

AN ELECTRODE MATERIAL AND A METHOD OF GENERATING THE ELECTRODE MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application makes reference to and claims the benefit of priority of an application for “Carbon Coating Strategies To Improve Electrode Performance of Fluorine Ion Batteries” filed on March 2, 2011, with the United States Patent and Trademark Office, and there duly assigned serial number 61/464,270. The content of said application filed on March 2, 2011, is incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

10 [0002] The present invention relates to an electrode material and a method of generating the electrode material. The present invention also relates to an electrode, in particular, a cathode for a lithium battery.

BACKGROUND

15 [0003] As the energy consumption rate per year increases rapidly, energy storage devices have become more and more important, for example, to regulate or buffer the peak energy flow in portable electronics and for energy transportation. Of the various energy storage devices available currently, lithium ion secondary batteries provide good charge-discharge characteristics and thus have been widely adopted as power sources, in particular in portable electronic devices, amounting to a market of US\$ 5 billion in the energy storage industry.

20 [0004] Notwithstanding the above, limitations in terms of cell voltage, specific capacity and cycle life are still present in existing energy storage devices, which need to be overcome to meet the rapidly increasing demand for high performance electronic devices with improved energy density, reduced fabrication cost, and enhanced safety to users.

25 [0005] In view of the above, there exists a need in the art for improved electrochemical cells that exhibit enhanced performance while maintaining improved stability and safety. In particular, there exists a need for improved electrode materials for electrodes, which
30 constitute an integral part of such electrochemical cells.

SUMMARY OF THE INVENTION

[0006] In a first aspect, the present invention refers to a method of generating an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix. The method comprises

- 5 a) forming a dispersion or a solution comprising a carbon precursor and rare earth metal fluoride nanoparticles;
 - b) drying the dispersion or the solution to obtain a mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles; and
 - c) thermally decomposing the mixture to form the carbon nanostructured matrix
- 10 comprising the rare earth metal fluoride nanoparticles.

[0007] In a second aspect, the present invention refers to an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix obtainable by the method according to the first aspect.

[0008] In a third aspect, the present invention refers to an electrode material comprising

15 rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix.

[0009] In a fourth aspect, the present invention refers to an electrode for an electrochemical cell comprising an electrode material according to the second aspect or the third aspect.

[0010] In a fifth aspect, the present invention refers to a cathode for a lithium battery, the

20 cathode comprising an electrode material according to the second aspect or the third aspect.

[0011] In a sixth aspect, the present invention refers to use of an electrode material according to the second aspect or the third aspect for the manufacture of an electrode.

[0012] In a seventh aspect, the present invention refers to use of an electrode according to the fourth aspect as a cathode in a lithium battery or an anode in a fluoride ion battery.

25 [0013] In an eighth aspect, the present invention refers to a lithium electrochemical cell or battery. The lithium electrochemical cell or battery comprises an anode comprising a material selected from the group consisting of metallic lithium, a lithium alloy and a lithium intercalation material; a cathode comprising an electrode material according to the second aspect or the third aspect; and an electrolyte comprising a lithium ion conductor, wherein the

30 lithium ion conductor allows lithium ion transport between the anode and the cathode during charge and discharge of the lithium electrochemical cell or battery.

[0014] In a ninth aspect, the present invention refers to a fluoride ion electrochemical cell or battery. The fluoride ion electrochemical cell or battery comprises an anode comprising an electrode material according to the second aspect or the third aspect; a cathode comprising a fluoride-containing material; and an electrolyte comprising a fluoride ion conductor, wherein the fluoride ion conductor allows fluoride ion transport between the anode and the cathode during charge and discharge of the fluoride ion electrochemical cell or battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0016] **Figure 1** is a schematic diagram of a state of the art fluoride ion electrochemical cell. In fluoride ion electrochemical cells, the anion charge carrier is fluoride ion (F^-). Similar to lithium ion batteries, fluoride ion electrochemical cells operate on the principle of simultaneous fluoride ion insertion and de-insertion reactions occurring at positive and negative electrodes in concert with electron transport between electrodes as shown in **Figure 1**. During charge and discharge of a fluoride ion electrochemical cell, F^- ions are shuttled between the negative and positive electrodes. The maximum voltage in a fluoride ion electrochemical cell results from differences in the chemical potential of the fluoride ions in the negative electrode and the positive electrode. The positive electrode and negative electrode are respectively high voltage and low voltage fluorides, which are able to reversibly exchange fluoride ions (F^-).

[0017] **Figure 2** is a schematic diagram showing the average working potential for an example fluoride ion electrochemical cell having a LaF_{3-x} negative electrode and a CF_x positive electrode. As can be seen from **Figure 2**, the open-circuit voltage between the typical anodes and cathodes can reach a value of greater than 4.5 V. This is determined by their electrochemical reduction potential. As shown in **Figure 2**, the difference in the electrode potentials for this example is about 4.5 V. The theoretical cell voltage takes into account the La^{3+}/La and the CF_x/F^- redox couples and the open circuit voltage at the end of charge is expected to be 4.5 V, which is larger than that of a conventional lithium ion battery.

[0018] **Figure 3** is a table ("Table I") summarizing the performance comparison of a lithium ion battery and a fluoride ion battery. Theoretical energy density calculated for this

particular cell system is 1560 Wh/kg. We can compare this value with conventional lithium ion battery using LiC_6 and LiCoO_2 as the positive and negative electrodes, which are two representative electrodes. The cell reaction is given as $2\text{LiCoO}_2 + 6\text{C} \rightarrow 2\text{Li}_{0.5}\text{CoO}_2 + \text{LiC}_6$. The theoretical energy density of this particular cell is 420 Wh/kg. It gives rise to a ratio of 3.7 as compared to the theoretical energy density for the example fluoride ion electrochemical cell and the example lithium ion battery described above. Other than the specific energy density, other advantages in term of cost, safety, achievable voltage are listed in Table I.

[0019] **Figure 4** is a schematic flow diagram depicting a procedure for LaF_2 nanofibers synthesis.

[0020] **Figure 5** is a schematic flow diagram depicting a procedure for LaF_3 particles in carbon matrix synthesis.

[0021] **Figure 6** is a schematic flow diagram depicting a procedure for carbon coated LaF_3 particles in carbon matrix synthesis.

[0022] **Figure 7** are scanning electron microscope (SEM) images of LaF_2 nanofibers (A) before, and (B) after heat treatment. The scale bar in (A)(i) and (B)(i) denotes a length of 10 μm . The scale bar in (A)(ii) and B(ii) denotes a length of 5 μm .

[0023] **Figure 8** is a schematic diagram depicting LaF_2 nanofibers.

[0024] **Figure 9** is a x-ray diffraction (XRD) spectrum of carbon coated LaF_2 nanofibers.

Referring to the spectrum, Point A denotes the peak which signifies the presence of LaF_2 lanthanum fluoride, while Point B denotes the diffraction angle for experimental pattern-carbon coated LaF_3 nanofibers where no such peak is present.

[0025] **Figure 10** is an energy-dispersive x-ray spectroscopy (EDX) spectrum of carbon coated LaF_2 nanofibers.

[0026] **Figure 11** are scanning electron microscope (SEM) images of LaF_3 particles in carbon matrix (A) before, and (B) after heat treatment. The scale bar in (A)(i) and (B)(i) denotes a length of 10 μm . The scale bar in (A)(ii) and (B)(ii) denotes a length of 5 μm .

[0027] **Figure 12** are field emission scanning microscope (FESEM) images of LaF_3 particles in carbon matrix after heat treatment.

[0028] **Figure 13** is a schematic diagram depicting LaF_3 particles in carbon matrix.

[0029] **Figure 14** is a x-ray diffraction (XRD) spectrum of LaF_3 particles in carbon matrix.

[0030] **Figure 15** is an energy-dispersive x-ray spectroscopy (EDX) spectrum of LaF_3 particles in carbon matrix.

[0031] **Figure 16** is a thermal gravimetric analysis (TGA) spectrum of LaF_3 particles in carbon matrix before heat treatment.

5 [0032] **Figure 17** is a thermal gravimetric analysis (TGA) spectrum of LaF_3 particles in carbon matrix after heat treatment.

[0033] **Figure 18** are scanning electron microscope (SEM) images of 7.5 wt% LaF_3 particles in carbon matrix (A) before, and (B) after heat treatment. The scale bar in (A)(i) and (B)(i) denotes a length of 10 μm . The scale bar in (A)(ii) and (B)(ii) denotes a length of 5 μm .

10 [0034] **Figure 19** are scanning electron microscope (SEM) images of 5 wt% LaF_3 particles in carbon matrix (A) before, and (B) after heat treatment. The scale bar in (A)(i) and (B)(i) denotes a length of 10 μm . The scale bar in (A)(ii) and (B)(ii) denotes a length of 5 μm .

[0035] **Figure 20** are scanning electron microscope (SEM) images of polyethylene glycol (PEG) (8 wt%) coated LaF_3 particles in carbon matrix.

15 [0036] **Figure 21** are field emission scanning electron microscope (FESEM) images of PEG (8 wt%) coated LaF_3 particles in carbon matrix.

[0037] **Figure 22** is a x-ray diffraction (XRD) spectrum of (A) PEG coated LaF_3 powder and (B) pure LaF_3 powder.

20 [0038] **Figure 23** is a thermal gravimetric analysis (TGA) spectrum of PEG coated LaF_3 powder compared with pure LaF_3 powder.

[0039] **Figure 24** are scanning electron microscope (SEM) images of carbon coated LaF_3 particles with carbon matrix. The scale bar in (A)(i) and (B)(i) denotes a length of 10 μm . The scale bar in (A)(ii) and (B)(ii) denotes a length of 5 μm .

25 [0040] **Figure 25** are field emission scanning electron microscope (FESEM) images of carbon coated LaF_3 particles with carbon matrix.

[0041] **Figure 26** is a schematic diagram depicting carbon coated LaF_3 in carbon matrix.

[0042] **Figure 27** is a x-ray diffraction (XRD) spectrum of carbon coated LaF_3 particles in carbon matrix.

30 [0043] **Figure 28** is an energy-dispersive x-ray spectroscopy (EDX) spectrum of carbon coated LaF_3 particles in carbon matrix.

[0044] **Figure 29** is a thermal gravimetric analysis (TGA) spectrum of carbon coated LaF_3 particles in carbon matrix before heat treatment.

[0045] **Figure 30** is a thermal gravimetric analysis (TGA) spectrum of carbon coated LaF_3 particles in carbon matrix after heat treatment.

[0046] **Figure 31** is a schematic diagram showing the set-up of a electrochemical cell used for the electrochemical testing of the electrode.

5 [0047] **Figure 32** is a graph of voltage (V) against specific capacity (mA.h/g) comparing the performance of (1) LaF_3 powder; (2) LaF_3 particles in carbon matrix; (3) LaF_3 particles in carbon matrix sintered at 300 °C; and (4) LaF_3 particles in carbon matrix sintered at 400 °C.

[0048] **Figure 33** is a graph of voltage (V) against specific capacity (mA.h/g) comparing the performance of (1) LaF_3 powder; and (2) PEG (8 wt%) coated LaF_3 powder.

10 [0049] **Figure 34** is a graph of voltage (V) against specific capacity (mA.h/g) comparing the performance of (1) LaF_3 particles in carbon matrix sintered at 400 °C; (2) LaF_3 particles in carbon matrix sintered at 300 °C; (3) PEG (8 wt%) coated LaF_3 particles in carbon matrix at 300 °C; (4) PEG (16 wt%) coated LaF_3 particles in carbon matrix at 300 °C; (5) PEG (24 wt%) coated LaF_3 particles in carbon matrix at 300 °C.

15 [0050] **Figure 35** is a graph of voltage (V) against specific capacity (mA.h/g) comparing the performance of (1) LaF_3 particles in carbon matrix sintered at 400 °C; (2) PEG (8 wt%) coated LaF_3 particles in carbon matrix at 400 °C; (3) PEG (16 wt%) coated LaF_3 particles in carbon matrix at 400 °C; (4) PEG (24 wt%) coated LaF_3 particles in carbon matrix at 400 °C.

[0051] **Figure 36** is (A) scanning electron microscope (SEM) image of synthesized LaF_3 particles; and (B) a x-ray diffraction (XRD) spectrum of synthesized LaF_3 .

20 [0052] **Figure 37** shows the x-ray diffraction (XRD) spectra of (A) $\text{Pb}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$; (B) $\text{Ca}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$; (C) $\text{Pb}_{0.50}\text{La}_{0.50}\text{F}_{2.50}$; (D) $\text{Ca}_{0.50}\text{La}_{0.50}\text{F}_{2.50}$.

[0053] **Figure 38** is a graph showing the discharge performance of (1) pure LaF_3 , (2) $\text{Pb}_{0.5}\text{La}_{0.5}\text{F}_{2.5}$; and (3) $\text{Ca}_{0.5}\text{La}_{0.5}\text{F}_{2.5}$.

25 [0054] **Figure 39** is (A) a scanning electron microscope (SEM) image; and (B) x-ray diffraction (XRD) spectra for carbon coated LaF_3 electrospun nanofiber.

[0055] **Figure 40** is a graph showing the discharge performance of (1) carbon coated LaF_3 electrospun nanofiber; and (2) pure LaF_3 .

[0056] **Figure 41** are graphs showing the performance of synthesized electrode material in
30 lithium batteries as cathode. **Figure 41A** is a graph showing the electrochemical discharge behaviour of nanoparticles comprising fluorides, for (1) $\text{La}_{0.5}\text{Pb}_{0.5}\text{F}_{2.5}$; (2) LaF_3 ; (3) PbF_2 ; and (4) $\text{La}_{0.3}\text{Pb}_{0.7}\text{F}_{2.3}$; embedded in a carbon nanostructured matrix in lithium battery as a cathode.

Figure 41B is a graph showing the electrochemical discharge behaviour of nanoparticles comprising fluorides, for (1) LaF_3 ; (2) $\text{La}_{0.3}\text{Pb}_{0.7}\text{F}_{2.3}$; (3) $\text{La}_{0.5}\text{Pb}_{0.5}\text{F}_{2.5}$; (4) $\text{La}_{0.7}\text{Pb}_{0.3}\text{F}_{2.7}$ and (4) PbF_2 , embedded in a carbon nanostructured matrix in lithium battery as a cathode, as a function of dopant amount. The dopant used is lead (Pb).

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DETAILED DESCRIPTION OF THE INVENTION

[0057] In a first aspect, the present invention refers to a method of generating an electrode material, where the electrode material includes rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix.

10 [0058] The method comprises, in a first step, forming a dispersion or a solution comprising a carbon precursor and rare earth metal fluoride nanoparticles. The term ‘carbon precursor’ as used herein refers to a material that can be carbonized by thermal decomposition. A carbon precursor may include an inorganic carbon-containing compound or an organic carbon-containing compound. Examples of inorganic carbon-containing
15 compounds include, but are not limited to, carbides, carbonates, simple oxides of carbon, and cyanides. Examples of organic carbon-containing compounds include, but are not limited to, hydrocarbons such as alkanes, olefins, arenes, alcohols, aldehydes, ketones and thioethers, and polymers.

[0059] Examples of carbon precursor that may be used include, but are not limited to,
20 polyvinyl alcohol (PVA), polyacrylonitrile (PAN), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), polycarbonate, polyester, polyether, polyalkene, polyimide, natural crop, natural sugar, synthetic sugar, natural oil, synthetic oil, petrochemical, polyol, resorcinol–formaldehyde polymer, and mixtures thereof. In various embodiments, the carbon precursor is a polymer. Polymers may broadly be classified as natural occurring polymers,
25 such as proteins, starches, cellulose, and latex, and synthetic polymers such as synthetic rubber, and bakelite, for example. Generally, any polymer may be used to form the dispersion or the solution of the present invention. For example, the carbon precursor may be polyvinyl alcohol. As another example, the carbon precursor may be polyacrylonitrile.

[0060] The method includes forming a dispersion or a solution comprising the carbon
30 precursor and rare earth metal fluoride nanoparticles. The term “dispersion” as used herein refers to a suspension of solid particles finely dispersed in a liquid medium. For example, the carbon precursor may be dispersed in a non-solvent to form a dispersion of the carbon

precursor(s). The term “solution”, on the other hand, refers to a liquid medium having one or more substances dissolved therein. For example, a solvent may be used to at least substantially dissolve the carbon precursor(s) to form a solution. In embodiments in which the carbon precursor is in the form of a liquid, such as, natural oil or a polymer melt, the term “solution” is also used to refer to the liquid carbon precursor.

[0061] One or more carbon precursors may be used in combination to form the dispersion or the solution. Depending on the type of carbon precursor(s) used, one or more liquid media may optionally be used to form the dispersion or the solution. Examples of a liquid medium include, but are not limited to, water; hydrocarbon solvents such as n-hexane, benzene and toluene; alcohol based solvents such as methanol and ethanol; ketone solvents such as acetone, methylethyl ketone and methyl-isobutyl ketone; ester-based solvents such as ethyl acetate and butyl acetate; ether-based solvents such as diethylether, diethylene glycol, dimethylether, tetrahydrofuran and dioxane; halogen-based solvents such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, tetrachloroethylene, chlorobenzene and ortho-chlorobenzene; and polar solvents such as acetonitrile, N,N-dimethylformamide (DMF), N,N-dimethylimidazolidinone, dimethylsulfoxide and sulfolane. Each liquid medium may be used singly or in combination with another liquid medium. In some embodiments, a polymer may be dissolved in a liquid medium, such as a solvent, to form a polymer solution. In one embodiment, the liquid medium is water, and polyvinyl alcohol (PVA) is dissolved in water to form the solution. In another embodiment, the liquid medium is N,N-dimethylformamide and polyacrylonitrile (PNA) is dissolved in N,N-dimethylformamide to form the solution.

[0062] The method includes adding rare earth metal fluoride nanoparticles to the dispersion or the solution comprising the carbon precursor. In various embodiments, a liquid medium may additionally be used, and the rare earth metal fluoride nanoparticles may be added to the liquid medium prior to adding the carbon precursor. The carbon precursor may also be added to the liquid medium prior to adding the rare earth metal fluoride nanoparticles. In embodiments in which the carbon precursor is a liquid, the rare earth metal fluoride nanoparticles may be added directly to the carbon precursor.

[0063] In some embodiments, the rare earth metal fluoride nanoparticles are doped with another metal. The term “doped rare earth metal fluoride nanoparticles” as used herein refers to rare earth metal fluoride nanoparticles that comprise other metal atoms (“dopants”) in the

nanoparticles, while maintaining its parent structure. It does not require formation of a single phase in which the dopant or the doped metal substitutes the rare earth metal atoms.

[0064] In various embodiments, the rare earth metal fluoride nanoparticles may be doped with another metal to form mixed metal fluoride nanoparticles, so as to enhance the performance of the rare earth metal fluoride nanoparticles. In some embodiments, metals such as calcium, lead, zinc and copper are doped into lanthanum fluoride nanoparticles. The presence of dopants in the rare earth metal fluoride nanoparticles may result in improved fluoride ion conduction in the electrode material formed.

[0065] The rare earth metal fluoride nanoparticles that are used in the present invention may be described by Formula (I)



[0067] where M^1 is a trivalent metal; M^2 is a divalent metal; M^3 is a monovalent metal; wherein either one or both M^1 and M^2 comprises a rare earth metal; and $0 \leq x \leq 0.75$; $0 \leq y \leq 0.75$; $0 \leq x + y \leq 0.75$; and $x + 2y < 3$.

[0068] M^1 may be a trivalent metal or an alloy formed from two or more trivalent metals. Examples of M^1 that may be used to form the rare earth metal fluoride nanoparticles include scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), beryllium (B), aluminium (Al), gallium (Ga), indium (In), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), niobium (Nb), molybdenum (Mo), ruthenium (Ru), and rhodium (Rh), and mixtures thereof.

[0069] In various embodiments, M^1 is a trivalent rare earth metal. As used herein, the term "trivalent rare earth metal" refers to a rare earth element having a valence or oxidation state of +3. For example, M^1 may be a trivalent rare earth metal selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. The rare earth elements are trivalent in their most common form, with some rare earth elements, such as cerium (Ce) and praseodymium (Pr), also exhibiting a valence of +4, and other rare earth elements, such as europium (Eu) and thulium (Tm) also exhibiting a valence of +2. In one embodiment, M^1 is lanthanum.

[0070] M^2 may be a divalent metal, or an alloy formed from two or more divalent metals. As used herein, the term "divalent metal" refers to an element having a valence or oxidation state of +2. Examples of a divalent metal include, but are not limited to, an element from the

class of alkaline earth metals belonging to Group 2 of the Periodic Table of Elements, such as beryllium, magnesium, calcium, strontium, and barium. A divalent metal may also refer to a transition metal element having a valence or oxidation state of +2. Examples of transition metal elements exhibiting a valence of +2 include, but are not limited to, manganese (Mn), iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn). M^2 may also be a divalent rare earth metal, such as europium.

[0071] In various embodiments, M^2 is a divalent metal selected from the group consisting of magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), iron (Fe), zinc (Zn), copper (Cu), lead (Pb), europium (Eu), samarium (Sm), ytterbium (Yb), titanium (Ti), manganese (Mn), germanium (Ge), molybdenum (Mo), ruthenium (Ru), palladium (Pd), silver (Ag), cadmium (Cd), and mixtures thereof. In some embodiments, M^2 is lead or calcium.

[0072] M^3 may be a monovalent metal, or an alloy formed from two or more monovalent metals. As used herein, the term "monovalent metal" refers to an element having a valence or oxidation state of +1. Examples of a monovalent metal include, but are not limited to, an element from the class of alkali metals belonging to Group 1 of the Periodic Table of Elements, such as lithium (Li), sodium (Na), potassium (K), cesium (Cs), rubidium (Rb), silver (Ag), copper (Cu), gold (Au), mercury (Hg), and thallium (Tl). In some embodiments, M^3 is lithium, sodium or potassium.

[0073] Either one or both M^1 and M^2 comprises a rare earth metal to form the rare earth metal fluoride nanoparticles. For example, M^1 may be lanthanum and M^2 may be magnesium. In some embodiments, M^1 and M^2 may refer to the same metal. For example, both M^1 and M^2 may be europium. M^2 and M^3 may otherwise be termed as the "dopants" of the rare earth metal fluoride nanoparticles. Generally, M^1 , M^2 and/or M^3 are present in the rare earth metal fluoride nanoparticles in a molar ratio according to that set out in Formula (I). In various embodiments, the value of x is such that $0 \leq x \leq 0.75$. For example, x may be in the range: $0 \leq x \leq 0.5$, such as $0 \leq x \leq 0.25$. In various embodiments, the value of y is such that y is $0 \leq y \leq 0.75$. For example, y may be in the range: $0 \leq y \leq 0.5$, such as $0 \leq y \leq 0.25$. The values of x and y may relate to each other by the equations $0 \leq x + y \leq 0.75$, and $x + 2y < 3$. For example, the values of x and y may be in the range of $0 \leq x + y \leq 0.5$ or $0 \leq x + y \leq 0.25$. Generally, the smaller the values of x and/or y translates into a smaller percentage of dopants in the rare

earth metal fluoride nanoparticles, and decreases the likelihood of forming a second phase of the fluoride compound of the dopants.

[0074] In some embodiments, $x = 0$ and $y = 0$, i.e. the rare earth metal nanoparticles are not doped with another metal. Referring to Formula (I), the rare earth metal nanoparticles may be described by M^1F_3 . When $M^1 = La$, for example, such a nanoparticle may be LaF_3 .

[0075] The method according to the present invention includes forming the rare earth metal fluoride nanoparticles, by reacting a M^1 -salt with an ammonium-based fluoride via a co-precipitation mechanism.

[0076] Suitable M^1 -salts that may be used in the present invention include the respective nitrate, chloride, iodide, bromide, sulphate, oxalate, citrate, acetate, formate, oxide, hydroxide, oxide-hydroxide, or carbonate of M^1 . Suitable ammonium-based fluorides that may be used include ammonium fluoride or tetra alkyl ammonium fluoride. Generally, the M^1 -salt and ammonium-based fluoride are reacted in amounts that correspond to the stoichiometric ratio of M^1 to F in the rare earth metal nanoparticles. For example, to form lanthanum fluoride (LaF_3) nanoparticles, lanthanum nitrate hexahydrate and ammonium fluoride may be used as the M^1 -salt and ammonium-based fluoride respectively, and reacted in water in amounts sufficient to achieve a La:F ratio of 1:3 in the formed particles.

[0077] In some embodiments, $y = 0$, i.e. M^3 is not present and the rare earth metal nanoparticles is doped with M^2 only. Referring to Formula (I), the rare earth metal nanoparticles may be described by $M^1_{1-x}M^2_xF_{3-x}$. When $M^1 = La$, $M^2 = Ca$, and $x = 0.5$ for example, the nanoparticle may be $La_{0.5}Ca_{0.5}F_{2.5}$. When $M^1 = La$, $M^2 = Pb$, and $x = 0.25$ for example, the nanoparticle may be $La_{0.75}Pb_{0.25}F_{2.75}$. The method according to the present invention includes forming the rare earth metal fluoride nanoparticles, by reacting a M^1 -salt with M^2 -nitrate and an ammonium-based fluoride via a co-precipitation mechanism. Suitable M^1 -salts and ammonium-based fluorides that may be used have already been discussed herein. Generally, the M^1 -salt and M^2 -nitrate are reacted in amounts that correspond to the stoichiometric ratio of M^1 to M^2 in the doped rare earth metal nanoparticles. For example, to form $La_{0.75}Pb_{0.25}F_{2.75}$ nanoparticles, the M^1 -salt, the M^1 -nitrate and the ammonium-based fluoride may refer respectively to lanthanum nitrate hexahydrate, lanthanum nitrate and ammonium fluoride. The molar ratio of lead nitrate to lanthanum nitrate hexahydrate in the solution may be 0.25:0.75, which translates into a molar ratio 1:3. In various embodiments,

M¹-nitrate hexahydrate and M²-nitrate are mixed in water, afterwhich ammonium fluoride solution may be added to the solution.

[0078] The co-precipitation reaction to obtain the rare earth metal nanoparticles may be conducted at any suitable temperature and for a length of time sufficient to form the rare earth metal nanoparticles. In embodiments where water is used as the solvent, the reaction is also referred to as a water-based co-precipitation reaction. In various embodiments, the reaction between lanthanum nitrate hexahydrate ammonium fluoride in water to form LaF₃ nanoparticles is allowed to take place for 45 minutes.

[0079] An optional separation process such as centrifugation may be used to separate the formed rare earth metal nanoparticles from the excess reagent. The rare earth metal nanoparticles collected may be purified by washing the nanoparticles, for example, with deionized water and/or ethanol.

[0080] The weight percentage of the rare earth metal fluoride nanoparticles in the dispersion or the solution comprising the carbon precursor may range from about 5 % to about 25 %, such as about 5 % to about 10 %, about 10 % to about 25 % or about 8 % to about 15 %. In an embodiment, the weight percentage of rare earth metal fluoride nanoparticles in the dispersion or the solution is about 10 %, which has been found by the inventors of the present invention to be an optimal value in achieving an improved yield of nanofibers in embodiments where electrospinning of the dispersion or the solution is used to form nanofibers comprising the carbon precursor and the rare earth metal fluoride nanoparticles..

[0081] Typically, the rare earth metal fluoride nanoparticles do not react with the liquid medium or the carbon precursor. In other words, the rare earth metal fluoride nanoparticles may remain dispersed in the dispersion or the solution comprising the carbon precursor. The rare earth metal fluoride nanoparticles may be dispersed homogeneously in the dispersion or the solution. The term “homogeneously” is used to describe a composition, solution or mixture whose elements are at least substantially uniformly dispersed in each other. Accordingly, the rare earth metal fluoride nanoparticles may be at least substantially uniformly dispersed in the dispersion or the solution to form a homogeneous solution.

[0082] In various embodiments, the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 500 nm, such as between about 5 nm to about 200 nm, between about 5 nm to about 100 nm, between about 5 nm to about 20 nm or

between about 20 nm to about 200 nm. The term “maximal dimension” as used herein refers to the maximal dimension of the nanoparticle in any direction, since the dimension of a nanoparticle is not always regular, i.e. perfectly spherical. In one embodiment, the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 20 nm.

[0083] The method according to the present invention includes drying the dispersion or the solution to obtain a mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles. The dispersion or the solution comprising the carbon precursor and the rare earth metal fluoride nanoparticles may be dried using any suitable means. For example, the dispersion or the solution comprising the carbon precursor and the rare earth metal fluoride nanoparticles may be dried using an oven. Another suitable means to dry the dispersion or the solution is by spray drying and by spray coating. The drying temperature may be any suitable temperature that is able to drive away the liquid medium comprised in the dispersion or the solution. In embodiments in which a liquid polymer is used, the drying temperature may be any suitable temperature that is able to drive away the water molecules, for example, that may be absorbed or adsorbed by the polymer. The drying temperature may depend on the type of liquid medium and carbon precursor used. In one embodiment, a drying temperature of 90 °C is used when the liquid medium is water and the carbon precursor is polyvinyl alcohol.

[0084] In various embodiments, the method of generating an electrode material may further comprise electrospinning the dispersion or the solution to form nanofibers comprising the carbon precursor and the rare earth metal fluoride nanoparticles prior to the drying step. In one embodiment, the carbon precursor is a polymer, and electrospinning is used to form polymeric nanofibers. In various embodiments, electrospinning is used to form polymeric nanofibers from a solution formed from a water-soluble polymer, such as polyvinyl alcohol, dissolved in water. In general terms, electrospinning refers to a process that is used to produce fibers from a polymer solution or polymer melt. Typically, an electrospinning apparatus useful for spinning nanofibers from a polymer solution includes a spinneret, such as a metallic needle, a syringe and syringe pump, a high voltage supply, and a metal collector which is grounded. The solution, which typically includes a polymer and a solvent, is loaded into the syringe and is driven to the needle tip by the syringe pump, so that a droplet is formed at the needle tip. An electrostatic field is used to generate a positively charged jet

from the syringe to the grounded collector. When the polymer solution within the syringe is charged, the droplet is drawn toward the grounded collector. Moving with high velocity as the jet of solution from the needle tip to the grounded collector, the jet is stretched and the solvent in the polymer solution evaporates. This result in the nanofibers being formed, which are spread out onto the collector.

[0085] Generally, the polymeric nanofibers formed may comprise rare earth metal fluoride nanoparticles which are embedded in the polymeric nanofibers. Depending on the relative dimensions of the polymeric nanofibers and rare earth metal fluoride nanoparticles, for example, the rare earth metal fluoride nanoparticles may be entirely contained within each polymeric nanofiber and/or partially contained within each polymeric nanofiber, i.e. a portion of the nanoparticle may be exposed outside of each polymeric nanofiber. The dimensions of the polymeric nanofibers may depend on factors such as the type of polymer and solvent used, the concentration of rare earth metal nanoparticles in the polymer solution, and parameters such as driving voltage used for electrospinning. The width of the nanofibers may be between about 5 nm to about 500 nm, such as about 50 nm to about 500nm, about 200 nm to about 500 nm, about 100 nm to about 400 nm or about 400 nm.

[0086] The method of generating an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix according to the present invention includes thermally decomposing the mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles to form the carbon nanostructured matrix comprising the rare earth metal fluoride particles.

[0087] Generally, the temperature at which the thermal decomposition of the mixture is carried out depends on the type of carbon precursor(s) used. Typically, thermal decomposition of the carbon precursor(s) is carried out at a temperature of about 300 °C to about 900 °C, such as about 300 °C, about 400 °C, about 500 °C or about 900 °C. In one embodiment, polymeric nanofibers formed from polyvinyl alcohol is decomposed at a temperature of about 300 °C. In another embodiment, polymeric nanofibers formed from polyacrylonitrile (PAN) is decomposed at a temperature of about 900 °C. The heat treatment of the mixture may be carried out in an inert gas environment, whereby inert gases, such as argon and helium, may be used.

[0088] The term “nanostructured” refers to the building structure of a material, such as grains, particles, fibers, and filaments, having a size with order of magnitude in the

nanometer range. In various embodiments, the carbon nanostructured matrix comprises carbon present in the form of nanograins, nanoparticles, nanofibers, nanofilaments, or mixture thereof. In various embodiments, the carbon nanostructured matrix comprising the rare earth metal fluoride particles forms a network of interconnecting carbon nanostructures, which may further enhance the electrical conductivity of the sample and facilitate the electrolyte transport through the electrode. By interconnecting the rare earth metal fluoride particles using the network of carbon nanostructures, this may lead to a better energy storage performance and the rate performance of the resultant material due to reduction of the ohmic resistance across the material. In the nanostructured matrix comprising the rare earth metal fluoride nanoparticles, carbon can be present on the surface of the rare earth metal fluoride nanoparticles and/or be present between the rare earth metal fluoride nanoparticles so as to provide a continuous easy path for electrons and for ion transport in the electrode.

[0089] In some specific embodiments, the carbon precursor is a polymer and electrospinning is used to form polymeric nanofibers, which are thermally decomposed to form carbon nanofibers. The dimensions of the carbon nanofibers may be affected by factors such as the dimensions of the polymeric nanofibers and the concentration of rare earth metal nanoparticles in the matrix. In various embodiments, the width of the carbon nanofibers is between about 5 nm to about 200 nm, such as about 5 nm to about 100 nm, about 5 nm to about 50 nm, or about 50 to about 150 nm.

[0090] The method of generating an electrode material according to the present invention may further comprise coating the rare earth metal fluoride nanoparticles with a layer of carbon. The rare earth metal fluoride nanoparticles may be coated with a layer of carbon prior to adding to the dispersion or the solution comprising the carbon precursor. In preparing the carbon coating on the rare earth metal fluoride nanoparticles, the nanoparticles may first be dispersed in a dispersion or a solution comprising a second carbon precursor to form a mixture comprising the second carbon precursor and the rare earth metal fluoride nanoparticles.

[0091] Examples of carbon precursors that may be used for this purpose include, but are not limited to, polyethylene glycol (PEG), polycarbonate, polyester, polyether, polyalkene, polyimides, natural crops, natural sugar, synthetic sugar, natural oil, synthetic oil, petrochemical, polyol, resorcinol-formaldehyde polymer, and mixtures thereof. Generally, the second carbon precursor that is used to coat the nanoparticles is different from the carbon

precursor that is used to form the carbon nanostructured matrix. In one embodiment, the second carbon precursor is polyethylene glycol, which is dissolved in water is used to coat the rare earth metal fluoride nanoparticles, while polyvinyl alcohol is used as the carbon precursor to form the carbon nanostructured matrix.

5 [0092] The concentration of carbon precursor in the dispersion or the solution may range from about 5 wt % to about 25 wt %, such as about 5 wt % to about 10 wt %, or about 8 %. In one embodiment, a polymer solution containing 8 wt % polyethylene glycol in water is used to coat the rare earth metal fluoride nanoparticles.

[0093] The mixture comprising the second carbon precursor and the rare earth
10 nanoparticles may be subjected to a heat treatment to thermally decompose the mixture comprising the second carbon precursor and rare earth metal fluoride nanoparticles to form a layer of carbon on the rare earth metal fluoride nanoparticles. Generally, the temperature at which thermal decomposition of the mixture is carried out depends on the type of second carbon precursor(s) used. Typically, thermal decomposition of the mixture is carried out at a
15 temperature of between about 300 °C to about 500 °C. In one embodiment, polymeric coating formed from polyethylene glycol on the nanoparticles is decomposed at a temperature of about 300 °C.

[0094] In a second aspect, the present invention refers to an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix
20 obtainable by the method according to the first aspect. The invention also provides for an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix, according to a third aspect. In some embodiments, the electrode material according to the second aspect or the third aspect consists of rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix.

25 [0095] The rare earth metal fluoride nanoparticles may be doped with another metal. Suitable metals that may be used to dope the rare earth metal fluoride nanoparticles have already been discussed herein.

[0096] The rare earth metal fluoride nanoparticles may have Formula (I). In various embodiments, the electrode material includes rare earth metal fluoride particles comprising
30 LaF_3 , $\text{Pb}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$, $\text{Ca}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$, $\text{Pb}_{0.50}\text{La}_{0.50}\text{F}_{2.50}$, $\text{Ca}_{0.50}\text{La}_{0.50}\text{F}_{2.50}$, and combinations thereof. In one embodiment, the rare earth metal fluoride nanoparticles are nanocrystalline LaF_3 . It has been found by the inventors from the present invention that nanocrystalline LaF_3

have a much better ionic conductance than single crystal LaF_3 , or LaF_3 with much larger crystalline size, and are therefore very suitable for use in electrode material.

[0097] The electrode material may include rare earth metal fluoride particles which are at least partially coated with a second layer of carbon. Methods in which the second layer of carbon may be formed on the rare earth metal fluoride particles have already been discussed herein.

[0098] The average thickness of the second layer of carbon may be in the range of about 25 nm to about 80 nm, such as about 25 nm to about 60 nm, or about 25 nm to about 40 nm. The carbon coated rare earth metal fluoride particles may be embedded within the carbon nanostructured matrix. In some embodiments, the carbon nanostructured matrix comprises carbon nanofibers. In some embodiments, the carbon nanostructured matrix consists of carbon nanofibers. The carbon nanofibers may have a width of about 5 nm to about 500 nm. In various embodiments, the weight percentage of the rare earth metal fluoride particles in the carbon nanostructured matrix ranges from about 50 % to about 95 %, such as about 70 % to about 80 %.

[0099] In a fourth aspect of the invention, the electrode material formed by a method of generating an electrode material according to the first aspect and the electrode material according to the third aspect of the invention may be used to form an electrode for an electrochemical cell.

[00100] The term “electrochemical cell” refers to a device that converts chemical energy into electrical energy, and from electrical energy into chemical energy. The term “battery” in the general sense refers to a device comprising one or more electrochemical cells for the production of electricity. Each electrochemical cell may comprise an electrolyte, a cathode, and an anode.

[00101] The term “electrolyte” as used herein refers to an ionic conductor through which electricity may be conducted. Examples of electrolyte include, but are not limited to, inorganic lithium salts such as LiF , LiClO_4 , LiAsF_6 , LiPF_6 , Li_2CO_3 , and LiBF_4 ; fluorine containing organic lithium salts such as LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, lithium 1,2-tetrafluoroethane disulfonylimide; dicarboxylic acid containing lithium salt complexes, such as lithium bi(oxalate)borate; and sodium salts and potassium salts, such as KPF_6 , NaPF_6 , NaBF_4 and NaCF_3SO_3 , and their combination. In various embodiments, LiF and LiPF_6 in ethylene carbonate:diethyl carbonate (EC:DEC) is used as the electrolyte.

[00102] The terms “cathode” and “anode” refer respectively to the electrodes at which reduction and oxidation occur during battery discharge. During charging of the battery, the sites of oxidation and reduction are reversed. In an electrochemical cell, the cathode or positive electrode has a higher electrode potential compared to the anode or negative electrode. The term “electrode potential” refers to a voltage, which may be measured against a reference electrode, due to the presence within or in contact with the electrode of chemical species at different oxidation or valance states.

[00103] The electrode according to various embodiments of the invention may further comprise a conductive diluent, such as carbon black, powdered graphite, coke, carbon fiber and metallic powder. In further embodiments, a binder, such as a fluoropolymer, may additionally be present to keep the ion and electron conduction in the electrodes stable. In one embodiment, polyvinylidene fluoride (PVDF) is used as the binder.

[00104] The electrode may be formed by depositing a slurry comprising the electrode material, the conductive diluent, the binder and a suitable liquid carrier on an electrode current collector, with subsequent evaporation of the liquid carrier. In various embodiments, a solvent such as N-methyl-2-pyrrolidone is used as the liquid carrier. The electrode current collector may be any suitable electrical conductor. In one embodiment, copper foil is used as the electrode current collector, onto which the slurry is coated to form the electrode.

[00105] The electrode according to various embodiments of the present invention may be used as an anode in a fluoride ion battery. In various embodiments, the positive electrode and negative electrode reversibly exchange fluoride ions with the electrolyte during charging and discharging of the battery. Accordingly, the fluoride ions may function like anion charge carriers in the electrochemical cell. For example, during discharge of the battery, fluoride ions may be released from the positive electrode and accommodated by the negative electrode. Similarly, during charging of the battery, fluoride ions may be released from the negative electrode and accommodated by the positive electrode. The term “accommodating” refers generally to intercalation of fluoride ions into a host material, and may also include reaction of fluoride ions with the host material. The electrode material that is used to form the electrode may therefore function as a fluoride ion host material to accommodate the ions.

[00106] In various embodiments, the electrode may also be used as a cathode in a lithium battery, such as a lithium primary battery or a lithium ion rechargeable battery. In this regard, a fifth aspect of the invention refers to a cathode for a lithium battery, the cathode comprising

an electrode material according to the second aspect or the third aspect. It has been surprisingly found by the inventors of the present invention that the electrode formed from an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix has an improved electrode potential, which makes it suitable as a cathode in a lithium ion battery. Referring to Example 8 and Figures 32 to 35, for example, it has been found that the electrode potential is increased by a factor of more than 2.5 times as compared to an electrode formed using rare earth metal nanoparticles alone, the value of which is in the range of about 2.5 V to about 3.5 V. As a further example, it can be seen from Figure 41, which are graphs showing the electrochemical discharge behavior of a cathode in a lithium electrochemical cell, wherein the cathode comprises an electrode material according to various embodiments of the invention, that rare earth metal fluoride nanoparticles which are doped with another metal, as in the case for $\text{La}_{0.7}\text{Pb}_{0.3}\text{F}_{2.7}$ and $\text{La}_{0.5}\text{Pb}_{0.5}\text{F}_{2.5}$, increases the capacity of the electrochemical cell. Of these, the cathode which comprises rare earth metal fluoride nanoparticles of $\text{La}_{0.5}\text{Pb}_{0.5}\text{F}_{2.5}$ demonstrated a largest increase in capacity, or amount of electric charge, of the lithium electrochemical cell.

[00107] The electrode according to various embodiments of the invention may be used in many areas. For example, it may be used in both primary and secondary cationic, anionic and mixed ion-type electrochemical cells. Specific examples of application areas of the electrode include, but are not limited to, a supercapacitor, a sensor, a hybrid electrochemical device, or a rechargeable battery or a metal-air battery.

[00108] In another aspect, the present invention refers to a lithium electrochemical cell or battery. The lithium electrochemical cell or battery comprises an anode, a cathode and an electrolyte. The anode comprises a material selected from the group consisting of metallic lithium, a lithium alloy, a lithium alloying material and a lithium intercalation material. For example, the anode may be formed from a lithium alloying material such as Al, Bi, Cd or a lithium intercalation material, such as carbon and graphite. The cathode comprises an electrode material in accordance with the second aspect or the third aspect. The electrolyte comprises a lithium ion conductor, wherein the lithium ion conductor allows lithium ion transport between the anode and the cathode during charge and discharge of the lithium electrochemical cell or battery. In various embodiments, an inorganic lithium salt, such as LiF, LiClO_4 , and Li_2CO_3 , dissolved in a suitable solvent is used as the electrolyte.

[00109] In a further aspect, the present invention refers to a fluoride ion electrochemical cell or battery. The fluoride ion electrochemical cell or battery comprises an anode, a cathode and an electrolyte. The anode comprises an electrode material in accordance with the second aspect or the third aspect. The cathode comprises a fluoride-containing material. Examples of fluoride-containing material include, but are not limited to, metal fluorides such as LaF_3 , CaF_2 , MgF_2 , BaF_2 , CeF_3 , and CaCeF_2 . Generally, any type of fluoride-containing material, in which the electrode potential of a cathode comprising or consisting the fluoride-containing material is higher compared to the anode, may be used. Accordingly, the fluoride-containing material of the cathode in a fluoride ion electrochemical cell is different from the inventive electrode material used to form the anode. The electrolyte in the fluoride ion electrochemical cell or battery according to the present invention comprises a fluoride ion conductor, wherein the fluoride ion conductor allows fluoride ion transport between the anode and the cathode during charge and discharge of the fluoride ion electrochemical cell or battery. In various embodiments, the electrolyte is a metal fluoride, comprising Na, K, Rb, Mg, and/or Ca, for example, dissolved in a suitable solvent so as to generate fluoride ions in the electrolyte.

[00110] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[00111] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[00112] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

5

EXPERIMENTAL SECTION

[00113] **Example 1: Formation of polyvinyl alcohol (PVA) solution**

[00114] A polyvinyl alcohol (PVA) polymer solution was prepared using the following procedure. A suitable amount of PVA was dissolved in water at 140 °C to make a 15 wt%
10 PVA solution, in view that a higher concentration of PVA gives a more viscous solution and is easier to form fibers (less droplets). The PVA polymer was added slowly to allow dissolution of the polymer in solution, and the solution was stirred overnight at 140 °C.

[00115] **Example 2: Synthesis of carbon coated LaF₂ nanofibers**

[00116] **Figure 4** is a schematic flow diagram depicting a procedure for LaF₂ nanofibers
15 synthesis.

[00117] 10 wt% of lanthanum nitrate and ammonium fluoride, which are LaF₂ precursors, were dissolved using a stoichiometric ratio of La:F = 1:3 directly into the PVA solution and stirred overnight at 80°C.

[00118] Subsequently, the solution was electrospun to obtain nanofibers. The parameters
20 for electrospinning are as follow:

[00119] A) Voltage: 15 kV; B) Needle size: 0.4 mm (27 G) – 0.6 mm (23 G); C) Flowrate: 2 ml/h; D) Distance from needle tip to collector: 10 cm.

[00120] In view that a high temperature and quick temperature increase may result in heterogeneous nanofibers and broken fibers, heat treatment of lanthanum fluoride / PVA
25 composite nanofibers was carried out at 500 °C for 7 hours at a heating rate of 4 °C/min, , to convert PVA into carbon. Carbon coated LaF₂ nanofibers were attained.

[00121] **Example 3: Synthesis of LaF₃ particles in carbon matrix**

[00122] **Figure 5** is a schematic flow diagram depicting a procedure for LaF₃ particles in carbon matrix synthesis.

30 [00123] Lanthanum nitrate and ammonium fluoride (LaF₃ precursors) were dissolved in water at a stoichiometric ratio of La:F = 1:3. The resultant solution was stirred for at least 45

minutes, and centrifuged for 3 cycles (1st and 3rd cycles with deionized (DI) water and 2nd cycle with ethanol). Subsequently, the solution was dried using an oven to form LaF_3 powder.

[00124] Various weight concentrations of LaF_3 powder in solution, at 10 wt%, 7.5 wt% and 5 wt% of LaF_3 , were prepared. For a 10 wt% LaF_3 solution, for example, 10 wt% of the LaF_3 powder was added into PVA solution (refer Example 1), and the solution was stirred overnight at a temperature of 80 °C. Electrospinning of the solution was to obtain nanofibers.

[00125] Lanthanum fluoride / PVA composite nanofibers were heat treated at 300 °C for 1 hour at a heating rate of 1 °C/min. LaF_3 particles in carbon matrix was obtained.

[00126] **Example 4: Synthesis of carbon coated LaF_3 particles in carbon matrix**

[00127] **Figure 6** is a schematic flow diagram depicting a procedure for carbon coated LaF_3 particles in carbon matrix synthesis. Carbon coating of LaF_3 particles was carried out to increase the conductivity of the fluoride material. LaF_3 powder was first coated with polyethylene glycol (PEG) before mixing with the PVA solution (refer Example 1). The procedure used is as follows:

[00128] Various concentrations of PEG, at 8 wt%, 16 wt% and 24 wt% PEG in solution, were used for carbon optimization. For preparing a 8 wt% PEG solution, for example, LaF_3 powder was mixed and stirred in PEG solution using a weight ratio of 92:8 for 24 hours. The solution was dried at 90 °C to evaporate off the water and PEG coated LaF_3 powder was collected. The PEG coated LaF_3 powder was coated at 300 °C for 1 hour to convert PVA to carbon, and carbon coated LaF_3 powder was obtained.

[00129] 10 wt% of carbon coated LaF_3 powder was dissolved into the PVA solution and stirred overnight at a temperature of 80 °C. Electrospinning was carried out obtain nanofibers. Heat treatment of Lanthanum fluoride / PVA composite nanofibers was carried out at 300 °C for 1 hour using a heating rate of 1 °C/min. Carbon coated LaF_3 particles in carbon matrix were obtained.

[00130] **Example 5: Characterization of LaF_2 nanofibers**

[00131] Scanning Electron Microscope was used to characterize the LaF_2 nanofibers that were obtained using the general methodology outlined in Example 2. **Figure 7** are scanning electron microscope (SEM) images of LaF_2 nanofibers (A) before, and (B) after heat treatment. From **Figure 7**, it can be seen that nanofibers of LaF_2 were obtained after electrospinning. The fibers do not break and retain their shapes after heat treatment. It was also observed that after heat treatment, the carbon coated LaF_2 nanofibers are thinner and

their structures assume a more wavy/curly appearance. **Figure 8** is a schematic diagram depicting LaF_2 nanofibers.

[00132] It is first expected that LaF_3 nanofibers will be formed from this experiment. However, from the x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX) results shown in **Figure 9** and **Figure 10** respectively, it can be seen that the nanofibers attained using lanthanum fluoride (LaF) precursors (at a ratio of 1:3) are carbon coated LaF_2 nanofibers and not LaF_3 . A few possible reasons for this may be due to firstly, the high sintering temperature of 300°C may have resulted in the decomposition of LaF_3 into LaF_2 , or LaF_2 is formed instead of LaF_3 when the precursors are mixed into PVA solution. The presence of carbon is due to the conversion of PVA into carbon after heat treatment at 300°C . Thus in the next experiment, preformed LaF_3 powder is mixed directly into PVA solution with the aim of spinning out LaF_3 fibers.

[00133] **Example 6: Characterization of LaF_3 particles in carbon matrix**

[00134] **Example 6.1: 10 wt % of LaF_3 powder**

[00135] **Figure 11** are scanning electron microscope (SEM) images of LaF_3 particles in carbon matrix (A) before, and (B) after heat treatment. From the SEM pictures, it can be seen that fibers with embedded particles are formed. Before heat treatment, the particles were LaF_3 and the long, straight fibers were PVA. After heat treatment at 300°C , the fibers became thinner and curlier, which may be due to the conversion of PVA into carbon matrix, while the particles remain as LaF_3 .

[00136] **Figure 12** are field emission scanning microscope (FESEM) images of LaF_3 particles in carbon matrix after heat treatment. From the images, it can be seen that LaF_3 particles were irregularly stacked on top of carbon matrix. The dark colored spots denote the LaF_3 particles, while the light colored lines / tubes denote the carbon matrix. **Figure 13** is a schematic diagram depicting LaF_3 particles in carbon matrix.

[00137] **Figure 14** is a x-ray diffraction (XRD) spectrum of LaF_3 particles in carbon matrix. **Figure 15** is an energy-dispersive x-ray spectroscopy (EDX) spectrum of LaF_3 particles in carbon matrix. The XRD and EDX results show the presence of LaF_3 and carbon in the spun out fibers. It confirms the analysis that LaF_3 particles with carbon matrix have been synthesized using the general methodology outlined in Example 3.

[00138] **Figure 16** is a thermal gravimetric analysis (TGA) spectrum of LaF_3 particles in carbon matrix before heat treatment. The decomposition temperature of PVA to carbon was

about 300 °C. From **Figure 16**, it can be seen that all of the PVA fibers (61.47 %) have been decomposed off as carbon at a temperature of about 500 °C, leaving 38.53 % of LaF₃ as residue. As the spun out fiber was heated up to 300 °C, it can be concluded that out of 61.47 % of PVA, about 39 % (100 % - 61.73 %) of PVA would have evaporated off at 300 °C, which contributed to the weight loss. The remaining 23.7 % (61.73 % - 38.03 %) of PVA remained as carbon matrix. This acted as further support that LaF₃ particles with carbon matrix were successfully synthesized.

[00139] **Figure 17** is a thermal gravimetric analysis (TGA) spectrum of LaF₃ particles in carbon matrix after heat treatment. The thermal gravimetric analysis (TGA) result after heat treatment as shown in **Figure 17** justified the presence of carbon even after heat treatment, as there is a weight loss of 20.76 % at 800 °C due to evaporation of carbon.

[00140] Example 6.2: 7.5 wt% and 5 wt% of LaF₃ powder

[00141] Specific capacitance of a battery is dependent on the weight of active material. The active material in this case was LaF₃. Therefore, the amount of LaF₃ powder to be mixed into PVA solution was reduced to 7.5 wt% and 5 wt% for battery performance comparison and optimization.

[00142] **Figure 18** are scanning electron microscope (SEM) images of 7.5 wt% LaF₃ particles in carbon matrix (A) before, and (B) after heat treatment. **Figure 19** are scanning electron microscope (SEM) images of 5 wt% LaF₃ particles in carbon matrix (A) before, and (B) after heat treatment.

[00143] There were no structural changes to the fibers by reducing the amount of LaF₃ powder to 7.5 wt% and 5 wt%. Just like the results from 10 wt%, long straight fibers were obtained before heat treatment, and thinner, curlier fibers after heat treatment. However, by reducing the amount of LaF₃ powder, the yield of spun out fibers was very little (less than 20 milligrams for 4 hours of electrospinning). As a result, the amount of LaF₃ powder to be mixed into PVA solution was fixed at 10 wt%.

[00144] **Example 7: Characterization of carbon coated LaF₃ particles in carbon matrix**

[00145] For this experiment, LaF₃ powder was first coated with PEG and sintered to form carbon coated LaF₃ powder, before mixing into PVA solution. The characterization results are as follow:

[00146] **Figure 20** are scanning electron microscope (SEM) images of polyethylene glycol (PEG) (8 wt%) coated LaF_3 particles in carbon matrix. **Figure 21** are field emission scanning electron microscope (FESEM) images of PEG (8 wt%) coated LaF_3 particles in carbon matrix.

[00147] From the FESEM pictures in **Figure 21**, it can be seen that carbon coating was successfully done on LaF_3 powder. The thickness of the carbon layer (light colored) surrounding LaF_3 particles varied from about 25 nm to about 80 nm.

[00148] **Figure 22** is a x-ray diffraction (XRD) spectrum of (A) PEG coated LaF_3 powder and (B) pure LaF_3 powder. Comparing with the XRD spectra of pure LaF_3 powder, it can be concluded that the composition of carbon coated LaF_3 powder did not change and the lanthanum fluoride particles remained as LaF_3 . The presence of carbon is confirmed by the TGA results below.

[00149] The presence of carbon in carbon coated LaF_3 powder was established from the TGA results shown in **Figure 23**. **Figure 23** is a thermal gravimetric analysis (TGA) spectrum of PEG coated LaF_3 powder compared with pure LaF_3 powder. There was a weight loss of 16 % at 500 °C for PEG coated LaF_3 powder compared to negligible weight loss for pure LaF_3 powder. This is because of carbonization that occurred after 300 °C due to the presence of PEG.

[00150] The successfully synthesized carbon coated LaF_3 was then mixed with PVA solution and spun out. The characterization results were as follows.

[00151] **Figure 24** are SEM pictures of the carbon coated LaF_3 particles in carbon matrix, which showed the same results as the previous sample (LaF_3 particles in carbon matrix) in **Figure 11**. Fibers with embedded particles were formed. Before heat treatment, the particles were LaF_3 and the long, straight fibers were PVA. After heat treatment at 300 °C, the fibers became thinner and curlier due to conversion of PVA into carbon to form the carbon matrix, while the particles remained as LaF_3 .

[00152] **Figure 25** are field emission scanning electron microscope (FESEM) images of carbon coated LaF_3 particles with carbon matrix. Comparing the FESEM pictures between carbon coated LaF_3 particles with carbon matrix in **Figure 25**, and LaF_3 particles with carbon matrix in **Figure 12**, it can be seen that there was an extra layer of carbon covering the LaF_3 particles in **Figure 25** which was not seen in **Figure 12**. This means that carbon coated LaF_3 particles were successfully spun out with carbon matrix. The average thickness of the carbon

layer ranged from about 25 nm to about 80 nm. **Figure 26** is a schematic diagram depicting carbon coated LaF_3 in carbon matrix.

[00153] **Figure 27** is a x-ray diffraction (XRD) spectrum of carbon coated LaF_3 particles in carbon matrix. **Figure 28** is an energy-dispersive x-ray spectroscopy (EDX) spectrum of carbon coated LaF_3 particles in carbon matrix. The XRD and EDX results showed the presence of LaF_3 and carbon in the spun out fibers. It confirmed the analyses that carbon coated LaF_3 particles with carbon matrix had been synthesized.

[00154] The decomposition temperature of PVA to carbon was about 300 °C. **Figure 29** is a thermal gravimetric analysis (TGA) spectrum of carbon coated LaF_3 particles in carbon matrix before heat treatment. **Figure 30** is a thermal gravimetric analysis (TGA) spectrum of carbon coated LaF_3 particles in carbon matrix after heat treatment. From **Figure 29**, it can be seen that all of the PVA fibers (76.75 %) were decomposed off as carbon at a temperature of about 500 °C, and 22.65 % of LaF_3 was left behind as residue. As the spun out fiber was heated up to 300 °C, it can be concluded that out of 76.75 % of PVA, 25 % (100 % - 75 %) of PVA would have evaporated off at 300 °C which contributed to the weight loss. While the remainder 51.75 % (76.75 % - 25 %) of PVA remained as carbon matrix. Comparing with the TGA result of LaF_3 particles with carbon matrix (**Figure 16** and **Figure 17**), it can be observed that the amount of carbon in carbon coated LaF_3 particles with carbon matrix was more, which was due to the carbon coating layer surrounding LaF_3 particles. This further demonstrated that carbon coated LaF_3 particles with carbon matrix were successfully synthesized.

[00155] The TGA result after heat treatment (**Figure 30**) was to justify the presence of carbon even after heat treatment as there was a weight loss of 36.85 % at 800 °C due to evaporation of carbon.

[00156] **Example 8: Electrochemical Cell Testing**

[00157] Battery performances of the electrospun lanthanum fluorides were tested as a coin cell in half-cell configuration. The fluoride ion cell construction is shown in **Figure 31** in which lithium metal foil acted as the cathode, and LaF active material as the anode. LaF was first mixed and stirred with polyvinylidene difluoride (PVDF) and carbon black using a weight ratio of 80:15:5 to form a slurry solution, with N-Methyl-2-pyrrolidone (NMP) as the solvent. The slurry was then coated on copper foil with a thickness of 25 μm to form the anode.

[00158] The charge/discharge condition of LaF_3 half cell used, using battery tester for testing, was as follow:

[00159] Charge / Discharge current: 0.1 mA

[00160] Cycle 1: Charge up to 3.5

5 [00161] Discharge to 0.01 V

[00162] Electrolyte: 0.5 M LiF + 1 M LiPF_6 in EC:DEC

[00163] The 1st cycles of the electrochemical cell testing of the various LaF_3 based active materials are shown in **Figures 32 to 34**. In **Figure 32**, it was observed that the spun out LaF_3 particles in carbon matrix (56 mAh/g) produced higher specific capacity than pure LaF_3 powder (28 mAh/g). The specific capacity of the LaF_3 particles in carbon matrix was further increased after heat treatment. This was due to presence of carbon which was converted from PVA at high temperature. Specific capacity values of LaF_3 particles of 108 mAh/g at 300 °C, and 132 mAh/g at 400 °C were obtained.

15 [00164] As carbon helped to increase the specific capacity of the fluoride-ion battery, LaF_3 powder was coated with polyethylene glycol (PEG). This was to increase the amount of carbon, contributed by PEG, in the active material. PEG indeed increased the specific capacity of LaF_3 powder as shown in **Figure 33**, whereby the specific capacity of LaF_3 powder was increased from 28 mAh/g to 41 mAh/g.

20 [00165] Although PEG (8%) coated LaF_3 powder has higher specific capacity than pure LaF_3 powder, it was not reflected in the spun out fibers as shown in **Figure 34**. All three weight concentration of PEG (carbon) coated LaF_3 particles in carbon matrix have lower specific capacity than LaF_3 particles in carbon matrix. This may be due to the presence of an excessive amount of carbon in the active material which reduced the overall capability of the battery.

25 [00166] Increasing the heating temperature to 400 °C would reduce the amount of carbon. However, it increased the performance of the PEG (carbon) coated LaF_3 particles in carbon matrix to almost the same level as the LaF_3 particles in carbon matrix as shown in **Figure 35**. This indicates that carbon indeed improved the performance of the battery but not in excessive amount.

30 [00167] Currently, the lithium ion battery has a market of US\$ 5 billion in the energy storage industry. New technology and concept to improve the battery performance that exceeds that of lithium ion battery would explore this market further. Based on the test on the

prototype fluoride ion battery, the energy density may be increased to a much higher value than that of state of the art lithium ion battery. Meanwhile, the fluoride ion battery can eliminate safety issues regarding the usage of lithium ion battery. In lithium ion battery, the possible formation of lithium metal on the cathodes may cause short circuit or even explosion, which would not happen in the fluoride ion battery. The overall fabrication cost will also reduce as the electrode materials are much cheaper for fluoride ion battery.

[00168] The lithium ion battery has demonstrated its important applications in various fields, including portable electronic devices, air and space craft technologies, and biomedical instrumentation. The fluoride battery with cheaper fabrication, wider operation voltage, wider operation temperature, safer operation will expand the market and give impact on the renovation of the technology.

[00169] From the experimental results according to various embodiments of the invention, it can be seen that there is a great potential in developing fluoride ion batteries which can be integrated into equipments. Therefore, the performance of fluoride ion battery has been improved. Using various embodiments of the invention, energy industry would benefit while maintaining environmental remediation sustainability, as well as enriching the fundamental understanding of the renewable energy storage.

[00170] **Example 9: Synthesis of nanostructured LaF₃ and doped LaF₃**

[00171] The synthesis of nanostructured LaF₃ and doped LaF₃ were done by a simple and cheap water based co-precipitation method. Calcium, lead, copper, cerium and zinc were chosen as dopants in the experiments. First, metal nitrate and ammonium fluoride in were dissolved in deionized water (DI) separately. Then the ammonium fluoride solution will be added into the metal nitrate solution drop by drop under rapid stirring.

[00172] **Example 9.1: Synthesis of nanostructured LaF₃ particles**

[00173] For the synthesis of pure LaF₃, lanthanum nitrate hexahydrate was dissolved in DI water with a concentration of 0.25 M. Subsequently, 2 M of ammonium fluoride salt was dissolved in DI water separately. The molar ratio of lanthanum nitrate hexahydrate to ammonium fluoride used was at least 1:3 to ensure sufficient fluoride ions in solution to form LaF₃. The ammonium fluoride solution was then added to lanthanum nitrate hexahydrate solution in a drop by drop fashion using burette, and which is carried out under vigorous stirring. The solution was stirred for 2 hours after the titration, and the precipitated LaF₃ particles were collected and washed by centrifuging. The LaF₃ particles were centrifuged 3

times, first with DI water, followed by isopropyl alcohol, then lastly with DI water. The sample was left to dry at 90 °C overnight.

[00174] Example 9.2: Synthesis of nanostructured doped LaF₃ particles

[00175] For doped LaF₃ samples, the desired metal nitrate was dissolved with lanthanum nitrate hexahydrate in DI water in a single solution. The ratio of the metal nitrate to the lanthanum nitrate hexahydrate used to prepare the solution was the same as that of the desired molar ratio of the metal ion to the lanthanum ion in the resulted compound. For example, to obtain Pb_{0.25}La_{0.75}F_{2.75}, the molar ratio of lead nitrate to lanthanum nitrate hexahydrate in the solution will be 0.25:0.75 which is 1:3. Subsequently, the ammonium fluoride solution was added in a drop by drop fashion under vigorous stirring. The collection and washing of the sample was the same as that carried out in the synthesis of pure LaF₃ (Example 9.1).

[00176] Example 10: Characterization of the morphology of samples by SEM and XRD

[00177] The morphology and structure of the samples were characterized by scanning electron microscope (SEM) and x-ray diffraction technique (XRD).

[00178] From the XRD results shown in **Figure 36(B)** and **Figure 37**, it can be seen that pure LaF₃ and doped LaF₃ particles were successfully synthesized using a simple and cost effective co-precipitation method, which is suitable for mass production of the material. Dopants such as calcium, lead, zinc and copper have been successfully doped into the lanthanum fluoride, while maintaining the parent structure of lanthanum fluoride, ensuring the excellent fluoride ion conduction in the material.

[00179] Although from **Figure 36(A)**, the particles size of the synthesized LaF₃ seemed to range from few tens of nm to μm in size. However, by applying Scherrer Equation $D = 0.9 \lambda / (B \cos \theta)$, where D is the diameter of nanoparticles (nm); B is the full width at half maximum for the diffraction peak under consideration (rad); λ is the wavelength of the monochromatic X-ray beam; and θ is the diffraction angle (deg), on the XRD result of LaF₃, the crystallite size of the material was calculated to be less than 20 nm in size. In view of the above, it may be concluded that the particles depicted in **Figure 36(A)** were agglomerates of LaF₃ nanocrystals of not more than 20 nm in size.

[00180] Nanocrystalline LaF₃ was shown to have much better ionic conductance than single crystal LaF₃ or LaF₃ with a much larger crystalline size. This proved that excellent

LaF₃ ionic conductor can be produced by a cheap and yet effective water based co-precipitation method.

[00181] XRD spectra in **Figure 37** revealed that up to 25 mole percent of the dopants were successfully doped into LaF₃ while maintaining the LaF₃ parent structure. However, with further addition of a higher amount of dopant of up to 50 mole percent, presence of the second phase, which is the fluoride compound of the dopant, was observed.

[00182] **Example 11: Electrochemical performance of nanostructured LaF₃ particles and doped LaF₃ particles**

[00183] The energy storage performance of the material was tested in a 2 electrodes half-cell with a lithium metal piece as a counter electrode, and the electrolyte used was 0.5 M of LiF dissolved in 1.0 M of LiPF₆ in EC: DEC.

[00184] **Figure 38** shows that by doping LaF₃ with other dopants, it is possible to increase the specific capacitance of LaF₃ from 166 mAh/g to 650 mAh/g for lead doped LaF₃, and from 166 mAh/g to 425mAh/g for calcium doped LaF₃, which amounts to almost 300% and 150% increment respectively.

[00185] **Example 12: Synthesis of carbon-coated electrospun LaF₃ and doped LaF₃ nanofibers**

[00186] Electrical conductivity of the materials has been identified as one of the important factors that would affect the performance of the device. To improve the electrical conductivity of LaF₃, an attempt to interconnect these synthesized LaF₃ and LaF₃ based doped compound into fibrous carbon has been done using electrospinning method.

[00187] To synthesize the carbon coated LaF₃ electrospun nanofiber, the electrospinning solution was prepared by first dissolving 0.5 g of polyacrylonitrile (PAN) into 8 ml of dimethylformamide (DMF) under stirring at 60 °C. Then 1.0 g of the pre-synthesized LaF₃ was added into the PAN solution, and the solution was stirred overnight to obtain a homogenous solution.

[00188] The fibers were electrospun at 12 kV using a feed rate of 1.0 ml/h. The heat treatment of the as-spun fibers was first stabilize the fibers at 280 °C for 1 hour, using a heat ramping rate of 1 °C/min. The fibers were then calcined at 900 °C for 15 minutes, with a ramping rate of 2 °C/min. The heat treatment was carried out under argon. The morphology and structure of the resultant fibers were characterized by SEM and XRD, and the energy

storage performance was studied using a 2 electrodes half-cell with lithium metal piece as counter electrode and 0.5 M of LiF dissolved in 1.0 M of LiPF₆ in EC: DEC as electrolyte.

[00189] Carbon coated LaF₃ electrospun nanofiber were successfully synthesized by electrospinning. The diameter of the fibers was about 400 nm as can be seen in **Figure 39(A)**.

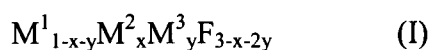
5 A thin layer of carbon was coated on LaF₃ particles, and these particles were interconnected by a carbon nanofiber network, which further enhanced the electrical conductivity of the sample and resulted in a better energy storage performance by reducing the ohmic resistance of the material.

[00190] **Example 13: Electrochemical performance of carbon-coated electrospun LaF₃ and doped LaF₃ nanofibers**

10 [00191] The energy storage performance of the samples was tested in a 2 electrodes half cell with the lithium metal piece as counter electrode, and using an electrolyte of 0.5 M LiF dissolved in 1.0 M of LiPF₆ in EC: DEC. As observed from the discharge curves illustrated in **Figure 40**, the capacitance of the material was increased to 370 mAh/g, which amounted to
15 an increase of about 122 % compared to that for pure LaF₃.

CLAIMS

1. A method of generating an electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix, the method comprising
 - a) forming a dispersion or a solution comprising a carbon precursor and rare earth metal fluoride nanoparticles;
 - b) drying the dispersion or the solution to obtain a mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles; and
 - c) thermally decomposing the mixture to form the carbon nanostructured matrix comprising the rare earth metal fluoride nanoparticles.
2. The method according to claim 1, wherein the carbon precursor is selected from the group consisting of polyvinyl alcohol (PVA), polyacrylonitrile (PAN), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), polycarbonate, polyester, polyether, polyalkene, polyimide, natural crop, natural sugar, synthetic sugar, natural oil, synthetic oil, petrochemical, polyol, resorcinol-formaldehyde polymer, and mixtures thereof.
3. The method according to claim 1 or 2, further comprising doping the rare earth metal fluoride nanoparticles with another metal.
4. The method according to claim 3, wherein the rare earth metal fluoride nanoparticles have Formula (I)



where

M^1 is a trivalent metal;

M^2 is a divalent metal;

M^3 is a monovalent metal;

wherein either one or both M^1 and M^2 comprises a rare earth metal; and

$0 \leq x \leq 0.75$; $0 \leq y \leq 0.75$; $0 \leq x + y \leq 0.75$; and $x + 2y < 3$.

5. The method according to claim 4, wherein $0 \leq x \leq 0.5$ and $0 \leq y \leq 0.5$.
6. The method according to claim 5, wherein $0 \leq x \leq 0.25$ and $0 \leq y \leq 0.25$.
- 5 7. The method according to any one of claims 4 to 6, wherein M^1 is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Cr, Fe, Co, Ni, Nb, Mo, Ru, Rh, and mixtures thereof.
- 10 8. The method according to any one of claims 4 to 7, wherein M^2 is selected from the group consisting of Mg, Ca, Sr, Ba, V, Cr, Co, Ni, Fe, Zn, Cu, Pb, Eu, Sm, Yb, Ti, Mn, Ge, Mo, Ru, Pd, Ag, Cd, and mixtures thereof.
- 15 9. The method according to any one of claims 4 to 8, wherein M^3 is selected from the group consisting of Li, Na, K, Rb, Cs, Ag, Cu, Au, Hg, Tl, and mixtures thereof.
10. The method according to any one of claims 4 to 9, wherein $x = 0$ and $y = 0$.
11. The method according to claim 10, wherein the rare earth metal fluoride nanoparticles are obtained by reacting M^1 -salt with ammonium-based fluoride.
- 20 12. The method according to claim 11, wherein the M^1 -salt is selected from the group consisting of a nitrate, a chloride, an iodide, a bromide, a sulphate, an oxalate, a citrate, an acetate, a formate, an oxide, a hydroxide, an oxide-hydroxide, and a carbonate.
- 25 13. The method according to claim 11, wherein the ammonium-based fluoride is ammonium fluoride or tetra alkyl ammonium fluoride.
- 30 14. The method according to any one of claims 4 to 10, wherein $y = 0$.

15. The method according to claim 14, wherein the rare earth metal fluoride nanoparticles are obtained by reacting M^1 -salt with M^2 -nitrate and ammonium-based fluoride.
- 5 16. The method according to claim 15, wherein the M^1 -salt is selected from the group consisting of a nitrate, a chloride, an iodide, a bromide, a sulphate, an oxalate, a citrate, an acetate, a formate, an oxide, a hydroxide, an oxide-hydroxide and a carbonate.
- 10 17. The method according to claim 15, wherein the ammonium-based fluoride is ammonium fluoride or tetra alkyl ammonium fluoride.
- 15 18. The method according to any one of claims 1 to 17, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the dispersion or the solution is about 5 % to about 25 %.
19. The method according to claim 18, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the dispersion or the solution is about 10 %.
- 20 20. The method according to any one of claims 1 to 19, wherein the rare earth metal fluoride nanoparticles are dispersed homogeneously in the dispersion or the solution.
21. The method according to any one of claims 1 to 20, wherein thermally decomposing the carbon precursor is carried out at a temperature of about 300 °C to about 900 °C.
- 25 22. The method according to claim 1, further comprising coating the rare earth metal fluoride nanoparticles with a layer of carbon prior to step a).
23. The method according to claim 22, wherein the rare earth metal fluoride nanoparticles are coated with a layer of carbon by
- 30 a) dispersing the rare earth metal fluoride nanoparticles in a dispersion or a solution comprising a second carbon precursor to form a mixture

comprising the second carbon precursor and the rare earth metal fluoride nanoparticles; and

- b) thermally decomposing the mixture to form carbon coated rare earth metal fluoride nanoparticles.

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24. The method according to claim 23, wherein the second carbon precursor is selected from the group consisting of polyethylene glycol (PEG), polycarbonate, polyester, polyether, polyalkene, polyimide, natural crop, natural sugar, synthetic sugar, natural oil, synthetic oil, petrochemical, polyol, resorcinol-formaldehyde polymer, and mixtures thereof.

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25. The method according to claim 23 or 24, wherein the second carbon precursor is a different material from the carbon precursor used to form the carbon nanostructured matrix.

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26. The method according to any one of claims 22 to 25, wherein thermally decomposing the mixture is carried out at a temperature between about 300 °C to about 500 °C.

27. The method according to any one of claims 1 to 26, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 500 nm.

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28. The method according to claim 27, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 200 nm.

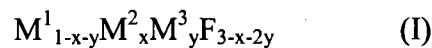
29. The method according to claim 28, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 20 nm to about 200 nm.

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30. The method according to any one of claims 1 to 29, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the carbon nanostructured matrix ranges from about 50 % to about 95 %.

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31. The method according to claim 30, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the carbon nanostructured matrix ranges from about 70 % to about 80 %.
- 5 32. The method according to claim 1, further comprising electrospinning the dispersion or the solution to form nanofibers comprising the carbon precursor and the rare earth metal fluoride nanoparticles prior to step b).
- 10 33. The method according to claim 32, wherein the width of the nanofibers is between about 5 nm to about 500 nm.
34. The method according to claim 1, wherein drying of the dispersion or the solution to obtain a mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles is by spray drying.
- 15 35. The method according to claim 1, wherein drying of the dispersion or the solution to obtain a mixture comprising the carbon precursor and the rare earth metal fluoride nanoparticles is by spray coating.
- 20 36. An electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix obtainable by the method according to any one of claims 1 to 35.
- 25 37. An electrode material comprising rare earth metal fluoride nanoparticles embedded in a carbon nanostructured matrix.
38. The electrode material according to claim 37, wherein the rare earth metal fluoride nanoparticles is doped with another metal.
- 30 39. The electrode material according to claim 37 or 38, wherein the rare earth metal fluoride nanoparticles have Formula (I)



where

M^1 is a trivalent metal;

5 M^2 is a divalent metal;

M^3 is a monovalent metal;

wherein either one or both M^1 and M^2 comprises a rare earth metal; and

$0 \leq x \leq 0.75$; $0 \leq y \leq 0.75$; $0 \leq x + y \leq 0.75$; and $x + 2y < 3$.

- 10 40. The electrode material according to claim 39, wherein $0 \leq x \leq 0.5$ and $0 \leq y \leq 0.5$.
41. The electrode material according to claim 40, wherein $0 \leq x \leq 0.25$ and $0 \leq y \leq 0.25$.
- 15 42. The electrode material according to any one of claims 37 to 41, wherein M^1 is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Cr, Fe, Co, Ni, Nb, Mo, Ru, Rh, and mixtures thereof..
- 20 43. The electrode material according to any one of claims 37 to 42, wherein M^2 is selected from the group consisting of Mg, Ca, Sr, Ba, V, Cr, Co, Ni, Fe, Zn, Cu, and Pb, Eu, Sm, Yb, Ti, Mn, Ge, Mo, Ru, Pd, Ag, Cd, Sm, and mixtures thereof.
- 25 44. The electrode material according to any one of claims 37 to 43, wherein M^3 is selected from the group consisting of Li, Na, K, Rb, Cs, Ag, Cu, Au, Hg, Tl, and mixtures thereof.
45. The electrode material according to any one of claims 37 to 44, wherein $y = 0$.
- 30 46. The electrode material according to claim 45, wherein the rare earth metal fluoride particles are selected from the group consisting of LaF_3 , $Pb_{0.25}La_{0.75}F_{2.75}$, $Ca_{0.25}La_{0.75}F_{2.75}$, $Pb_{0.50}La_{0.50}F_{2.50}$, $Ca_{0.50}La_{0.50}F_{2.50}$, and combinations thereof.

47. The electrode material according to claim 46, wherein the rare earth metal fluoride nanoparticles are nanocrystalline LaF_3 .
- 5 48. The electrode material according to any one of claims 37 to 47, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 500 nm.
49. The electrode material according to claim 48, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 5 nm to about 200 nm.
- 10 50. The electrode material according to claim 49, wherein the maximal dimension of the rare earth metal fluoride nanoparticles is between about 20 nm to about 200 nm.
51. The electrode material according to any one of claims 37 to 50, wherein the carbon nanostructured matrix comprises carbon nanofibers.
- 15 52. The electrode material according to claim 51, wherein the width of the carbon nanofibers is between about 5 nm to about 500 nm.
- 20 53. The electrode material according to any one of claims 37 to 52, wherein the rare earth metal fluoride nanoparticles are at least partially coated with a second layer of carbon.
54. The electrode material according to claim 53, wherein the average thickness of the second layer of carbon is between about 25 nm to about 80 nm.
- 25 55. The electrode material according to any one of claims 37 to 54, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the carbon nanostructured matrix ranges from about 50 % to about 95 %.
- 30 56. The electrode material according to claim 55, wherein the weight percentage of the rare earth metal fluoride nanoparticles in the carbon nanostructured matrix ranges from about 70 % to about 80 %.

57. An electrode for an electrochemical cell comprising an electrode material as referred to in any one of claims 36 to 56.
- 5 58. The electrode according to claim 57, wherein the electrode is a cathode in a lithium battery or an anode in a fluoride ion battery.
59. The electrode according to claim 58, wherein the electrode is an electrode comprised in a supercapacitor; or a sensor; or a hybrid electrochemical device; or a rechargeable
10 battery; or a metal-air battery.
60. A cathode for a lithium battery, the cathode comprising an electrode material as referred to in any one of claims 36 to 56.
- 15 61. Use of an electrode material according to any one of claims 36 to 56 for the manufacture of an electrode.
62. Use of an electrode according to any one of claims 36 to 56 as a cathode in a lithium battery or an anode in a fluoride ion battery.
- 20 63. A lithium electrochemical cell or battery comprising
- a) an anode, the anode comprising a material selected from the group consisting of metallic lithium, a lithium alloy and a lithium intercalation material;
- 25 b) a cathode, the cathode comprising an electrode material according to any one of claims 36 to 56; and
- c) an electrolyte, the electrolyte comprising a lithium ion conductor allowing lithium ion transport between the anode and the cathode during charge and discharge of the lithium electrochemical cell or battery.
- 30 64. A fluoride ion electrochemical cell or battery comprising

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- a) an anode, the anode comprising an electrode material according to any one of claims 36 to 56;
- b) a cathode, the cathode comprising a fluoride-containing material; and
- c) an electrolyte, the electrolyte comprising a fluoride ion conductor allowing fluoride ion transport between the anode and the cathode during charge and discharge of the fluoride ion electrochemical cell or battery.