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(54) Title: POSITIVE ELECTRODE COMPOSITION

(57) Abstract: The present invention relates to an NVPF-based composition and to its use in the field of batteries as electrochemically active material. It also relates to a conductive composition comprising said composition and to a process for obtaining said composition.



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POSITIVE ELECTRODE COMPOSITION

This application claims priority to European patent application No. 23306118.3
5 filed on June 30, 2023, the whole content of this application being incorporated
herein by reference for all purposes.

The present invention relates to an NVPF-based composition and to its use in the
field of batteries as electrochemically active material. It also relates to a conductive
composition comprising said composition and to a process for obtaining said
10 composition.

[Technical background]

The demand for lithium-ion batteries has increased in recent years with regard to
their application in a wide variety of electronic devices, such as portable
15 telephones and electric vehicles. In point of fact, lithium-based compounds are
relatively expensive and natural lithium sources are unequally distributed over the
planet and are not readily accessible as they are localized in a small number of
countries. Alternatives to this element have thus been sought. To this end, sodium-
ion batteries have been developed. This is because sodium is very abundant and
20 distributed homogeneously, and is advantageously nontoxic and economically
more advantageous.

However, the redox potential of the Na^+/Na couple is (-2.71 V vs SHE) and is thus
greater than that of the Li^+/Li couple (-3.05 V vs SHE), for a triple molar mass.
25 These specificities make it difficult to choose a host material. In this context, the
material $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (or NVPF) has proved to be a particularly advantageous
electrochemically active material with regard to its electrochemical performance
qualities. Indeed, NVPF usually shows a reversible capacity of more than 120
mAh/g and exhibits good cycling performance at room temperature.

30 To be used as a cathode active material (CAM), NVPF composition has to possess
not only high ionic conductivity but also good electronic conductivity in order to
efficiently drain electrons towards the current collector during working of the
battery. If both criteria are gathered then high power density can be achieved.

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For this purpose, NVPF particles are generally coated with conductive materials. The conductive material can be of different nature and should not be involved in the electrochemical process contributing to the cycling of the battery. Moreover, the conductive material has to be present in a moderate content in order to maximize the content of pure cathode active material and thus to maximize the energy density of the electrode.

Generally carbon is preferred to play the role of electron conductor while keeping the electrochemical properties of NVPF unchanged.

US2018/0297847 describes NVPF particles obtained through exposing under an inert atmosphere, a mixture of VPO_4 material with an effective amount of sodium fluoride NaF and at least one hydrocarbon- and oxygen- containing compound which is a source of elementary carbon, to temperature conditions that are favourable for calcining said mixture so as to form $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ compound e.g. 800°C during one hour. Cellulose is used as source of carbon. The carbon coating represents 0.5% to 5.0% by weight of the total weight of the material.

US2021/0305549 relates to a NVPF-based composition comprising particles of NVPF as well as carbon in graphitized form. The composition is obtained through calcination at 800°C of an intimate mixture of VPO_4 , NaF and cellulose as source of carbon. The carbon content represents between 1.0% to 3.5% by weight of the total weight of the composition.

The Applicant has experienced that NVPF-based composition prepared from calcination of intimate mixtures of VPO_4 , NaF and at least one hydrocarbon- and oxygen- containing compound as source of elementary carbon (namely cellulose), leads to coated NVPF with only moderate electronic conductivity when keeping a reasonable carbon amount to maintain energy density.

Chemical vapor deposition (CVD) which is generally admitted to be an efficient route to prepare highly conductive carbon, is sometimes used to deposit carbon material onto electrochemically active material for electrode application.

For example, Y.Fang et Al., disclose in Advanced Materials, 2015, 27, 5895-5900, chemical vapor deposition of conductive carbon onto $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP). For this purpose NVP material is introduced in a CVD furnace where acetylene gas

pyrolysis is conducted to generate conductive carbon structure. Acetylene, in mixture with argon, is introduced into the furnace while the furnace temperature is increased to 690°C. The decomposition of acetylene leads to carbon deposition on the surface of NVP.

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Similarly, Y.Zhang et Al., disclose in Journal of Materials Chemistry , 2018, 6, 4525-4534, the chemical vapor deposition of conductive carbon onto $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (or NVPF) . For this purpose NVPF material is introduced in a CVD furnace where acetylene gas pyrolysis is conducted to generate conductive carbon structure. A flow of acetylene, in mixture with argon, is introduced into the furnace while the furnace temperature is increased to 500°C. The decomposition of acetylene leads to carbon deposition on the surface of NVPF. In the particular case of NVPF, working under a gas flow can lead to fluorine departure associated with a partial oxidation of NVPF leading to lower electrochemical performances. Therefore a relatively low temperature (500°C) is set for pyrolysis with the risk of a reduced graphitization of carbon deposit and, finally, of a reduced electronic conductivity.

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Moreover, the handling of acetylene remains difficult because it is a highly flammable gas with some intrinsic instability. Therefore, the use of acetylene generates difficulties linked to its gaseous nature, safety issues and thus additional costs when compared to the use of hydrocarbon- and oxygen- containing compounds such as cellulose which are readily available, stable and easy to handle raw materials.

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[The technical problem]

There is a need for a cathode active material presenting a good trade-off between power density and energy density for Na-ion battery application. $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (or NVPF) is considered as a material of choice for building such cathode active material either considering its high ionic conductivity or considering its high gravimetric energy density i.e. the amount of energy which it may store per unit of weight.

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There is a need for a composition comprising NVPF particles coated with conductive material suitable to efficiently drain electrons generated during the working of the battery towards the current collector.

There is a need for a composition comprising NVPF particles coated with conductive carbon showing an enhanced electronic conductivity. Such composition having a tapped density of at least 0.9 g/ml is also desirable.

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There is a need for a composition comprising NVPF particles coated with conductive carbon having all the desired features described above, wherein resistance of the carbon coating towards oxidation under demanding thermal conditions is improved.

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There is also a need for a process suitable to prepare the above composition.

There is a need for a process involving CVD ensuring thin, pure and highly conductive carbon coating onto NVPF particles. Such a process involving CVD should be performed in conditions not demanding very sophisticated equipment.

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Ideally, this process has to involve readily available and easy to handle raw materials.

An electrode is generally composed of an active material which guarantees the extraction and the reinsertion of the sodium ions as well as a suitable proportion of electrochemically inactive materials, such as the binder or the conductive additive. The conductive additive ensures electron percolation through the electrode. The binder ensures the adhesion to the current collector and the mechanical strength of the composite electrode. The porosity is for its part necessary for the ion percolation between the electrolyte and the active material.

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In order to maximize the gravimetric capacity (expressed in this patent application in mAh/g), an attempt is made to limit the amount of electrochemically inactive materials in the composite, without however compromising the extraction and the reinsertion of the sodium ions of the active material.

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Therefore, there is a need for a composition comprising NVPF particles coated with conductive carbon having all the desired features above described, to be able to be easily formulated with the electrochemically inactive materials and for the resulting conductive composition to be able to be easily coated to form electrode films.

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Finally, there is a need for a sodium ion battery comprising the electrode above described presenting good cycle life durability.

All these needs and more are fulfilled by the composition according to the invention
5 obtained by the process of the invention.

[Brief description of drawings]

Figure 1 represents a plot of electronic conductivity values in mS/cm, as measured at 22°C by a DC method with a two-electrode set-up, as a function of the content,
10 in weight %, of carbon in the NVPF based compositions according to the invention (black solid circles ●) and for comparative NVPF based compositions (white squares □).

[The invention]

15 The invention relates to a process for the preparation of a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, comprising the following steps:
a) providing a mixture of VPO_4 and sodium fluoride;
b) introducing the mixture of step a) next to an oxygen-comprising hydrocarbon
20 compound, which thermally decomposes to give carbon, in a container and closing the container so as to obtain a confined reaction medium;
c) heating the reaction medium of step b) up to a temperature ranging from 700°C to 900°C and maintaining this temperature for a time ranging from 0.5h to 6h so as to form concomitantly NVPF and carbon to arrive to the desired composition
25 wherein carbon is introduced in said composition by chemical vapor deposition.

In step a), the VPO_4 is mixed with the stoichiometric amount of sodium fluoride (NaF) both being in solid form, for example as powders. It is advantageous to use a mixture in which the solids are intimately mixed. In order to obtain a thoroughly
30 intimate mixture, it is possible to use a VPO_4 which has been ground and/or sieved beforehand. For example, use may be made of a ground and sieved VPO_4 which exhibits a Dv_{50} of between 5 and 40 μm and a Dv_{90} between 40 and 100 μm , the distribution itself being determined from a suspension in anhydrous ethanol. The mixture can be prepared by any means suitable to mix solid materials, well known
35 by the person of ordinary skill in the art.

Just for the sake of example, suitable VPO_4 can be prepared according to the method described in US2021/0305549 starting from V_2O_5 and $NH_4H_2PO_4$ as raw materials. Commercially available NaF of high purity can be used. NaF can also be ground and sieved before mixing with VPO_4 .

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In step b), the oxygen-comprising hydrocarbon compound may, for example, be a sugar, such as, for example, glucose, fructose, galactose, saccharose, sucrose or lactose, or a carbohydrate, such as, for example, starch, agar-agar or a cellulose derivative, or lignin. Preferentially, it is a cellulose derivative and more particularly still microcrystalline cellulose. The oxygen-comprising hydrocarbon compound results, by thermal decomposition, in the carbon, in particular in graphitized form or partially graphitized form, which is present in the composition. Therefore, the oxygen-comprising hydrocarbon compound is considered as the carbon source in the process according to the invention.

15

In step b), the stoichiometric mixture of VPO_4 and NaF is not mixed with the oxygen-comprising hydrocarbon compound. The mixture of VPO_4 and NaF is introduced next to an oxygen-comprising hydrocarbon in a container. By next is meant that the mixture of VPO_4 and NaF is not directly in contact with the oxygen-comprising hydrocarbon compound, despite the fact that they are in the same container. There is no limitation in the form and the structure of the container. For example, at lab scale the container can be a parallelepiped rectangle crucible made of alumina that can be introduced in a tubular furnace. The mixture of VPO_4 and NaF, on one hand, and the oxygen-comprising hydrocarbon compound, on the other hand, can be placed in two different small crucibles. The latter can be further placed in the larger parallelepiped rectangle crucible which is then closed with a lid also made of alumina to obtain a confined reaction medium and introduced in the tubular furnace. Still for example, the mixture of VPO_4 and NaF, can be placed on one side of a container separated in two parts by a wall permeable to gas but not to solids, while the oxygen-comprising hydrocarbon compound is placed on the other side.

In step c) the reaction medium of step b) is heated up to a temperature ranging from 700°C to 900°C. In some embodiments, the temperature ranges from 750°C to 850°C. Good results were obtained with a temperature of 800 °C. Generally, the heating is performed using a heating rate of from 4°C/ minute to 50°C/ minute. In

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some embodiments, the heating rate is of from 5°C/ minute to 20°C/ minute. Good results were obtained with a heating rate of 10°C/minute. This temperature is generally maintained for a time ranging from 0.5h to 6h so as to form concomitantly NVPF by calcination of VPO₄ and NaF and carbon by thermal decomposition of the oxygen-comprising hydrocarbon compound to arrive to the desired composition. Preferably the temperature is maintained from 0.5h to 3h, more preferably for 1h. Good results were obtained when maintaining the temperature for 1h at 800°C. For the sake of example, step c) can be conducted by placing the container of step b), which is closed so as to obtain a confined reaction medium, in any furnace such as tubular furnace for heating.

The proportion of the oxygen-comprising hydrocarbon compound in the container, based on VPO₄ and on NaF, was surprisingly found to be related to the final content of carbon in the resulting composition. This proportion may be between 0.5% and 30.0% by weight, indeed even between 5.0% and 25.0%, this proportion being calculated with respect to the combination of the VPO₄ and NaF mixture.

Without being bound by any theory, the inventors assume that during the process the carbon is introduced in the composition by chemical vapor deposition (CVD). The chemical vapor deposition (CVD) may occur onto NVPF particles or onto VPO₄ before NVPF formation. Chemical vapor deposition (CVD) is generally defined as a controlled, gas-phase, chemical process for depositing thin film layers of various materials onto a substrate. According to K.E.Spear, in Pure & Appl.Chem., Vol.54, No 7, p1297-1311,1982, "chemical vapor deposition process is one in which a gaseous phase chemically reacts to produce one or more condensed phases (deposit) plus gaseous product species".

During steps a), b) or c), it is advisable to minimize contact of the reaction medium with oxygen by performing these steps under an inert gas, such as nitrogen or argon. As the calcination is carried out in a confined environment, the presence of oxygen may be limited by the introduction, into the container in which the calcination takes place, of an inert gas, such as nitrogen or argon. The presence of oxygen may be limited by the introduction, into the furnace wherein is placed the container of step b), of an inert gas, such as nitrogen or argon during the calcination for example as a flow. However, since the container of step b), is closed

so as to obtain a confined reaction medium, the contact of the reaction medium with oxygen is rather limited and the use of inert gas is not always required.

The invention also relates to a process for the preparation of a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, comprising the following steps:

a') introducing NVPF next to an oxygen-comprising hydrocarbon compound in a container and closing the container so as to obtain a confined reaction medium;

b') heating the reaction medium of step a') up to a temperature ranging from 700°C to 900°C and maintaining this temperature for a time ranging from 0.5h to 6h so as to arrive to the desired composition wherein carbon is introduced in said composition by chemical vapor deposition.

In step a'), the NVPF is in solid form, for example as powder. It is possible to use a NVPF which has been ground and/or sieved beforehand. For example, use may be made of a ground and sieved NVPF which exhibits a D_{v50} of between 1 and 30 μm and a D_{v90} between 5 and 100 μm , the distribution itself being determined from a suspension in anhydrous ethanol.

Just for the sake of example, suitable NVPF can be prepared according to the method described in the example 1 of US2021/0305549 starting from VPO_4 and NaF as raw materials without adding microcrystalline cellulose. By next is meant as previously described that the NVPF is not directly in contact with the oxygen-comprising hydrocarbon compound, despite the fact that they are in the same container. The set up suitable to operate the process previously described for the mixture of VPO_4 and NaF can also be used for NVPF.

In step b') the reaction medium of step a') is heated up to a temperature ranging from 400°C to 900°C. In some embodiments, the temperature ranges from 500°C to 850°C. Good results were obtained with a temperature of 800 °C. Generally, the heating is performed using a heating rate of from 4°C/ minute to 50°C/ minute. In some embodiments, the heating rate is of from 5°C/ minute to 20°C/ minute. Good results were obtained with a heating rate of 10°C/minute. This temperature is generally maintained for a time ranging from 0.5h to 6h so as to form carbon by thermal decomposition of the oxygen-comprising hydrocarbon compound to arrive to the desired composition. Preferably the temperature is maintained from 0.5h to

3h, more preferably for 1h. Good results were obtained when maintaining the temperature for 1h at 800°C.

5 The proportion of the oxygen-comprising hydrocarbon compound in the container, based on NVPF, was surprisingly found to be related to the final content of carbon in the resulting composition. This proportion may be between 0.5% and 30.0% by weight, indeed even between 5.0% and 25.0%, this proportion being calculated with respect to the NVPF.

10 Without being bound by any theory, the inventors assume that during the process the carbon is introduced in the composition by chemical vapor deposition (CVD) onto NVPF particles.

15 During steps a') or b'), it is advisable to minimize contact of the reaction medium with oxygen by performing these steps under an inert gas, such as nitrogen or argon. As the calcination is carried out in a confined environment, the presence of oxygen may be limited by the introduction, into the container in which the calcination takes place, of an inert gas, such as nitrogen or argon. The presence of oxygen may be limited by the introduction, into the furnace wherein is placed
20 the container of step b), of an inert gas, such as nitrogen or argon during the calcination for example as a flow. However, since the container of step b), is closed so as to obtain a confined reaction medium, the contact of the reaction medium with oxygen is rather limited and the use of inert gas is not always required.

25 The inventors have found that surprisingly, performing the processes according to the invention, it was possible to prepare a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, comprising a carbon content that can be controlled. They also found that these compositions have an enhanced electronic conductivity measured at 4.75 MPa by
30 a direct current (DC) method even for carbon content as low as 0.2%, this content being expressed by weight of the element carbon with respect to the total weight of the composition. This electronic conductivity is generally higher than the conductivity NVPF based composition obtained by process disclosed in prior art at same carbon content.

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Moreover, the inventors have found that, surprisingly, the composition prepared by the process according to the invention allows preparing sodium-ion battery having improved first discharge capacity, expressed in mAh/g measured at different C-rates such as C/10.

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Given the higher electronic conductivity of the product obtained by the process according to the invention, higher capacity retention is expected at high charge rates (such as 1C, 2C, or 5C) in sodium or Na-ion electrochemical cells compared to electrodes prepared with state of the art material.

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Given the higher electronic conductivity of the product obtained by the process according to the invention, higher capacity retention is expected at high discharge rates (such as 2C, 5C, or 10C) in sodium or Na-ion electrochemical cells compared to electrodes prepared with state of the art material.

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Therefore, the invention also relates to a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, characterized by :

- (1) a carbon content of between 0.17% and 3.0%, this content being expressed by weight of the element carbon with respect to the total weight of the composition,
- (2) an electronic conductivity σ expressed in mS/cm such as $\sigma > 4.3717 \times +0.2186$ with x being the carbon content expressed in % by weight with respect to the total weight of the composition;
- wherein the electronic conductivity σ is measured on a sample of said composition pressed at 4.75 MPa by a Direct Current (DC) method.

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The composition of the invention is characterized by its carbon content. The latter is of between 0.17% and 3.0%, this content being expressed by weight of the element carbon with respect to the total weight of the composition. The carbon content is determined by microanalysis.

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Generally, the carbon content is of between 0.17% and 3.0%. In some preferred embodiments, the carbon content is of between 0.17% and 1.0%, more preferably of between 0.20% and 0.9% and even more preferably of between 0.25% and 0.8%, this content being expressed by weight of the element carbon with respect to the total weight of the composition.

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The composition of the invention is also characterized by its electronic conductivity. The electronic conductivity of the NVPF based composition powder can be measured via a Direct Current method. A sample of powder is introduced in a PEEK cell (10mm diameter) with stainless steel plungers (10mm diameter).

5 The cell is placed in a mechanical jig with a force sensor in order to control the applied pressure. The thickness of the powder bed is measured with a digital dial indicator (Mitutoyo). At room temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$), a voltage of 1V is applied on the pressed sample using a VMP-3 potentiostat available from BioLogic at a pressure of 4.75 MPa, the thickness of the powder bed is measured at each step
10 and the value of the current is recorded after 30 seconds when equilibrium is reached .

The electronic conductivity is obtained with the following formula : $\sigma = I \cdot t / (S \cdot V)$ with I the current measured expressed in A, t the thickness of the powder bed expressed in cm, V the voltage expressed in Volt (1V here) and S the surface
15 expressed in cm^2 .

Generally, the electronic conductivity σ expressed in mS/cm is such that $\sigma > 4.3717 \times +0.2186$, with x being the carbon content expressed in % by weight with respect to the total weight of the composition. In some preferred embodiments, the electronic conductivity is such that $\sigma > 6.0730 \times -0.0607$; or such that $\sigma > 8.9879$
20 $\times -0.5393$; or such that $\sigma > 14.5900 \times -1.4590$; or such that $\sigma > 23.9010 \times -2.9876$.

The composition of the invention comprises particles of NVPF, which is optionally partially oxidized. NVPF, which is optionally partially oxidized, is the predominant element of the composition. Its proportion by weight is generally greater than or
25 equal to 92 %, generally greater than or equal to 95 %, generally greater than or equal to 97 % this proportion being expressed with respect to the total weight of the composition. This proportion may be between 92.0% and 99.83% by weight, preferably between 95.0% and 99.83% by weight, more preferably between 97.0% and 99.83% by weight.

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In NVPF of molecular formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, vanadium is present in the +III oxidation state. The NVPF may be partially oxidized. In this case, the product is characterized by the presence also of vanadium in the +IV oxidation state as well as by the partial replacement of fluorine atoms by oxygen atoms. The partially
35 oxidized NVPF may be represented by the formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-x}\text{O}_x$, x being an integer between 0 and 1.0.

The optionally partially oxidized NVPF crystallizes in an orthorhombic unit cell of Amam space group. The unit cell parameter c may be greater than or equal to 10.686 angstroms, indeed even greater than or equal to 10.750 angstroms. It may
5 be substantially equal to 10.750 angstroms. The unit cell parameter a may for its part be between 9.027 and 9.036 angstroms, preferably substantially equal to 9.029 angstroms. The unit cell parameter b may for its part be between 9.038 and 9.045 angstroms, preferably substantially equal to 9.044 angstroms. The unit cell volume V is for its part between 872.604 and 878.390 angstroms³, preferably
10 substantially equal to 878.000 angstroms³.

For NVPF, the unit cell parameter c is between 10.741 and 10.756 angstroms. The unit cell parameter a is between 9.028 and 9.031 angstroms. The unit cell parameter b is between 9.043 and 9.045 angstroms. The unit cell volume V is for
15 its part between 877.335 and 878.390 angstroms³, preferably substantially equal to 878.000 angstroms³.

The composition comprises carbon in graphitized form. Carbon in graphitized form contributes to the electron conductivity at the surface of the NVPF particles. The
20 presence of carbon in graphitized form in the composition may be demonstrated using Raman spectroscopy. More specifically, carbon in graphitized form may be demonstrated by Raman spectroscopy by the presence of a vibration band located between 1580 and 1600 cm⁻¹, more particularly centered around 1590 cm⁻¹. Carbon in graphitized form is obtained by high-temperature thermal decomposition
25 of an oxygen-comprising hydrocarbon compound, as described above. The thermal decomposition also results in the formation of amorphous carbon.

The composition of the invention may exhibit a ratio R of less than or equal to 1.1, preferably of less than or equal to 1.0, indeed even of less than or equal to 0.9, in
30 which:

- R denotes the arithmetic mean of the ratio I_D/I_G calculated over at least 6 measurements carried out at various points of a sample of the composition;
- I_D denotes the intensity of the Raman vibration band centered around 1340 cm⁻¹;
- I_G denotes the intensity of the Raman vibration band centered around 1590 cm⁻¹.

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The vibration band around 1340 cm^{-1} is attributable to amorphous (or disordered) carbon. This band is generally located between 1330 and 1360 cm^{-1} . The vibration band around 1590 cm^{-1} is attributable to graphitized carbon. This band is generally located between 1580 and 1600 cm^{-1} .

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The composition of the invention furthermore exhibits a tapped density TD which is greater than or equal to 0.9 g/ml , indeed even greater than or equal to 1.0 g/ml , indeed even more greater than or equal to 1.1 g/ml or 1.2 g/ml . The tapped density is measured in a known way using a powder tapping device. The tapped
10 density is generally less than or equal to 2.0 g/ml , indeed even less than or equal to 1.8 g/ml , indeed even more less than or equal to 1.5 g/ml .

The composition of the invention may be used as electrochemically active material of electrodes for sodium-ion batteries. The invention also relates to an electrode
15 comprising a conductive composition (CC) comprising the composition of the invention, at least one electron-conducting material and optionally a binder. The proportion of the composition of the invention in the conductive composition (CC) is generally greater than 70.0% by weight, this proportion being with respect to the total weight of the conductive composition. This proportion may be between 70.0%
20 and 98.0% . The proportion of the conductive material is generally less than 30.0% by weight, this proportion being with respect to the total weight of the conductive composition (CC). This proportion may be between 1.0% and 20.0% . More particularly, a conductive composition (CC) may comprise from 80.0% to 98.0% by weight of the composition of the invention, from 1.0% to 15.0% by weight of the
25 conductive material and from 1.0% to 15.0% by weight of binder.

The electron-conducting material may be chosen from carbon fibers, carbon black, carbon nanotubes, graphene and their analogs. An example of conductive material is Super C45 Carbon Black Conductive Additive for Battery Cathode and Anode,
30 available from MSE Supplies®. The binder may advantageously be a polymer. The binder may advantageously be chosen from polytetrafluoroethylene, polyvinylidene fluoride or a copolymer of vinylidene fluoride and of at least one comonomer, such as, for example, hexafluoropropylene, polymers derived from carboxymethylcellulose, polysaccharides and latexes, in particular of
35 styrene/butadiene rubber type. The binder is preferably a copolymer of vinylidene

fluoride and of at least one comonomer, such as, for example, hexafluoropropylene. It may, for example, be the Solef 5130 grade sold by Solvay.

5 The conductive composition may be prepared by mixing together the ingredients which constitute it in the presence of a polar solvent, such as N-methylpyrrolidone. When the viscosity of the mixture is high, a kneader suitable for high viscosities may be used. In the case of a polymeric binder, it is possible, for example, to first dissolve the binder in the NMP, to subsequently add the conductive material with stirring, then the composition according to the invention. The mixture may
10 subsequently be deposited on an aluminum sheet and then the NMP may be evaporated, for example using heating.

The electrode of the invention may be used as a positive electrode of a sodium generator. Advantageously, it is favored for use as a positive electrode for a
15 sodium or sodium-ion storage battery.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description
20 shall take precedence.

[Examples]

Determination of the carbon content

The carbon content is measured by microanalysis using a Horiba EMIA 320 V2
25 brand carbon/sulfur analyzer. The measurement is performed on 80 to 120 mg of sample. The sampled powder is covered by tin, tungsten and iron combustion accelerators.

Electronic conductivity measurement

30 The electronic conductivity of the NVPF powder is measured via a Direct Current method with a two-electrode set-up. A certain quantity of powder (444mg) is introduced in a PEEK cell (10 mm diameter) with stainless steel plungers (10mm diameter). The cell is placed in a mechanical jig with a force sensor in order to control the applied pressure. The thickness of the powder bed is measured with a
35 digital dial indicator (Mitutoyo). At room temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$), a voltage of 1V is applied on the sample using a VMP-3 potentiostat available from BioLogic at a

pressure of 4.75 MPa, the thickness of the powder bed is measured at each step and the value of the current is recorded after 30 seconds when equilibrium is reached. The electronic conductivity is obtained with the following formula : $\sigma = I \cdot t / (S \cdot V)$ with I the current measured expressed in A, t the thickness of the powder bed expressed in cm, V the voltage expressed in Volt (1V here) and S the surface expressed in cm².

Determination of the particle size distribution

The particle size distribution is measured by laser diffraction on a suspension of the particles in ethanol. A Malvern Mastersizer 3000 appliance equipped with the Hydro SV module is used. The tank of the appliance is filled with ethanol (refractive index for ethanol of 1.360) and stirred at 3500 rpm. A few milligrams of powder are then introduced directly into the tank so as to have an obscuration of between 8% and 12%. The optical model used is Fraunhofer.

Determination of the tapped density

A 10 ml (± 0.1 ml at 20°C) class A+ standardized graduated measuring cylinder is used and filled with exactly approximately 7 ml of the loose composition. 2500 blows are imposed before reading the final volume occupied by the tapped powder. The tapped density is then determined by the following formula:

$$TD \text{ (in g/ml)} = \text{weight of composition} / \text{final volume determined}$$

Determination of the powder X-ray diffraction diagram

Powder X-ray diffractograms were obtained in Bragg-Brentano geometry, with fixed slits. Acquisition is carried out between $2\theta = 5^\circ$ and $2\theta = 90^\circ$, on an X Pert Pro MPD assembly from Malvern Panalytical, equipped with a X-ray source with copper anticathode, at a voltage of 45 kV and a current of 40 mA. The detector is an X'Celerator linear detector with an active length of 2.122° . The PHD interval is by default of 37-80%. The K beta emission of copper is filtered with a Bragg-BrentanoHD module. The exposure time is typically 40 seconds with steps of 0.017° . The phase analysis is carried out on HighScore Plus software equipped with the latest version of the ICDD PDF4+ database. The linearity of the goniometer is checked periodically using a polycrystalline silicon standard.

The cell parameters of NVPF phases are obtained by Full Profile Matching using FullProf software, in the Amam space group.

Recording and processing of the Raman spectroscopy spectra

The spectra were recorded on a Horiba HR800 spectrometer between 50 and 2000 cm^{-1} with a 532 nm laser (150 mW nominal power), a 10X objective, a 600 rpm grating, a 10% filter, a 100 μm confocal hole and a 30 x 5 s acquisition time. The software used for the acquisitions and the processing operations is the Labspec version 6.6.1.11. from Horiba. In order to carry out the acquisition, the sample is deposited in the powder form on a calcium fluoride window, itself deposited on a glass slide covered with aluminum. Focusing is carried out on the sample with a 10X objective. After acquisition, the spectra are smoothed and then deconvoluted into two Gaussian-shaped contributions: one centered around 1340 cm^{-1} and the other centered around 1580 cm^{-1} . The intensities are determined from the baseline drawn between two points on the spectrum located at 700 cm^{-1} and at 2000 cm^{-1} .

Preparation of the positive electrodes from the composition of the invention

The conductive compositions (or electrode inks) are prepared by mixing the NVPF-based compositions with carbon black (Super C45 Carbon Black Conductive Additive for Battery Cathode and Anode obtained from MSE Supplies®) and a fluoropolymer (PVDF Solef 5130) in respective proportions by weight of 92:4:4 in the N-methyl-2-pyrrolidone solvent in order to obtain a viscous ink. Mixing is performed using an Ultra-Turrax® Tube Drive, in ST20 tubes, operating at 2000rpm for 30 minutes and then at 4000 rpm for 1.5 hours. This ink, comprising 45 wt% of solid content, is subsequently deposited using a film applicator with a wet thickness of 275 μm on an aluminum sheet of 15 μm thick, then dried at 90°C until complete evaporation of the solvent. The dried electrodes are calendared at 60°C using a MSK-HRP-01 Electric Hot Rolling Cylinder Press available from MTI Corporation, at 100 μm and then 70 μm . They are then cut in 12mm diameter discs and dried under primary vacuum at 120 °C for 12 h before being transferred to a glove box under an argon atmosphere.

Assembly of electrochemical cells of "coin cell" type

The NVPF electrodes are assembled in a half-cell configuration, facing a metallic sodium negative electrode, in a 2032 (20 mm in diameter by 3.2 mm in thickness) button cell geometry. The electrolyte used is composed of an equimassic mixture of ethylene carbonate and of dimethyl carbonate containing one mole per liter of

dissolved sodium hexafluorophosphate salt, a mixture to which is added 1% by weight of mono-fluoroethylene carbonate.

The coin cell consists of the positive electrode of NVPF, the negative electrode of metallic sodium, 100 μ l of electrolyte, a stainless steel current collector with a thickness of 1 mm, a ring-shaped spring with a thickness of 1.4 mm, a fiberglass separator with a 16 mm diameter and of the rigid casing of the cell (two hollow pieces interlocking with a seal). A thin flat layer of metallic sodium is deposited on the current collector, the weight of sodium being sufficient not to be limiting in the system. The separator is placed on top of the cathode, impregnated with electrolyte and the metallic sodium is then added, facing the cathode. These elements are kept under pressure by the spring inside the rigid casing, which is subsequently crimped in order to guarantee the leaktightness of the system.

Electrochemical tests

The cells assembled from NVPF electrodes are electrochemically tested under galvanostatic conditions, between 2.0 V and 4.3 V vs Na^+/Na , starting with the charge (positive current). The current used in charge and in discharge is expressed in C-rate. The C-rate is the measure of the speed at which a battery is charged or discharged. It is defined as the applied current divided by the theoretical current necessary to deliver the theoretical capacity of the battery in one hour. In the present case, it corresponds to the exchange of 2 sodium ions per NVPF. The electrochemical tests are carried out at a C-rate of C/10, corresponding to a theoretical charge or theoretical discharge in 10 hours.

The electrochemical tests make it possible to determine the reversible charging capacity of the NVPF electrodes. This capacity is reported by weight of the composition (active material) and is expressed in mAh/g. Tests are performed at room temperature ($22^\circ\text{C} \pm 2^\circ\text{C}$).

C-rate capability evaluation

The electrochemical tests are carried out following the program consisting of 3 cycles done at C/10 in charge and C/10 in discharge. For each cycle, the capacity and polarization is extracted. For some products, these 3 cycles at C/10 are followed by 3 to 5 cycles at C/5 in charge and C/5 in discharge, C/2 in charge and C/2 in discharge, C/2 in charge and 1C in discharge, C/2 in charge and 2C in

discharge, C/2 in charge and 5C in discharge, C/10 in charge and C/10 in discharge.

Example 1: Preparation of the VPO_4

- 5 Stoichiometric amounts of V_2O_5 and $NH_4H_2PO_4$ are mixed in the presence of 100% by weight of water in a kneader of Controlab L0031.2 type. The proportion of water is calculated by weight with respect to the combination of the two reactants V_2O_5 and $NH_4H_2PO_4$. At the end of approximately 2 hours, the mixture thickens and a yellow-colored paste formed of $NH_4VO_2HPO_4$ (presence confirmed by XRD) and
- 10 of water is obtained. This wet paste is placed in a well-confined environment i.e. the paste is poured into a SiC crucible closed by a SiC lid. The paste is subsequently calcined at 800°C for 3 hours with a temperature rise gradient of 5.5°C/min.
- 15 The VPO_4 which results from the calcination is friable and consists of pieces of between 1 mm and 5 cm. This product is ground using a jar mill for approximately 2.7 hours at a speed of rotation of 27 rpm. Polyethylene jars with a diameter of 10 cm are used, which make it possible to charge the product to be ground with yttria-stabilized zirconia balls with a diameter of 10 mm. The charging ratio may
- 20 be 1 kg of VPO_4 for a charge of 4 kg of balls. The VPO_4 thus ground is extracted from the jars, separated from the balls and sieved at 400 μm using a vibrating sieve which may have a vibrational amplitude of between 0.5 and 1.6. The VPO_4 sieved at 400 μm represents a fraction of between 95% and 98% of the total weight of VPO_4 ground. The product thus ground and sieved exhibits a particle size, the
- 25 Dv_{50} of which is between 5 and 40 μm and the Dv_{90} of which is between 40 and 100 μm .

Example 2: Preparation of the NVPF

- 30 The VPO_4 obtained in example 1 is mixed with a stoichiometric amount of NaF and the mixture of the solids is homogenized and ground beforehand in a polyethylene jar filled with yttria-stabilized zirconia balls by agitating the filled jar in a Turbula® type 3D mixer (balls of 10 mm in a ratio by weight of [VPO_4 + NaF] mixture to balls of 1 to 7). The mixture is then sieved in order to remove zirconia balls.

The intimate mixture of the powders is subsequently calcined at 800°C for 1 hour with a temperature rise gradient of 10°C/min. The powder should be well confined during the calcination. The NVPF is obtained according to XRD with a unit cell parameter c equal to 10.738 angstrom.

5

The NVPF which is obtained is finally deagglomerated in order to obtain the desired particle size distribution. For example, it is possible to carry out a ball milling or an air jet milling. For the air jet milling, an air mill of AFG-100 reference sold by Hosokawa was used. The NVPF is introduced into the grinding chamber using a metering screw. The feed rate of the grinding chamber is adjusted in order to be placed under "steady state" conditions of the fluidized bed thus formed. The pressurized air is introduced into the grinding chamber using nozzles with a diameter of 2 mm at a pressure of 5.5 bars. The finest particles rise into the top part of the grinding chamber. A selector, the rotation of which is between 3000 and 5000 rpm, makes it possible to recover the deagglomerated product.

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Examples 3 to 5: Preparation of the NVPF-based compositions according to the invention (Process A)

The VPO_4 obtained in example 1 is mixed with a stoichiometric amount of NaF and the mixture of the solids is homogenized and ground beforehand in a polyethylene jar filled with yttria-stabilized zirconia balls by agitating the filled jar in a Turbula® type 3D mixer (balls of 10 mm in a ratio by weight of $[VPO_4 + NaF]$ mixture to balls of 1 to 7). The mixture is then sieved in order to remove zirconia balls.

20
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The intimate mixture of the powders is subsequently introduced in a crucible made of alumina, next to 5%, 10% or 20% by weight of microcrystalline cellulose, with respect to the total weight of $VPO_4 + NaF$. Prior to its introduction, the microcrystalline cellulose is ground in a polyethylene jar filled with yttria-stabilized zirconia balls, by agitating the filled jar in a Turbula® type 3D mixer (balls of 10 mm in a ratio by weight of cellulose to balls of 1 to 7). Then the crucible is covered with an alumina lid and placed in a tubular furnace under nitrogen flow (30L/h). The furnace is heated up to 800°C with a temperature rise gradient of 10°C/min and maintained at this temperature for one hour before natural cooling.

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The powder is kept well confined during the calcination. The NVPF-based composition is finally obtained according to XRD. The unit cell parameter c of the

NVPF is respectively equal to 10.753, 10.754 and 10.754 angstrom. The carbon content represents respectively 0.52%, 0.65% and 0.81% by weight of the total weight of the composition. The electronic conductivity measured at 22°C on samples pressed at 4.75 MPa is respectively 17.0 mS/cm, 27.0 mS/cm and 30.0 mS/cm. Example 6: Preparation of the NVPF-based compositions according to the invention (Process B)

NVPF powder of example 2 is introduced in a crucible made of alumina, next to 13% by weight of microcrystalline cellulose, with respect to the total weight of NVPF powder. Prior to its introduction, the microcrystalline cellulose is ground in a polyethylene jar filled with yttria-stabilized zirconia balls, by agitating the filled jar in a Turbula® type 3D mixer (balls of 10 mm in a ratio by weight of cellulose to balls of 1 to 7). Then the crucible is covered with an alumina lid and placed in a tubular furnace under nitrogen flow (30L/h). The furnace is heated up to 800°C with a temperature rise gradient of 10°C/min and maintained at this temperature for one hour before natural cooling.

The powder is kept well confined during the calcination. The NVPF-based composition is finally obtained according to XRD with a unit cell parameter c equal to 10.737 angstrom. The carbon content represents 0.23% by weight of the total weight of the composition. The electronic conductivity measured at 22°C on sample pressed at 4.75 MPa is 3.70 mS/cm.

Example 7: Preparation of the NVPF-based composition according to the invention (Process A)

Example 7 is performed in the same conditions as example 5 except that the intimate mixture of the powders is introduced in a crucible made of alumina, next to 2 distinct portions of microcrystalline cellulose, representing each 10% by weight with respect to the total weight of $VPO_4 + NaF$. Example 7 results in a NVPF-based composition confirmed by XRD. The unit cell parameter c of the NVPF is equal to 10.755 angstrom. The carbon content represents 0.56 % by weight of the total weight of the composition. The electronic conductivity measured at 22°C on samples pressed at 4.75 MPa is 34.0 mS/cm.

Comparative example 1: open crucible

Comparative example 1 is performed in the same conditions as example 6, except that the crucible is not covered with a lid. The NVPF-based composition is finally

obtained according to XRD. The carbon content represents 0.001% by weight of the total weight of the composition. The electronic conductivity measured at 22°C on a sample pressed at 4.75 MPa is $1.56 \cdot 10^{-5}$ mS/cm.

5 Comparative examples 2 to 4:

Comparative examples 2 to 4 are performed in the same conditions as examples 3 to 5, except that the VPO_4 is mixed with a stoichiometric amount of NaF and with respectively 5%, 10% and 20% by weight of microcrystalline cellulose, with respect to the total weight of $VPO_4 + NaF$. The mixture of the solids is homogenized and
10 ground in a polyethylene jar filled with yttria-stabilized zirconia balls by agitating the filled jar in a Turbula® type 3D mixer (balls of 10 mm in a ratio by weight of [$VPO_4 + NaF$] mixture to balls of 1 to 7). The mixture is sieved in order to remove zirconia balls. The mixture is then introduced in the crucible and the crucible is covered with an alumina lid and placed in a tubular furnace under nitrogen flow
15 (30L/h). The furnace is heated up to 800°C with a temperature rise gradient of 10°C/min and maintained at this temperature for one hour before natural cooling. The powder is kept well confined during the calcination. The NVPF-based composition is obtained according to XRD. The unit cell parameter c of the NVPF is respectively equal to 10.755, 10.755 and 10.756 angstrom. The carbon content
20 represents respectively 0.93%, 2.12% and 4.39% by weight of the total weight of the composition. The electronic conductivity measured at 22°C on samples pressed at 4.75 MPa is respectively 1.9 mS/cm, 7.6 mS/cm and 11.4 mS/cm.

Some features of the compositions obtained in examples 3-6 and comparative
25 examples 1 to 4 are reported in table 1.

The composition obtained in comparative example 1 with an open crucible, comprises a very low amount of carbon thus highlighting the importance of operating with a confined reaction medium.

30

Results reported in table 1 show that, by setting the amount of cellulose engaged in the process according to the invention, it is possible to monitor the final content of carbon in the composition (compare examples 3-5).

35 It is clear that, at a similar carbon content, the composition obtained by the process according to the invention has an electronic conductivity at 22°C which is much

higher than a composition obtained as disclosed in prior art (e.g. compare example 5: 0.81wt % of C and $\sigma=30\text{mS/cm}$ with comparative example 2: 0.93wt % of C and $\sigma=1.9\text{mS/cm}$). This statement is even more clear when considering the results reported in figure 1.

5

Moreover, by comparing example 5 and comparative example 2 it is clear that, at a similar carbon content, an electrode prepared from the composition obtained by the process according to the invention has a higher first discharge capacity expressed in mAh/g than an electrode prepared from a composition obtained by a process according to the prior art.

10

Given the higher electronic conductivity of the product obtained by the process according to the invention (see figure 1), higher capacity retention is expected at high charge rates (such as 1C, 2C, or 5C) in sodium or Na-ion electrochemical cells compared to electrodes prepared with state of the art material.

15

Given the higher electronic conductivity of the product obtained by the process according to the invention (see figure 1), higher capacity retention is expected at high discharge rates (such as 2C, 5C, or 10C) in sodium or Na-ion electrochemical cells compared to electrodes prepared with state of the art material.

20

The results reported in Table II relates to the discharge capacity, expressed in mAh/g, of Example 7 according to the invention and of comparative Example 2 for different C-rates. These results evidence that the product according to the invention has advantageously higher discharged capacity in sodium or Na-ion electrochemical cells compared to electrodes prepared with state of the art material for each C-rate.

25

Table I

	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Comp.Ex. 1	Comp.Ex. 2	Comp.Ex. 3	Comp.Ex. 4
wt % of cellulose engaged	5	10	20	15	20	15	5	10	20
Carbon content (wt %)	0.52	0.65	0.81	0.23	0.56	0.001	0.93	2.12	4.39
Electronic conductivity at 22°C (mS/cm)	17.0	27.0	30.0	3.7	34.0	1.56.10 ⁻⁵	1.9	7.6	11.4
c parameter (angstrom Å)	10.753	10.754	10.754	10.737	10.755	n.d.	10.755	10.755	10.756
Raman spectroscopy R=I _D /I _G	0.84	0.86	0.74	n.d.	n.d.	n.d.	0.79	0.80	0.76
Tapped density (g/cm ³)	n.d.	0.99	n.d.	n.d.	n.d.	n.d.	1.02	n.d.	n.d.
First discharge capacity at C/10 (mAh/g)*	n.d.	n.d.	114	n.d.	119	n.d.	111	n.d.	n.d.

*The electrochemical properties have been measured on example 5 with a cathode loading of 11.5 mg/cm² (+/- 10%) and comparative example 2 with a cathode loading of 11.5 mg/cm² (+/- 10%).

Table II

Example	C-rate in charge / discharge	C/10-D/10	C/5-D/5	C/2-D/2	C/2-1D	C/2-2D	C/2-5D	C/10-D/10
	Example 7	119	114	106	103	95	80	117
	Comparative example 2	111	108	91	93	85	70	111

CLAIMS

1. A process for the preparation of a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, comprising the following steps:
- 5 a) providing a mixture of VPO_4 and sodium fluoride;
- b) introducing the mixture of step a) next to an oxygen-comprising hydrocarbon compound, which thermally decomposes to give carbon, in a container and closing the container so as to obtain a confined reaction medium;
- 10 c) heating the reaction medium of step b) up to a temperature ranging from 700°C to 900°C and maintaining this temperature for a time ranging from 0.5h to 6h so as to form concomitantly NVPF and carbon to arrive to the desired composition, wherein carbon is introduced in said composition by chemical vapor deposition.
- 15 2. A process for the preparation of a composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, comprising the following steps:
- a') introducing NVPF next to an oxygen-comprising hydrocarbon compound in a container and closing the container so as to obtain a confined reaction medium;
- 20 b') heating the reaction medium of step a') up to a temperature ranging from 700°C to 900°C and maintaining this temperature for a time ranging from 0.5h to 6h so as to arrive to the desired composition, wherein carbon is introduced in said composition by chemical vapor deposition.
- 25 3. A composition comprising particles of NVPF material of formula $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which is optionally partially oxidized, as well as carbon, characterized by :
- (1) a carbon content of between 0.17% and 3.0%, this content being expressed by weight of the element carbon with respect to the total weight of the composition,
- (2) an electronic conductivity at 22°C σ expressed in mS/cm such as $\sigma > 4.3717 \times$
- 30 $+0.2186$ with x being the carbon content expressed in % by weight with respect to the total weight of the composition;
- wherein the electronic conductivity σ is measured on a sample of said composition pressed at 4.75 MPa by a Direct Current (DC) method.
- 35 4. The composition as claimed in claim 3, in which the proportion by weight of NVPF, which is optionally partially oxidized, is between 92.0% and 99.83% by

weight, this proportion being expressed with respect to the total weight of the composition.

5 5. The composition as claimed in one of claims 3 to 4, in which the unit cell parameter c is greater than or equal to 10.686 angstroms, indeed even greater than or equal to 10.750 angstroms.

10 6. The composition as claimed in one of claims 3 to 5, in which the unit cell volume V is between 872.604 and 878.390 angstroms³.

7. The composition as claimed in one of claims 3 to 6, exhibiting a ratio R of less than or equal to 1.1, preferably of less than or equal to 1.0, indeed even of less than or equal to 0.9, in which:

15 - R denotes the arithmetic mean of the ratio ID/IG calculated over at least 6 measurements carried out at various points of a sample of the composition;

- ID denotes the intensity of the Raman vibration band centered around 1340 cm^{-1} ;

20 - IG denotes the intensity of the Raman vibration band centered around 1590 cm^{-1} .

8. The composition as claimed in one of claims 3 to 7, in which the tapped density is greater than or equal to 0.9 g/ml and less than or equal to 2.0 g/ml.

25 9. The use of the composition as claimed in one of claims 3 to 8 as electrochemically active material of electrodes for sodium-ion batteries.

10. A conductive composition comprising the composition as claimed in one of claims 3 to 8, at least one electron-conducting material and optionally a binder.

30 11. The conductive composition as claimed in claim 10, in which the electron-conducting material is chosen from carbon fibers, carbon black, carbon nanotubes, graphene and their analogs.

35 12. The conductive composition as claimed in claim 10 or 11, in which the binder is chosen from polytetrafluoroethylene, polyvinylidene fluoride or a copolymer of vinylidene fluoride and of at least one comonomer, such as, for example,

hexafluoropropylene, polymers derived from carboxymethylcellulose, polysaccharides and latexes, in particular of styrene/butadiene rubber type.

13. A positive electrode comprising a conductive composition as claimed in one of
5 claims 10 to 12 or a composition as claimed in one of claims 3 to 8.

14. A sodium-ion battery comprising the positive electrode of claim 13.

Figures

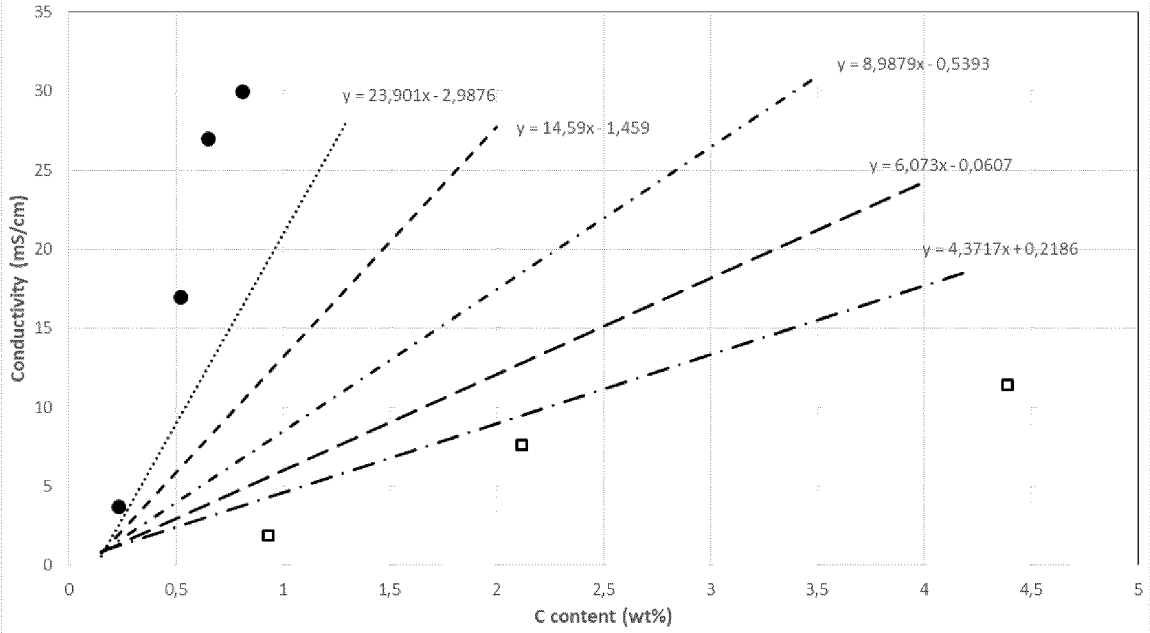


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068205

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/58 H01M10/054 H01M4/136 ADD. H01M4/62		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) H01M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/297847 A1 (HALL NIKITA [FR] ET AL) 18 October 2018 (2018-10-18) cited in the application paragraph [0032] - paragraph [0119] -----	1 - 14
X	LI LONG ET AL: "Ion transport through carbon nanotubes enable highly crystalline Na3V2(PO4)2F3 cathode for ultra-stable sodium-ion storage", JOURNAL OF POWER SOURCES, ELSEVIER, AMSTERDAM, NL, vol. 576, 24 May 2023 (2023-05-24), XP087326700, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2023.233226 [retrieved on 2023-05-24] supportive information: "Synthesis" -/-	3
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 August 2024		Date of mailing of the international search report 02/10/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Radeck, Stephanie

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068205

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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