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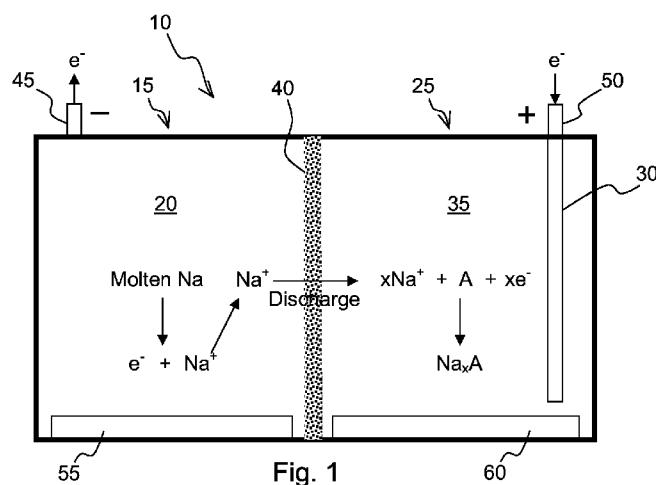
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(54) Title: LOW TEMPERATURE SECONDARY CELL WITH SODIUM INTERCALATION ELECTRODE



(57) Abstract: The present invention provides a molten sodium secondary cell. In some cases, the secondary cell includes a sodium metal negative electrode, a positive electrode compartment that includes a positive electrode disposed in a molten positive electrolyte comprising Na-FSA (sodium-bis(fluorosulfonyl)amide), and a sodium ion conductive electrolyte membrane that separates the negative electrode from the positive electrolyte. One disclosed example of electrolyte membrane material includes, without limitation, a NaSICON-type membrane. The positive electrode includes a sodium intercalation electrode. Non-limiting examples of the sodium intercalation electrode include Na_xMnO_2 , Na_xCrO_2 , Na_xNiO , and $\text{Na}_x\text{Fey}(\text{PO}_4)_z$. The cell is functional at an operating temperature between about 100 C and about 150 C, and preferably between about 110 C and about 130 C.

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LOW TEMPERATURE SECONDARY CELL WITH SODIUM INTERCALATION ELECTRODE

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent No. 61/779,857 filed on March 13, 2013. This application is also a continuation-in-part and claims priority to United States Application No. 13/290,716 filed November 7 2011 and titled LOW TEMPERATURE MOLTEN SODIUM SECONDARY CELL WITH SODIUM ION CONDUCTIVE ELECTROLYTE MEMBRANE which application claimed priority to United States Application No. 61/410,812 filed on November 5, 2010. These applications are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates in general to batteries. More particularly, the present invention provides a molten sodium-based secondary cell (or rechargeable battery) that operates at a temperature between about 100° Celsius (“C”) and about 150° C. The disclosed secondary cell utilizes a sodium ion conductive electrolyte membrane separating the molten sodium negative electrode from a sodium intercalation electrode in a molten sodium-FSA (sodium-bis(fluorosulfonyl)amide) electrolyte.

BACKGROUND OF THE INVENTION

[0003] 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 electrolyte(s), which can either be in a solid or a liquid state, or in combination. 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.

[0004] 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.

[0005] While rechargeable batteries based on sodium can comprise a variety of materials and designs, most, if not all, sodium batteries requiring 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.

[0006] The primary electrolyte separators used in sodium batteries that require a high Faradaic efficiency often consist of ionically conducting polymers, porous materials infiltrated with ionically conducting liquids or gels, or dense ceramics. In this regard, most, if not all, 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), or molten NiCl_2 , NaCl , and NaAlCl_4 (called a ZEBRA 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.

[0007] 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.

[0008] Thus, while molten 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 molten sodium-based rechargeable batteries with other molten sodium-based rechargeable batteries.

BRIEF SUMMARY OF THE INVENTION

[0009] The present invention provides a molten sodium secondary cell (or rechargeable battery) that functions at a temperature between about 100° C and about 150° C. While the described molten sodium secondary cell can include any suitable component, in some non-limiting implementations, the cell includes a sodium metal negative electrode, a positive electrode compartment that includes a positive electrode comprising a sodium intercalation material in a molten sodium FSA electrolyte. The disclosed secondary cell utilizes a sodium ion conductive electrolyte membrane physically separating the molten sodium negative electrode from the sodium intercalation electrode.

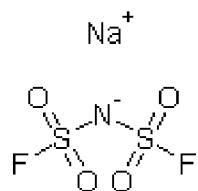
[0010] Generally, the sodium negative electrode comprises an amount of sodium metal. In this regard, as the cell operates, the sodium negative electrode is in a liquid or molten state. While the sodium negative electrode may comprise any suitable type of sodium, including without limitation, a pure sample of sodium or a sodium alloy, in some non-limiting implementations, the negative electrode comprises a sodium sample that is substantially pure.

[0011] The positive electrode in the positive electrode compartment can comprise any suitable material that allows the cell to function as intended. Indeed, in some non-limiting implementations, the positive electrode comprises a sodium intercalation material. Non-limiting examples of sodium intercalation materials include Na_xMnO_2 , Na_xCrO_2 , Na_xNiO ,

and $\text{Na}_x\text{Fe}_y(\text{PO}_4)_z$ where x, y, and z are between 0 and about 4. In one embodiment, the sodium intercalation materials include Na_xMnO_2 , Na_xCrO_2 , Na_xNiO where x is between 0 and 1.

[0012] The positive electrode may further comprise a current collector configured in the form of a wire, felt, mesh, plate, tube, foam, or other suitable electrode configuration.

[0013] The positive electrode compartment can comprise a molten sodium-FSA (sodium-bis(fluorosulfonyl)amide) electrolyte that is capable of conducting sodium ions to and from the electrolyte membrane and that otherwise allows the cell to function as intended. Na-FSA has the following structure:



Na-FSA has a melting point of about 107° C, such that it is molten at typical operating temperatures of the molten sodium secondary cell. Na-FSA has a conductivity in the range of about 50-100 mS/cm².

[0014] The sodium ion conductive electrolyte membrane can comprise any membrane (which is used herein to refer to any suitable type of separator) that: selectively transports sodium ions, that is stable at the cell's operating temperature, that is stable when in contact with molten sodium and the molten sodium-FSA electrolyte, and that otherwise allows the cell to function as intended. Indeed, in some non-limiting implementations, the electrolyte membrane comprises a NaSICON-type membrane.

[0015] Where the electrolyte membrane comprises a NaSICON-type membrane, the membrane can comprise any suitable kind of NaSICON-type membrane, including, without limitation, a composite NaSICON membrane. In this regard, and by way of non-limiting illustration, the membrane can comprise any known or novel composite NaSICON membrane that includes a dense NaSICON layer and a porous NaSICON layer.

[0016] The described secondary cell may operate at any suitable operating temperature. Indeed, in some non-limiting implementations, the cell functions (e.g., is discharged or recharged) while the temperature of the cell is at least as high as a temperature selected from about 100° C, about 110° C, 120° C, and about 130° C. In some non-limiting implementations, the cell functions at a temperature less than a temperature selected from about 150° C and about 130° C. Indeed, in some non-limiting implementations, as the cell

functions, the temperature of the negative electrode is about $120^{\circ}\text{ C} \pm$ about 10° C . In some non-limiting implementations, as the cell functions, the temperature of the positive electrode is sufficient to melt the sodium-FSA electrolyte. Such temperatures will typically be above about 107° C . The temperature of the positive electrode may be about $120^{\circ}\text{ C} \pm$ about 10° C . In some embodiments, the cell is pressurized ranging from about 1 psi to about 30 psi. In some embodiments, the cell is pressurized ranging from about 1 psi to about 30 psi. In one embodiment, the cell may be pressurized in a range of about 10 psi to about 15 psi.

[0017] These features and advantages of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL DRAWINGS

[0018] In order that the manner in which the above-recited and other features and advantages of the invention are obtained and 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 the drawings are not made to scale, depict only some representative 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:

[0019] Figure 1 depicts a schematic diagram of a representative embodiment of a molten sodium secondary cell, wherein the cell is in the process of being discharged.

[0020] Figure 2 depicts a schematic diagram of a representative embodiment of the molten sodium secondary cell, wherein the cell is in the process of being recharged.

DETAILED DESCRIPTION OF THE INVENTION

[0021] 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,” 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.

[0022] 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 negative electrodes, positive electrode materials, liquid positive electrode solutions, sodium ion conductive electrolyte membrane, 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 instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

[0023] 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.

[0024] The present invention provides a molten sodium secondary cell that functions at an operating temperature between about 100° C and about 150° C. While the described cell can comprise any suitable component, Figure 1 shows a representative embodiment in which the molten 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 positive electrode. The positive electrode includes a current collector 30 and a sodium intercalation electrode material “A” disposed in a molten sodium-FSA (sodium-bis(fluorosulfonyl)amide) electrolyte 35. A sodium ion conductive electrolyte membrane 40 separates the negative electrode from the positive electrolyte and 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.

[0025] Turning now to the manner in which the molten 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.

[0026] 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).

[0027] 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.

[0028] 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.

[0029] 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 sodium intercalation material, shown generically as “A” in Figs. 1 and 2, in a molten sodium-FSA electrolyte 35.

[0030] In some embodiments, the positive current collector may comprise a wire, felt, plate, tube, mesh, foam, and/or other suitable current collector configuration. In some non-limiting embodiments, the sodium intercalation material (“A”) is selected from Na_xMnO_2 , Na_xCrO_2 , Na_xNiO , and $\text{Na}_x\text{Fe}_y(\text{PO}_4)_z$ where x, y, and z are between 0 and about 4. In one embodiment, the sodium intercalation materials include Na_xMnO_2 , Na_xCrO_2 , Na_xNiO where x is between 0 and 1.

[0031] In some non-limiting embodiments, the reactions that occur at the negative electrode and at the positive electrode and the overall reaction as the cell 10 is discharged may occur as illustrated below:



[0035] Accordingly, some embodiments of the describe cell 10, at least theoretically, are capable of producing about $3.2\text{V} \pm 0.5\text{V}$ at standard temperature and pressure.

[0036] Moreover, some examples of overall reactions that may occur during the discharging and charging of a cell in which the positive electrode 30 comprises a Na_xMnO_2 intercalation material, the negative electrode 20 comprises sodium, and the positive electrolyte 35 comprises molten sodium-FSA, are shown below:



[0039] With respect now to the molten sodium-FSA positive electrolyte 35, the positive electrolyte has been found to have good sodium ion conductivity that allows the cell 10 to function as intended. It is intended for the positive electrolyte to have a higher sodium ion conductivity than the electrolyte membrane 40. The molten sodium-FSA conductivity ranges between about 50 mS/cm and 100 mS/cm. The NaSICON conductivity may range between about 20 and about 50 mS/cm. The NaSICON conductivity may range between about 30 and about 45 mS/cm.

[0040] 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 the molten sodium negative electrode and the positive electrolyte. In some embodiments, the electrolyte membrane comprises a NaSICON-type (sodium Super Ion CONductive) material. In such embodiments, the NaSICON-type

material may comprise any known or novel NaSICON-type material that is suitable for use with the described cell 10. Some non-limiting 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 selected from 1.6 to 2.4), Y-doped NaSICON ($Na_{1+x+y}Zr_{2-y}Y_ySi_xP_{3-x}O_{12}$, $Na_{1+x}Zr_{2-y}Y_ySi_xP_{3-x}O_{12-y}$ (where x = 2, y = 0.12), and Fe-doped NaSICON ($Na_3Zr_{2/3}Fe_{4/3}P_3O_{12}$). Indeed, in certain embodiments, the NaSICON-type membrane comprises $Na_3Si_2Zr_2PO_{12}$. In still other embodiments, the NaSICON-type membrane comprises known or novel composite, cermet-supported NaSICON membrane. In such embodiments, the composite NaSICON membrane can comprise any suitable component, including, without limitation, a porous NaSICON-cermet layer that comprises NiO/NaSICON or any other suitable cermet layer, and a dense NaSICON layer. In yet other embodiments, the NaSICON membrane comprises a monoclinic ceramic.

[0041] Where the cell's electrolyte membrane 40 comprises a NaSICON-type material, the NaSICON-type material may provide the cell 10 with several beneficial characteristics. In one example, because such membranes selectively transport sodium ions but do not allow the negative electrode 20 and the positive electrolyte 35 to mix, such membranes can help the cell to have minimal capacity fade and to have a relatively stable shelf life at ambient temperatures.

[0042] 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, including without limitation, to one or more cells. In this regard, the terminals can comprise any suitable material and any suitable shape of any suitable size.

[0043] In addition to the aforementioned components, the cell 10 can optionally comprise any other suitable component. By way of non-limiting illustration Figure 2 shows 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. 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, one or more temperature sensors, and appropriate temperature control circuitry.

[0044] 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 operating temperature that is as high as a temperature selected from about 120° C, about 130° C, and about 150° C. Moreover, in such embodiments, as the cell functions, the temperature of the negative and/or positive electrode compartments can be as low as a temperature selected from about 120° C, about 115° C, about 110° C, and about 100° C. Indeed, in some embodiments, as the cell functions, the temperature of the negative and/or positive electrode compartments may be between about 100° C and about 150° C. In other embodiments, the cell functions at a temperature between about 110° C and about 130° C. In yet other embodiments, however, as the cell functions, the temperature of the negative and/or positive electrode compartments is about 120° C ± about 10° C.

[0045] In addition to the aforementioned benefits of the cell 10, the described cell may have several other beneficial characteristics. By way of example, by being able to operate in a temperature range between about 100° and about 150° C, the cell 10 may operate in a temperature range that is significantly lower the operating temperature of certain conventional molten sodium rechargeable batteries. Accordingly, the described cell may require less energy to heat and/or dissipate heat from the cell as the cell functions, may be less dangerous use or handle, and may be more environmentally friendly.

[0046] 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.

[0047] While specific embodiments and examples 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.

CLAIMS:

1. A molten sodium secondary cell, comprising:
 - a negative electrode compartment comprising a sodium metal negative electrode, which electrochemically oxidizes to release sodium ions during discharge and electrochemically reduces sodium ions to sodium metal during recharging;
 - a positive electrode compartment comprising a positive electrode disposed in a molten positive electrolyte comprising NaFSA (sodium bis(fluorosulfonyl)amide), wherein the positive electrode comprises a sodium intercalation electrode; and
 - a sodium ion conductive electrolyte membrane that separates the sodium metal negative electrode from the molten positive electrolyte,
wherein the sodium metal negative electrode is molten and in contact with the conductive electrolyte membrane as the cell operates, and wherein the cell functions at an operating temperature between about 100° C and about 150° C.
2. The secondary cell of claim 1, wherein the sodium ion conductive electrolyte membrane comprises a NaSICON-type material.
3. The secondary cell of claim 2, wherein the NaSICON-type material comprises a composite membrane having a porous layer and a dense functional layer.
4. The secondary cell of claim 1, wherein the cell functions when the operating temperature is between about 110° C and about 130° C.
5. The secondary cell of claim 1, wherein the sodium intercalation electrode comprises Na_xMnO_2 .
6. The secondary cell of claim 1, wherein the sodium intercalation electrode comprises Na_xCrO_2 .
7. The secondary cell of claim 1, wherein the sodium intercalation electrode comprises Na_xNiO or $\text{Na}_x\text{Fe}_y(\text{PO}_4)_z$, wherein x is between 0 and 4, y is between 0 and 4, and z is between 0 and 4.
8. The secondary cell of claim 1, further comprising a heat management system to control the operating temperature of the cell.
9. The secondary cell of claim 1, further comprising a heat management system disposed in the negative electrode compartment to control the operating temperature of the negative electrode compartment.
10. The secondary cell of claim 1, further comprising a heat management system disposed in the positive electrode compartment to control the operating temperature of the positive electrode compartment.

11. A method for providing electrical potential from a molten sodium secondary cell, the method comprising:

providing a molten sodium secondary cell, comprising:

a sodium metal negative electrode, which electrochemically oxidizes to release sodium ions during discharge and electrochemically reduces sodium ions to sodium metal during recharging;

a positive electrode compartment comprising a positive electrode disposed in a molten positive electrolyte comprising NaFSA (sodium bis(fluorosulfonyl)amide), wherein the positive electrode comprises a sodium intercalation electrode; and

a sodium ion conductive electrolyte membrane that separates the sodium metal negative electrode from the molten positive electrolyte; and

heating the sodium metal negative electrode to a temperature between about 100° C and about 150° C so that the sodium metal negative electrode is molten and in contact with the sodium ion conductive electrolyte membrane and so that the sodium metal negative electrode oxidizes to release the sodium ions and allows the cell to discharge electricity.

12. The method of claim 11, wherein the sodium ion conductive electrolyte membrane comprises a NaSICON-type material.

13. The method of claim 11, further comprising maintaining the temperature of the sodium metal negative electrode between about 110° and about 130° C.

14. The method of claim 11, further comprising recharging the cell by passing an electrical potential between the sodium metal negative electrode and the positive electrode to cause the sodium negative electrode to electrochemically reduce sodium ions to sodium metal.

15. The method of claim 11, wherein the sodium intercalation electrode comprises Na_xMnO_2 .

16. The method of claim 11, wherein the sodium intercalation electrode comprises Na_xCrO_2 .

17. The method of claim 11, wherein the sodium intercalation electrode comprises Na_xNiO or $\text{Na}_x\text{Fe}_y(\text{PO}_4)_z$, wherein x is between 0 and 4, y is between 0 and 4, and z is between 0 and 4.

18. The method of claim 11, wherein the molten sodium secondary cell further comprises a heat management system.

19. A molten sodium secondary cell, comprising:

a negative electrode compartment comprising a sodium metal negative electrode, which electrochemically oxidizes to release sodium ions during discharge and electrochemically reduces sodium ions to sodium metal during recharging;

a positive electrode compartment comprising a positive electrode disposed in a molten positive electrolyte comprising NaFSA (sodium bis(fluorosulfonyl)amide), wherein the positive electrode comprises a sodium intercalation electrode selected from Na_xMnO_2 , Na_xCrO_2 , Na_xNiO and $\text{Na}_x\text{Fe}_y(\text{PO}_4)_z$, wherein x is between 0 and 4, y is between 0 and 4, and z is between 0 and 4;

a sodium ion conductive electrolyte membrane comprising a NaSICON-type material that separates the sodium metal negative electrode from the molten positive electrolyte; and

a heat management system to control the operating temperature of the cell,

wherein the sodium metal negative electrode is molten and in contact with the conductive electrolyte membrane as the cell operates, and wherein the cell functions at an operating temperature between about 110° C and about 130° C.

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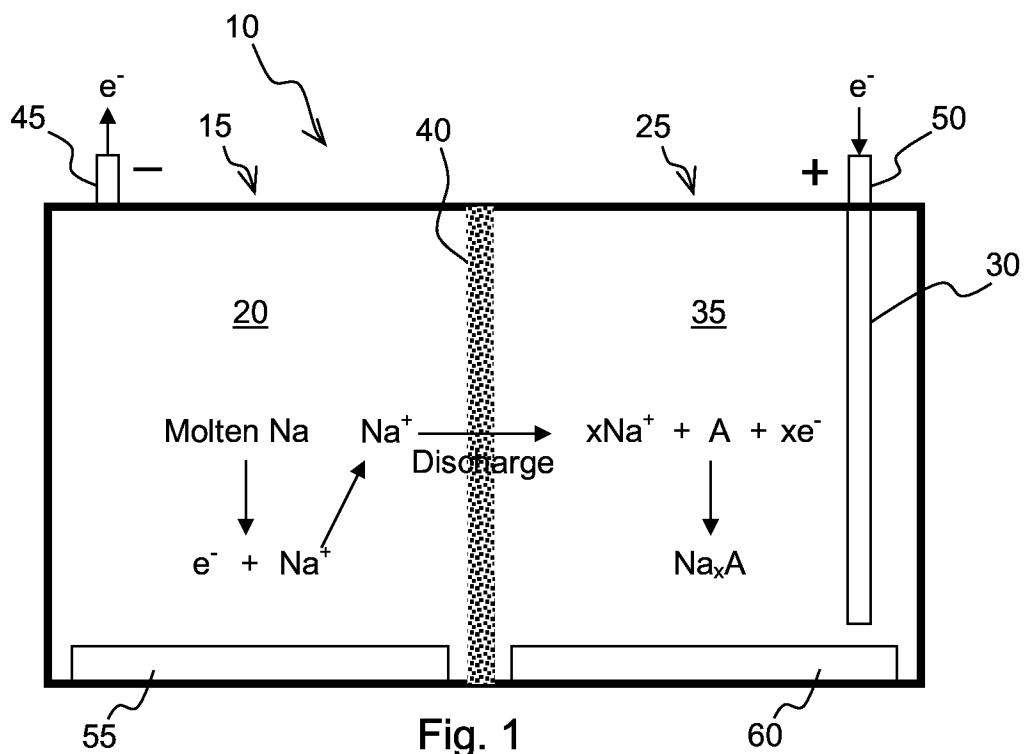


Fig. 1

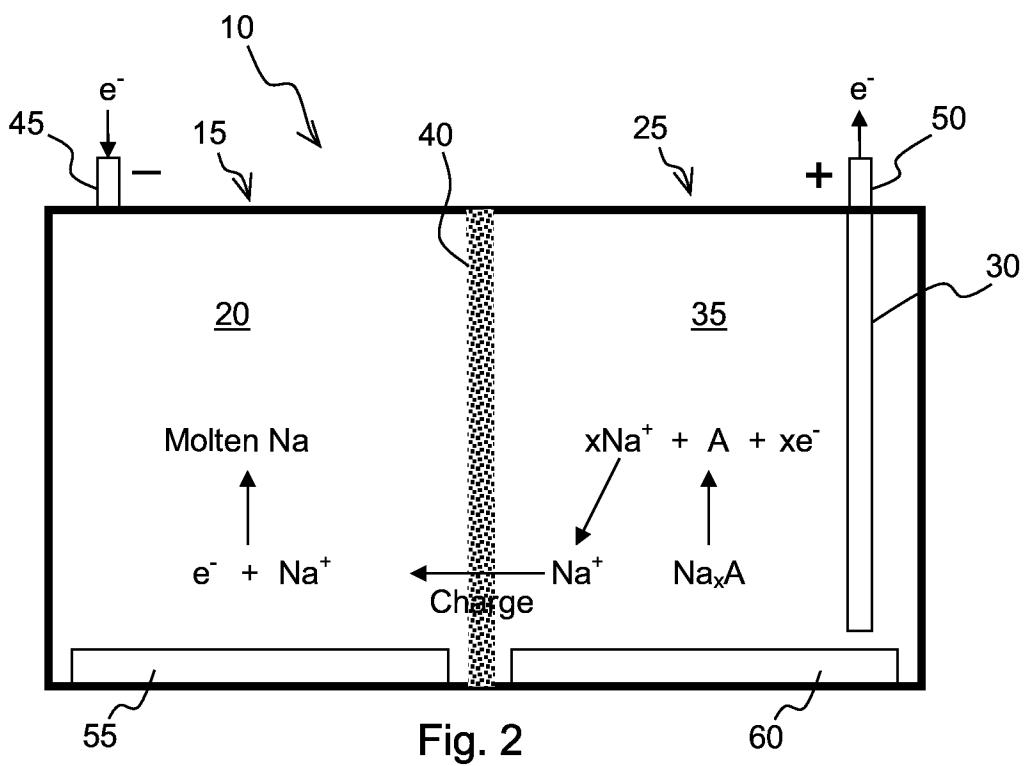


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/023698

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/39(2006.01)i, H01M 10/38(2006.01)i, H01M 10/04(2006.01)i, H01M 4/02(2006.01)i, H01M 4/38(2006.01)i, H01M 4/58(2010.01)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 10/39; H01M 4/40; H01B 1/06; H01M 6/36; H01M 10/42; H01M 4/36; H01M 6/24; H01M 10/02; H01M 2/02; H01M 10/38; H01M 10/04; H01M 4/02; H01M 4/38; H01M 4/58

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: molten sodium secondary cell, Na-FSA, low temperature, NaSICON, sodium intercalation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012-0219833 A1 (COORS, W. G. et al.) 30 August 2012 See claims 1-3, 9, 16-17, 19-20, 22; paragraph [0046]; and figure 2.	1-19
Y	WO 2012-114951 A1 (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 30 August 2012 See abstract; claims 1, 3; and paragraph [0019].	1-19
Y	WO 2012-132813 A1 (NISSAN MOTOR CO., LTD. et al.) 04 October 2012 See paragraph [0035].	5, 7, 15, 17
A	JP 2009-009933 A (PANASONIC CORP.) 15 January 2009 See abstract; and claims 1-3.	1-19
A	US 2008-0268327 A1 (GORDON, J. H. et al.) 30 October 2008 See abstract; and claims 1-11.	1-19

 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

28 July 2014 (28.07.2014)

Date of mailing of the international search report

29 July 2014 (29.07.2014)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/023698

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