Title: NOVEL CATHODE AND LITHIUM ION RECHARGEABLE CELLS

Abstract: Provided is a cathode for lithium ion rechargeable cells, comprising: a) a composite of VS₄ and graphene; and a) binder, comprising polyacrylic acid and/or carboxymethyl cellulose. Also provided is a lithium ion rechargeable cell containing the cathode.
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NOVEL CATHODE AND LITHIUM ION RECHARGEABLE CELLS

TECHNICAL FIELD

The present invention relates to a cathode and a lithium ion rechargeable cell containing the same.

BACKGROUND

Lithium ion rechargeable batteries have now been widely used in energy storage systems and electric vehicles. There is an on-going demand for providing more attractive and reliable power sources.

SUMMARY OF THE INVENTION

After intensive study, the inventors have surprisingly found that a composite of $\text{VS}_4$ and graphene (hereinafter abbreviated to "VS-\text{i}/graphene composite") can be used to provide a novel cathode for lithium ion rechargeable batteries.

Based on such discovery, a cathode for lithium ion rechargeable cells is provided which comprises:

a1) a composite of $\text{VS}_4$ and graphene; and
a2) a binder, comprising polyacrylic acid and/or carboxymethyl cellulose.

Also provided is a lithium ion rechargeable cell which comprises:
a) a cathode, wherein the cathode comprises:
   a1) a composite of $\text{VS}_4$ and graphene; and
   a2) a binder, comprising polyacrylic acid and/or carboxymethyl cellulose;
b) an anode;
c) a liquid electrolyte; and
d) a separator located between the cathode and the anode.

Optionally, the cathode according to the present disclosure further comprises: a3) a conductive additive.

For the first time, the inventors propose that $\text{VS}_4$/graphene composite can be used in cathodes of lithium ion rechargeable batteries. In particular, the inventors provide a novel cathode by employing a $\text{VS}_4$/graphene composite in combination with polyacrylic acid (PAA) and/or carboxymethyl cellulose (CMC). Surprisingly, it is found that by using the cathode according to the present disclosure, the lithium ion rechargeable batteries exhibit high initial Coulombic efficiencies and reversible capacities.

These and other features, aspects and advantages of the present disclosure will
become evident to those skilled in the art from the following description of various examples taken in conjunction with the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1(a) is a transmission electron microscopy (TEM) image of a VS₄/graphene composite prepared according to an Example of the present disclosure.

Figure 1(b) is a high-resolution transmission electron microscopy (HRTEM) image of a VS₄/graphene composite prepared according to an Example of the present disclosure.

Figure 2 is an X-ray diffraction (XRD) pattern of a VS^graphene composite prepared according to an Example of the present disclosure.

Figure 3 shows the cyclic voltammogram profiles of a lithium ion rechargeable cell prepared according to a Comparative Example of the present disclosure.

Figure 4 compares the discharge/charge profiles of the cells prepared according to a Comparative Example and an Example.

Figure 5 compares the cycling performances of the cells prepared according to a Comparative Example and an Example.

Figure 6 compares the discharge/charge profiles of the cells prepared according to a Comparative Example and an Example.

Figure 7 compares the cycling performances of the cells prepared according to a Comparative Example and an Example.

Each of Figure 8 to Figure 11 shows the discharge/charge profiles of the cells prepared according to some Examples of the present disclosure.

Figure 12 shows the cycling performances of the cells prepared according to some Examples of the present disclosure.

These drawings are shown here to help illustrate various examples of the disclosure, and as such, are not necessarily drawn to scale.

**DETAILED DESCRIPTION OF THE INVENTION**

Throughout this disclosure, all the scientific and technical terms, unless otherwise indicated, shall have the same meanings as those known to a person skilled in the art. Where there is inconsistency, the definition provided in the present disclosure should
It should be understood that the detailed description of all materials, processes, examples and drawings are presented for the purposes of illustration, and therefore, unless expressly specified otherwise, are not construed as limitations of the present disclosure.

Herein, the terms "cell" and "battery" may be interchangeably used. The terms "lithium ion rechargeable cell (or battery)" may also be abbreviated to "cell (or battery)".

Herein, the term "comprising" means that other ingredients or other steps which do not affect the final effect can be included. This term encompasses the terms "consisting of" and "consisting essentially of. The product and process according to the present disclosure can comprise, consist of, and consist essentially of the essential technical features and/or limitations of the present disclosure described herein, as well as any additional and/or optional ingredients, components, steps, or limitations described herein.

The use of the terms "a", "an" and "the" and similar referents in the context of describing the subject matter of this application (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

Unless otherwise specified, every numerical range in this context intends to include both endpoints and any numbers and sub-ranges falling within said numerical ranges.

Unless specially indicated, all materials and agents used in the present disclosure are commercially available.

Examples of the present disclosure are described in detail as follows.

a): Cathode

In some examples, the cathode may comprise:
   al) a composite of VS₄ and graphene; and
   a2) a binder, comprising polyacrylic acid and/or carboxymethyl cellulose.

Optionally, the cathode may further comprise: a3) a conductive additive.

According to some examples, the cathode may comprise:
   al) no less than 70 but less than 100 weight parts of the composite of VS₄ and graphene;
   a2) more than 0 but no more than 20 weight parts of the binder; and
   a3) from 0 to 20 weight parts of conductive additive.
In some examples, components al), a2) and optional a3) of the cathode are mixed in water or a water-miscible solvent so as to form a slurry.

al): VS$_4$/graphene composite
According to some examples of the present disclosure, the cathode may comprise component al): a VS$_4$/graphene composite as the cathode active material. Owing to the high theoretical capacity of VS$_4$ and the high conductivity of graphene, the VS$_4$/graphene composite exhibits a high energy density.

Preferably, the VS$_4$/graphene composite may have a structure that VS$_4$ particles chemically bond with or physically embed in graphene sheets. Preferably, VS$_4$ particles are uniformly distributed on the graphene sheets. Preferably, VS$_4$ is a vanadium sulfide in patronite form.

According to some examples of the present disclosure, the graphene is a reduction product of graphene oxide.

Preferably, VS$_4$/graphene composite is in the form of powders or particles.

According to some examples of the present disclosure, the content of the graphene may be more than 0% by weight but no more than 20% by weight, and the content of the VS$_4$ particles may be no less than 80% by weight but less than 100% by weight, based on the total weight of the VSV/graphene composite.

According to some examples of the present disclosure, the content of the VS$_4$/graphene composite may be no less than 70% by weight but less than 100% by weight, preferably less than 95% by weight, based on the total weight of the cathode.

a2): Binder
In some examples, the cathode according to the present disclosure may comprise component a2): a binder. In some examples, the binder does not contain polyvinylidone fluoride (PVDF). Preferably, the binder is carboxymethyl cellulose (CMC) and/or polyacrylic acid (PAA).

Comparing with PVDF, carboxymethyl cellulose (CMC) is often used in the form of an aqueous solution. The aqueous CMC may have a low swelling ability and a high elastic modulus. During repeated charge/discharge cycles, the aqueous CMC could accommodate large changes in the spacing between the powders or particles contained in the cathode.

Furthermore, in the case where a conductive additive is contained in the cathode, CMC serves as a dispersant and thus favors a much more homogeneous distribution of the conductive additive particles than PVDF. Besides, since the cathode
components are mixed in the form of a slurry, CMC may provide a network that
efficiently bridges the conductive additive particles and active material (i.e., the
VS-j/graphene composite) particles, owing to the extended conformation of the slurry.

Compared with PVDF, PAA is regarded as a better binder for use in
large-volume-change electrodes. In addition to a low swelling ability and a good
elasticity, PAA can be dissolved in both water and a variety of organic solvents, such
as ethanol. Furthermore, PAA may offer a much higher concentration of carboxyl
groups which can form hydrogen bonds. PAA may also provide many possible
modifications via copolymerization.

According to some examples of the present disclosure, the content of the binder may
be more than 0 but no more than 20% by weight, for example, from 2.5 % by weight
to 15 % by weight, based on the total weight of the cathode.

a3): Conductive additive
Optionally, the cathode according to the present disclosure may comprise component
a3): a conductive additive. The conductive additive may increase the conductivity
and/or capacity of the cathode.

There no specific limitation to the conductive additives, and those which are known
for use in lithium ion rechargeable batteries may be used. Preferably, the conductive
additive may be selected from carbon black, super P, acetylene black, Ketjen black,
graphite, graphene, carbon nanotubes, vapour grown carbon fibers (VGCF) and their
combinations; with super P being more preferable. For example, super P may be
commercially available from TTMical.

Preferably, the conductive additive is in the form of powders or particles, or is ground
into powders or particles.

According to some examples of the present disclosure, the content of the conductive
additive may be from 0 to 20% by weight, based on the total weight of the cathode.

Lithium ion rechargeable cell
In some examples, the lithium ion rechargeable cell comprises:
a) a cathode, wherein the cathode comprises:
   a1) a composite of VS₄ and graphene; and
   a2) a binder, comprising polyacrylic acid and/or carboxymethyl cellulose; and optionally
      a3) a conductive additive; and
b) an anode;
c) a liquid electrolyte; and
d) a separator located between the cathode and the anode.
There is no specific limitation to the anode, and those which are known for use in lithium ion rechargeable batteries may be used. In some examples, the anode may be a lithium-based anode. Non-limiting examples of the lithium-based anode include lithium metal; lithium alloys, such as Li-In alloy; stacks consisting of a layer of lithium metal and one or more layers of other metals, such as Li-In stack; pre-lithiated graphite, for example, graphite which contains a desired amount of lithium intercalated or absorbed therein; pre-lithiated silicon, for example, silicon which contains a desired amount of lithium intercalated or absorbed therein; and any combination thereof.

In some examples, the liquid electrolyte may be a lithium salt dissolved in an organic solvent. There is no specific limitation to the lithium salts, and those which are known for use in lithium ion rechargeable batteries may be used. Suitable lithium salts include, but not limited to lithium bis(oxalate) borate (LiBOB), LiPF$_6$, LiAsFe, LiBF$_4$, L1CIO$_4$, etc. Suitable organic solvents include, but not limited to, cyclic carbonates, such as ethylene carbonate (EC), propylene carbonate, fluoroethylene carbonate, difluoroethylene carbonate, etc; linear carbonates, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate, and their fluorides; cyclic lactones, such as γ-butyrolactone, γ-valerolactone, etc; or any combinations thereof.

There is no specific limitation to the separator, and those which are known for use in lithium ion rechargeable batteries may be used. In some examples, the separator may be made from polyolefin, such as polyethylene, polypropylene and polybutylene; polyesters, such as polyethylene glycol terephthalate. The separator may be in the form of microporous film or microporous sheet. The separator may be a single layer, a two-layer stack, or a multi-layer stack consisting of three or more layers. A commercially available example for the separator is Celgard 2300, which is a trilayer membrane containing one layer of polyethylene between two layers of polypropylene.

In addition, the lithium ion rechargeable cells of the present disclosure may optionally contain further additives, so long as they do not adversely affect the electrochemical properties of the batteries. The further additives may be contained within or between any one of the cathode, the anode, the electrolyte and the separator.

The lithium ion rechargeable cells according to the present disclosure may be used in energy storage systems and electric vehicles.

**EXAMPLES**

[Synthesis of graphene oxide solution]
1.5 g of graphite powder (SP-1, Bay carbon) and 1.5 g of KNO$_3$ (Sigma Aldrich, ≥ 99.0%) were taken in 69 ml of H$_2$SO$_4$ (Sigma Aldrich, 98.0%) at 0°C, and 9 g of KMnO$_4$ (Sigma Aldrich, ≥ 99.0%) was added gradually. The mixture was then stirred at 35°C for 6h, and 120 ml of deionized (DI) water was added. After 15 min, the...
reaction was terminated by the addition of 300 ml of a solution of deionized water and 9 ml of H₂O₂ (SAMCHUN pure chemical, 34.5% extra pure), and the color of the mixture changed to yellow. The mixture was filtered and washed with 500 ml of HCl (SAMCHUN pure chemical, 10% by weight) solution. The resulting graphite oxide was suspended in 200 ml of distilled water again, followed by dialysis (dialysis membrane: Spectrum Laboratories, MWCO-21-14,000) to remove excess HCl. The graphite oxide is exfoliated to give about 2.15 mg/ml graphene oxide solution by a high-pressure homogenizer at 15,000 psi. After exfoliation, the solution was centrifuged at 400 rpm for 10 min to remove the non-exfoliated graphite oxide, and the top supernatant graphene oxide solution was used for the synthesis of VS₄/graphene composite.

[Synthesis of VS₄/graphene composite]
1.1g of sodium orthovanadate (Na₃V0₄, Sigma-Aldrich, ≥90%) and 2.25g of thioacetamide (C₂H₃NS, aladdin, ≥99%) were dissolved in 20 ml of deionized water. Then, 37 ml of graphene oxide solution (2.15 mg/ml) was added to the mixture and a total volume of the solution was adjusted to 80 ml. After that, the solution was transferred to a 100ml Teflon-lined stainless steel autoclave and heated to 160 °C for 24 h. After cooling naturally, the product was filtered, washed with DI water, and dried in vacuum at 110 °C for 24 h.

[ Determination and characterization of the structure of the VS₄/graphene composite]
The obtained sample was detected to demonstrate and characterize its structure. The detection results are summarized as below:

As shown in Fig. 1(a), the transmission electron microscopy (TEM) image indicates that the graphene is in the shape of sheets, and the VS₄ nanoparticles are uniformly distributed on the graphene sheets, with the lateral lengths of the VS₄ particles being 25-50 nm and the longitudinal lengths of the VS₄ particles being 50-200 nm. The TEM image was obtained on an FEI Tecnai G² F20 transmission electron microscopy at an accelerating voltage of 200 kV.

In the high-resolution TEM (HRTEM) image shown in Fig 1(b), an interplanar distance of around 0.56 nm was observed, which matches well with the d(110) spacing of known monoclinic VS₄ [PDF No. 072-1294]. The HRTEM image was also obtained on an FEI Tecnai G² F20 transmission electron microscopy at an accelerating voltage of 200 kV.

As shown in Fig. 2, The XRD pattern of the VS₄/graphene composite further confirms the formation of a monoclinic VS₄ phase since all peaks can be indexed to known monoclinic VS₄ [JCPDS No. 072-1294]. Furthermore, the diffraction peak corresponding to the (110) plane is present at 15.8°, corresponding to a distance of 0.56 nm, which is also consistent with the HRTEM result shown in Fig 1(b). The
XRD pattern was obtained on a D8-Advance (Bruker AXS, Germany) powder diffractometer, operated at a voltage of 40 kV and scanning from 10° to 80°.

In Fig. 2, no impurities or other phase were detected in the VS₄/graphene composite sample. The characteristic diffraction peaks for the graphene were not observed. It is presumably attributed to a low content of graphene in the final VS₄/graphene composite. The low diffraction intensity of graphene is also responsible for the lack of graphene peaks.

Therefore, the combination of Fig. 1(a), Fig. 1(b) and Fig. 2 clearly demonstrates and characterizes the structure of the VSV-graphene composite.

Comparative Example 1
[Preparation of a cathode]
80 mg of VS₄/graphene, 10mg of PVDF and 10 mg of Super P (40nm, available from Timical) were mixed together in 300 mg N-methyl-2-pyrrolidone (NMP) so as to from a uniform slurry. The resultant slurry was spread on an aluminum foil, dried in vacuum and pressed to obtain a cathode.

[Preparation of the cell]
A coin cell (CR2032) for electrochemical measurements was assembled in an Argon filled glovebox by using the cathode obtained above. A Li metal foil was used as a counter electrode, Celgard 2300 (20 µ m-25 µ m) was employed as the separator, and 1 M LiPF₆ dissolved in EC/DMC/DEC (volume ratio: 1:1:1, available from Guangzhou Tianci Materials Technology Co, Ltd) was used as electrolyte.

[Electrochemical measurements]
The cell thus obtained was galvanostatically cycled at room temperature within a voltage range of 0.01 to 3.0 V (vs. Li/Li⁺) at a current density of 100 mA g⁻¹. The cyclic voltammogram profiles and discharge/charge profiles of the cell in Comparative Example 1 were plotted in Fig. 3 and Fig. 4, respectively.

Fig. 3 shows the cyclic voltammogram (CV) profiles of the cathode containing VS-i/graphene measured in the voltage range of 0.01 to 3.0 V (vs Li/Li⁺) at a scan rate of 0.1 mV s⁻¹ during the first five cycles.

Based on the CV test result and the discharge/charge profiles described later, the possible electrochemical reaction process of the VS₄/graphene in the cell of Comparative Example 1 (also applicable to Examples 1-5 described later) is shown as follow:

At initial discharge (see the 1st discharge curve):
1.8V/1.6 V: \( \text{VS}_4 + 3\text{Li}^+ + 3\text{e}^- \rightarrow \text{Li}_3\text{VS}_4 \)

0.6 V: \( \text{VS}_4 + 5\text{Li}^+ + 5\text{e}^- \rightarrow 4\text{Li}_2\text{S} + \text{V} \)

Followed by (see the 1\textsuperscript{st} charge curve):

1.9V/2.5 V: \( \text{Li}_2\text{S} \leftrightarrow \text{S} + 2\text{Li}^+ + 2\text{e}^- \)

Example 1
A coin cell was prepared in the same way as described above for Comparative Example 1, except that 10mg of PAA in DI water was used instead of 10mg of PVDF in NMP for the cathode.

Example 2
A coin cell was prepared in the same way as described above for Comparative Example 1, except that 10mg of CMC in DI water was used instead of 10mg of PVDF in NMP for the cathode.

Example 3
A coin cell was prepared in the same way as described above for Comparative Example 1, except that 5mg of PAA in DI water was used instead of 10mg of PVDF in NMP, and 85 mg of VSVgraphene was used instead of 80 mg of VS-i/graphene in the cathode.

Example 4
A coin cell was prepared in the same way as described above for Comparative Example 1, except that 15mg of PAA in DI water was used instead of 10mg of PVDF in NMP, and 75 mg of VSVgraphene was used instead of 80 mg of VS-i/graphene in the cathode.

Example 5
A coin cell was prepared in the same way as described above for Comparative Example 1, except that 20 mg of PAA in DI water was used instead of 10mg of PVDF in NMP, and 70 mg of VS-i/graphene was used instead of 80 mg of VSVgraphene in the cathode.

[Electrochemical measurements]
The electrochemical properties of Comparative Example 1 and Example 1 to Example 5 were each measured in the voltage range of 0.01 to 3.0 V (\( \text{Li/Li}^+ \)) at a current density of 100 mA g\(^{-1}\) during the first three cycles, and then at a current density of 500 mA g\(^{-1}\) during the four to thirty cycles.
Fig. 4 compares the discharge/charge profiles of the cells of Comparative Example 1 and Example 1. Fig. 5 compares the cycling performances of the cells of Comparative Example 1 and Example 1. The 1<sup>st</sup>, 4<sup>th</sup>, 15<sup>th</sup> and 30<sup>th</sup> discharge/charge capacities of these two cells are summarized in Table 1 below.

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Binder</th>
<th>1st capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>4th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>15th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>30th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Discharge</td>
<td>Charge</td>
<td>Discharge</td>
<td>Charge</td>
</tr>
<tr>
<td>Example 1</td>
<td>PAA</td>
<td>1630.1</td>
<td>1230.4</td>
<td>1170.7</td>
<td>1065.0</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>PVDF</td>
<td>1629.3</td>
<td>1062.9</td>
<td>713.6</td>
<td>683.0</td>
</tr>
</tbody>
</table>

It can be seen from Table 1 that the cathodes containing VS-<i>i</i>/graphene with PAA (Example 1) and PVDF (Comparative Example 1) have similar initial discharge capacities of 1630.1 and 1629.3 mAh g<sup>-1</sup> but quite different initial Coulombic efficiencies of 75.5% and 65.2%. After discharging/charging at 100mA g<sup>-1</sup> for 3 cycles, the reversible capacity of the cathodes containing VS<sub>4</sub>/graphene with PAA (Example 1) and PVDF (Comparative Example 1) are 1170.7 and 713.6 mAh/g, respectively, at a discharge current of 500mA g<sup>-1</sup>. Therefore, the cathodes containing VS<sub>4</sub>/graphene with PAA (Example 1) shows significantly improved initial Coulombic efficiency and reversible capacity.

Fig. 6 compares the discharge/charge profiles of the cells of Comparative Example 1 and Example 2. Fig. 7 compares the cycling performances of the cells of Comparative Example 1 and Example 2. The 1<sup>st</sup>, 4<sup>th</sup>, 15<sup>th</sup> and 30<sup>th</sup> discharge/charge capacities of these two cells are summarized in Table 2 below.

### Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Binder</th>
<th>1st capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>4th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>15th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>30th capacity (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Discharge</td>
<td>Charge</td>
<td>Discharge</td>
<td>Charge</td>
</tr>
<tr>
<td>Example 2</td>
<td>CMC</td>
<td>1557.9</td>
<td>1177.0</td>
<td>1143.8</td>
<td>1133.9</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>PVDF</td>
<td>1629.3</td>
<td>1062.9</td>
<td>713.6</td>
<td>683.0</td>
</tr>
</tbody>
</table>

It can be seen from Table 2 that the cathodes containing VS-<i>s</i>/graphene with CMC (Example 2) and PVDF (Comparative Example 1) have similar initial discharge capacities of 1557.9 and 1629.3 mAh g<sup>-1</sup> but quite different initial Coulombic efficiencies of 75.6% and 65.2%. After discharging/charging at 100mA g<sup>-1</sup> for 3 cycles, the reversible capacity of the cathodes containing VS<sub>4</sub>/graphene with CMC (Example 2) and PVDF (Comparative Example 1) are 1143.8 and 713.6 mAh/g, respectively, at a discharge current of 500mA g<sup>-1</sup>. Therefore, the cathodes containing VS<sub>4</sub>/graphene with CMC (Example 1) shows significantly improved initial Coulombic efficiency.
and reversible capacity.

Fig. 8 shows the discharge/charge profiles of the cell of Example 3. Fig. 9 shows the discharge/charge profiles of the cell of Example 1. Fig. 10 shows the discharge/charge profiles of the cell of Example 4. Fig. 11 shows the discharge/charge profiles of the cell of Example 5. Fig. 12 shows the cycling performances of Example 3, Example 1, Example 4 and Example 5.

It can be seen from Fig. 8 to Fig. 12 that the initial Coulombic efficiencies in Example 3, Example 1, Example 4 and Example 5 were as high as 76.0% 75.5% 74.8% and 68.9%, respectively. The cycling stabilities with 15 wt% of PAA (Example 4), 10 wt% of PAA (Example 1), 5 wt% of PAA (Example 3) and 20 wt% of PAA (Example 5) in the cathode were all satisfactory.

While the disclosure has been described with reference to certain examples, those skilled in the art will appreciate that various modifications, changes, omissions, and substitutions can be made without departing from the spirit of the disclosure. It is intended, therefore, that the present disclosure be limited only by the scope of the following claims.
CLAIMS

1. A cathode for lithium ion rechargeable cells, comprising:
   a1) a composite of VS₄ and graphene; and
   a2) a binder, comprising polyacrylic acid and/or carboxymethyl cellulose.

2. The cathode according to claim 1, wherein the composite of VS₄ and graphene has a structure that VS₄ particles chemically bond with or physically embed in graphene sheets.

3. The cathode according to claim 1 or 2, wherein the graphene is a reduction product of graphene oxide.

4. The cathode according to any one of the preceding claims, wherein the content of the graphene is more than 0% by weight but no more than 20% by weight, based on the total weight of the composite of VS₄ and graphene.

5. The cathode according to any one of the preceding claims, further comprising: a3) a conductive additive.

6. The cathode according to claim 5, wherein the conductive additive is selected from carbon black, super P, acetylene black, Ketjen black, graphite, graphene, carbon nanotubes, vapour grown carbon fibers and their combinations.

7. The cathode according to any one of the preceding claims, comprising:
   a1) no less than 70 but less than 100 weight parts of the composite of VS₄ and graphene;
   a2) more than 0 but no more than 20 weight parts of the binder; and
   a3) from 0 to 20 weight parts of conductive additive.

8. A lithium ion rechargeable cell, comprising:
   a) a cathode according to any one of claims 1 to 7;
   b) an anode;
   c) a liquid electrolyte; and
   d) a separator located between the cathode and the anode.

9. The cell according to claim 8, wherein the anode is a lithium-based anode.

10. The cell according to claim 9, wherein the anode is selected from lithium metal, lithium alloys, pre-lithiated graphite, pre-lithialed silicon, stacks consisting of a layer of lithium metal and one or more layers of other metals, and any combination thereof.
Fig. 2

Fig. 3
Fig. 4

Fig. 5
Fig. 8

Fig. 9
Fig. 10

Fig. 11
Fig. 12
A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/1397(2010.01)i; H01M 4/133(2010.01)i; H01M 10/0525(2010.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

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

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

WPI, EPODOC, CNKI, CNPAT, IEEE: VS4, vanadium, sulphide, graphene, electrode, LiMn2O4, cathode, anode, cell, battery

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>SUN, Ruimin et al. &quot;Vanadium Sulfide on Reduced Graphene Oxide Layer as a Promising Anode for Sodium Ion Battery,&quot; ACS Applied Materials &amp; Interfaces, Vol. 7, No. 37, 02 September 2015 (2015-09-02), ISSN: 1944-8252, page 20903, right column, last paragraph to page 20904, right column, first paragraph</td>
<td>1-7</td>
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<tr>
<td>Y</td>
<td>SUN, Ruimin et al. &quot;Vanadium Sulfide on Reduced Graphene Oxide Layer as a Promising Anode for Sodium Ion Battery,&quot; ACS Applied Materials &amp; Interfaces, Vol. 7, No. 37, 02 September 2015 (2015-09-02), ISSN: 1944-8252, page 20903, right column, last paragraph to page 20904, right column, first paragraph</td>
<td>1-10</td>
</tr>
<tr>
<td>Y</td>
<td>CN 104393303 A (SHANGHAI INST. SPACE POWER SOURCES) 04 March 2015 (2015-03-04) description, paragraphs 4-7</td>
<td>1-10</td>
</tr>
<tr>
<td>Y</td>
<td>XU, Xiaodong et al. 'Lithium Reaction Mechanism and High Rate Capability of VS4-graphene Nanocomposite as an Anode Material for Lithium Batteries,' Journal of Materials Chemistry A, Vol. 2, No. 28, 05 March 2014 (2014-03-05), ISSN: 2050-7488, page 10847, right column, last paragraph to page 10848, right column, first paragraph</td>
<td>8-10</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:
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- "E" earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search: 28 March 2016
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### DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>CN 104393303 A</td>
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