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(54) Title: CATHODE MATERIAL CONTAINING GRAPHENE FOR LI-S BATTERY AND METHOD FOR FORMING THE SAME

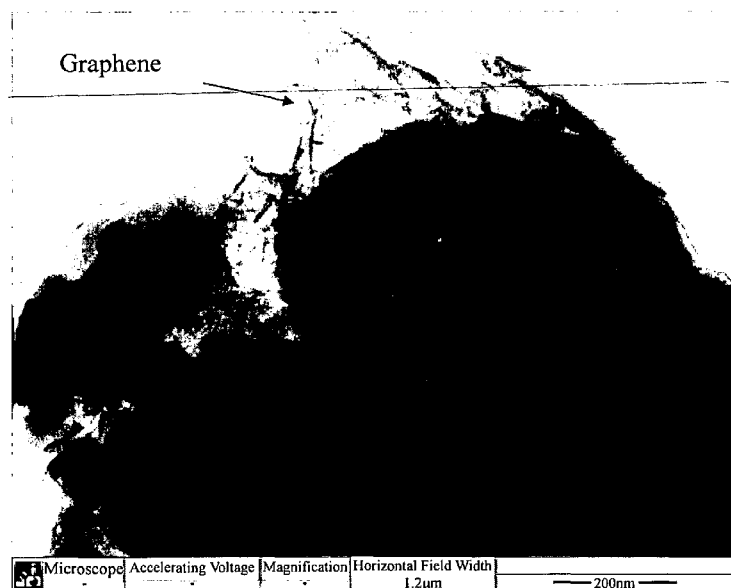


Fig. 2

(57) Abstract: The present invention provides a cathode material for Li-S battery, comprising an acrylonitrile based polymer, sulfur and graphene. Also provided are a cathode and a Li-S battery that comprise said cathode material, as well as a method for preparing said cathode material.



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Cathode material containing graphene for Li-S Battery and method for forming the same

Field of the Invention

5 The present invention relates to a cathode material for Li-S battery, a cathode and a Li-S battery that comprise said cathode material, as well as a method for preparing said cathode material.

Background Art

10 The lithium sulfur battery (Li-S battery) is a rechargeable cell with a very high energy density, wherein the high electrochemical potential of lithium is combined with sulfur (Li-S) to attain superior rechargeable performance. Battery energy is stored and released when sulfur and lithium atoms are separated or combined.

15 Compared with conventional batteries, a Li-S battery has higher energy density, because sulfur offers higher charge capacity per gram than other common cathode materials.

20 Li-S batteries may succeed lithium-ion cells because of their higher energy density and lower cost. Also, in contrast with most cathode materials, sulfur is almost non-toxic, making these batteries relatively safe for human touch. Therefore, there is much interest in using Li-S batteries for various applications.

25 However, poor electrochemical stability, cycle stability and low utilizable rate of cathode materials have long been problems that block the rapid development of Li-S batteries.

30 Chinese patent application publication CN1396202A discloses a composite cathode material for electrochemical cells comprising sulfur and polymer, wherein the polymer is used as a matrix, and electrochemical active sulfur is incorporated therein. CN1396202A discloses that polypropylene, polyacrylonitrile, polystyrene, polyoxyethylene, polyvinyl alcohol etc, can be used as polymer precursors in Li-S batteries.

35 Chinese patent application publication CN101577323A discloses a cathode material for Li-S battery, which is prepared by mixing sulfur based composite material, cyclodextrin binder and carbon conductivity agent, coating the mixture on an aluminum foil current collector, which is dried and pressed to obtain a cathode. The sulfur based composite material comprises carbon nanotubes, sulfur and polyacrylonitrile.

Despite all these prior arts, there is still a need for cathode materials that

have better charge and discharge performances and are less expensive.

Summary of the Invention

Accordingly, it is an object of the present invention to provide a cathode material that has better charge and discharge performances and is less expensive.

This object is achieved via the following technical solutions.

The present invention provides a cathode material for Li-S battery, comprising an acrylonitrile based polymer, sulfur and graphene.

In one embodiment, based on the total weight of the cathode material, the cathode material comprises from 10wt% to 70% of acrylonitrile based polymer, from 20wt% to 80% of sulfur, and from 0.1wt% to 20wt% of graphene.

In one embodiment, the graphene used has a thickness of 0.34-10 nm, a length of 10-500 nm, and a width of 10-500 nm.

In a preferred embodiment, the cathode material further comprises carbon nanotubes.

The present invention also provides a cathode for Li-S battery, which comprises the inventive cathode material.

Also provided are three methods for preparing said cathode material for Li-S battery.

The first method for preparing said cathode material includes the following steps:

dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 20-200 parts by weight of sulfur; and
the thus obtained mixture is homogenized before being heated to a temperature of 200-400°C under a inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

The second method for preparing said cathode material includes the following steps:

dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 0.1-10 parts by weight of a reducing agent;

obtaining a homogeneous mixture of graphene and acrylonitrile based polymer at room temperature to 100°C;

adding 20-200 parts by weight of sulfur to said mixture; and

the thus obtained mixture is homogenized before being heated to a
5 temperature of 200-400°C under a inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

The third method for preparing said cathode material includes the following steps:

10 dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;

adding 0.1-5 parts by weight of graphene;

adding 20-200 parts by weight of sulfur to said mixture; and

the thus obtained mixture is homogenized before being heated to a
15 temperature of 200-400°C under a inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

Compared with prior art, advantages of the inventive gasket include:

- Graphene is used as a conductive filler in cathode materials;
- 20 - Graphene is homogeneously dispersed in cathode materials by in situ reduction of graphite oxide to graphene;
- Sources of conductive fillers are broadened while the costs of cathode materials are reduced.

25 Various other features, aspects, and advantages of the present invention will become more apparent with reference to the following description, examples, and appended claims.

Brief Description of the Drawings

30 Fig. 1 is a TEM picture of graphene, which was obtained by reducing graphite oxide with polysulfide.

Fig. 2 is a TEM picture of a cathode material that contains graphene for Li-S battery.

Fig. 3 shows charge-discharge curves obtained using a cathode material
35 that contains graphene for Li-S battery.

Fig. 4 compares the discharge performances of an inventive cathode material (PAN/S/GNS) and a cathode material without graphene (PAN/S) at different discharge rates, wherein C indicating discharge power rate, for

example 0.1 C is referred to as a 10-hour discharge, and 1 C is referred to as a 1-hour discharge.

Detailed Description of the Invention

5 The present invention is further described by way of embodiment below without any intention that the scope of the present invention is limited to the embodiments.

10 All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

15 Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

 When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless
20 otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

 When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.
25

 Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component.
30 Therefore, "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

 The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods
35 and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

 The invention is described in detail herein under.

Battery costs primarily depend on the materials and preparation processes. As sulfur is much less expensive than the typical components of other battery systems, the Li-S technology starts with a lower material cost than lithium-ion or lithium-polymer batteries.

To further reduce costs of Li-S batteries, the present invention is to provide a cathode material that has better charge/discharge performances and is less expensive.

In the present invention, the acrylonitrile based polymer plays the role of polymer matrix that envelopes elemental sulfur. The preferable weight percentage of acrylonitrile based polymer is from 10wt% to 70wt%.

Useful polymers include polyacrylonitrile and acrylonitrile copolymers. In this application, polyacrylonitrile refers to homopolymers of acrylonitrile, which is prepared by the polymerization of acrylonitrile. Homopolymers of acrylonitrile have been used as fibers in hot gas filtration systems, outdoor awnings, sails for yachts, and even fiber reinforced concrete.

Acrylonitrile copolymers refer to copolymers that contain acrylonitrile units. Acrylonitrile copolymers are often used as fibers to make knitted clothing, like socks and sweaters, as well as outdoor products like tents and similar items.

In the cathode material of the present invention, the acrylonitrile copolymer may be bipolymer or terpolymer.

As bipolymer, the acrylonitrile copolymer may be preferably selected from a group consisting of acrylonitrile-butadiene copolymer, acrylonitrile-vinyl chloride copolymer, acrylonitrile-methyl acrylate copolymer, acrylonitrile-methyl methacrylate copolymer, and acrylonitrile-styrene copolymer, and in the acrylonitrile copolymer the molar percentage of acrylonitrile unit is 90%-99%.

As terpolymer, the acrylonitrile copolymer may be acrylonitrile-butadiene-styrene copolymer or acrylonitrile-butadiene-methyl methacrylate copolymer, and in the acrylonitrile copolymer the molar percentage of acrylonitrile unit is 60%-95%, the molar percentage of butadiene unit is 2.5%-20%, and the molar percentage of other units is 2.5%-20%.

There is no special limit on the molecular weight of acrylonitrile based polymers used in the present invention, polymers with molecular weights ranging from 10,000 to 1 million are suitable.

Elemental sulfur is an active species in the inventive cathode material.

The higher the content of sulfur, the higher the energy density of the cathode material. But if its content is higher than 80%, part of the elemental sulfur will be left out of the polymer matrix formed by dehydrogenization of acrylonitrile based polymer.

5 Graphene is a one-atom-thick planar sheet of graphite, possesses a unique two-dimensional structure and excellent electrical, mechanical, and thermal properties.

Compared with carbon nanotubes, graphene has lower density, better heat conductivity, higher conductivity and larger specific surface. Moreover,
10 graphene prepared by chemical methods are less expensive and easily assessable, therefore, is desirable conductive filler for composite cathode materials.

The size of graphene used in the present invention is not specifically limited, for example, the graphene may have a thickness of 0.34-10 nm, a
15 length of 10-500 nm, a width of 10-500 nm.

The cathode material of the present invention may further comprise carbon nanotubes as conductive filler. Suitable carbon nanotubes may be multi-wall carbon nanotubes or single wall carbon nanotubes, with outer diameters of 1nm-60nm and lengths of 500nm-50 μ m. Specifically, the outer
20 diameter of carbon nanotubes may be 1nm-20nm, 20nm-40nm or 40nm-60nm.

It is surprising and interesting to find that the combined use of graphene and carbon nanotubes in the inventive cathode material leads to excellent performances, including superior discharge performances at high discharge rates.

25 It is assumed that the combination of graphene and carbon nanotubes helps to form a stable 3-dimensional conductive network in the cathode material.

The inventors found that it is desirable to control the total amount of graphene and carbon nanotubes at 0.1-20 wt%, preferably 0.1-10 wt%, based
30 on the total weight of the cathode material.

The present invention also provides a cathode and a Li-S battery using the inventive cathode material.

Besides the inventive cathode material, a cathode for Li-S battery may further comprise a binder, such as PTFE, a conductive filler, such as Super P.
35 Generally, a cathode for Li-S battery is formed on a metal substrate, such as Nickel foam or Aluminum foil.

A Li-S battery according to the present invention may comprise a negative

electrode made of Li, electrolyte, such as EC-DMC-1M LiPF₆, and a separator, such as a porous polyethylene membrane.

5 The present invention also provides three methods for preparing said cathode material for Li-S battery.

The first method for preparing said cathode material includes the following steps:

10 dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 20-200 parts by weight of sulfur; and
the thus obtained mixture is homogenized before being heated to a temperature of 200-400°C under a inert atmosphere and kept at said
15 temperature for 1-20 hours, so as to obtain a cathode material.

The inventors are of the view that, without being bound to a particular theory, during the above described heat treatment, acrylonitrile based polymers react with elemental sulfur to form H₂S, which plays the role of a
20 reducing agent and convert graphite oxide to graphene in situ. It is assumed that the in situ formed graphene contributes the excellent charge/discharge performances of the inventive cathode materials.

25 The second method for preparing said cathode material includes the following steps:

dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 0.1-10 parts by weight of a reducing agent;
30 obtaining a homogeneous mixture of graphene and acrylonitrile based polymer at room temperature to 100°C;
adding 20-200 parts by weight of sulfur to said mixture; and
the thus obtained mixture is homogenized before being heated to a temperature of 200-400°C under a inert atmosphere and kept at said
35 temperature for 1-20 hours, so as to obtain a cathode material.

Suitable reducing agents include hydrazine hydrate, sodium borohydride, potassium borohydride, glucose and aqueous ammonia, sodium polysulfide.

The third method for preparing said cathode material includes the following steps:

- 5 dispersing 10-30 parts by weight of acrylonitrile based polymer in
30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphene;
adding 20-200 parts by weight of sulfur to said mixture; and
the thus obtained mixture is homogenized before being heated to a
temperature of 200-400°C under a inert atmosphere and kept at said
10 temperature for 1-20 hours, so as to obtain a cathode material.

It is preferable to add graphene in the form of dispersion, so as avoid undesirable folding or rolling of graphene.

15 Materials used in experiments

Polyacrylonitrile, with molecular weights ranging from 10,000 to 1 million.

Super P, conductive graphite, provided by TIMCAL Graphite & Carbon.

PTFE, polytetrafluoroethylene emulsion, provided by SHANGHAI 3F NEW
20 MATERIALS CO., LTD.

Preparation of graphite oxide

- 5g graphite was added into a beaker that contained 115ml 98%
concentrated sulfuric acid. The beaker was then placed in an ice-bath. 15g
KMnO₄ was slowly added into the beaker under stirring, so that the
25 temperature of the mixture was kept at no higher than 20°C. After that, the
ice-bath was removed, and the beaker was placed in an oil-bath and kept at
30°C for 30 minutes. Then 230ml of de-ionized water was added into the
beaker to raise the temperature of the mixture to 90°C, and the mixture was
kept at this temperature for 4 hours. The mixture thus obtained was separated
30 via filtration and washed with de-ionized water until the pH of the eluate
reached 7. The filter cake was then dried at 60°C in a vacuum oven. As a result,
graphite oxide was obtained.

Assembly of coin cells and charge/discharge tests

- 35 Li-S batteries of coin cell form were prepared by using the inventive
composite materials as active materials, PTFE as a binder and Super P as
conductive filler.

10mg Super P, 10mg PTFE and 80mg active materials were

homogeneously mixed, and heated while being stirred. As the result, a mixture was obtained in the form of lumps, which was rolled into a plate. The plate was dried in an oven that was kept at 80°C and pressed onto Nickel foam to form a cathode. The cathode was then dried in a vacuum oven that was kept at 80°C.

5 In a glove box that was filled with argon, a CR2016 coin cell was prepared using the above prepared cathode, a lithium plate as an anode, a porous polyethylene membrane as the separator, and 1 mol·L⁻¹ LiPF₆/EC:DMC (wherein EC:DMC (by volume) =1:1, EC represents ethylene carbonate, DMC represents dimethyl carbonate) as electrolyte.

10 The thus prepared coin cell was subjected to charge/discharge tests conducted on LAND battery test system (provided by Wuhan Landian Electronics Co., Ltd) at room temperature, with the cut-off voltages set at 1~3V (vs Li/Li⁺).

15 Example 1

0.1g graphite oxide and 1g sodium polysulfide were added into 50g water, and was refluxed at 80°C, resulting in graphene as shown in Fig. 1. 1g polyacrylonitrile was dispersed in 100g water; 0.1g graphene and 8g sulfur were added into the dispersion. The thus obtained mixture was heated to 300
20 °C under nitrogen and kept at said temperature for 5 hours, so as to obtain a cathode material containing graphene, wherein the content of graphene is 6 wt%, and sulfur content is 48 wt%.

The charge/discharge test of the above prepared cathode material demonstrated the discharge capacity of the first cycle is 827 mAh/g, the
25 discharge capacity of the second cycle is 685 mAh/g, and the discharge capacity of the tenth cycle is 630 mAh/g.

Example 2

1g polyacrylonitrile was dispersed in 50g water. 0.1g graphite oxide and
30 0.3g hydrazine hydrate were added into the dispersion. The resulted mixture was refluxed at 70°C. A homogeneous mixture of graphene and polyacrylonitrile was obtained.

7g sulfur was added into said mixture. The thus obtained mixture was heated to 300°C under nitrogen and kept at said temperature for 6 hours, so as
35 to obtain a cathode material containing graphene, Fig. 2 is a TEM picture of this cathode material.

The charge/discharge test of the above prepared cathode material demonstrated that the discharge capacity of the first cycle is 821.5 mAh/g, the

discharge capacity of the second cycle is 663.6 mAh/g, as is shown in Fig. 3.

Example 3

1g polyacrylonitrile was dispersed in 20g water. 0.1g graphite oxide and
5 1g glucose and 0.1ml aqueous ammonia were added into the dispersion. The
resulted mixture was refluxed at 95°C. A homogeneous mixture of graphene
and polyacrylonitrile was obtained.

8g sulfur was added into said mixture. The thus obtained mixture was
heated to 300°C under nitrogen and kept at said temperature for 5 hours, so as
10 to obtain a cathode material containing graphene.

The charge/discharge test of the above prepared cathode material
demonstrated that the discharge capacity of the first cycle is 823 mAh/g, the
discharge capacity of the second cycle is 681 mAh/g, and the discharge
capacity of the tenth cycle is 627 mAh/g.

15

Example 4

1g polyacrylonitrile was dispersed in 50g water. 0.3g graphite oxide and
10g sulfur were added into the dispersion. The thus obtained mixture was
heated to 280°C under nitrogen and kept at said temperature for 8 hours, so as
20 to obtain a cathode material containing graphene.

The charge/discharge test of the above prepared cathode material
demonstrated that the discharge capacity of the first cycle is 750 mAh/g, the
discharge capacity of the second cycle is 623 mAh/g.

25 Example 5

1g acrylonitrile-butadiene copolymer was dispersed in 50g water. 0.1g
graphite oxide and 8g sulfur were added into the dispersion. The thus obtained
mixture was heated to 300°C under nitrogen and kept at said temperature for 5
hours, so as to obtain a cathode material containing graphene.

30 The charge/discharge test of the above prepared cathode material
demonstrated the discharge capacity of the first cycle is 823 mAh/g, the
discharge capacity of the second cycle is 663 mAh/g, and the discharge
capacity of the tenth cycle is 610 mAh/g.

35 Example 6

1g polyacrylonitrile was dispersed in 50g water. 0.05g graphite oxide and
1g hydrazine hydrate were added into the dispersion. The resulted mixture
was refluxed at 90°C. A homogeneous mixture of graphene and

polyacrylonitrile was obtained.

0.05g carbon nanotubes and 8g sulfur were added into said mixture. The thus obtained mixture was heated to 300°C under nitrogen and kept at said temperature for 5 hours, so as to obtain a cathode material containing
5 graphene, contents of graphene and carbon nanotubes are 3 wt% respectively and sulfur content is 48 wt%..

The charge/discharge test of the above prepared cathode material demonstrated the discharge capacity of the first cycle is 863 mAh/g, the discharge capacity of the second cycle is 712 mAh/g, and the discharge
10 capacity of the tenth cycle is 657 mAh/g.

Comparative Example 1

In order to exhibit the effects of graphene, a cathode material containing no graphene was prepared as below.

15 1g polyacrylonitrile was dispersed in 100g water. 7g sulfur was added into the dispersion. The thus obtained mixture was heated to 300°C under argon and kept at said temperature for 6 hours, so as to obtain a cathode material without graphene.

Fig. 4 compares the discharge performances of an inventive cathode material (Example 2) and a cathode material without graphene (Comparative
20 Example 1) at different discharge rates, wherein C indicating the discharge power rate, for example 0.1 C is referred to as a 10-hour discharge, and 1 C is referred to as a 1-hour discharge.

As is shown in Fig. 4, for the cathode material that contains graphene, the
25 discharge capacity of the first cycle is 816.2 mAh/g, the discharge capacity of the second cycle is 659.5 mAh/g, and the discharge capacity at 1C is 535.8 mAh/g.

For the cathode material without graphene, the discharge capacity of the first cycle is 819 mAh/g, the discharge capacity of the second cycle is 623.5
30 mAh/g, and the discharge capacity at 1C is 413.6 mAh/g.

Thus, it is clear that the addition of graphene significantly improves the discharge performances of cathode materials, especially at high discharge rates.

35 While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions are possible without departing from the spirit of the present invention. As such, modifications and equivalents of the invention

herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.

What is claimed is:

1. A cathode material for Li-S battery, comprising an acrylonitrile based polymer, sulfur and graphene.

2. The cathode material for Li-S battery according to claim 1, wherein based on the total weight of the cathode material, the weight percentage of acrylonitrile based polymer is from 10wt% to 70wt%, the weight percentage of sulfur is from 20wt% to 80wt%, and the weight percentage of graphene is from 0.1wt% to 20wt%.

3. The cathode material for Li-S battery according to claim 1 or 2, wherein the graphene has a thickness of 0.34-10 nm, a length of 10-500 nm, a width of 10-500 nm.

4. The cathode material for Li-S battery according to anyone of claims 1-3, which further comprises carbon nanotubes.

5. The cathode material for Li-S battery according to claim 1, wherein said acrylonitrile based polymer is selected from polyacrylonitrile or acrylonitrile copolymers.

6. A cathode, which comprises the cathode material for Li-S battery according to anyone of claims 1-5.

7. A Li-S battery, which comprises the cathode of claim 6.

8. A method for preparing a cathode material for Li-S battery, including:
dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 20-200 parts by weight of sulfur; and
the thus obtained mixture is homogenized before being heated to a temperature of 200-400°C under an inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

9. A method for preparing a cathode material for Li-S battery, including:
dispersing 10-30 parts by weight of acrylonitrile based polymer in

30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphite oxide;
adding 0.1-10 parts by weight of a reducing agent;
obtaining a homogeneous mixture of graphene and acrylonitrile based polymer at room temperature to 100°C;
adding 20-200 parts by weight of sulfur to said mixture; and
the thus obtained mixture is homogenized before being heated to a temperature of 200-400°C under an inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

10. The method of claim 9, wherein the reducing agent is selected from hydrazine hydrate, sodium borohydride, potassium borohydride, glucose and aqueous ammonia, sodium polysulfide.

11. A method for preparing a cathode material for Li-S battery, including:
dispersing 10-30 parts by weight of acrylonitrile based polymer in 30-1000 parts by weight of water;
adding 0.1-5 parts by weight of graphene;
adding 20-200 parts by weight of sulfur to said mixture; and
the thus obtained mixture of acrylonitrile based polymer/sulfur/graphite oxide is homogenized before being heated to a temperature of 200-400°C under an inert atmosphere and kept at said temperature for 1-20 hours, so as to obtain a cathode material.

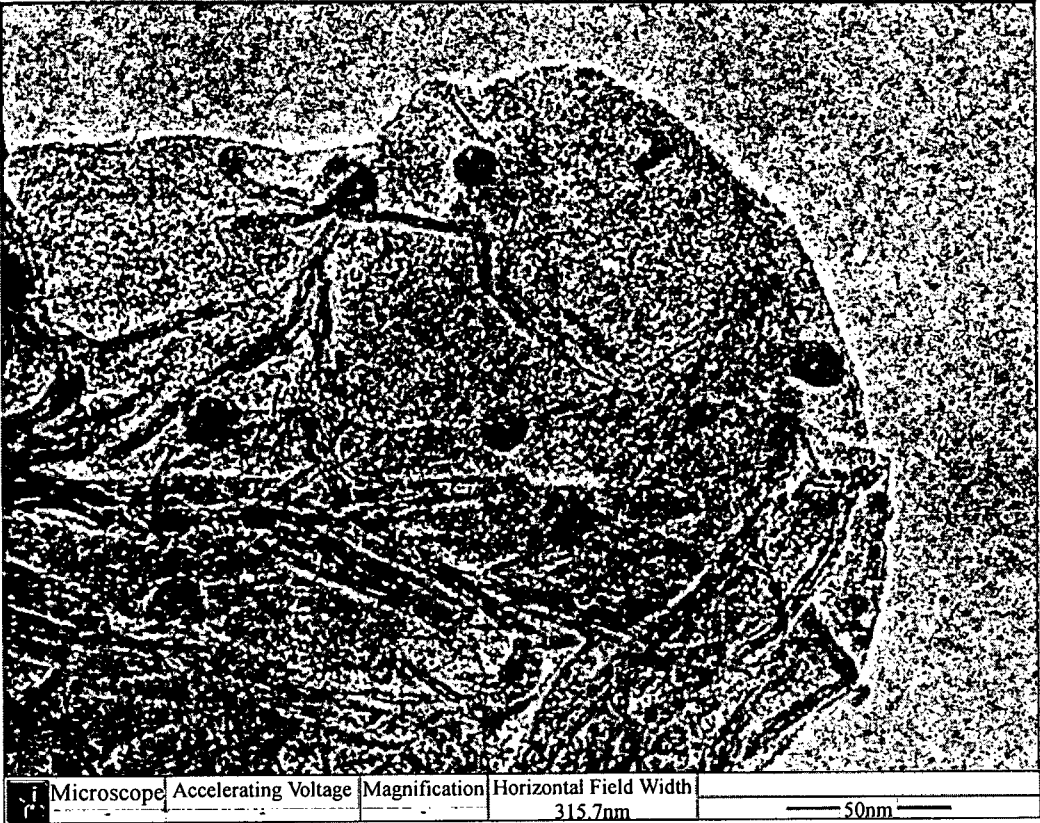


Fig.1

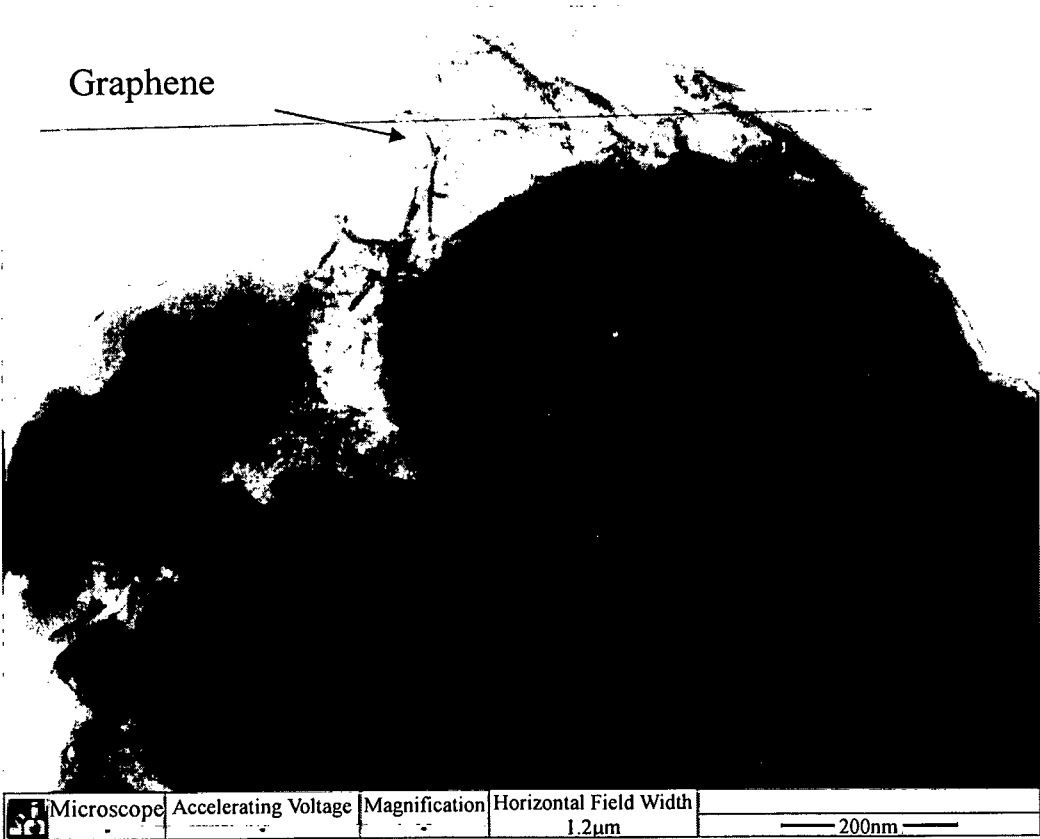


Fig. 2

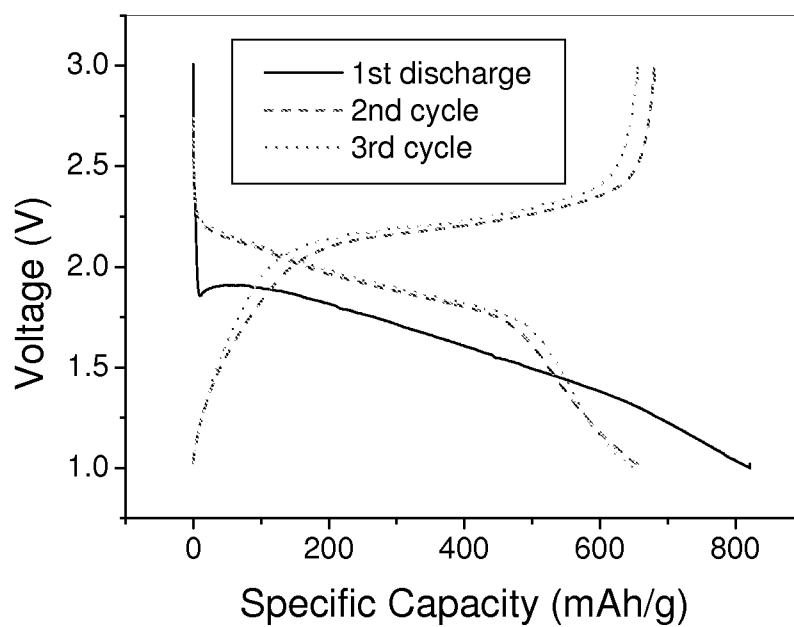


Fig. 3

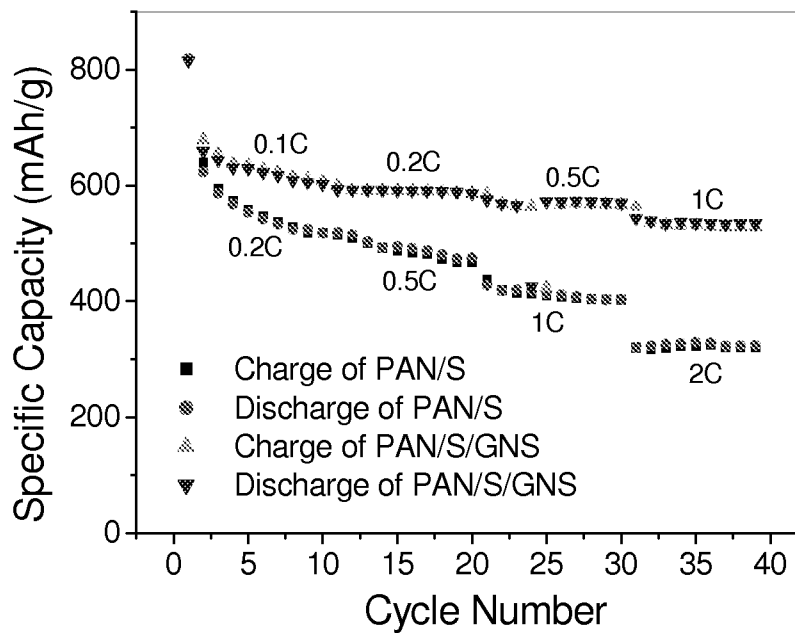


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/073598

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/137(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)

IPC: 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)

WPI, EPODOC; CNPAT Li-S, lithium, sulfur, battery, acrylonitrile, polymer, graphene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN101577323A (SHANGHAI JIAO TONG UNIV) 11 November 2009 (11.11.2009) Page 3, line 6 to 15	1-7
Y	CN101916849A (SHANGHAI JIAO TONG UNIV) 15 December 2010 (15.12.2010) Claim 1	1-7
Y	WO2009029984A1 (NEWSOUTH INNOVATIONS PTY LTD) 12 March 2009 (12.03.2009) Page 6, line 13 to 25, page 7, line 30 to 34	1-7
Y	CN101794874A (TIANJIN UNIV) 04 August 2010 (04.08.2010) Claim 1	1-7
A	US7150840B2 (Yamamoto et al) 19 December 2006 (19.12.2006) The whole document	1-11

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

* Special categories of cited documents:	“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
“A” document defining the general state of the art which is not considered to be of particular relevance	“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
“E” earlier application or patent but published on or after the international filing date	“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
“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)	“&” document member of the same patent family
“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	

Date of the actual completion of the international search 21 June 2011 (21.06.2011)	Date of mailing of the international search report 14 Jul. 2011 (14.07.2011)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer WANG Weijia Telephone No. (86-10) 62411553

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/073598

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

See Extrat Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/073598

I: Independent claims 1,6,7,11 directed to a cathode material comprising acrylonitrile based polymer, sulfur and graphene, a cathode using the material and a method for preparing the same.

II: Independent claims 8,9 directed to a method for preparing a cathode material comprising acrylonitrile based polymer, sulfur and graphite oxide.

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

The prior art has been identified as document 1(CN101577323A) and discloses a sulfur-based composite active material comprises 4-11% of carbon nanotube, 35-43% of elemental sulfur, and polyacrylonitrile cyclization product.

It follows that the following technical feature of claim 8 or claim 9 makes a contribution over the prior art and can be considered as a special technical feature within the meaning of Rule 13.2 PCT: the material contains graphite oxide.

In conclusion, the groups of claims are not linked by common or corresponding special technical features and define 2 different inventions not linked by a single general inventive concept.

The application, hence does not meet the requirements of unity of invention as defined in Rules 13.1 and 13.2 PCT.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/073598

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101577323A	11.11.2009	NONE	
CN101916849A	15.12.2010	NONE	
WO2009029984A1	12.03.2009	WO2009029984A8	11.06.2009
CN101794874 A	04.08.2010	NONE	
US7150840 B2	19.12.2006	US2004041130A1	04.03.2004
		JP2004143652A	20.05.2004
		JP4376564B2	02.12.2009