DESCRIPTION

TITLE OF THE INVENTION: ELECTROLYTE MATERIAL FOR AN ALL-SOLID-STATE BATTERY

[0001] The present invention relates to the field of materials used in batteries and relates, more specifically, to a layer of electrolyte material and a stack of material for the production of an all-solid-state battery.

[0002] The bibliographic references in the following text are denoted as follows in the text of the description: **[]**; they are also listed in the reference table.

PRIOR ART

[0003] Standalone and portable applications often require a large amount of energy. Most of these apparatuses rely on rechargeable batteries, provided that they can deliver higher volumetric and gravimetric energy densities. Li-ion batteries, which are known in the state-of-the-art, are the most commonly used for high-energy-density applications. These Li-ion batteries use liquid organic electrolytes and specific polymers. As a result, these batteries require airtight and durable packaging which increases the weight of the batteries and reduces their energy density. Additionally, there are several known problems associated with the use of an organic liquid electrolyte, such as leakage, accelerated aging, flammability, etc.

[0004] Li-ion batteries known in the prior art have a maximum energy storage capacity that remains too limited for the intended applications (< 300 Wh/kg). In addition, these Li-ion batteries use materials that are expensive and/or whose mining poses environmental problems, as is the case with cobalt. Such Li-ion batteries use a liquid electrolyte, which, in addition to the technical problems mentioned hereinbefore, complicates their recycling at the end of

their life due to the presence of toxic compounds that they contain, which are difficult to separate and dispose of.

[0005] More high-performance batteries are needed, particularly for use in electrified transportation such as electric cars or in aviation, specifically with an energy density greater than 500 Wh/kg; these batteries must be safer and therefore free from thermal runaway and flammability; and more environmentally friendly by virtue of using less toxic materials, with a smaller environmental footprint and greater recyclability.

[0006] Batteries incorporating solid electrolytes are known from the prior art: **[1–5]**. However, such batteries have the following drawbacks associated with the use of solid electrolytes:

- chemically unstable when exposed to air or moisture;
- electrically unstable at the operating potentials of the electrode materials;
- that use materials that are difficult to obtain in sufficient quantities, such as lanthanum and germanium, and generally require complex manufacturing processes; and
- have low resistance to the propagation of lithium dendrites during cycling.

[0007] The present invention aims to propose alternative solid-state electrolytes based on the high-entropy oxide family, by replacing critical metals such as cobalt and nickel, which have been used to date, with compositions containing iron and/or manganese. Such materials exhibit ionic conductivity properties that allow them to be used as solid electrolytes for all-solid-state batteries. Such next-generation batteries are designed to deliver high performance by incorporating a metal with high energy density, such as lithium and/or sodium, into the negative electrode and by using an insertion material that typically comprises alkali metal ions in the positive electrode.

DESCRIPTION OF THE INVENTION

[0008] To overcome the drawbacks of the prior art described above, the present invention relates to a solid inorganic material for use as an electrolyte comprising an oxide of formula $A_x(MgM_1M_2Cu_yZn)_{1-x}O$, M_1 and M_2 being independently selected from among the metals of block d of the periodic table, excluding Co, and A being an alkali metal, x is between 0.15 and 0.35, and y is selected from the two integer values 0 and 1, preferably, the oxide is a high-entropy oxide. Such high-entropy oxides are referred to as "HEOx" and are defined as a class of materials discovered in 2015 by an American team, as reported in the journal Nature communication **[6]**. Such alkali metal doping of these high-entropy oxides gives the inorganic material excellent thermal conductivity.

[0009] Advantageously, M_1 and M_2 are selected independently from Fe, Ni and Mn.

[0010] Advantageously, the oxide of the solid inorganic material according to the invention is selected from $A_x(MgFeNiCuZn)_{1-x}O$; $A_x(MgMnNiCuZn)_{1-x}O$ and $A_x(MgFeMnCuZn)_{1-x}O$, and A is selected from Na and Li. These electrolytes have the advantage of being excellent ionic conductors at room temperature, eliminating the need to reach an operating temperature, typically through heating, to realize the full potential of the material.

[0011] Advantageously, the oxide is selected from $(MgFeNiCuZn)_{0.70}Li_{0.30}O$; $(MgMnNiCuZn)_{0.75}Li_{0.25}O$; $(MgFeNiCuZn)_{0.70}Na_{0.30}O$ and $(MgFeNiCuZn)_{0.75}Na_{0.25}O$.

[0012] Advantageously, the oxide does not comprise either one of the elements selected from Ni or Cu, or the material contains neither of the two elements Ni and Cu. The inventors have demonstrated that it is possible to eliminate not only Co but also Ni and/or Cu, which opens the door to a wider variety of materials for new applications.

[0013] Advantageously, the value of x is greater than or equal to 0.20. The inventors demonstrated, in a completely unexpected way, that doping alkali metals with high-entropy oxides in these proportions can significantly improve ionic conductivity. Preferably, the value of x is greater than or equal to 0.25.

[0014] The present invention also relates to a solid electrolytic material, and more particularly to a solid electrolyte comprising the inorganic solid material described previously within the scope of the invention. Such a solid electrolyte is advantageously incorporated into an energy storage and/or delivery system, such as a cell, a battery or a rechargeable battery. The inventors demonstrated, in a completely unexpected way, that such a storage system according to the invention, was particularly efficient by virtue of energy densities greater than 500 Wh/kg, while also being safer than existing systems in terms of health, safety and environmental (HSE) criteria. Such a solid electrolyte also serves as a separator layer between the cathode and anode electrodes in an energy storage system, such as a battery. Such a battery does not form an unstable passivation layer (SEI), resulting in very low self-discharge rates. It allows energy to be stored for several years with minimal loss and is expected to last 50 to 100 times longer than conventional liquid-electrolyte batteries.

[0015] The present invention also relates to a method for manufacturing a solid inorganic material as described previously within the scope of the invention, obtained from a ground and compacted mixture of metal oxides and alkali carbonate. Alkali carbonates are preferably selected from lithium carbonate Li_2CO_3 and sodium carbonate Na_2CO_3. The inventors demonstrated that it was possible to compact the powders to reduce porosity without altering the conductive properties.

[0016] Preferably, the ground mixture of metal oxides and alkali carbonate is subjected to a compression step of 10^7 to 2.10^8 Pa and a temperature between 25 and 250°C. Such a compaction step makes the powder mixture dense,

ensuring that the high-temperature solid-state chemical reactions proceed efficiently and uniformly throughout the entire sample. Preferably, the pressure is applied to the sample using a uniaxial press, applying a conversion pressure of 1 metric ton per square centimeter or 100 MPa. Ideally, the pressure is applied using a hydraulic press manufactured by Eurolab®. The pressure gage of the device displays the applied pressure in metric tons. The pellets have a diameter of 13 mm; the pressure in pascals is obtained by converting the value.

[0017] Preferably, the method according to the invention comprises two additional steps:

1- performing heat treatment at a temperature $T \geq 900°C$ in an air atmosphere; and

2- performing a quenching treatment immediately after step 1, under a partial pressure of oxygen Pox, where $0\ Pa \leq Pox < 2.104\ Pa$. The press used and the methods for applying pressure are as described previously and involve a hydraulic press manufactured by Eurolab®.

[0018] The present invention also relates to a solid-state battery comprising the following three layers of materials:

- a negative electrode layer;
- a positive electrode layer; and
- a solid electrolyte as described previously within the scope of the invention, positioned between the negative and positive electrode layers.

[0019] Preferably, the negative electrode layer comprises at least one metal selected from Li and Na, and the positive electrode layer comprises a ceramic and graphite, wherein the ceramic is preferably a ceramic having a content of more than 50% of an active material comprising an alkali metal ion, the content, expressed as a percentage, being a mass percentage with respect to the total mass of the ceramic. Preferably, said active material is selected from

at least one of the materials selected from the following oxides: $LiNi_xCo_yMn_zO_2$, $LiFePO_4$/C, $LiMn_2O_4$, $LiCoO_2$, $Na_{0.7}MnO_2$ and $NaCoO_2$.

[0020] The present invention also relates to a thin film comprising the solid-state battery described previously within the scope of the invention, for its integrated use in an electronic apparatus, wherein said electronic apparatus is preferably selected from a smart card, a biotechnology apparatus and a graphing calculator.

[0021] The present invention also relates to the use of a solid-state battery as described previously within the scope of the invention, selected from integration into an electric vehicle, transportation, large-scale stationary storage, integration into aerospace aircraft, the medical sector and robotics.

[0022] The present invention is also described in the following detailed description, by means of the experimental part which details some embodiments by means of examples, given only by way of illustration and which should not be considered as limiting, and the figures that are briefly described in the following section.

BRIEF DESCRIPTION OF THE FIGURES

[0023] [Fig.1] – Figure 1 shows the ionic conductivities of $(MgFeNiCuZn)_{0.70}Li_{0.30}O$ at 20°C and 100°C;

[0024] [Fig.2] – Figure 2 shows the ionic conductivities of $(MgMnNiCuZn)_{0.75}Li_{0.25}O$ at 20°C and 100°C;

[0025] [Fig.3] – Figure 3 shows the stability of $(MgFeNiCuZn)_{0.70}Na_{0.30}O$ in air and a comparison with the same Heox sample stored under vacuum;

[0026] [Fig.4] – Figure 4 shows the assembly of a positive electrode (composite)/electrolyte according to the invention (cold-pressed);

[0027] [Fig.5] – Figure 5 shows cyclic voltammetry of $(MgFeNiCuZn)_{0.75}Na_{0.25}O$; and

[0028] [Fig.6] – Figure 6 shows the charge curve of an all-solid-state battery containing $(MgFeNiCuZn)_{0.75}Na_{0.25}O$;

[0029] [Fig.7] Figure 7 shows the EDX chemical analysis of the compound $(MgMnNiCuZn)_{0.70}Li_{0.30}O$, which is consistent with the expected stoichiometry.

[0030] [Fig.8(a)]–[Fig.8(c)] Figures 8(a), 8(b) and 8(c) show the X-ray diffraction patterns of the compositions $(MgFeNiCuZn)_{0.80}Li_{0.20}O$, $(MgMnNiCuZn)_{0.80}Li_{0.20}O$ and $(MgMnNiCuZn)_{0.75}Na_{0.25}O$; and

[0031] [Fig.9] Figure 9 shows the complex impedance of the compound $(MgFeNiCuZn)_{0.80}Na_{0.20}O$ at two different temperatures.

Experimental part

[0032] **<u>Material and methods</u>**

In the scope of the invention, the diffractometer used for X-ray diffraction is a Philips Panalytical® X-Pert Pro MPD diffractometer.

[0033] All high-entropy solid electrolyte samples are prepared from oxides such as magnesium (II) oxide (MgO - Alfa Aesar® 99.95%), iron (III) oxide (Fe_2O_3 - Alfa Aesar®), manganese (II) oxide (Mn_2CO_3 - Alfa Aesar®), copper (II) oxide (CuO - Alfa Aesar® 99. 7%), nickel (II) oxide (NiO), zinc (II) oxide (ZnO - Alfa Aesar® 4N), and carbonates such as lithium carbonate (Li_2CO_3 - Alfa Aesar® 99.998%) and sodium carbonate (Na_2CO_3). The chemical composition (formula) of the resulting materials is determined by energy-dispersive X-ray spectroscopy, also known by the abbreviation EDX, using a Philips Panalytical® X-Pert Pro MPD diffractometer.

Results and discussion

[0034] **<u>Preparation of oxides</u>**

[0035] The starting powders of the precursors, in stoichiometric quantities, are mixed in equimolar ratios of all cations Mg, Fe or Mn or both, Ni, Cu and Zn, for a total mass of 4 g, by adding the ingredients to a mortar or agate bowls, with a capacity of 20 mL, followed by processing in a Fritsch® planetary micro-mill, under the reference Pulverisette 7 Premium Line, with 5 agate grinding balls, 1 cm in diameter, for one hour at 350 rpm, with a one-minute pause after each five-minute cycle.

[0036] The resulting mixture is then uniformly pressed into a rectangular die measuring 12x3x3 mm^3 or a cylindrical die measuring 13x13 mm^2 under a hydraulic pressure of 10^7 to 2.10^8 Pa, while the applied temperature ranges from 25 to 250°C; the resulting pellets are then placed and held in an alumina crucible, and heated to a temperature selected based on the composition of the sample and ranging from 850°C to 1100°C for 12 hours in air at a constant heating rate of 2°C/minute (120°C/h) (for a total of 20 hours of sintering). Next, a quenching step is performed in liquid nitrogen or directly on a metal plate under vacuum (partial pressure of oxygen Pox, where 0 Pa ≤ Pox < 2. 104 Pa). Solid mixtures prepared with a high concentration of lithium/sodium (x > 0.25) must be stored in a glovebox to prevent them from absorbing moisture (hygroscopic compounds).

[0037] The geometric density of all samples, after heat treatment, is calculated to be between 75 and 80% of the theoretical density. Since the reaction is complete, the resulting chemical formula is the same as that expected based on the molar ratios of the starting compounds.

[0038] The resulting solid materials have the following general formulas:

$(MgFeNiCuZn)_{1-x}Li_xO$

$(MgMnNiCuZn)_{1-x}Li_xO$

$(MgFeNiCuZn)_{1-x}Na_xO$

$(MgMnNiCuZn)_{1-x}Na_xO$

$(MgFeMnCuZn)_{1-x}Li_xO$

$(MgFeMnCuZn)_{1-x}Na_xO$;

and, more specifically, have the following formula:

$(MgFeNiCuZn)_{0.70}Li_{0.30}O$; $(MgMnNiCuZn)_{0.75}Li_{0.25}O$;

$(MgFeNiCuZn)_{0.70}Na_{0.30}O$; $(MgFeNiCuZn)_{0.75}Na_{0.25}O$;

$(MgFeNiCuZn)_{0.80}Li_{0.20}O$; $(MgMnNiCuZn)_{0.80}Li_{0.20}O$ and

$(MgFeNiCuZn)_{0.75}Na_{0.25}O$.

[0039] **Results**

The high-entropy oxides obtained as described above exhibit good ionic conductivity at room temperature, making them good candidates for use as solid electrolytes, as shown for the compounds $(MgFeNiCuZn)_{0.70}Li_{0.30}O$ and $(MgMnNiCuZn)_{0.75}Li_{0.25}O$ in Figure 1 and Figure 2.

[0040] The chemical stability of high-entropy oxides is tested in the presence of air (oxygen) and moisture (water), and they prove to be very stable under both conditions. The resulting high-entropy oxides also exhibit chemical stability with respect to the negative and positive electrodes when used in a battery, which eliminates solid-solid interface protection issues and reduces the ohmic drop within the battery itself, as shown by X-ray diffraction for $(MgFeNiCuZn)_{0.70}Na_{0.30}O$ in Figure 3.

[0041] Figure 4 shows the assembly of a positive electrode (composite)/electrolyte according to the invention, incorporating the solid organic material according to the invention (cold-pressed). More particularly, Figure 4 shows the positive electrode (at the bottom of the figure), which consists of a mixture of inorganic material according to the invention and solid electrolyte; the positive electrode is therefore a composite. Shown above in Figure 4 is the solid electrolyte alone. The white line marks the interface between the solid electrolyte alone (above) and the positive electrode (below).

[0042] Figure 5 and Figure 6 show the electrical properties characterized for the material $(MgFeNiCuZn)_{0.75}Na_{0.25}O$.

[0043] Figure 7 shows the EDX chemical analysis of the compound $(MgMnNiCuZn)_{0.70}Li_{0.30}O$, which is consistent with the expected stoichiometry.

[0044] Figures 8(a) to 8(c) show the variety of possible compositions, with three X-ray diffraction patterns corresponding to stoichiometries different from those shown in previous Figures 1 to 7

[0045] Figure 9 shows the complex impedance of the compound $(MgFeNiCuZn)_{0.80}Na_{0.20}O$ at a temperature of 25°C (corresponding to an ionic conductivity of $2.3x10^{-6}$ S/cm) and at a temperature of 50°C (corresponding to an ionic conductivity of $3.2x10^{-6}$ S/cm).

References

[0046] The following Table 1 lists the references cited previously in the text:

[Table 1]

1	Y. Wang et al., Chem (2019), vol. 5, pp. 2547-2570 Developments and Perspectives on Emerging High-Energy Density Sodium-Metal Batteries
2	Y. Lu et al., Joule (2018), vol. 2, pp. 1747-1770 Electrolyte and Interface Engineering for Solid State Sodium Batteries
3	H. Gao et al., Chem (2018), vol. 4, pp. 833-844 Stabilizing a High-Energy Density Rechargeable Sodium Battery with a Solid Electrolyte
4	C. Zhou et al., ACS Energy Letters (2018), vol.3, pp.2181-2198 Engineering Materials for Progressive All Solid State Na Batteries

5	W. Zhou et al., ACS Central Science (2017), vol. 3, pp. 52–57 Rechargeable sodium all solid state battery
6	Rost *et al*., Nature Communications 6, 8485 (2015)

Claims

[Claim 1] A solid inorganic material for use as an electrolyte material comprising an oxide of formula $A_x(MgM_1M_2Cu_yZn)_{1-x}O$, M_1 and M_2 being independently selected from among the metals of block d of the periodic table, with the exception of Co, and A being an alkali metal, x is between 0.15 and 0.35 and y is selected from the two integer values 0 and 1, preferably, the oxide is a high-entropy oxide.

[Claim 2] The material according to claim 1, wherein M_1 and M_2 are independently selected from Fe, Ni and Mn.

[Claim 3] The material according to one of claims 1 or 2, wherein the oxide is selected from $A_x(MgFeNiCuZn)_{1-x}O$; $A_x(MgMnNiCuZn)_{1-x}O$ and $A_x(MgFeMnCuZn)_{1-x}O$, and A is selected from Na and Li.

[Claim 4] The material according to one of claims 1 to 3, wherein the oxide is selected from $(MgFeNiCuZn)_{0.70}Li_{0.30}O$; $(MgMnNiCuZn)_{0.75}Li_{0.25}O$; $(MgFeNiCuZn)_{0.70}Na_{0.30}$ and $(MgFeNiCuZn)_{0.75}Na_{0.25}O$.

[Claim 5] The material according to one of claims 1 or 2, wherein the oxide does not comprise any of the elements selected from Ni and Cu, or the material contains neither of elements Ni or Cu.

[Claim 6] The material according to any one of claims 1 to 5, wherein the value of x is greater than or equal to 0.20.

[Claim 7] A solid electrolyte comprising the solid inorganic material according to one of claims 1 to 6.

[Claim 8] A method for manufacturing a solid inorganic material according to one of claims 1 to 6, obtained from a ground mixture of metal oxides and

alkali carbonate, comprising a step of compression of 10^7 to 2.10^8 Pa at a temperature between 25 and 250°C, to obtain a ground and compacted mixture.

[Claim 9] The method for manufacturing a solid inorganic material according to claim 8, obtained from said ground and compacted mixture of metal oxides and alkali carbonate, comprising the following two steps:

1- performing heat treatment to the ground and compacted mixture at a temperature T ≥ 900°C in an air atmosphere; and

2- performing a quenching treatment immediately after step 1, under a partial pressure of oxygen Pox, where 0 Pa ≤ Pox < 2.104 Pa.

[Claim 10] A solid-state battery comprising the following three layers of materials:

- a negative electrode layer;
- a positive electrode layer; and
- a solid electrolyte according to claim 7, positioned between the negative and positive electrode layers.

[Claim 11] The battery according to claim 10, wherein the negative electrode layer comprises at least one metal selected from Li and Na, and the positive electrode layer comprises a ceramic and graphite.

[Claim 12] A thin film comprising the solid-state battery according to one of claims 10 or 11, intended for integration into an electronic apparatus, preferably selected from a smart card, a biotechnology apparatus and a graphing calculator.

[Claim 13] Use of a solid-state battery according to one of claims 10 or 11, selected from integration into an electric vehicle, transportation, large-scale stationary storage, integration into aerospace aircraft, the medical sector and robotics.