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(54) Title: IONICALLY-CONDUCTIVE AMORPHOUS LITHIUM LANTHANUM ZIRCONIUM OXIDE

(57) Abstract: Amorphous lithium lanthanum zirconium oxide (LLZO) is formed as an ionically- conductive electrolyte medium. The LLZO comprises by percentage of total number of atoms from about 0.1% to about 50% lithium, from about 0.1% to about 25% lanthanum, from about 0.1% to about 25% zirconium, from about 30% to about 70%> oxygen and from 0.0% to about 25% carbon. At least one layer of amorphous LLZO may be formed through a sol-gel process wherein quantities of lanthanum methoxyethoxide, lithium butoxide and zirconium butoxide are dissolved in an alcohol-based solvent to form a mixture which is dispensed into a substantially planar configuration, transitioned through a gel phase, dried and cured to a substantially dry phase.

TITLE OF THE INVENTION

[0001] Ionically-Conductive Amorphous Lithium Lanthanum Zirconium Oxide

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application claims the benefit of U.S. Patent Application No. 12/848,991, filed August 2, 2010, the disclosure of which is herein incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

[0003] This invention relates to ionically-conductive materials useful as electrolyte mediums in electrochemical cells, and more particularly, the invention relates to an ionically-conductive amorphous lithium lanthanum zirconium oxide composition formable as an electrolyte medium for an electrochemical cell such as a battery cell.

[0004] A battery cell is a useful article that provides stored electrical energy that can be used to energize a multitude of devices, particularly portable devices that require an electrical power source. The cell is an electrochemical apparatus typically formed of at least one ion-conductive electrolyte medium disposed between a pair of spaced-apart electrodes commonly known as an anode and a cathode. Electrons flow through an external circuit connected between the anode and cathode. The electron flow is caused by the chemical-reaction-based electric potential difference between the active anode material and active cathode material. The flow of electrons through the external circuit is accompanied by ions being conducted through the electrolyte between the electrodes.

[0005] Electrode and electrolyte cell components typically are chosen to provide the most effective and efficient battery for a particular purpose. Lithium is a desirable active anode material because of its light weight and characteristic of providing a favorable reduction potential with several active cathode materials. Liquid and aqueous electrolytes have often been chosen because of favorable ion-conducting capabilities. Despite the benefits provided by certain anode materials and electrolytes, the materials themselves and, often, the combination of a particular electrode material and a particular electrolyte can cause problems in cell performance and, in some instances, can create a hazardous condition. For example, as advantageous as lithium can be as an active anode material, it can be degraded and otherwise react undesirably with such common mediums as air and water, and certain solvents. As a further example of problems, certain liquids that are useful as effective electrolytes can create hazardous conditions when serving as components of a lithium-ion battery.

[0006] For the reasons broadly stated above, it is often desirable to use a non-aqueous and non-liquid electrolyte medium in cells. Non-aqueous electrolyte mediums are desired because water can interact undesirably with some desirable electrode materials such as lithium. Non-liquid electrolyte mediums are desired for several reasons. One reason is that liquid electrolytes often react detrimentally with desirable electrode substances such as lithium even though the liquid is non-aqueous. Another reason that liquid electrolytes can be undesirable is the need to prevent electrolytic material from freely flowing beyond a predetermined geometric boundary configuration. For example, leakage of electrolyte solution from the battery container is typically undesirable. Another problem with liquid electrolytes is that some solvents that are used as effective non-aqueous, liquid electrolytes are flammable and have a relatively high vapor pressure. The combination of flammability and high-vapor pressure creates a likelihood of combustion. Further in this regard, batteries that use lithium-based anodes can pose severe safety issues due to the combination of a highly volatile, combustible electrolyte and the active nature of lithium metal.

[0007] Some of the problems associated with particular cell electrodes and electrolyte can result in internal failure of the cell. One type of internal failure is the discharge of electric current internally, within the cell, rather than externally of the cell. Internal discharge may also be referred to as "self-discharge." Self-discharge can result in high current generation, overheating and ultimately, a fire. A primary cause of self-discharge has been dendritic lithium growth during recharge of a rechargeable battery. In rechargeable cells having lithium anodes, dendrites are protuberances extending from the anode base that are formed during imperfect re-plating of the anode during recharge. Dendrites or growths resulting from low-density lithium plating during recharge can grow through the separator that separates anode from cathode particularly if the separator is porous or solid but easily punctured by the growth. When the growths extend far enough to interconnect the anode and cathode, an internal electrical short circuit is created through which current can flow. Electrical current produces heat that will vaporize a volatile electrolyte substance. In turn, vaporization of the electrolyte can produce extreme pressure within the battery housing or casing which can ultimately lead to rupture of the housing or casing. The temperatures that result from an electrical short circuit within a battery are sometimes high enough to ignite escaping electrolyte vapors thereby causing continuing degradation and the release of violent levels of energy. Lithium-ion batteries were developed to eliminate dendritic lithium growth by utilizing the lithium ions inserted into graphite anodes rather than re-platable lithium metal anodes. Although these lithium-ion batteries are much safer than earlier designs, violent failures still occur.

[0008] Ion-conductive, solid-glass electrolytes and ceramic electrolytes have been developed in the past to address the need for an electrolyte medium without the shortcomings described above. These solutions have included glass electrolyte materials such as Lithium Phosphorous Oxy-Nitride (LiPON) and a class of glass-ceramic materials generally referred to as LiSICON (an acronym for Lithium Super-Ionic Conductor) structure-type materials and NaSICON (an acronym for Sodium Super-Ionic Conductor, wherein the "Na" portion of the acronym is the chemical symbol for sodium) structure-type materials. However, these materials have limitations. LiPON has low ionic conductivity, in the range of 1.2E-6 S/cm, and generally can only be applied or used as thin films less than 10μm thick. In addition, it has to be produced using a reactive sputtering process in a low vacuum environment which can be very expensive. LiPON is also unstable in contact with water which eliminates its possible use as a protective electrolyte in battery systems where exposure to moisture or ambient air may occur. On the other hand LiSICON and NaSICON structure-type materials are stable in contact with water but are unstable in contact with lithium. When in contact with lithium this class of materials turns dark and can conduct electric current by electron flow thus minimizing usefulness as electrolyte separators.

[0009] Thus it can be appreciated that it would be useful to have a cell electrolyte medium that is a conductor of ions, that is protective of and stable in contact with lithium, that is non-aqueous, that is non-liquid, that is non-flammable and that does not produce short circuits that are associated with dendritic plating of lithium.

BRIEF SUMMARY OF THE INVENTION

[0010] According to a first embodiment the invention provides an amorphous oxide-based compound having a general formula $M_wM'_xM''_yM'''_z$,

wherein

M comprises at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

M' comprises at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

M'' comprises at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

M''' comprises at least one oxygen-set element from an oxygen set consisting of oxygen, sulfur, selenium, and the halogen family of the Periodic Table of Elements, and

wherein w, x, y, and z are positive numbers including various combinations of integers and fractions or decimals.

[0011] In accordance with an aspect of the first embodiment, M comprises lithium, M' comprises lanthanum, M'' comprises zirconium and M''' comprises oxygen.

[0012] In accordance with another aspect of the first embodiment, by percentage of total number of atoms, M comprises from about .1% to about 50%, M' comprises , from about .1% to about 25%, M'' comprises from about .1% to about 25%, M''' comprises from about 30% to about 70%, and carbon comprises from 0.0% to about 25%.

[0013] According to a second embodiment of the present invention, an electrolyte medium for an electrochemical cell comprises a layer of amorphous lithium lanthanum zirconium oxide.

[0014] In accordance with an aspect of the second embodiment, the layer of amorphous lithium lanthanum zirconium oxide comprises by percentage of total number of atoms from about .1% to about 50% lithium, from about .1% to about 25% lanthanum, from about .1% to about 25% zirconium, from about 30% to about 70% oxygen and from 0.0% to about 25% carbon.

[0015] According to a third embodiment of the present invention, a method for synthesizing an amorphous oxide-based compound comprises

substantially dissolving in a quantity of an alcohol-based solvent to produce a mixture, quantities of

an alkoxide of at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

an alkoxide of at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

an alkoxide of at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

an alcohol-soluble precursor of at least one of sulfur, selenium, and the halogen family of the Periodic Table of Elements,

dispensing said mixture in a substantially planar configuration, transitioning through a gel phase, and drying and curing to a substantially dry phase.

[0016] According to a fourth embodiment of the invention, amorphous lithium lanthanum zirconium oxide is synthesized by substantially dissolving quantities of a lanthanum alkoxide, a lithium alkoxide, and a zirconium alkoxide in a quantity of an alcohol-based solvent to produce a mixture; then dispensing the mixture into a substantially planar configuration, transitioning through a gel phase, and drying and curing to a substantially dry phase.

[0017] In accordance with an aspect of the fourth embodiment, the alcohol-based solvent comprises methoxyethanol.

[0018] In accordance with another aspect of the fourth embodiment, the lanthanum alkoxide comprises lanthanum methoxyethoxide, the lithium alkoxide comprises lithium butoxide and the zirconium alkoxide comprises zirconium butoxide.

[0019] In accordance with yet another aspect of the fourth embodiment, the quantity of lanthanum methoxyethoxide comprises an amount of lanthanum methoxyethoxide pre-dissolved in an amount of the alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight lanthanum methoxyethoxide.

[0020] In accordance with an additional aspect of the fourth embodiment, the quantity of zirconium butoxide comprises an amount of zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

[0021] In accordance with yet an additional aspect of the fourth embodiment, the quantity of lanthanum methoxyethoxide comprises about 4.5 grams of the lanthanum methoxyethoxide solution, the quantity of lithium butoxide comprises about 0.65 grams thereof, the quantity of zirconium butoxide comprises about 0.77 grams of the zirconium butoxide solution and the alcohol-based solvent comprises about 5 grams of methoxyethanol.

[0022] In accordance with a further aspect of the fourth embodiment, the mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing or ink-jet printing.

[0023] According to a fifth embodiment of the invention, amorphous lithium lanthanum zirconium oxide is synthesized by substantially dissolving quantities of a lanthanum alkoxide, a lithium alkoxide, a zirconium alkoxide and a polymer in a quantity of an alcohol-based solvent to produce a mixture; then dispensing the mixture into a substantially planar configuration, transitioning through a gel phase, and drying and curing to a substantially dry phase.

[0024] In accordance with an aspect of the fifth embodiment, the alcohol-based solvent comprises methoxyethanol and the polymer comprises polyvinyl pyrrolidone.

[0025] In accordance with another aspect of the fifth embodiment, the lithium alkoxide comprises lithium butoxide, the lanthanum alkoxide comprises lanthanum methoxyethoxide, and the zirconium alkoxide comprises zirconium butoxide.

[0026] In accordance with yet another aspect of the fifth embodiment, the quantity of lanthanum methoxyethoxide comprises an amount of lanthanum methoxyethoxide pre-dissolved in an amount of the alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight lanthanum methoxyethoxide.

[0027] In accordance with an additional aspect of the fifth embodiment, the quantity of zirconium butoxide comprises an amount of zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

[0028] In accordance with yet another additional aspect of the fifth embodiment, the quantity of polymer comprises an amount of polymer pre-dissolved in an amount of alcohol-based solvent to produce a polymer solution

[0029] In accordance with a further aspect of the fifth embodiment, the quantity of lanthanum methoxyethoxide comprises about 4.5 grams of lanthanum methoxyethoxide solution, the quantity of lithium butoxide comprises about 0.65 grams thereof, the quantity of zirconium butoxide comprises about 0.77 grams of said zirconium butoxide solution, the quantity of polymer solution comprises not more than about 2 grams of polyvinyl pyrrolidone dissolved in about 5 grams of methoxyethanol, and the quantity of alcohol-based solvent comprises about 5 grams of methoxyethanol.

[0030] In accordance with yet a further aspect of the fifth embodiment, the mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing or ink-jet printing.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0031] The foregoing summary, as well as the following detailed description of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown.

[0032] In the drawings:

[0033] Fig. 1 is schematic representation of a cell suitable for incorporating an electrolyte medium in accordance with the present invention.

[0034] Fig. 2 shows XPS Spectra Graphs for atomic species for amorphous LLZO films of the invention.

[0035] Fig. 3 is an electrochemical impedance spectroscopy spectra of LLZO films of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0036] Embodiments of the present invention are described herein. The disclosed embodiments are merely exemplary of the invention that may be embodied in various and alternative forms, and combinations thereof. As used herein, the word “exemplary” is used expansively to refer to embodiments that serve as illustrations, specimens, models, or patterns. The figures are not necessarily to scale and some features may be exaggerated or minimized to show details of particular components. In other instances, well-known components, systems, materials, or methods have not been described in detail in order to avoid obscuring the present invention. Therefore, at least some specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention.

[0037] Referring to Fig. 1, therein is illustrated a cross-sectional, schematic representation of a battery cell, or electrochemical cell, 10 suitable for incorporating an electrolyte medium in accordance with the present invention. A centrally-disposed cathode current collector 11 is flanked on either side by a cathode 12. An electrolyte medium 13 is disposed in a U-shaped, face-contacting relationship with the cathodes 12. An anode 14 is disposed in a U-shaped, face-contacting relationship with the electrolyte medium 13. An anode current collector 15 is disposed in a U-shaped, face-contacting relationship with the anode 14. A cathode terminal 16 is disposed in contacting relationship with the cathode current collector 11 and cathode 12.

Overview

[0038] Lithium is a desirable substance to use as an electrode (particularly an anode) in a cell. This is because lithium is one of the lightest of elements while possessing high energy density and high specific energy. However, lithium is extremely undesirably reactive with water and is likewise undesirably reactive with many highly ionically-conductive liquid electrolytes. Thus it is desirable to have an electrolyte medium that is non-aqueous and non-liquid so as to be compatible with electrodes containing or consisting of lithium. A solid electrolyte is non-aqueous and non-liquid; however, some solid electrolytes still react undesirably with lithium. Thus, it is desirable to have an electrolyte medium that not only is non-aqueous and non-liquid but that is also otherwise compatible with electrodes that contain or comprise lithium.

[0039] Often, batteries are used in applications that require unique geometries and physical specifications for the battery package. For example, batteries are used in very small electronic devices that require that batteries therefor be sized on the order of millimeters or less. For applications requiring batteries of very small dimensions, it is important that the components of these battery cells perform effectively even though produced at a very small size. Thus it is important to have an electrolyte medium that is effective even though produced on an extremely small scale.

[0040] One method of producing cells of very small dimensions is to construct what are known as "thin-film" batteries. Typically, in thin-film battery cells the electrodes and electrolyte medium comprise substrates having a thin, film-like configuration. Thin-film batteries also have the advantage of potentially being flexible. The electrolyte medium for thin-film battery cells has to be effective even though produced at very small dimensions.

The Invention in Detail

[0041] The invention is an effective, ionically-conductive composition for an electrolyte medium. The invention further encompasses a method for producing the composition in general and a method for forming an electrolyte medium comprising the composition. The electrolyte medium taught by the invention is non-aqueous, non-liquid, inorganic, and compatible with lithium and lithium-containing compositions, and can be manufactured in thin-dimensioned and small-dimensioned configurations.

[0042] In an embodiment, the composition of the invention is amorphous lithium lanthanum zirconium oxide (for convenience, sometimes this composition is referred to herein as "LLZO"). The amorphous LLZO is highly ionically-conductive. It is inorganic and compatible with lithium. It can be used to produce a solid, thin-film electrolyte medium that facilitates incorporation into a small-dimensioned energy cell.

[0043] The amorphous LLZO is unique as an electrolyte medium as well as in and of itself. The invention teaches that the amorphous compound may have a chemical make-up wherein certain other elements may be partially or fully substituted for the four primary constituent elements lithium, lanthanum, zirconium and oxygen. Substitutes for lithium constituent include elements in the alkali-metal family of the Periodic Table. Substitutes for lanthanum constituent include barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table. Substitutes for zirconium constituent include tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium.

Substitutes for the oxygen constituent include sulfur, selenium, and the halogen family of the Periodic Table.

[0044] In an embodiment, an amorphous compound has a general formula $M_wM'_xM''_yM'''_z$, wherein

M comprises at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

M' comprises at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

M'' comprises at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

M''' comprises at least one oxygen-set element from an oxygen set consisting of oxygen, sulfur, selenium, and the halogen family of the Periodic Table of Elements,

wherein w, x, y, and z are positive numbers including various combinations of integers and fractions or decimals.

[0045] The amorphous compound of the invention can be produced by a relatively simple and inexpensive processes. One broad category of process is a sol-gel class of process. In an embodiment, the invention teaches adaptation of a sol-gel technique, which is generally known in chemistry, to form the ultimate, substantially solid compound and medium of the invention. In the invention's application of a sol-gel process a precursor solution mixture is derived from substantial dissolution of liquid or/and solid solutes in a solvent. The sol-gel technique is advantageous because it is not necessary to subject the amorphous-LLZO precursor ingredients to extreme high temperatures as is necessary in the case of solid-state reactions and other processes for producing solid-electrolyte mediums. Extreme high temperatures are unwanted because such temperatures can produce undesirable effects in electrolyte membranes that are formed and/or in associated components.

[0046] In an embodiment, the amorphous compound of the invention is created through a sol-gel methodology by processing alkoxides that contain desired end constituent elements. In an embodiment of methodology of the invention, alkoxides of each of four primary constituents described above are dissolved in a quantity of an alcohol-based solvent to produce a mixture; the mixture is dispensed in a substantially planar configuration, transitioned through a gel phase, and dried and cured to a substantially dry phase.

[0047] In an embodiment, alkoxides of other elements may be substituted for the four primary constituent element alkoxides. Thus, in an embodiment, an amorphous compound is synthesized by substantially dissolving quantities of

an alkoxide of at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

an alkoxide of at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

an alkoxide of at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

an alcohol-soluble precursor of at least one of sulfur, selenium, and the halogen family of the Periodic Table of Elements,

in a quantity of an alcohol-based solvent to produce a mixture; dispensing the mixture in a substantially planar configuration, transitioning through a gel phase, and drying and curing to a substantially dry phase.

[0048] In an embodiment of the invention, in a method for synthesizing amorphous LLZO quantities of a lanthanum alkoxide, a lithium alkoxide, and a zirconium alkoxide are dissolved in a quantity of an alcohol-based solvent to produce a mixture. Suitable lanthanum alkoxide is lanthanum methoxyethoxide. Suitable lithium alkoxide is lithium butoxide. Suitable zirconium alkoxide is zirconium butoxide. Suitable alcohol-based solvent is methoxyethanol. The solutes and solvent are mixed in quantities and percentages to bring about substantially complete dissolution. The mixture (the precursor solution formed by mixing) is dispensed into a substantially planar configuration, processed through a "gel" phase, dried and cured to a substantially dry phase.

Synthesis Examples

[0049] The ingredients in the examples described below are readily-obtainable chemical compositions that may be purchased from many different chemical suppliers in the United States such as but not limited to Gelest, Inc., which at the time of this writing is believed to have an address of Gelest, Inc., 11 E Steel Rd, Morrisville, PA 19067, and a website at www.gelest.com and Alfa Aesar, which at the time of this writing is believed to have an address at 26 Parkridge Rd, Ward Hill, MA 01835, and a website at http://www.alfa.com/en/gh100w.pgm.

[0050] Lithium butoxide is also know as lithium tert-butoxide (LTB); lithium t-butoxide; lithium tert-butoxide; lithium tert-butylate; 2-methyl-2-propanolithium salt; 2-methyl-2-propanol lithium salt; lithium tert-butanolate; tert-butoxylithium; tert-butylalcohol, lithiumsalt; lithium tert-butoxide solution; lithium butoxide min off white powder; and lithium 2-methylpropan-2-olate. It has the molecular formula C_4H_9LiO. It in particular may be purchased from Gelest, Inc.

[0051] Lanthanum methoxyethoxide is also known as lanthanum (III) 2-methoxyethoxide, lanthanum 2-methoxyethoxide; lanthanum methoxyethoxide; lanthanum methoxyethylate; and lanthanum tri(methoxyethoxide). It has the molecular formula $C_9H_{21}LaO_6$. It in particular may be purchased from Gelest, Inc.

[0052] Zirconium butoxide is also known as 1-butanol, zirconium(4+) salt; butan-1-olate, zirconium(4+); butyl alcohol, zirconium(4+) salt; butyl zirconate; butyl zirconate(IV); tetrabutoxyzirconium; tetrabutyl zirconate; zirconic acid butyl ester; zirconium tetrabutanolate; and zirconium tetrabutoxide. It has the molecular formula $C_{16}H_{36}O_4Zr$. It in particular may be purchased from Gelest, Inc.

[0053] Methoxyethanol is also known as 2-methoxyethanol (2ME); ethylene glycol monomethyl ether (EGME) and methyl cellosolve. It has the molecular formula $C_3H_8O_2$. It in particular may be purchased from Alfa Aesar.

[0054] After thorough mixing of the ingredients and substantially complete dissolution of the solutes, the resulting mixture is processed through a fluidized stage that includes, at least briefly, aspects of a gel state. The fully-mixed, applied and processed components produce an amorphous substrate of LLZO.

[0055] In the amorphous LLZO compound of the invention, the number of atoms of lithium, lanthanum, zirconium, and oxygen are proportional to one another within ranges as set forth in the table of Atomic Percentage(s) below. For convenience, the amorphous compound is referred to herein simply as LLZO although the compound may also contain carbon as a result of the synthesis process. Further, for convenience, the compound may be denoted by the general formula $Li_wLa_xZr_yO_z$ wherein w, x, y, and z are positive numbers including various combinations of integers and fractions or decimals representative of the proportional relationship of the elements to one another.

[0056] Carbon as additional element: The production techniques described herein for producing amorphous LLZO may produce a product that contains some quantity of carbon. The carbon is left over as a by-product from one or more of the organic compositions used as precursors in formulating the amorphous LLZO. The atomic percentage of carbon in the amorphous composition is in the range from 0.0% to about 25%.

[0057] The percentages of the number of atoms of each element as a proportion of the total number of atoms in the amorphous composition is as shown in the following table:

Chemical Element in Amorphous Composition	Atomic Percentage of Each Element in the Composition
Lithium	from about 0.1% to about 50%
Lanthanum	from about 0.1% to about 25%
Zirconium	from about 0.1% to about25%
Oxygen	from about 30% to about 70%
Carbon	from 0.0% to about 25%

Example 1 of Production of Amorphous LLZO Electrolyte Medium

[0058] The amorphous LLZO precursor solution was prepared by dissolving about 4.5 grams of a lanthanum methoxyethoxide solution, about 0.65 gram of lithium butoxide and about 0.77 gram of a zirconium butoxide solution in about 5 grams of methoxyethanol.

[0059] Lanthanum methoxyethoxide and zirconium butoxide were used in solution form for convenience in mixing; however, the invention encompasses use of these compositions without being pre-dissolved. The lanthanum methoxyethoxide solution comprised lanthanum methoxyethoxide pre-dissolved in methoxyethanol whereby lanthanum methoxyethoxide comprised approximately 12 % by weight of the total weight of the lanthanum methoxyethoxide solution. Similarly, the zirconium butoxide solution comprised zirconium butoxide pre-dissolved in butanol whereby zirconium butoxide comprised approximately 80 % by weight of the zirconium butoxide solution.

[0060] The components may be mixed in any sequence as the sequence of mixing is not significant. The thoroughly-mixed precursor solution was left in a bottle in a dry environment for about 1 to 1.5 hours to help facilitate substantially complete dissolution of the lithium butoxide, the component that was not pre-dissolved. What is meant by "dry environment" is that moisture in the ambient air is low enough that lithium components are not degraded due to moisture.

Example 1(A) – Formation of Substrate by Spin Coating

[0061] The amorphous LLZO precursor solution was prepared as described above. The precursor solution was deposited by spin coating; however, it can be cast if so desired as described below. Spin coating was performed by known spin-coating processes at approximately 1200 rpm for about 15 seconds in a dry environment. The resulting layer of composition was placed in a closed container and exposed to an ozone-rich air environment (ozone concentration larger than 0.05 part per million (ppm)) for approximately 1 hour. The term "environment" refers to the enclosed space in which a process (or sub-process) is carried out in the methodology taught by the invention. A vaporous or gaseous element or composition in the enclosure facilitates the drying, curing or other desired chemical processing. A gas or vapor may be placed in a suitable enclosure by known chemical processing means. For example, a vapor or gas may be injected through a port. As a further example, a liquid may be placed in the enclosure and permitted (or caused) to vaporize thereby creating the desired vaporous or gaseous environment. In this step, as an alternative, the closed environment may be solvent-vapor-rich (for example wherein a quantity of a solvent such as methoxyethanol is disposed in the closed container in a liquid phase and permitted or caused to vaporize). As another alternative, the closed environment may contain a gaseous mixture of ozone-rich air and solvent-vapor-rich air. This was followed by heating at approximately 80°C for about 30 minutes, also in an ozone-rich air environment. The LLZO coating and substrate were then heated at approximately 300°C for 30 minutes in air. It is to be understood that the heating times and environmental factors such as humidity, temperature, and gaseous content of ambient air may be varied.

[0062] The described spin-coating process resulted in an amorphous LLZO layer whose thickness was approximately 250 nm. Thicker films or layers of amorphous LLZO may be formed by repeating the basic spin-coating processing steps multiple times until the desired thickness is achieved.

Example 1(B) Formation of Substrate by Casting

[0063] The amorphous LLZO precursor solution was prepared as described above. For casting, the precursor solution optionally may be heated at approximately 100°C under an inert gas to increase the density and viscosity of the solution. This optional step was utilized in some samples that were produced.

[0064] The amorphous LLZO precursor solution was cast on a suitable substrate that facilitated support and then selective release of the formed layer. The layer that was formed was initially a solution. After further processing the layer may transition into a film, or a powder, or a combination of two or more of solution, film and powder. The freshly-cast LLZO was placed in a closed container and exposed to ozone-rich air environment (ozone concentration larger than 0.05 ppm) for approximately 1 hour, although longer exposure times may be used as well. In this step, as an alternative, the closed environment may be solvent-vapor-rich (for example wherein a quantity of a solvent such as methoxyethanol is disposed in the closed container in a liquid phase and allowed to and/or caused to vaporize). As another alternative, the closed environment may contain a mixture of ozone-rich air and solvent-vapor-rich air. This was followed by heating at approximately 80°C for 30 minutes or longer, also in an ozone-rich air environment. The LLZO material was then heated at approximately 300°C for 30 minutes in air. It should be understood that the heating times and environmental factors such as humidity, temperature, and gaseous content of ambient air may be varied. The immediately-above described processing step for the layer of cast material may result in a thick layer of amorphous LLZO or amorphous LLZO powder, or, to some degree, a thin film.

Example 2 of Production of Amorphous LLZO Electrolyte Medium - Incorporation of PVP into Precursor

[0065] The LLZO precursor solution was prepared in the following fashion. First, a quantity of a polymer, polyvinyl pyrrolidone (PVP), generally not exceeding 2 grams, was added to about 5 grams of methoxyethanol (2ME) and the mixture was allowed to sit for approximately 1 hour so that the PVP could be fully dissolved and form a substantially homogeneous PVP/2ME solution. Then about 4.5 grams of lanthanum methoxyethoxide solution, about 0.65 gram of lithium butoxide and about 0.77gram of zirconium butoxide solution were dissolved in about 5 grams of methoxyethanol and approximately 1gram of the PVP/2ME solution.

[0066] Predissolution of PVP in 2ME is not required but may be carried out in this manner for convenience in mixing. For example, a suitable amount of PVP may be added to 2ME at the same time that the other solution components such as lanthanum methoxyethoxide and zirconium butoxide are mixed together in the solvent. The order of mixing has no bearing on the final composition and function of the solution.

[0067] As in Example 1, lanthanum methoxyethoxide and zirconium butoxide were provided in solution form for convenience in mixing. The invention also encompasses use of these compositions without being pre-dissolved. The lanthanum methoxyethoxide solution comprised lanthanum methoxyethoxide pre-dissolved in methoxyethanol whereby lanthanum methoxyethoxide comprised approximately 12 % by weight of the total weight of the lanthanum methoxyethoxide solution. Similarly, the zirconium butoxide solution comprised zirconium butoxide pre-dissolved in butanol whereby zirconium butoxide comprised approximately 80 % by weight of the zirconium butoxide solution.

[0068] The components may be mixed in any sequence as the sequence of mixing is not significant. The thoroughly-mixed precursor solution was left in a bottle in a dry environment for about 1 to 1.5 hours to help facilitate substantially complete dissolution of the lithium butoxide, the component that was not pre-dissolved.

[0069] The LLZO precursor solution containing some PVP may be dispensed into a substrate configuration by either spin coating or casting as described in Example 1 above. Spin coating was done at approximately 1200 rpm for about 15 seconds. Both spin coating and casting are done in a dry environment. The freshly-coated LLZO was placed in a closed container and exposed to ozone-rich air environment (ozone concentration larger than 0.05 ppm) for approximately 1 hour. In this step, as an alternative, the closed environment may be solvent-vapor-rich (for example wherein a quantity of a solvent such as methoxyethanol, in liquid phase, is disposed in the closed container and permitted or caused to vaporize). As another alternative, the closed environment may contain a mixture of ozone-rich air and a solvent-vapor-rich air. This was followed by heating at approximately 80°C for 30 minutes, also in an ozone-rich air environment. The LLZO coating and substrate were then heated at approximately 300°C for 30 minutes in air. It should be understood that the heating times and environmental factors such as humidity, temperature, and gaseous content of ambient air may be varied. The immediately preceding processing step results in a layer or powder of amorphous LLZO that also contains a small PVP component.

Alternative Embodiments

[0070] The invention may be practiced by synthesizing an amorphous compound in which a different element is substituted for one or more of the constituent elements of the amorphous LLZO compound. Thus, the invention may also be practiced by fully or partially substituting for lithium, one or more chemical elements from the alkali metal family (or group) of the Periodic Table such as but not limited to potassium and sodium. And the invention also may be practiced by fully or partially substituting for lanthanum, one or more chemical elements from the group consisting of barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, alkali metal elements in the alkali metal family (or group) of the Periodic Table such as but not limited to potassium, and elements in the lanthanoid (also know as lanthanide) series of the Periodic Table, such as but not limited to, for example, cerium and neodymium. And the invention also may be practiced by fully or partially substituting for zirconium, one or more chemical elements from the group consisting of tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium. And, lastly, the invention further may be practiced by fully or partially substituting for oxygen, one or more elements from the group consisting of sulfur, selenium, and the halogen family (or group) of the Periodic Table.

[0071] Alternative Processing. All or some of the processing steps during spin coating and in subsequent processing may be carried out in either pure ozone (O_3) or an ozone-enriched air environment that is provided. Or, as a further alternative the environment may be solvent-vapor-rich (for example wherein a quantity of a solvent such as methoxyethanol is disposed in the closed container). As another alternative, the environment may contain a mixture of ozone-rich air and solvent-vapor-rich air.

[0072] Two sol-gel-type related preparation processes have been described above, namely, one directed to spin-coating for making thin films, and the other directed to casting for making thick layers or powder. The invention also may be practiced by employing other sol-gel and non-sol-gel related processes for depositing at least one layer of composition that ultimately results in the production of at least one layer of amorphous lithium lanthanum zirconium oxide. Such additional depositing processes include but are not limited to dip coating, spray coating, screen printing or ink-jet printing as well as various forms of sputtering, chemical vapor deposition (CVD) and other fabrication and deposition techniques.

Representative Test Results and Analytical Data for Amorphous LLZO Produced

[0073] The table below shows depth profile of composition for a typical amorphous LLZO thin film produced under the invention. The data presented are in the form of atomic percentages of the constituent atoms. The depth profile was achieved by sputtering away the exposed LLZO film surface at an approximate rate of 0.3 nm/s. The table was constructed from the X-ray photoemission spectroscopy (XPS) results that are presented in Fig. 2. In the table, "3d" and "1s" are energy level subshell designations.

Depth Profile of Composition of an Amorphous LLZO film

	Atomic Concentration %				
Sputter time (s)	La 3d	O 1s	C 1s	Zr 3d	Li 1s
0	2.5	37.2	32.0	3.7	24.6
200	10.3	49.6	8.3	10.0	21.8
400	10.6	53.3	10.0	10.0	16.1
600	8.9	50.5	8.9	8.5	23.2
800	9.2	51.9	9.4	8.9	20.6
1000	8.1	45.8	7.8	7.5	30.8
1200	8.1	47.4	8.3	7.8	28.4
1400	8.8	46.7	7.1	7.8	29.6
1600	8.6	47.0	8.5	8.0	27.9
1800	9.7	49.2	8.0	8.8	24.5
2000	9.8	48.7	8.2	8.9	24.3

[0074] Referring now to Fig. 2, therein is shown XPS spectra graphs for atomic species constituting an amorphous LLZO film. The set of spectra for each atom corresponds to the set of depth profiling produced by sputtering times discussed and shown in the table above. In the graphs of Fig. 2, each horizontal axis (x-axis) displays “Binding Energy” measured in electronvolts (eV) and each vertical axis (y-axis) displays “intensity” measured in “counts per second” (cps).

[0075] Referring now to Fig. 3, the ionic conductivity of amorphous LLZO product as taught by the invention was observed. Ionic conductivity of an amorphous LLZO thin film was measured by electrochemical impedance spectroscopy (EIS) taking high frequency real-axis intercept as the lithium ionic resistance of the sample from which the ionic conductivity was estimated taking the sample geometry into account. Fig. 3 shows measured EIS spectra of an amorphous LLZO thin film, full spectra on the left and the real axis intercept in detail on the right. The spectra are presented in the form of Nyquist plots. Each horizontal axis (x-axis) displays impedance (Z’) in ohms and each vertical axis (y-axis) displays impedance (Z’’) in ohms. The impedance that is measured by the EIS method is a complex number having both a real and an imaginary component. The real portion is displayed as impedance Z’ on the horizontal axis and the imaginary portion is displayed as impedance Z’’ on the vertical axis.

[0076] The EIS results indicate pure ionic conductivity of the sample, i.e. no evidence of electronic conductivity is observed. The ionic conductivity, estimated from the sample’s film thickness of approximately 1.25 μm and area of 1 mm^2, is in the range 1 to 2 E-3 S/cm. This conductivity is very high for room-temperature ionic conductivity of an inorganic electrolyte.

[0077] Many variations and modifications may be made to the above-described embodiments without departing from the scope of the claims. All such modifications, combinations, and variations are included herein by the scope of this disclosure and the following claims.

[0078] The composition described herein is amorphous lithium lanthanum zirconium oxide (LLZO). It is ionically conductive and, if electronically conductive at all, only negligibly so. When formed as a thin layer, the amorphous LLZO is an effective electrolyte medium that is useful in an electrochemical cell in which lithium is employed as electrode material. The amorphous LLZO electrolyte medium is non-aqueous, non-liquid, inorganic, and non-reactive with lithium; will not leak or leach with respect to adjacent components of a battery cell; and can be manufactured in flexible, thin, useful layers.

[0079] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

We claim:

1. An amorphous oxide-based compound having a general formula $M_wM'_xM''_yM'''_z$,

wherein

M comprises at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

M' comprises at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

M'' comprises at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

M''' comprises at least one oxygen-set element from an oxygen set consisting of oxygen, sulfur, selenium, and the halogen family of the Periodic Table of Elements,

wherein w, x, y, and z are positive numbers including various combinations of integers and fractions or decimals.

2. The amorphous oxide-based compound of claim 1, wherein M comprises lithium, M' comprises lanthanum, M'' comprises zirconium and M''' comprises oxygen.

3. The amorphous oxide-based compound of claim 1, wherein by percentage of total number of atoms M comprises from about 0.1% to about 50%, M' comprises from about 0.1% to about 25%, M'' comprises from about 0.1% to about 25%, M''' comprises from about 30% to about 70%, and carbon comprises from 0.0% to about 25%.

4. The amorphous oxide-based compound of claim 1, having a substantially planar configuration for an electrolyte medium.

5. An electrolyte medium comprising at least one layer of amorphous lithium lanthanum zirconium oxide.

6. The electrolyte medium of claim 5, wherein said amorphous lithium lanthanum zirconium oxide comprises by percentage of total number of atoms from about 0.1% to about

50% lithium, from about 0.1% to about 25% lanthanum, from about 0.1% to about 25% zirconium, from about 30% to about 70% oxygen and from 0.0% to about 25% carbon.

7. A method for synthesizing an amorphous oxide-based compound comprising a sol-gel method comprising:

producing a mixture by substantially dissolving in a solvent,

a first precursor solute comprising a compound consisting of at least one of the alkali-metal family of the Periodic Table,

a second precursor solute comprising a compound of at least one of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

a third precursor solute comprising a compound of at least one of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

a fourth precursor solute comprising a compound of at least one of oxygen, sulfur, selenium, and the halogen family of the Periodic Table of Elements; and

dispensing said mixture in a substantially planar configuration, transitioning through a gel phase, and drying and curing to a substantially dry phase.

8. The method of claim 7, wherein the step of drying and curing said mixture comprises exposing and heating said mixture in an environment comprising air and ozone wherein a concentration of said ozone in said air is greater than 0.05 parts per million.

9. The method of claim 8, wherein the steps of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour; and

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes.

10. The method of claim 8, wherein the steps of exposing and heating said mixture in an environment comprising air and ozone are followed by the step of heating said mixture in air.

11. The method of claim 10, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour;

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes; and

then heating said mixture in air at about 300°C for about 30 minutes.

12. A method of synthesizing amorphous lithium lanthanum zirconium oxide comprising

producing a mixture by substantially dissolving in a solvent,

a first precursor solute comprising a compound of lithium,

a second precursor solute comprising a compound of lanthanum, and

a third precursor solute comprising a compound of zirconium; and

dispensing said mixture in a substantially planar configuration and drying and curing to a substantially dry phase.

13. The method of claim 12, wherein said solvent comprises an alcohol-based solvent, said first precursor solute comprises lithium alkoxide, said second precursor solute comprises lanthanum alkoxide, and said third precursor solute comprises zirconium alkoxide.

14. The method of claim 13, wherein said alcohol-based solvent comprises methoxyethanol.

15. The method of claim 13, wherein said lithium alkoxide comprises lithium butoxide, said lanthanum alkoxide comprises lanthanum methoxyethoxide, and said zirconium alkoxide comprises zirconium butoxide.

16. The method of claim 15, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide.

17. The method of claim 15, wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

18. The method of claim 15, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based

solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide; and wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

19. The method of claim 12, wherein said mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing and ink-jet printing.

20. The method of claim 12, wherein the step of drying and curing said mixture comprises exposing and heating said mixture in an environment comprising air and ozone wherein a concentration of said ozone in said air is greater than 0.05 parts per million.

21. The method of claim 20, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour; and

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes.

22. The method of claim 20, wherein the steps of exposing and heating said mixture in an environment comprising air and ozone are followed by the step of heating said mixture in air.

23. The method of claim 22, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour;

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes; and

then heating said mixture in air at about 300°C for about 30 minutes.

24. A method of synthesizing amorphous lithium lanthanum zirconium oxide comprising

producing a mixture by substantially dissolving in a solvent

a first precursor solute comprising a compound of lithium,

a second precursor solute comprising a compound of lanthanum, and a third precursor solute comprising a compound of zirconium, and

a polymer; and

dispensing said mixture in a substantially planar configuration and drying and curing to a substantially dry phase.

25. The method of claim 24, wherein said solvent comprises an alcohol-based solvent, said first precursor solute comprises lithium alkoxide, said second precursor solute comprises lanthanum alkoxide, and said third precursor solute comprises zirconium alkoxide.

26. The method of claim 25, wherein said alcohol-based solvent comprises methoxyethanol and said polymer comprises polyvinyl pyrrolidone.

27. The method of claim 25, wherein said lithium alkoxide comprises lithium butoxide, said lanthanum alkoxide comprises lanthanum methoxyethoxide, and said zirconium alkoxide comprises zirconium butoxide.

28. The method of claim 27, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide.

29. The method of claim 27, wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

30. The method of claim 25, wherein said polymer comprises an amount of said polymer pre-dissolved in an amount of said alcohol-based solvent to produce a polymer solution.

31. The method of claim 27,

wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide;

wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide; and wherein said polymer comprises an amount of said polymer pre-dissolved in an amount of said alcohol-based solvent to produce a polymer solution.

32. The method of claim 31, wherein said alcohol-based solvent comprises methoxyethanol and said polymer comprises polyvinyl pyrrolidone.

33. The method of claim 24, wherein said mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing and ink-jet printing.

34. The method of claim 24, wherein the step of drying and curing said mixture comprises exposing and heating said mixture in an environment comprising air and ozone wherein a concentration of said ozone in said air is greater than 0.05 parts per million.

35. The method of claim 34, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour; and

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes.

36. The method of claim 34, wherein the steps of exposing and heating said mixture in an environment comprising air and ozone are followed by the step of heating said mixture in air.

37. The method of claim 36, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour;

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes; and

then heating said mixture in air at about 300°C for about 30 minutes.

38. An amorphous oxide-based compound having a general formula $M_wCM'_xM''_yM'''_z$,

wherein

M comprises at least one lithium-set element from a lithium set consisting of the alkali-metal family of the Periodic Table,

C comprises carbon,

M' comprises at least one lanthanum-set element from a lanthanum set consisting of lanthanum, barium, strontium, calcium, indium, magnesium, yttrium, scandium, chromium, aluminum, lutetium, potassium, the alkali-metal family of the Periodic Table and the lanthanide series of the Periodic Table,

M'' comprises at least one zirconium-set element from a zirconium set consisting of zirconium, tantalum, niobium, antimony, tin, hafnium, bismuth, tungsten, silicon, selenium, gallium and germanium, and

M''' comprises at least one oxygen-set element from an oxygen set consisting of oxygen, sulfur, selenium, and the halogen family of the Periodic Table of Elements,

wherein w, x, y, and z are positive numbers including various combinations of integers and fractions or decimals.

39. The amorphous oxide-based compound of claim 38, wherein M comprises lithium, M' comprises lanthanum, M'' comprises zirconium and M''' comprises oxygen.

40. The amorphous oxide-based compound of claim 38, wherein by percentage of total number of atoms M comprises from about 0.1% to about 50%, carbon comprises up to about 25%, M' comprises from about 0.1% to about 25%, M'' comprises from about 0.1% to about 25%, and M''' comprises from about 30% to about 70%.

41. The amorphous oxide-based compound of claim 38, having a substantially planar configuration for an electrolyte medium.

42. An electrolyte medium comprising at least one layer of amorphous lithium carbon lanthanum zirconium oxide.

43. The electrolyte medium of claim 42, wherein said amorphous lithium carbon lanthanum zirconium oxide comprises by percentage of total number of atoms from about 0.1% to about 50% lithium, up to about 25% carbon, from about 0.1% to about 25% lanthanum, from about 0.1% to about 25% zirconium, and from about 30% to about 70% oxygen.

44. A method of synthesizing amorphous lithium carbon lanthanum zirconium oxide comprising

producing a mixture by substantially dissolving in a solvent, a first precursor solute comprising a compound of lithium,

a second precursor solute comprising a compound of lanthanum, and

a third precursor solute comprising a compound of zirconium; and

dispensing said mixture in a substantially planar configuration and drying and curing to a substantially dry phase.

45. The method of claim 44, wherein the step of drying and curing said mixture comprises exposing and heating said mixture in an environment comprising air and ozone wherein a concentration of said ozone in said air is greater than 0.05 parts per million.

46. The method of claim 45, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour; and

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes.

47. The method of claim 45, wherein the steps of exposing and heating said mixture in an environment comprising air and ozone are followed by the step of heating said mixture in air.

48. The method of claim 47, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour;

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes; and

then heating said mixture in air at about 300°C for about 30 minutes.

49. The method of claim 44, wherein said solvent comprises an alcohol-based solvent, said first precursor solute comprises lithium alkoxide, said second precursor solute comprises lanthanum alkoxide, and said third precursor solute comprises zirconium alkoxide.

50. The method of claim 49, wherein said alcohol-based solvent comprises methoxyethanol.

51. The method of claim 49, wherein said lithium alkoxide comprises lithium butoxide, said lanthanum alkoxide comprises lanthanum methoxyethoxide, and said zirconium alkoxide comprises zirconium butoxide.

52. The method of claim 51, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide.

53. The method of claim 51, wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

54. The method of claim 51, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide; and wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

55. The method of claim 46, wherein said mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing and ink-jet printing.

56. A method of synthesizing amorphous lithium carbon lanthanum zirconium oxide comprising:

producing a mixture by substantially dissolving in a solvent
a first precursor solute comprising a compound of lithium,
a second precursor solute comprising a compound of lanthanum, and
a third precursor solute comprising a compound of zirconium, and
a polymer; and

dispensing said mixture in a substantially planar configuration and drying and curing to a substantially dry phase.

57. The method of claim 56, wherein the step of drying and curing said mixture comprises exposing and heating said mixture in an environment comprising air and ozone wherein a concentration of said ozone in said air is greater than 0.05 parts per million.

58. The method of claim 57, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour; and

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes.

59. The method of claim 57, wherein the steps of exposing and heating said mixture in an environment comprising air and ozone are followed by the step of heating said mixture in air.

60. The method of claim 59, wherein the step of drying and curing said mixture further comprises:

exposing said mixture to said environment comprising air and ozone for about one hour;

then heating said mixture in said environment comprising air and ozone at about 80°C for about 30 minutes; and

then heating said mixture in air at about 300°C for about 30 minutes.

61. The method of claim 56, wherein said solvent comprises an alcohol-based solvent, said first precursor solute comprises lithium alkoxide, said second precursor solute comprises lanthanum alkoxide, and said third precursor solute comprises zirconium alkoxide.

62. The method of claim 61, wherein said alcohol-based solvent comprises methoxyethanol and said polymer comprises polyvinyl pyrrolidone.

63. The method of claim 61, wherein said lithium alkoxide comprises lithium butoxide, said lanthanum alkoxide comprises lanthanum methoxyethoxide, and said zirconium alkoxide comprises zirconium butoxide.

64. The method of claim 63, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide.

65. The method of claim 63, wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide.

66. The method of claim 61, wherein said polymer comprises an amount of said polymer pre-dissolved in an amount of said alcohol-based solvent to produce a polymer solution.

67. The method of claim 63, wherein said lanthanum methoxyethoxide comprises an amount of said lanthanum methoxyethoxide pre-dissolved in an amount of said alcohol-based solvent to produce a lanthanum methoxyethoxide solution comprising about 12% by weight said lanthanum methoxyethoxide;

wherein said zirconium butoxide comprises an amount of said zirconium butoxide pre-dissolved in an amount of butanol to produce a zirconium butoxide solution comprising about 80% by weight said zirconium butoxide; and

wherein said polymer comprises an amount of said polymer pre-dissolved in an amount of said alcohol-based solvent to produce a polymer solution.

68. The method of claim 67, wherein said alcohol-based solvent comprises methoxyethanol and said polymer comprises polyvinyl pyrrolidone.

69. The method of claim 56, wherein said mixture is dispensed into a substantially planar configuration by one of spin coating, casting, dip coating, spray coating, screen printing and ink-jet printing.

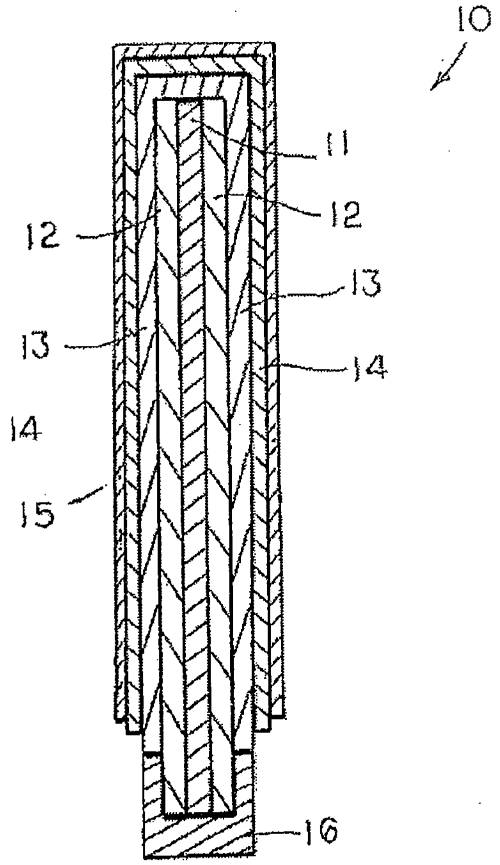


Fig. 1

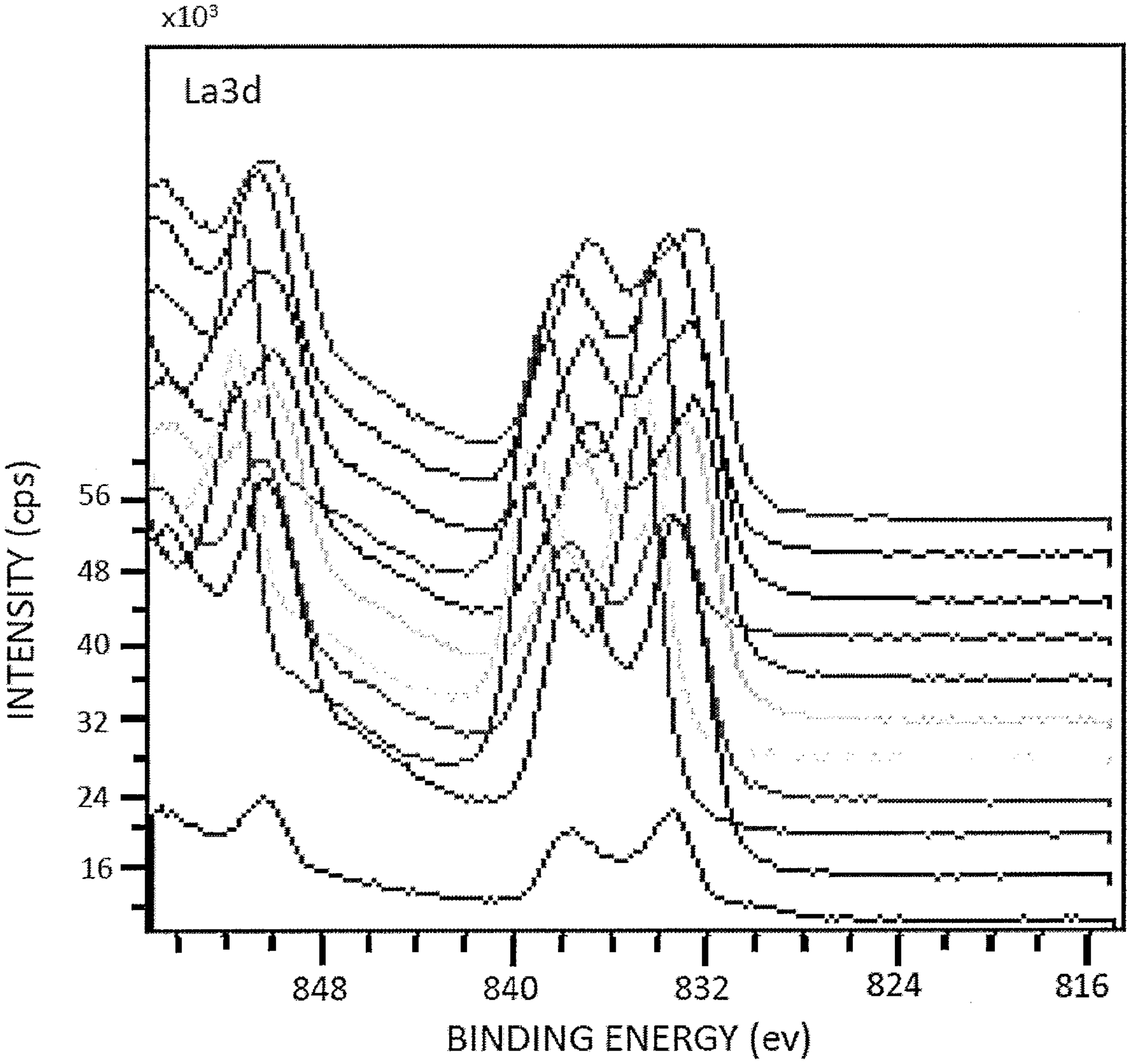

x10³
La3d
INTENSITY (cps)
56
48
40
32
24
16
848
840
832
824
816
BINDING ENERGY (ev)

Fig. 2(a)

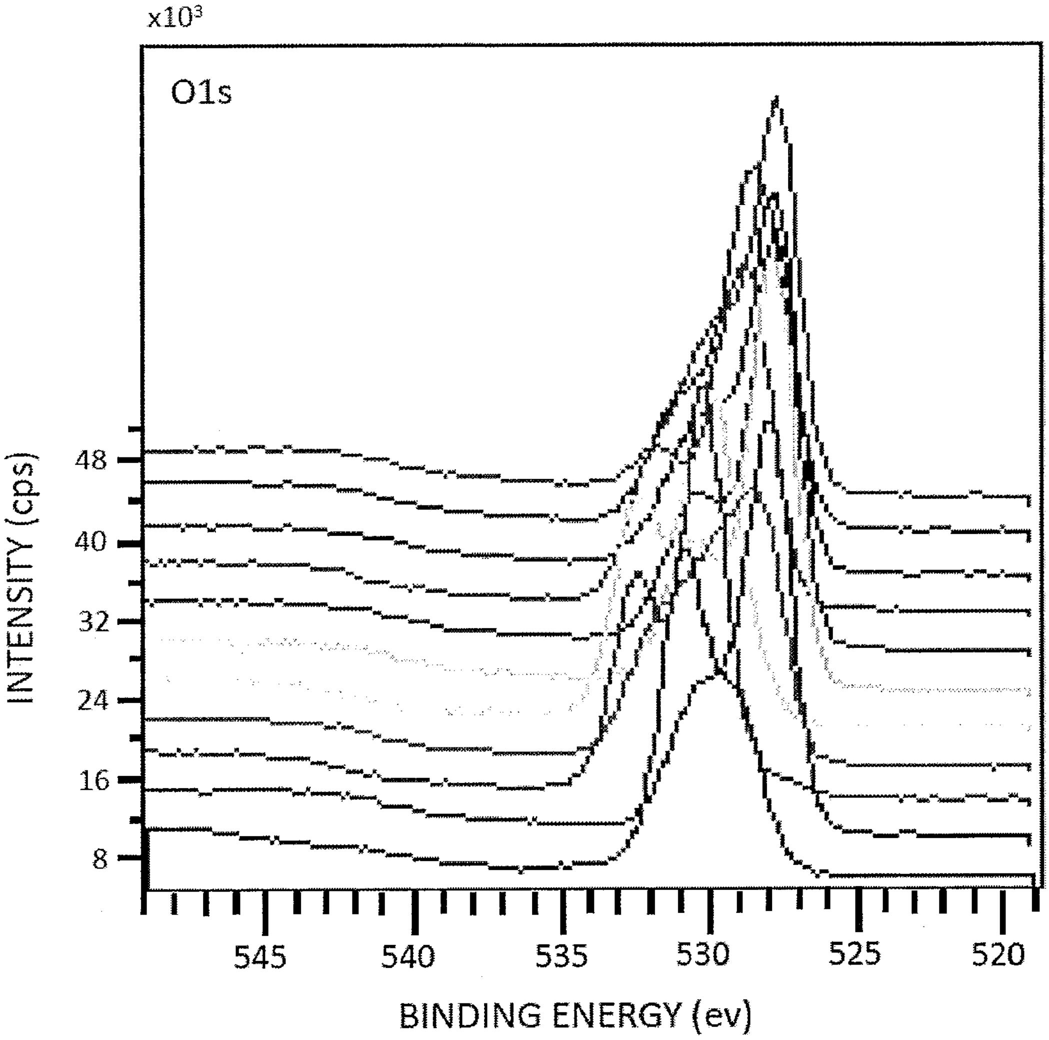
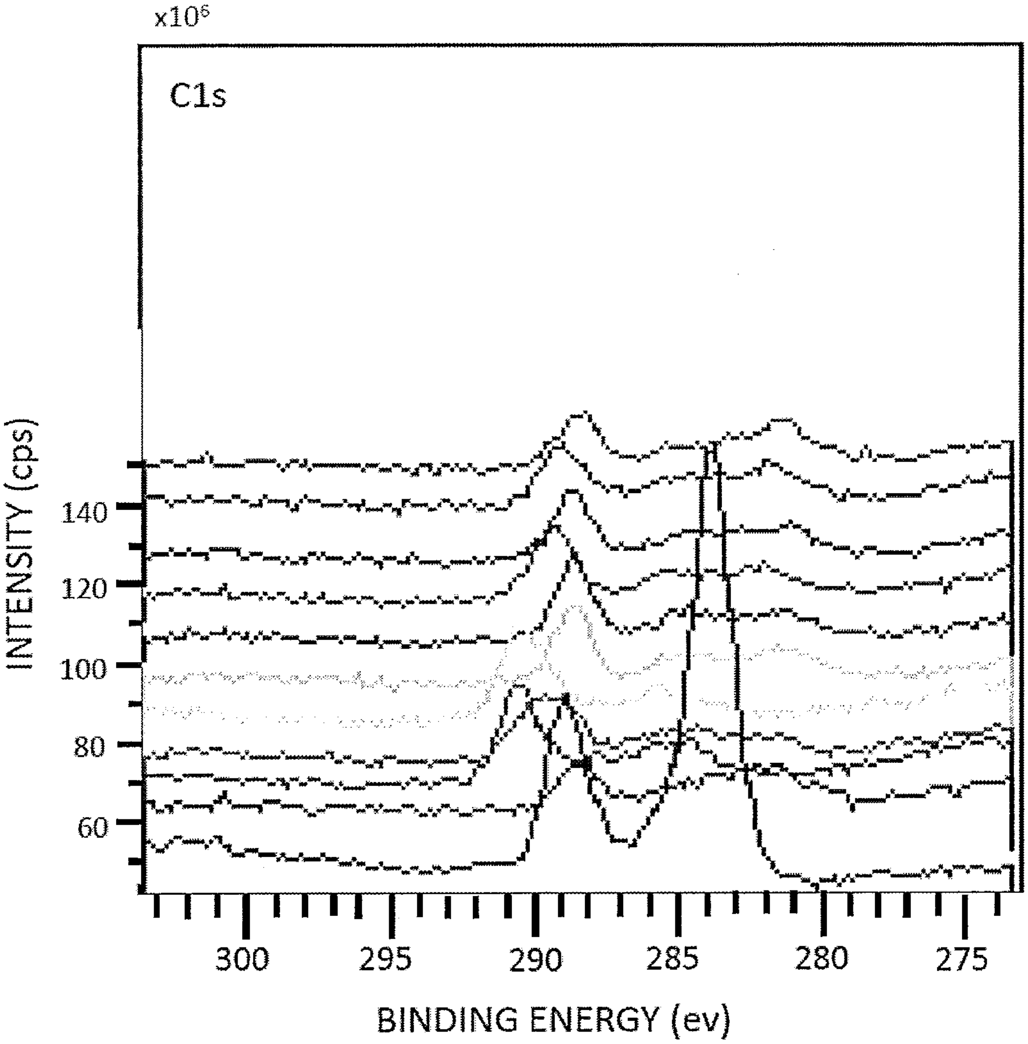

x10³
O1s
INTENSITY (cps)
48
40
32
24
16
8
545
540
535
530
525
520
BINDING ENERGY (ev)

Fig. 2(b)


x10⁶
C1s
INTENSITY (cps)
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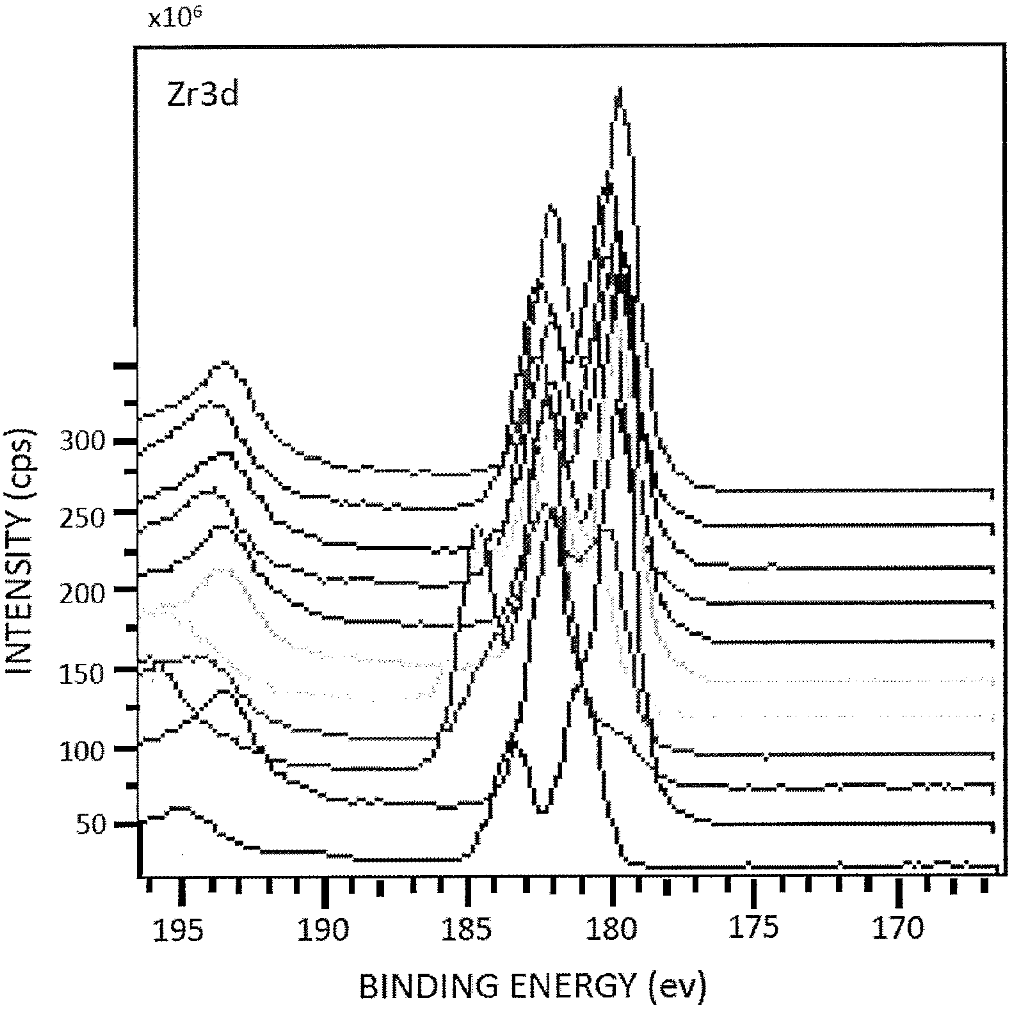
120
100
80
60
300
295
290
285
280
275
BINDING ENERGY (ev)

Fig. 2(c)


x10⁶
Zr3d
INTENSITY (cps)
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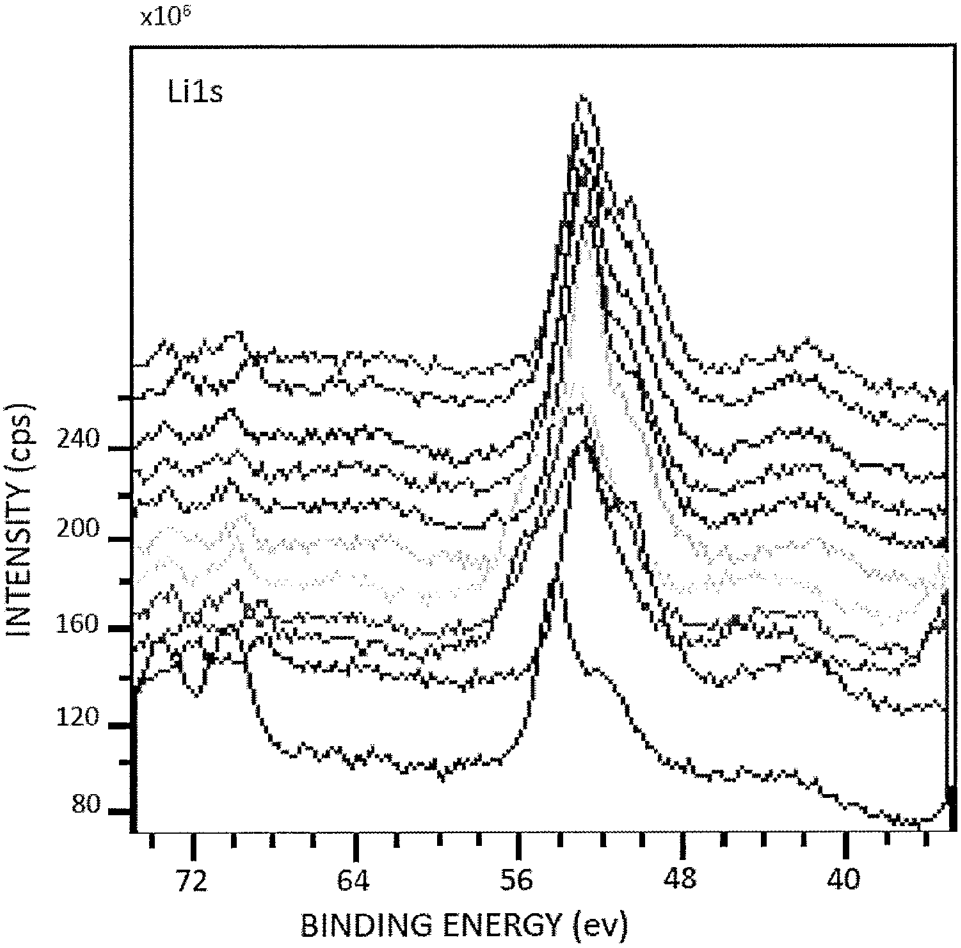
200
150
100
50
195
190
185
180
175
170
BINDING ENERGY (ev)

Fig. 2(d)


x10⁶
Li1s
INTENSITY (cps)
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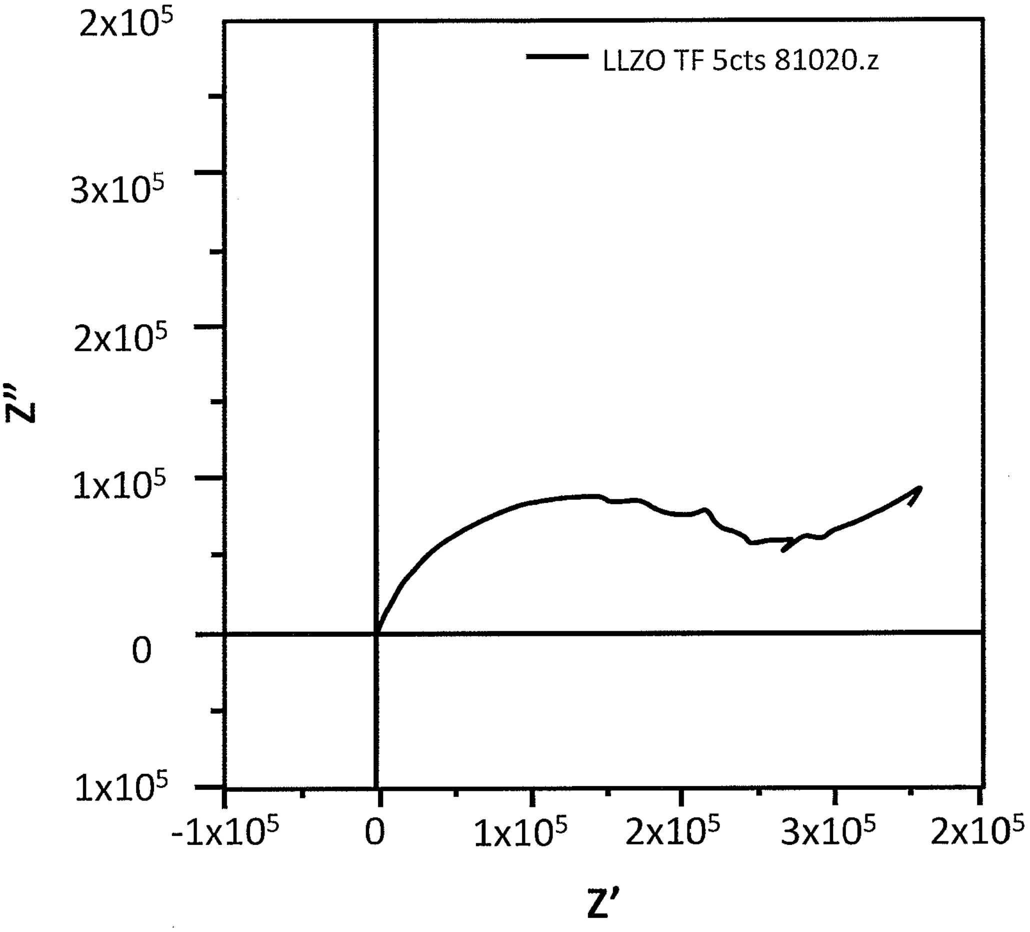
200
160
120
80
72
64
56
48
40
BINDING ENERGY (ev)

Fig. 2(e)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3x10^5
2x10^5
1x10^5
0
1x10^5
Z''
-1x10^5
0
1x10^5
2x10^5
3x10^5
2x10^5
Z'

Fig. 3(a)

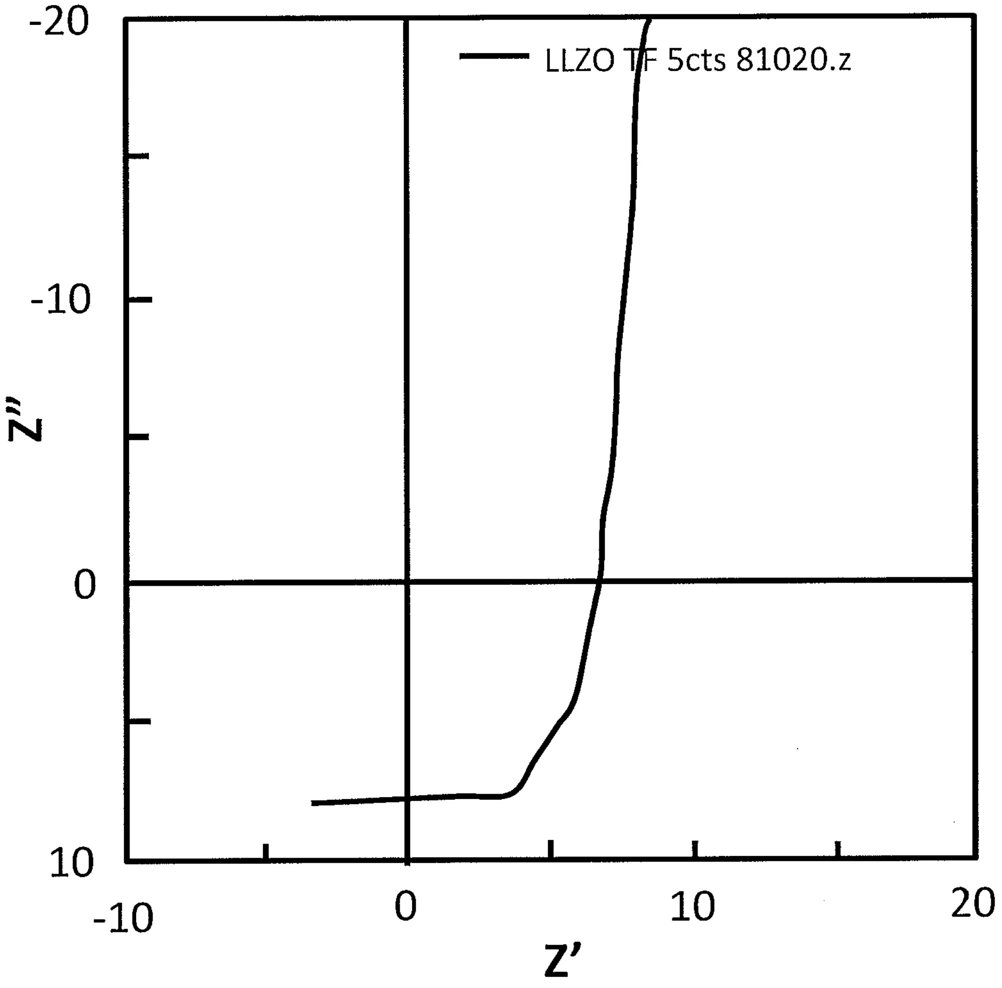

Fig. 3(b)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/046289

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B35/486 C04B35/624 H01M10/052 H01M10/0562
ADD.

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)
C04B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 037 527 A1 (SUMITOMO ELECTRIC INDUSTRIES [JP]) 18 March 2009 (2009-03-18) paragraph [0082] - paragraph [0083]; example 2; table II -----	1-6
X	JP 2010 080426 A (SUMITOMO ELECTRIC INDUSTRIES) 8 April 2010 (2010-04-08) paragraphs [0021], [0029], [0039] - [0043] -----	1-69
A	DE 10 2007 030604 A1 (WEPPNER WERNER [DE]) 8 January 2009 (2009-01-08) the whole document -----	1-69

☐ 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 document 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 21 December 2011	Date of mailing of the international search report 06/01/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bonneau, Sébastien

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/046289

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1, 7, 38(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1, 7, 38(all partially)

Present claims 1, 7 and 38 relate to an extremely large number of possible compounds or raw materials. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds or raw materials claimed, see specific examples. The alternative embodiments described in paragraph [0070] are not considered as a sufficient support since it appears to be a mere general statement which does not prove that all combinations would work and solve the technical problem. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1, 7 and 38 (PCT Guidelines 9.19 and 9.23). The search of claims 1, 7 and 38 was restricted to those claimed compounds or raw materials which appear to be supported,i.e. to a lithium lanthanum zirconium oxide compound optionally containing carbon and the raw materials leading to such a product.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/046289

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2037527 A1	18-03-2009	EP 2037527 A1	18-03-2009
		JP 2009245913 A	22-10-2009
		KR 20090027144 A	16-03-2009
		US 2009068563 A1	12-03-2009
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		JP 2010080426 A	08-04-2010
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		CN 101952223 A	19-01-2011
		DE 102007030604 A1	08-01-2009
		EP 2176190 A2	21-04-2010
		JP 2010534383 A	04-11-2010
		KR 20100053543 A	20-05-2010
		TW 200910671 A	01-03-2009
		US 2010203383 A1	12-08-2010
		WO 2009003695 A2	08-01-2009