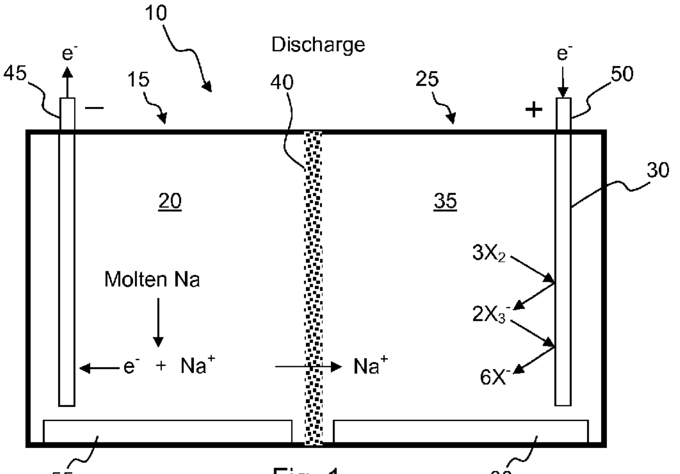

Fig. 1

(57) Abstract: An intermediate temperature sodium-halogen secondary cell that includes a negative electrode compartment housing a negative, molten sodium-based electrode and a positive electrode compartment housing a current collector disposed in a highly conductive molten positive electrolyte. A sodium halide (NaX) positive electrode is disposed in a molten positive electrolyte comprising one or more AlX3 salts, wherein X may be the same or different halogen selected from Cl, Br, and I, wherein the ratio of NaX to AlX_3 is greater than or equal to one. A sodium ion conductive solid electrolyte membrane separates the molten sodium negative electrode from the molten positive electrolyte. The secondary cell operates at a temperature in the range from about 80° C to 210° C.

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SODIUM-HALOGEN SECONDARY CELL

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH

[0001] This invention was made with government support under Contract No. 1189875 awarded by the Sandia National Lab. The government has certain rights in the invention.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application claims the benefit of and priority to U.S. Provisional Patent Application Serial No. 62/087,507 entitled "SODIUM-HALOGEN SECONDARY CELL" filed December 4, 2014. This application is also a continuation-in-part of U.S. Patent Application No. 14/511,031, entitled "SODIUM-HALOGEN SECONDARY CELL," filed October 9, 2014, which claims the benefit of U.S. Provisional Patent Application Serial No. 61/888,933 entitled "NASICON MEMBRANE BASED Na-I_2 BATTERY," filed October 9, 2013. This application is also a continuation-in-part of U.S. Patent Application No. 14/019,651, entitled "SODIUM-HALOGEN BATTERY," filed September 6, 2013, which claims the benefit of U.S. Provisional Patent Application Serial No. 61/697,608 entitled "SODIUM-HALOGEN BATTERY," filed September 6, 2012, and which also claims the benefit of U.S. Provisional Patent Application Serial No. 61/777,967 entitled "SODIUM-HALOGEN SECONDARY CELL," filed March 12, 2013, and which also claims the benefit of U.S. Provisional Patent Application Serial No. 61/781,530 entitled "SODIUM-HALOGEN SECONDARY FLOW CELL," filed March 14, 2013, and which also claims the benefit of U.S. Provisional Patent Application Serial No. 61/736,444 entitled "BATTERY WITH BROMINE OR BROMIDE ELECTRODE AND SODIUM SELECTIVE MEMBRANE," filed December 12, 2012. All of these prior patent applications are expressly incorporated herein by reference.

TECHNICAL FIELD

[0003] The disclosed invention relates to an intermediate temperature, sodium - halogen secondary cell (or rechargeable battery) with a sodium ion conductive electrolyte membrane and a positive electrolyte that comprises one or more sodium haloaluminate salts and a sodium halide. In some disclosed embodiments, the battery system utilizes a molten eutectic mixture of sodium haloaluminate salts having a relatively low melting point.

BACKGROUND

[0004] Batteries are known devices that are used to store and release electrical energy for a variety of uses. In order to produce electrical energy, batteries typically convert chemical energy directly into electrical energy. Generally, a single battery includes one or more galvanic cells, wherein each of the cells is made of two half-cells that are electrically isolated except through an external circuit. During discharge, electrochemical reduction occurs at the cell's positive electrode, while electrochemical oxidation occurs at the cell's negative electrode. While the positive electrode and the negative electrode in the cell do not physically touch each other, they are generally chemically connected by at least one (or more) ionically conductive and electrically insulative electrolytes, which can either be in a solid state, a liquid state, or in a combination of such states. When an external circuit, or a load, is connected to a terminal that is connected to the negative electrode and to a terminal that is connected to the positive electrode, the battery drives electrons through the external circuit, while ions migrate through the electrolyte.

[0005] Batteries can be classified in a variety of manners. For example, batteries that are completely discharged only once are often referred to as primary batteries or primary cells. In contrast, batteries that can be discharged and recharged more than once are often referred to as secondary batteries or secondary cells. The ability of a cell or battery to be charged and discharged multiple times depends on the Faradaic efficiency of each charge and discharge cycle.

[0006] While rechargeable batteries based on sodium can comprise a variety of materials and designs, most, if not all, sodium batteries that require a high Faradaic efficiency employ a solid primary electrolyte separator, such as a solid ceramic primary electrolyte membrane. The principal advantage of using a solid ceramic primary electrolyte membrane is that the Faradaic efficiency of the resulting cell approaches 100%. Indeed, in almost all other cell designs, electrode solutions in the cell are able to intermix over time and, thereby, cause a drop in Faradaic efficiency and loss of battery capacity.

[0007] The primary electrolyte separators used in sodium batteries that require a high Faradaic efficiency often consist of ionically conductive polymers, porous materials infiltrated with ionically conductive liquids or gels, or dense ceramics. In this regard, many rechargeable sodium batteries that are presently available for commercial applications comprise a molten sodium metal negative electrode, a sodium β''-alumina ceramic electrolyte separator, and a molten positive electrode, which may include a composite of molten sulfur and carbon (called a sodium/sulfur cell). Because these conventional high temperature sodium-based rechargeable batteries have relatively high specific energy densities and only modest power densities, such rechargeable batteries are typically used in certain specialized applications that require high specific energy densities where high power densities are typically not encountered, such as in stationary storage and uninterruptable power supplies.

[0008] Despite the beneficial characteristics associated with some conventional sodium-based rechargeable batteries, such batteries may have significant shortcomings. In one example, because the sodium β''-alumina ceramic electrolyte separator is typically more conductive and is better wetted by molten sodium at a temperature in excess of about 270° C and/or because the molten positive electrode typically requires relatively high temperatures (*e.g.*, temperatures above about 170° or 180° C) to remain molten, many conventional sodium-based rechargeable batteries operate at temperatures higher than about 270° C and are subject to significant thermal management problems and thermal sealing issues. For example, some sodium-based rechargeable batteries may have difficulty dissipating heat from the batteries or maintaining the negative electrode and the positive electrode at the relatively high operating temperatures. In another example, the relatively high operating temperatures of some sodium-based batteries can create significant safety issues. In still another example, the relatively high operating temperatures of some sodium-based batteries require their components to be resistant to, and operable at, such high temperatures. Accordingly, such components can be relatively expensive. In yet another example, because it may require a relatively large amount of energy to heat some conventional sodium-based batteries to the relatively high operating temperatures, such batteries can be expensive to operate and energy inefficient.

[0009] Thus, while sodium-based rechargeable batteries are available, challenges with such batteries also exist, including those previously mentioned. Accordingly, it would be an improvement in the art to augment or even replace certain conventional sodium-based rechargeable batteries with other sodium-based rechargeable batteries that operate effectively at intermediate temperatures.

SUMMARY OF THE INVENTION

[0010] Examples of sodium-halogen secondary cells are disclosed in Applicant's copending U.S. Patent Application No. 14/019,651, published as U.S. Publication No. 2014/0065456 entitled "Sodium-Halogen Secondary Cell." The disclosed secondary cells include a positive electrode compartment housing a current collector disposed in a liquid positive electrode solution. Some examples of suitable positive electrode solution materials include organic solvents such as dimethyl sulfoxide, NMF (N-methylformamide), and ionic liquids.

[0011] The present disclosure provides an improvement to the positive electrode solution of the sodium-halogen secondary cells disclosed in Applicant's copending application. More specifically, the disclosed invention utilizes a positive electrolyte that comprises sodium halide in a molten haloaluminate electrolyte. In some disclosed embodiments, the battery system utilizes a molten eutectic mixture of sodium haloaluminate salts having a relatively low melting point.

[0012] A sodium ion conductive solid electrolyte separates the negative electrode and the positive electrode. In a non-limiting embodiment, the sodium ion conductive solid electrolyte comprises a NaSICON electrolyte material. The NaSICON electrolyte material has high sodium conductivity at cell operating temperatures.

[0013] In one non-limiting embodiment, the battery operates at a temperature in the range from 80 °C to 210 °C.

[0014] In one non-limiting embodiment of the disclosed invention, the rechargeable sodium-halogen battery includes a negative electrode comprising metallic sodium in molten state. In another embodiment, the negative electrode may comprise metallic sodium in a solid state. The positive electrode comprises NaX, where X is a halogen selected from Cl, Br and I. The positive electrode is disposed in a molten salt positive electrolyte comprising AlX_3. In some embodiments, the positive electrolyte is a mixture of at least two AlX_3 salts that can be represented by the formula $NaAlX'_{4-\delta}X''_{\delta}$, where $0 < \delta < 4$, wherein X' and X" are different halogens selected from Cl, Br and I.

[0015] The mixed molten salt positive electrolyte comprises at least two salts of the general formula $NaAlX'_4$ and $NaAlX''_4$ at various molar ratios, wherein X' and X" are different halogens selected from Cl, Br and I. In one non-limiting embodiment, the molar ratio of $NaAlX'_4$ to $NaAlX''_4$ is in the range of 9:1 to 1:9 with corresponding δ values of 0.4 to 3.6.

[0016] The positive electrode comprises additional NaX or a mixture of NaX compounds added in a molar ratio to the mixed molten salt positive electrolyte ranging from 1:1 to 3:1 of NaX : $NaAlX'_{4-\delta}X''_{\delta}$. The excess NaX renders the positive electrolyte highly basic. At cell operating temperatures, the positive electrode and mixed molten salt positive electrolyte is a molten liquid or a two phase mixture wherein the mixed molten salt positive electrolyte is predominantly a liquid phase and the additional NaX or mixture of NaX compounds is a solid phase.

[0017] In other embodiments, the positive electrode is disposed in a mixed molten salt positive electrolyte comprising at least three salts that can be represented by the formula $NaAlX'_{4-\delta-\varpi}X''_{\delta}X'''_{\varpi}$, where X', X'' and X''' are three different halogens selected from Cl, Br, and I, where $0 < \delta < 4$, $0 < \varpi < 4$, and $0 < \delta + \varpi < 4$. The mixed molten salt positive electrolyte comprises $NaAlCl_4$, $NaAlBr_4$, and $NaAlI_4$, at various molar ratios.

[0018] The disclosed sodium haloaluminate molten salts are highly conductive at relatively low temperatures enabling the sodium-halogen battery to be highly efficient and reversible. These features and advantages of the present embodiments will become more fully apparent from the following description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] 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:

[0020] Fig. 1 depicts a schematic diagram of a representative embodiment of a molten sodium-halogen secondary cell, wherein the cell is in the process of being discharged.

[0021] Fig. 2 depicts a schematic diagram of a representative embodiment of the molten sodium-halogen secondary cell, wherein the cell is in the process of being recharged.

[0022] Fig. 3A depicts one potential reaction, designated Battery Chemistry 1, at the positive current collector.

[0023] Fig. 3B depicts another potential reaction, designated Battery Chemistry 2, at the positive current collector.

[0024] Fig. 4 is a graph comparing the conductivity of NaI in a molten salt electrolyte and in an organic solvent as a function of temperature.

[0025] Figs. 5A and 5B are graphs comparing the oxidation of iodide in a sodium-iodine secondary cell containing NaI in $AlCl_3$ at basic and acidic ratios of $NaI:AlCl_3$.

[0026] Fig. 6 is a graph of the current vs. voltage for the operation of the symmetrical cells described in Example 3.

DETAILED DESCRIPTION

[0027] Reference throughout this specification to "one embodiment," "an embodiment," or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment," "in an embodiment," "in another embodiment," and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment. Additionally, while the following description refers to several embodiments and examples of the various components and aspects of the described invention, all of the described embodiments and examples are to be considered, in all respects, as illustrative only and not as being limiting in any manner.

[0028] Furthermore, the described features, structures, or characteristics of the invention may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of suitable sodium-based negative electrodes, liquid positive electrode solutions, current collectors, sodium ion conductive electrolyte membranes, etc., to provide a thorough understanding of embodiments of the invention. One having ordinary skill in the relevant art will recognize, however, that the invention may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other embodiments, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

[0029] As stated above, secondary cells can be discharged and recharged and this specification describes cell arrangements and methods for both states. Although the term "recharging" in its various forms implies a second charging, one of skill in the art will understand that discussions regarding recharging would be valid for, and applicable to, the first or initial charge, and *vice versa*. Thus, for the purposes of this specification, the terms "recharge," "recharged," and "rechargeable" shall be interchangeable with the terms "charge," "charged," and "chargeable," respectively.

[0030] The present embodiments provide a sodium-halogen secondary cell, which includes a molten or solid state sodium negative electrode and a sodium halide positive electrode disposed in a molten positive electrolyte that comprises one or more haloaluminate salts. In some disclosed embodiments, the secondary cell utilizes a molten eutectic mixture of sodium haloaluminate salts having a relatively low melting point. Although the described cell can comprise any suitable component, Figure 1 shows a representative embodiment in which the sodium secondary cell 10 comprises a negative electrode compartment 15 that includes a sodium metal negative electrode 20 and a positive electrode compartment 25 that comprises a sodium halide positive electrode. The positive electrode includes a current collector 30 disposed in a positive electrolyte 35 comprising one or more molten haloaluminate salts ($AlCl_3$, $AlBr_3$, and AlI_3). A sodium ion conductive electrolyte membrane 40 separates the negative electrode from the positive electrode and positive electrolyte 35. The sodium ion conductive electrolyte membrane 40 separates a first terminal 45 from a second terminal 50. To provide a better understanding of the described cell 10, a brief description of how the cell functions is provided below. Following this discussion, each of the cell's components shown in Figure 1 is discussed in more detail.

[0031] Turning now to the manner in which the sodium secondary cell 10 functions, the cell can function in virtually any suitable manner. In one example, Figure 1 illustrates that as the cell 10 is discharged and electrons (e^-) flow from the negative electrode 20 (*e.g.*, via the first terminal 45), sodium is oxidized from the negative electrode 20 to form sodium ions (Na^+). Figure 1 shows that these sodium ions are respectively transported from the sodium negative electrode 20, through the sodium ion conductive membrane 40, and to the positive electrolyte 35.

[0032] In a contrasting example, Figure 2 shows that as the secondary cell 10 is recharged and electrons (e^-) flow into the sodium negative electrode 20 from an external power source (not shown), such as a recharger, the chemical reactions that occurred when the cell 10 was discharged (as shown in Figure 1) are reversed. Specifically, Figure 2 shows that as the cell 10 is recharged, sodium ions (Na^+) are respectively transported from the positive electrolyte 35, through the electrolyte membrane 40, and to the negative electrode 20, where the sodium ions are reduced to form sodium metal (Na).

[0033] Referring now to the various components of the cell 10, the cell, as mentioned above, can comprise a negative electrode compartment 15 and a positive electrode compartment 25. In this regard, the two compartments can be any suitable shape and have any other suitable characteristic that allows the cell 10 to function as intended. By way of example, the negative electrode and the positive electrode compartments can be tubular, rectangular, or be any other suitable shape. Furthermore, the two compartments can have any suitable spatial relationship with respect to each other. For instance, while Figure 2 shows that the negative electrode compartment 15 and the positive electrode compartment 25 can be adjacent to each other, in other embodiments (not shown), one compartment (*e.g.*, the negative electrode compartment) is disposed, at least partially, in the other compartment (*e.g.*, the positive electrode compartment), while the contents of the two compartments remain separated by the electrolyte membrane 40 and any other compartmental walls.

[0034] With respect to the negative electrode 20, the cell 10 can comprise any suitable sodium negative electrode 20 that allows the cell 10 to function (*e.g.*, be discharged and recharged) as intended. Some examples of suitable sodium negative electrode materials include, but are not limited to, a sodium sample that is substantially pure and a sodium alloy comprising any other suitable sodium-containing negative electrode material. In certain embodiments, however, the negative electrode comprises or consists of an amount of sodium that is substantially pure. In such embodiments, because the melting point of pure sodium is around 98° C, the sodium negative electrode will become molten above that temperature.

[0035] With respect to the positive current collector 30, the positive electrode compartment 25 can comprise any suitable positive electrode that allows the cell to be charged and discharged as intended. For instance, the positive electrode can comprise virtually any current collector 30 in combination with a halogen, shown generically as “X” in Figs. 1 and 2, in a positive electrolyte 35 comprising one or more sodium haloaluminate salts. The current collector 30 can be disposed in any suitable location in the positive electrode compartment 25 that allows the cell 10 to function as intended.

[0036] With respect to the current collector 30, the cell 10 can comprise any suitable current collector that allows the cell to be charged and discharged as intended. For instance, the current collector can comprise virtually any current collector configuration that has been successfully used in a sodium-based rechargeable battery system. In some embodiments, the current collector comprises at least one of wires, felts, foils, plates, parallel plates, tubes, meshes, mesh screens, foams, and/or other suitable current collector configuration. It will be appreciated by those of skill in the art that the foam may include, without limitation, metal foams and carbon foams. Indeed, in some embodiments, the current collector comprises a configuration having a relatively large surface area which may include one or more mesh screens and metal foams.

[0037] The current collector 30 can comprise any suitable material that allows the cell 10 to function as intended. In this regard, some non-limiting examples of suitable current collector materials include tungsten, stainless steel, carbon, molybdenum, titanium, platinum, copper, nickel, zinc, a sodium intercalation material (*e.g.*, Na_XMnO_2, etc.), nickel foam, nickel, a sulfur composite, a sulfur halide (*e.g.*, sulfuric chloride), and/or another suitable material. Furthermore, these materials may coexist or exist in combinations. In some embodiments, however, the current collector comprises tungsten, carbon, molybdenum, titanium.

[0038] In some non-limiting embodiments, the reactions that may occur at the negative electrode 20, the positive electrode/current collector 30, and the overall reaction as the cell 10 is discharged may occur in at least two steps. These two potential reactions are shown below and designated Battery Chemistry 1 (shown schematically in Fig. 3A for battery recharge) and Battery Chemistry 2 (shown schematically in Fig. 3B for battery recharge). It has been observed that these reactions may be individual steps of a multi-step reaction, or depending upon the battery conditions, one step may be favored over another step.

[0039] Negative electrode $Na \leftrightarrow Na^+ + 1e^-$

[0040] Positive electrode $X_3^- + 2e^- \leftrightarrow 3X^-$ (Battery Chemistry 1)

[0041] Positive electrode $3X_2 + 2e^- \leftrightarrow 2X_3^-$ (Battery Chemistry 2)

[0042] Overall $2Na + X_3^- \leftrightarrow 2Na^+ + 3X^-$ (Battery Chemistry 1)

[0043] Overall $2Na + 3X_2 \leftrightarrow 2Na^+ + 2X_3^-$ (Battery Chemistry 2)

[0044] Where X comprises iodine, bromine, or chlorine.

[0045] Where X comprises iodine, the cell 10 may have the following chemical reactions and the following theoretical voltage (V vs. SHE (standard hydrogen electrode)) and theoretical specific energy (Wh/kg):

[0046] Negative electrode $Na \leftrightarrow Na^+ + 1e^-$ (-2.71V)

[0047] Positive electrode $I_3^- + 2e^- \leftrightarrow 3I^-$ (0.29V, Chemistry 1)

[0048] Positive electrode $3I_2 + 2e^- \leftrightarrow 2I_3^-$ (0.74V, Chemistry 2)

[0049] Overall $2Na + I_3^- \leftrightarrow 2Na^+ + 3I^-$ (2.8V, Chemistry 1) (388 Wh/kg)

[0050] Overall $2Na + 3I_2 \leftrightarrow 2Na^+ + 2I_3^-$ (3.25V, Chemistry 2) (193 Wh/kg)

[0051] Where X is iodine, the charging reactions at the positive electrode may occur in two steps: 1) iodide to triiodide and 2) triiodide to iodine. Similarly, discharging reactions at the positive electrode may occur in two steps: 1) iodine to triiodide and 2) triiodide to iodide. Alternatively, the charging and discharging reactions may occur using the combination of reaction chemistries above.

[0052] Where X is bromine, the cell 10 may have the following chemical reactions and the following theoretical voltage (V vs. SHE) and theoretical specific energy (Wh/kg):

[0053] Negative electrode $Na \leftrightarrow Na^+ + 1e^-$ (-2.71V)

[0054] Positive electrode $Br_3^- + 2e^- \leftrightarrow 3Br^-$ (0.82V, Chemistry 1)

[0055] Positive electrode $3Br_2 + 2e^- \leftrightarrow 2Br_3^-$ (1.04V, Chemistry 2)

[0056] Overall $2Na + Br_3^- \leftrightarrow 2Na^+ + 3Br^-$ (3.53V, Chemistry 1) (658 Wh/kg)

[0057] Overall $2Na + 3Br_2 \leftrightarrow 2Na^+ + 2Br_3^-$ (3.75V, Chemistry 2) (329 Wh/kg)

[0058] The charging reactions at the positive electrode may occur in two steps: 1) bromide to tribromide and 2) tribromide to bromine. Similarly, discharging reactions at the positive electrode may occur in two steps: 1) bromine to tribromide and 2) tribromide to bromide. Alternatively, the charging and discharging reactions may occur using the combination of reaction chemistries above.

[0059] It will be appreciated by those of skill in the art that an alternative positive electrode chemistry may include:

[0060] Positive electrode $X_2 + 2e^- \leftrightarrow 2X^-$ (Battery Chemistry 3)

[0061] With an overall battery chemistry of:

[0062] Overall $2Na + X_2 \leftrightarrow 2Na^+ + 2X^-$ (Battery Chemistry 3)

[0063] With regards now to the sodium ion conductive electrolyte membrane 40, the membrane can comprise any suitable material that selectively transports sodium ions and permits the cell 10 to function with a positive electrolyte 35. In some embodiments, the electrolyte membrane comprises a NaSICON-type (sodium Super Ion CONductive) material. Where the electrolyte membrane comprises a NaSICON-type material, the NaSICON-type material may comprise any known or novel NaSICON-type material that is suitable for use with the described cell 10. Some suitable examples of NaSICON-type compositions include, but are not limited to, $Na_3Zr_2Si_2PO_{12}$, $Na_{1+x}Si_xZr_2P_{3-x}O_{12}$ (where x is between about 1.6 and about 2.4), Y-doped NaSICON ($Na_{1+x+y}Zr_{2-y}Y_ySi_xP_{3-x}O_{12}$, $Na_{1+x}Zr_{2-y}Y_y Si_xP_{3-x}O_{12-y}$ (where x = 2, y = 0.12)), $Na_{1-x}Zr_2Si_xP_{3-x}O_{12}$ (where x is between about 0 and about 3, and in some cases between about 2 and about 2.5), and Fe-doped NaSICON ($Na_3Zr_2/_3Fe_4/_3P_3O_{12}$). Indeed, in certain embodiments, the NaSICON-type membrane comprises $Na_3Si_2Zr_2PO_{12}$. In other embodiments, the NaSICON-type membrane comprises one or more *NaSELECT*® materials, produced by Ceramatec, Inc. in Salt Lake City, Utah.

[0064] The positive electrode comprises NaX, where X is a halogen selected from Cl, Br and I. The positive electrode is preferably NaI.

[0065] The positive electrode is disposed in a molten salt positive electrolyte comprising AlX_3. NaX and AlX_3 may combine to form $NaAlX_4$ as follows:

[0066] $NaX + AlX_3 \leftrightarrow AlX_4$

[0067] In some embodiments, the positive electrode is combined with a mixture of at least two AlX_3 salts. The combination of positive electrode and positive electrolyte can be represented by the general formula $NaAlX'_{4-\delta}X''_{\delta}$, where $0 < \delta < 4$, wherein X' and X" are different halogens selected from Cl, Br and I.

[0068] The mixed molten salt positive electrolyte comprises at least two salts of the general formula $NaAlX'_4$ and $NaAlX''_4$ at various molar ratios, wherein X' and X" are different halogens selected from Cl, Br and I. In one non-limiting embodiment, the molar ratio of $NaAlX'_4$ to $NaAlX''_4$ is in the range of 9:1 to 1:9 with corresponding δ values of 0.4 to 3.6.

[0069] The positive electrode comprises additional NaX or a mixture of NaX compounds added in a molar ratio to the mixed molten salt positive electrolyte ranging from 1:1 to 3:1 of NaX : $NaAlX'_{4-\delta}X''_{\delta}$. The excess NaX renders the positive electrolyte highly basic. At cell operating temperatures, the positive electrode and mixed molten salt positive electrolyte is a molten liquid or a two phase mixture wherein the mixed molten salt positive electrolyte is predominantly a liquid phase and the additional NaX or mixture of NaX compounds is a solid phase.

[0070] The following Table 1 illustrates some non-limiting combinations of NaX and AlX_3 to form $NaAlX_4$.

[0071] Table 1

NaX \ AlX_3	**$AlCl_3$**	**$AlBr_3$**	**AlI_3**
NaCl	$NaAlCl_4$	$NaAlBr_3Cl$	$NaAlI_3Cl$

NaBr	$NaAlCl_3Br$	$NaAlBr_4$	$NaAlI_3Br$
NaI	$NaAlCl_3I$	$NaAlBr_3I$	$NaAlI_4$

[0072] In other embodiments, the positive electrode is disposed in a mixed molten salt positive electrolyte comprising at least three salts that can be represented by the formula $NaAlX'_{4-\delta-\varpi}X''_{\delta}X'''_{\varpi}$, where X', X'' and X''' are three different halogens selected from Cl, Br, and I, where $0 < \delta < 4$, $0 < \varpi < 4$, and $0 < \delta + \varpi < 4$. The mixed molten salt positive electrolyte comprises $NaAlCl_4$, $NaAlBr_4$, and $NaAlI_4$, at various molar ratios.

[0073] In some embodiments, the positive electrolyte 35 also comprises one or more halogens and/or halides. In this regard, the halogens and halides, as well polyhalides and/or metal halides that form therefrom (*e.g.*, where the current collector 30 comprises a metal, such as copper, nickel, zinc, etc. (as discussed below)) can perform any suitable function, including, without limitation, acting as the positive electrode as the cell 10 operates. Some examples of suitable halogens include bromine, iodine, and chlorine. Similarly, some examples of suitable halides include bromide ions, polybromide ions, iodide ions, polyiodide ions, chloride ions, and polychloride ions. While the halogens/halides can be introduced into the positive electrode solution in any suitable manner, in some embodiments, they are added as NaX, wherein X is selected from Br, I, Cl, etc.

[0074] With reference now to the terminals 45 and 50, the cell 10 can comprise any suitable terminals that are capable of electrically connecting the cell with an external circuit (not shown), including without limitation, to one or more cells. In this regard, the terminals can comprise any suitable material, be of any suitable shape, and be of any suitable size.

[0075] In addition to the aforementioned components, the cell 10 can optionally comprise any other suitable component. By way of non-limiting illustration Figures 1 and 2 show an embodiment in which the cell 10 comprises a heat management system 55, 60. Independent heat management systems may be associated with the negative electrode and positive electrode compartments. Alternatively, a single heat management system may be disposed in only one compartment or to the exterior of the cell 10 generally. In such embodiments, the cell can comprise any suitable type of heat management system that is capable of maintaining the cell within a suitable operating temperature range. Some examples of such heat management systems include, but are not limited to, a heater, a cooler, one or more temperature sensors, and appropriate temperature control circuitry.

[0076] The described cell 10 may function at any suitable operating temperature. In other words, as the cell is discharged and/or recharged, the sodium negative electrode and the positive electrolyte may have any suitable temperature. The negative and positive electrode compartments may operate at the same or different temperatures. Indeed, in some embodiments, the cell functions at an intermediate operating temperature in the range from about 80 °C to about 210 °C. In other embodiments, the cell may function at an intermediate operating temperature in the range from about 110 °C to about 180 °C. In yet another embodiment, the operating temperature of the cell in the range of about 150 °C to about 170 °C.

[0077] The following examples are given to illustrate various embodiments within, and aspects of, the scope of the present invention. These are given by way of example only, and it is understood that the following examples are not comprehensive or exhaustive of the many types of embodiments of the present invention that can be prepared in accordance with the present invention.

[0078] **Example 1**

[0079] The conductivity of NaI in a molten salt positive electrolyte $AlCl_3$ was compared to the conductivity of NaI in an organic solvent solution that included N-methyl formamide. The molten salt positive electrolyte had a general formula of $NaAl_xI_yCl_z$. The conductivity of NaI in a molten salt positive electrolyte was approximately three times the conductivity of the organic solvent-based electrolyte at 120 °C, as shown in Fig. 4. Cells utilizing a molten salt positive electrolyte will be more energy dense due to higher molarity of NaI. Furthermore, cells utilizing a molten salt positive electrolyte are safer than organic solvent based positive electrolyte solutions because if molten sodium happens to contact the molten salt positive electrolyte, the chemical reaction would only produce non-flammable salts.

[0080] **Example 2**

[0081] A sodium-iodine secondary cell was prepared as described herein containing sodium iodide in molten $AlCl_3$ in a 60:40 NaI:$AlCl_3$ ratio (a "basic" electrolyte). Tungsten wire was used as the positive current collector. NaSICON was used to separate a molten sodium negative electrode from the positive electrode/positive electrolyte. The oxidation of iodide was measured and found to produce two oxidation peaks, consistent with Battery Chemistry 1 and Battery Chemistry 2, described herein. Experimental results are shown in Fig. 5A. The oxidation peaks were found to be reversible. Additional tests were performed using an "acidic" electrolyte comprising sodium iodide in molten $AlCl_3$ in a 40:60 NaI:$AlCl_3$

ratio. Experimental results are shown in Fig. 5B. The results suggest that the second oxidation peak in the basic electrolyte occurs at a similar potential as the first iodide oxidation peak in the acidic electrolyte. The reduction peak in acidic electrolyte occurs at a higher potential. This suggests that whether the electrolyte is acidic or basic affects the potential of I_2 generation.

[0082] **Example 3**

[0083] Three symmetrical sodium-iodine secondary cells were prepared to test the reversibility of the oxidation / reduction reactions that occur in the positive electrode / positive electrolyte. The symmetrical cells were prepared as set forth in Table 2, below:

[0084] Table 2

Cell	**Electrode**		**Electrolyte**	
	Outside of tube	Inside of tube	Outside of Tube	Inside of Tube
Symmetrical Cell 1	Graphite felt with tungsten wire	Graphite felt with tungsten wire	1M I_2 in 51:49mol% NaI:$AlCl_3$	1M I_2 in 51:49mol% NaI:$AlCl_3$
Symmetrical Cell 2	0.93g NaI/0.93g C/PTFE around tungsten mesh	Tungsten wire with graphite felt	60:40mol% NaI:$AlCl_3$	0.02475g I_2 in 51:49mol% NaI:$AlCl_3$
Symmetrical Cell 3	Graphite felt with tungsten wire	0.25" Carbon Rod	60:40mol% NaI:$AlCl_3$	50:50mol% NaI:$AlCl_3$

[0085] The symmetrical cells were operated as set forth in Table 3, below:

[0086] Table 3

Cell	**Temperature (°C)**	**EIS**		**Operating Range**		**Current Density (mA/cm^2)**
		Ohmic (Ω)	System (Ω)	Upper Voltage Limit (V)	Lower Voltage Limit (V)	
Symmetrical Cell 1	125	2.17	5.19	0.5	-0.5	91
Symmetrical Cell 2	125	3.60	16.40	0.5	-0.5	72
Symmetrical Cell 3	125	5.00	6.70	0.15	-0.15	20

[0087] A graph of the current vs. voltage for the operation of the symmetrical cells is shown in Fig. 6. Because there is little or no hysteresis shown in Fig. 6, it may be concluded that the oxidation / reduction reactions that occur in the positive electrode / positive electrolyte are highly reversible.

[0088] Embodiments of the present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments and examples are to be considered in all respects only as illustrative and not as restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

[0089] What is claimed is:

CLAIMS:

1. A sodium-halogen secondary cell, comprising:

a negative electrode compartment comprising a negative electrode that comprises metallic sodium in molten or solid state, wherein the negative electrode electrochemically oxidizes to release sodium ions during discharge and electrochemically reduces sodium ions to form sodium metal during recharge;

a positive electrode comprising NaX disposed in a molten positive electrolyte comprising one or more AlX_3 salts, wherein X may be the same or different halogen selected from Cl, Br, and I, wherein the ratio of NaX to AlX_3 is greater than or equal to one; and

a sodium ion conductive solid electrolyte membrane that separates the negative electrode from the liquid positive electrode solution.

2. The secondary cell of claim 1, wherein the molten positive electrolyte comprises two different AlX_3 salts and is represented by the general formula $NaAlX'_{4-\delta}X''_{\delta}$, where $0 < \delta < 4$, wherein X' and X" are different halogens selected from Cl, Br and I.

3. The secondary cell of claim 2, wherein the positive electrode and the molten positive electrolyte are in the form of a mixed molten salt comprising at least two salts of the general formula $NaAlX'_4$ and $NaAlX''_4$ at various molar ratios.

4. The secondary cell of claim 3, wherein the molar ratio of $NaAlX'_4$ to $NaAlX''_4$ is in the range of 9:1 to 1:9 with corresponding δ values of 0.4 to 3.6.

5. The secondary cell of claim 3, wherein the positive electrode comprises additional NaX or a mixture of NaX compounds added in a molar ratio to the mixed molten salt positive electrolyte ranging from 1:1 to 3:1 of NaX : $NaAlX'_{4-\delta}X''_{\delta}$.

6. The secondary cell of claim 1, wherein the secondary cell operates at a temperature between about 80 °C and 210° C.

7. The secondary cell of claim 1, wherein the electrolyte membrane comprises a NaSICON-type material.

8. The secondary cell of claim 1, wherein molten salt positive electrolyte comprises three different AlX_3 salts and is represented by the general formula $NaAlX'_{4-\delta-\varpi}X''_{\delta}X'''_{\varpi}$, where X', X'' and X''' are three different halogens selected from Cl, Br, and I, where $0 < \delta < 4$, $0 < \varpi < 4$, and $0 < \delta + \varpi < 4$.

9. The secondary cell of claim 8, wherein the positive electrode and the molten positive electrolyte are in the form of a mixed molten salt comprising at least three salts of the formula $NaAlCl_4$, $NaAlBr_4$, and $NaAlI_4$, at various molar ratios.

10. The secondary cell of claim 8, wherein the positive electrode comprises additional NaX or a mixture of NaX compounds added in a molar ratio to the mixed molten salt positive electrolyte ranging from 1:1 to 3:1 of NaX : $NaAlX'_{4-\delta-\varpi}X''_{\delta}X'''_{\varpi}$, where $0 < \delta < 4$, $0 < \varpi < 4$, and $0 < \delta + \varpi < 4$.

11. The secondary cell of claim 10, wherein the additional NaX is present as a solid phase within the current collector.

12. The secondary cell of claim 1, wherein the positive electrode comprises a current collector comprising at least one of carbon, tungsten, molybdenum, and titanium.

13. The secondary cell of claim 11, wherein the current collector comprises at least one of wires, felts, foils, plates, parallel plates, tubes, meshes, mesh screens, and foams.

14. A sodium-halogen secondary cell, comprising:

a negative electrode compartment comprising a negative electrode that comprises metallic sodium in molten state, wherein the negative electrode electrochemically oxidizes to release sodium ions during discharge and electrochemically reduces sodium ions to form sodium metal during recharge;

a positive electrode comprising NaI disposed in a molten positive electrolyte comprising one or more AlX_3 salts, wherein X may be the same or different halogen selected from Cl, Br, and I, wherein the ratio of NaI to AlX_3 is greater than one; and

a sodium ion conductive solid electrolyte membrane that separates the negative electrode from the liquid positive electrode solution.

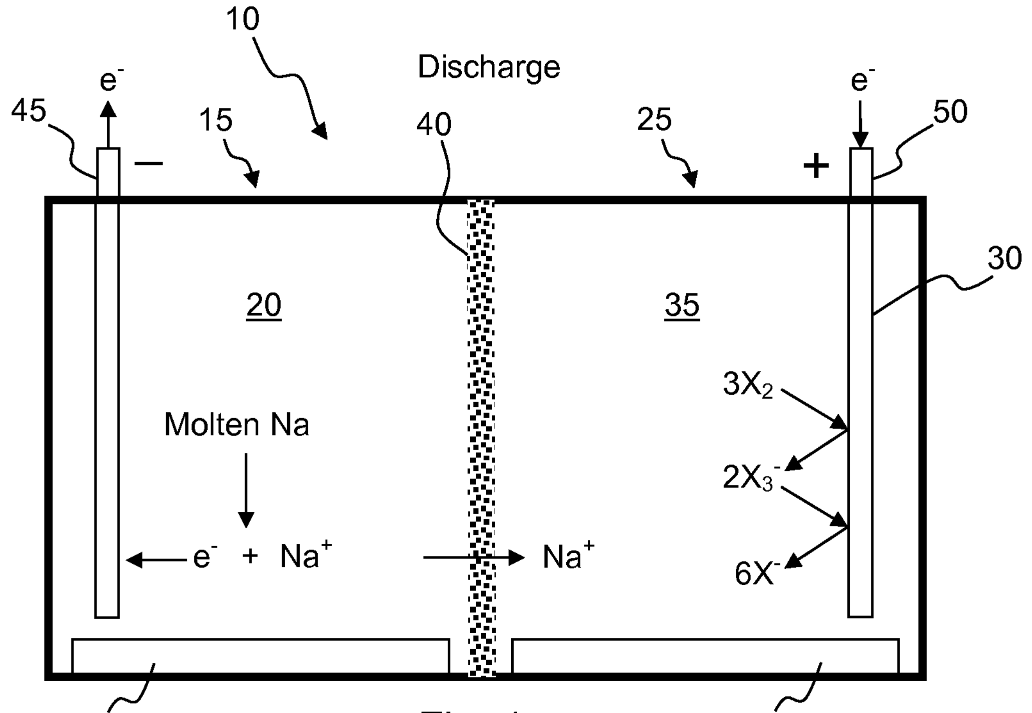
10
Discharge
45
e^-
15
40
25
e^-
50
−
+
20
35
30
Molten Na
$3X_2$
$2X_3^-$
e^- + Na^+
Na^+
$6X^-$
55
60

Fig. 1

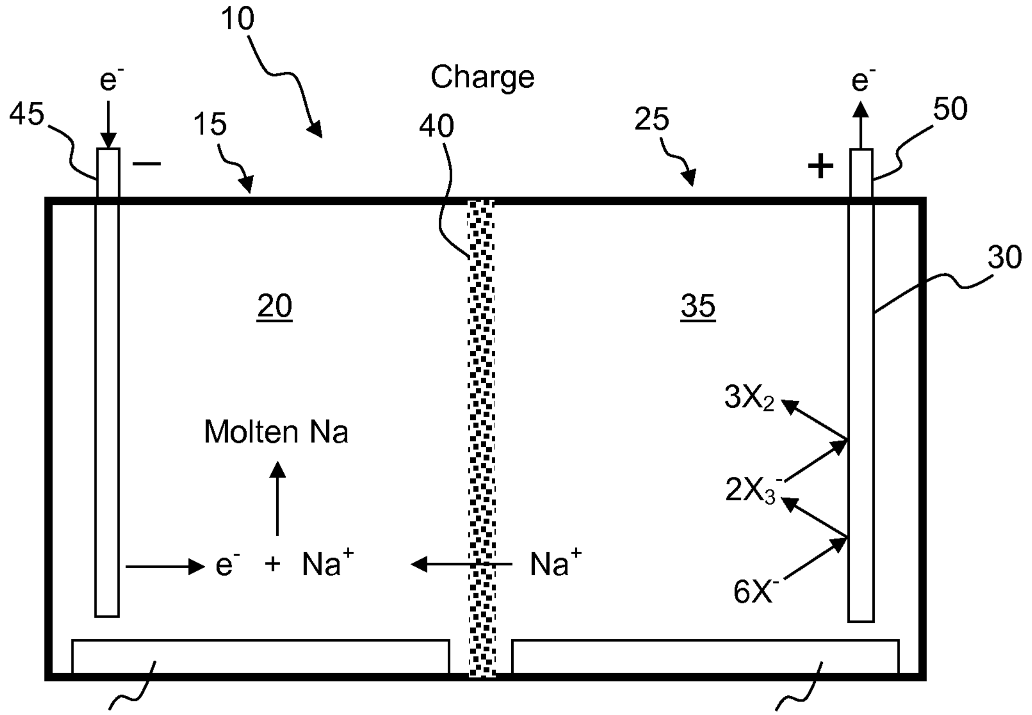
10
Charge
45
e^-
15
40
25
e^-
50
−
+
20
35
30
$3X_2$
Molten Na
$2X_3^-$
e^- + Na^+
Na^+
$6X^-$
55
60

Fig. 2

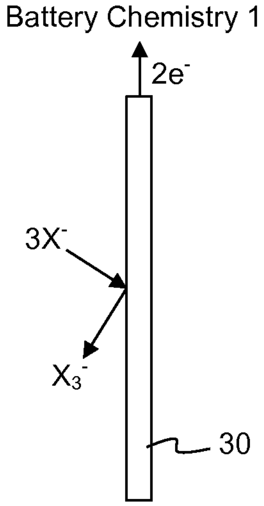
Battery Chemistry 1
2e$^-$
3X$^-$
X$_3^-$
30

Fig. 3A

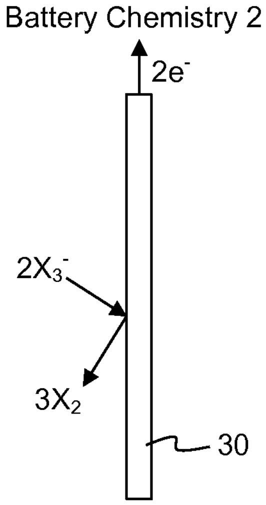
Battery Chemistry 2
2e$^-$
2X$_3^-$
3X$_2$
30

Fig. 3B

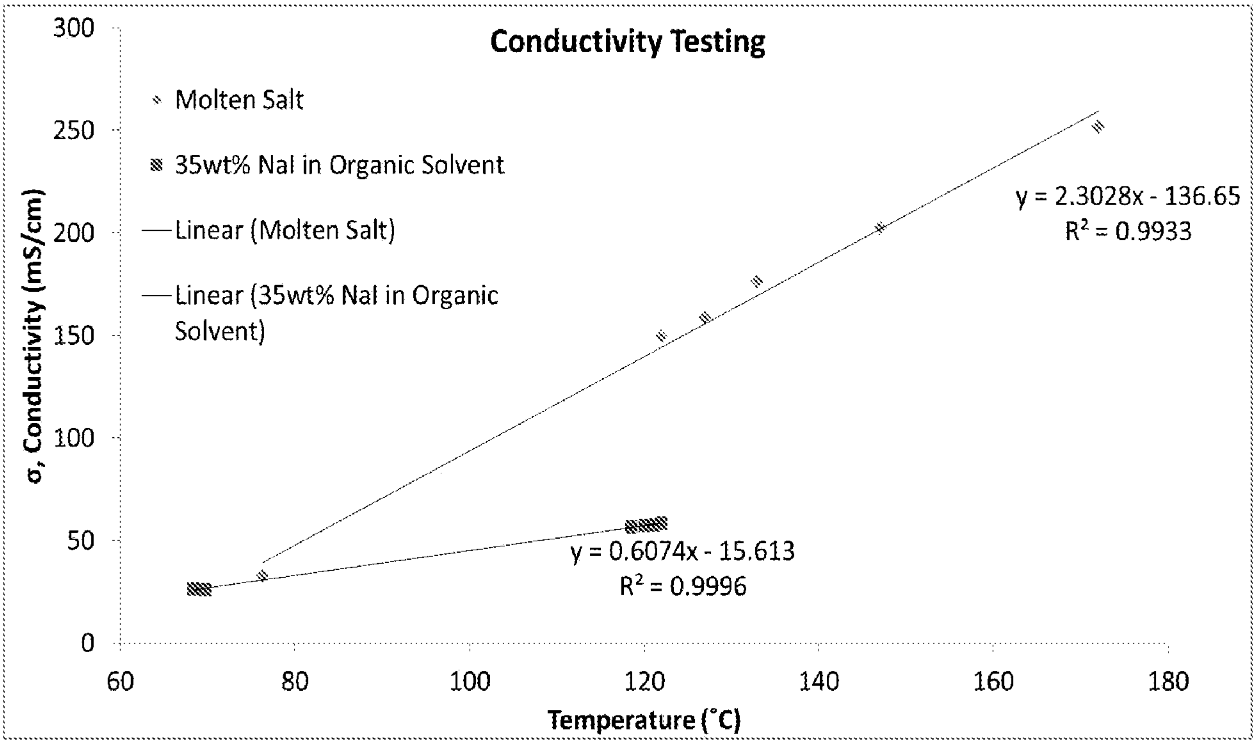
Conductivity Testing
Molten Salt
35wt% NaI in Organic Solvent
Linear (Molten Salt)
Linear (35wt% NaI in Organic Solvent)
y = 2.3028x - 136.65
R² = 0.9933
y = 0.6074x - 15.613
R² = 0.9996
σ, Conductivity (mS/cm)
300
250
200
150
100
50
0
60
80
100
120
140
160
180
Temperature (˚C)

Fig. 4

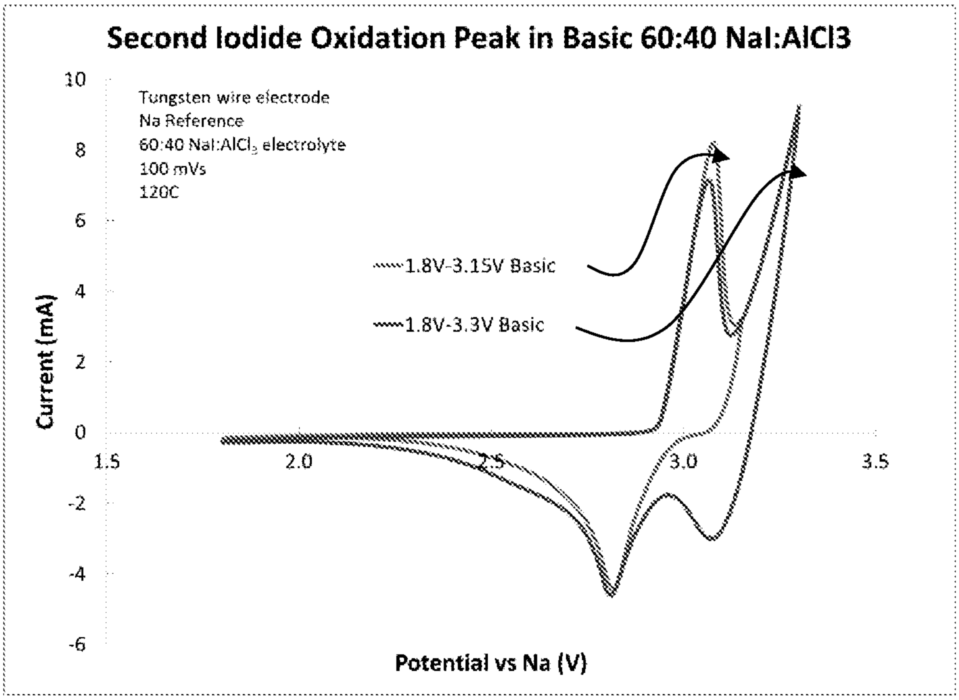
Second Iodide Oxidation Peak in Basic 60:40 NaI:AlCl3
Tungsten wire electrode
Na Reference
60:40 NaI:AlCl$_3$ electrolyte
100 mVs
120C
1.8V-3.15V Basic
1.8V-3.3V Basic
Current (mA)
Potential vs Na (V)
10
8
6
4
2
0
-2
-4
-6
1.5
2.0
2.5
3.0
3.5

Fig. 5A

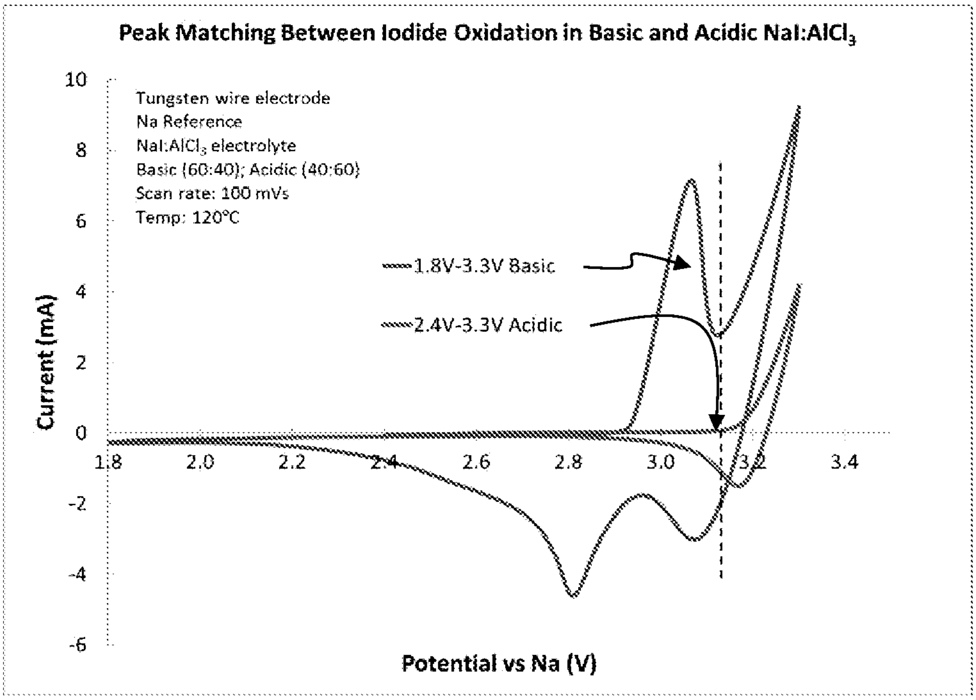
Peak Matching Between Iodide Oxidation in Basic and Acidic NaI:AlCl$_3$
Tungsten wire electrode
Na Reference
NaI:AlCl$_3$ electrolyte
Basic (60:40); Acidic (40:60)
Scan rate: 100 mVs
Temp: 120°C
1.8V-3.3V Basic
2.4V-3.3V Acidic
Current (mA)
Potential vs Na (V)
10
8
6
4
2
0
-2
-4
-6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4

Fig. 5B

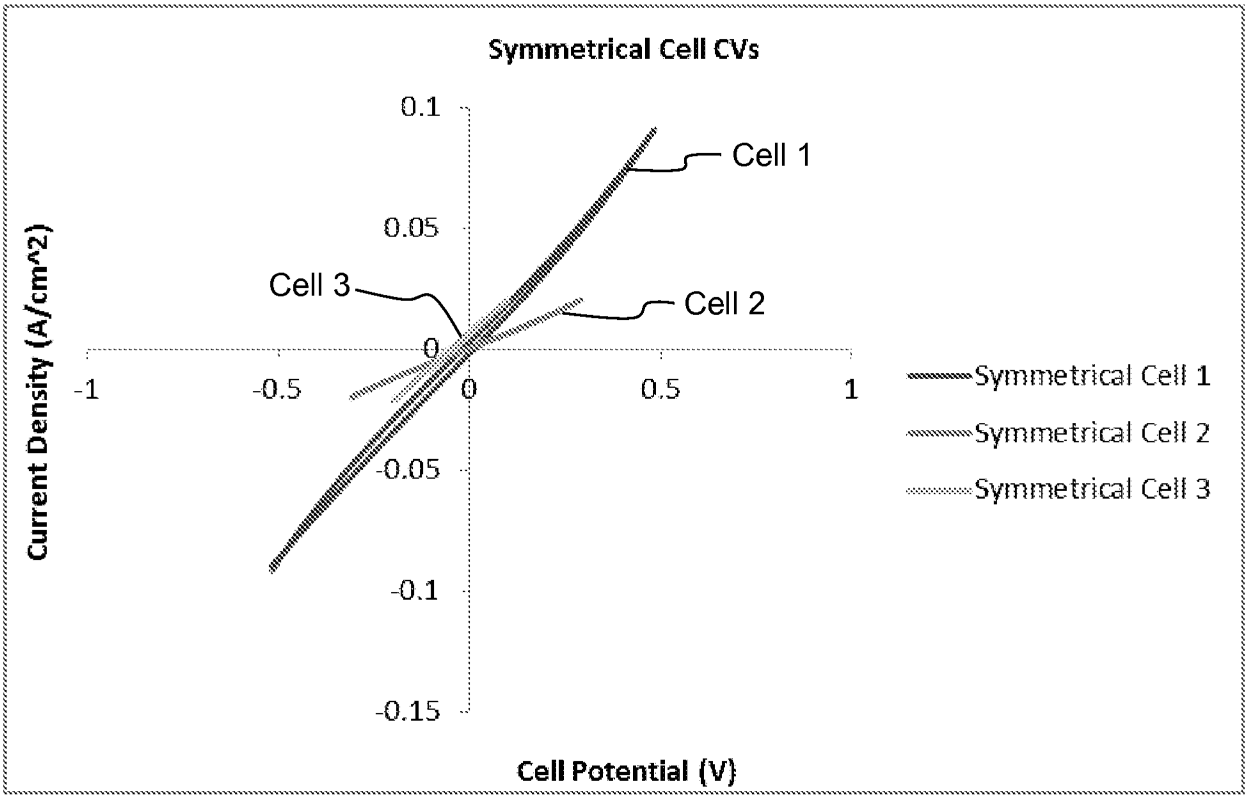
Symmetrical Cell CVs
0.1
0.05
0
-0.05
-0.1
-0.15
-1
-0.5
0
0.5
1
Current Density (A/cm^2)
Cell Potential (V)
Cell 1
Cell 2
Cell 3
Symmetrical Cell 1
Symmetrical Cell 2
Symmetrical Cell 3

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/063244

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/054(2010.01)i, H01M 4/38(2006.01)i, H01M 4/13(2010.01)i, H01M 4/66(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M 10/054; H01M 10/39; H01M 10/056; H01M 10/0569; H01M 4/133; H01M 10/02; H01M 2/00; H01M 10/0563; H01M 4/38; H01M 4/66

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: sodium, halogen, secondary, cell, halide, Na AlX, NaX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011-0104526 A1 (BOXLEY, CHETT et al.) 5 May 2011 See claim 1.	1-14
A	US 2013-0196224 A1 (BATTELLE MEMORIAL INSTITUTE) 1 August 2013 See claims 1-2.	1-14
A	WO 2013-154349 A1 (SK INNOVATION CO., LTD.) 17 October 2013 See claim 1.	1-14
A	US 2012-0015256 A1 (KOMABA SHINICHI et al.) 19 January 2012 See claim 1.	1-14
A	US 2013-0052525 A1 (KAGEURA JUN-ICHI et al.) 28 February 2013 See claim 1.	1-14

☐ Further documents are listed in the continuation of Box C.　　☒ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 March 2016 (17.03.2016)	**18 March 2016 (18.03.2016)**

Name and mailing address of the ISA/KR	Authorized officer
International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea	KIM, Yeon Kyung
Facsimile No. +82-42-472-7140	Telephone No. +82-42-481-3325

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0104526 A1	05/05/2011	CA 2770733 A1	12/05/2011
		EP 2497133 A2	12/09/2012
		JP 05753852 B2	22/07/2015
		JP 2013-510391 A	21/03/2013
		KR 10-2012-0095949 A	29/08/2012
		US 2014-363706 A1	11/12/2014
		US 8859141 B2	14/10/2014
		WO 2011-057135 A2	12/05/2011
		WO 2011-057135 A3	18/08/2011
		WO 2011-057135 A9	07/06/2012
		WO 2011-057135 A9	12/05/2011
US 2013-0196224 A1	01/08/2013	AU 2013-215308 A1	19/06/2014
		AU 2013-215308 A1	08/08/2013
		CA 2857047 A1	08/08/2013
		CN 104054211 A	17/09/2014
		EP 2810333 A1	10/12/2014
		EP 2810333 A4	29/07/2015
		KR 10-2014-0127211 A	03/11/2014
		WO 2013-116263 A1	08/08/2013
WO 2013-154349 A1	17/10/2013	KR 10-2013-0116022 A	22/10/2013
US 2012-0015256 A1	19/01/2012	CN 102362386 A	22/02/2012
		JP 05800316 B2	28/10/2015
		KR 10-2011-0139291 A	28/12/2011
		WO 2010-109889 A1	30/09/2010
US 2013-0052525 A1	28/02/2013	CN 102956921 A	06/03/2013
		JP 2013-062241A	04/04/2013