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KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
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(54) Title: CATHODE MATERIAL FOR LI-S BATTERY AND METHOD FOR FORMING THE SAME

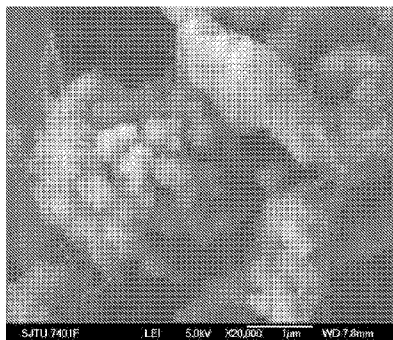


Fig. 1

(57) Abstract: The present invention provides a novel cathode material for Li-S battery, which is consisted of a dehydrogenized acrylonitrile copolymer, sulfur and carbon nanotubes, wherein the weight percentages of these components are as below: 20%≤dehydrogenized acrylonitrile copolymer ≤80%, 20%≤ sulfur ≤80%, 1%≤ carbon nanotubes ≤30%. Also provided are a cathode and a Li-S battery using said cathode material, as well as a method for preparing said cathode material.



Cathode Material for Li-S Battery and method for forming the same

Field of the Invention

The present invention relates to a cathode material for rechargeable lithium-sulfur (Li-S) battery and the method for forming the same.

Background Art

The lithium-sulfur (Li-S) battery is a rechargeable cell with a very high energy density. The theoretical specific energy density of lithium-sulfur batteries is 2600 Wh/kg, which is one of the highest energy densities for batteries. Li-S batteries may become a successor of lithium-ion cells because of their higher energy density and the lower cost. In contrast with most cathode materials, sulfur is also relatively non-toxic, making these batteries relatively safe for human contact. Therefore, there is much interest in using Li-S batteries for various applications.

However, Li-S battery's conventional cathode materials have a variety of problems, including low electronic conductivity, low utilizable rate of active material, poor circulatory stability, etc, which need to be solved in rechargeable lithium batteries.

A Chinese patent CN1396202A discloses a composite material comprising sulfur and an electrically conductive polymer, which is used as cathodes material for electrochemical cells, wherein the electrically conductive polymer is used as a matrix, and electrically active sulfur is incorporated therein. CN1396202A also discloses that polypropylene, polyacrylonitrile, polystyrene, polyoxyethylene, polyvinyl alcohol etc, can be used as electrically conductive polymer precursors.

Another Chinese patent CN101577323A discloses a cathode material for Li-S battery, which is prepared by mixing a 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.

Although the cathode materials using pure polyacrylonitrile as their matrixes have desirable charge and discharge performances, the high price of

pure polyacrylonitrile renders the Li-S batteries too expensive to be competitive on the market.

It is an object of the present invention to reduce the cost of polymer materials that are used as cathode materials of Li-S battery, while remaining desirable charge and discharge performances.

Summary of the Invention

An object of the present invention is to provide cheaper polymer materials, which can be used in cathode materials for Li-S battery as matrixes and achieve desirable charge and discharge performances.

This object is achieved via the following technical solutions.

In one aspect, the present invention provides a cathode material for Li-S battery, which is consisted of a dehydrogenized acrylonitrile copolymer, sulfur and carbon nanotubes, wherein the weight percentages of these components are as below: $20\% \leq \text{dehydrogenized acrylonitrile copolymer} \leq 70\%$, $20\% \leq \text{sulfur} \leq 80\%$, $0\% \leq \text{carbon nanotubes} \leq 20\%$.

In the present invention, dehydrogenized acrylonitrile copolymer plays the role of polymer matrix that envelopes elemental sulfur. On one hand, if the content of dehydrogenized acrylonitrile copolymer is higher than 70%, the energy density of the cathode material will be too low. On the other hand, if its content is lower than 20%, it is not enough to completely envelope all elemental sulfur.

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%.

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 of dehydrogenized acrylonitrile copolymer.

The carbon nanotubes used in the present invention may be multi-wall carbon nanotubes or single wall carbon nanotubes, with outer diameters of 10nm-60nm and lengths of 1 μ m-50 μ m. Specifically, the outer diameter of carbon nanotubes may be 10nm-30nm, 20nm-40nm or 40nm-60nm.

In the present invention, carbon nanotubes are used to enhance the electronic conductivity of the cathode material and to stabilize the frame of said cathode material. The present inventors found that it is desirable to control the content of carbon nanotubes at 0-20 wt%.

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

Preferably, the Li-S battery may comprises a negative electrode made of Li, EC-DMC-1M LiPF₆ as the electrolyte, and a porous polyethylene membrane as a separator.

The present invention also provides a method for preparing a cathode material for Li-S battery, including: mixing carbon nanotubes and acrylonitrile copolymer in a ball mill, wherein ethanol is used as a dispersant; adding sulfur into the ball mill and further mixing; drying the mixture under vacuum to remove ethanol; heat-treating the mixture under a inert atmosphere; and cooling at ambient temperature, so as to obtain a cathode material.

The heat-treating process is preferably conducted at a temperature of 200 $^{\circ}$ C-450 $^{\circ}$ C.

Further, it is preferable to dwell the material at a constant temperature for 1-20 hours, after the heat treating step and before the cooling step.

The inventors noticed that it is important to control the morphology of acrylonitrile copolymers. Also it is desirable to mix acrylonitrile copolymers with carbon nanotubes homogeneously. In the field of electrochemistry, the performances of batteries are largely determined by the morphologies of

materials used therein.

In order to accelerate the commercial utilization of Li-S batteries, the cost of cell materials must be further reduced while remaining the high performances of the battery.

In this connection, after numerous experiments, the inventors of the present invention surprisingly found that some acrylonitrile copolymers commonly used in other sectors are suitable matrix materials for Li-S batteries. These acrylonitrile copolymers are usually used as textile materials or engineering plastics. Therefore, the acrylonitrile copolymers used in the present invention are preferably those commonly used as textile materials or engineering plastics. These materials are commercially available at relatively cheaper prices.

Thus the present invention dramatically broadens the range of materials that are suitable as matrix materials for Li-S batteries and reduces the cost of raw materials, hence facilitates the commercial application of Li-S batteries.

Brief Description of the Drawings

Fig. 1 is a SEM picture of the cathode material obtained from Example 1.

Fig. 2 shows charge-discharge curves obtained using a cathode made of the cathode material obtained from Example 1.

Fig. 3 shows cycling response of a cathode made of the cathode material obtained from Example 1 at various current rates.

Detailed Description of the Invention

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.

Embodiments 1-4 respectively illustrate four specific acrylonitrile copolymers, which are widely used as textile materials or engineering plastics and hence, acrylonitrile copolymers are available at reasonable prices.

Embodiment 1

0.1g multi-wall carbon nanotubes with a diameter of 10-30nm were mixed

with 1g acrylonitrile-methyl methacrylate copolymer (wherein the molar percentage of methyl methacrylate unit is 5%) in a ball mill for 10 hours, using ethanol as a dispersant.

10g sulfur was added into the ball mill, and the mixing was continued for another 10 hours. The mixture thus obtained was dried under vacuum to remove ethanol.

The mixture was then heated to 320°C and dwelled under a nitrogen atmosphere. After that it was kept at a constant temperature for 6 hours, and then cooled at ambient temperature. The cathode material thus prepared had a sulfur content of 39 wt%. Fig.1 shows the microstructure of this cathode material, wherein carbon nanotubes were homogeneously dispersed.

The cathode material thus prepared was made into a cathode, which used polytetrafluoroethylene as a binder, acetylene black as a conductive agent, ethanol as a dispersant, and nickel foam as a current collector.

This cathode was then fitted into a battery, which comprised a negative electrode made of Li, EC-DMC-1M LiPF₆ as the electrolyte, and a porous polyethylene membrane as a separator.

Fig. 2 shows that the battery thus prepared demonstrated a first capacity of 775 mAh/g and a reversible capacity of 588 mAh/g.

Fig. 3 shows that the cathode material had a capacity of 430 mAh/g at a high current (5C).

Embodiment 2

0.05g single wall carbon nanotubes with a diameter of 20-40nm were mixed with 1g acrylonitrile-butadiene copolymer (wherein the molar percentage of butadiene unit is 10%) in a ball mill for 5 hours, using ethanol as a dispersant.

20g sulfur was added into the ball mill, and the mixing was continued for another 5 hours. The mixture thus obtained was dried under vacuum to remove ethanol.

The mixture was then heated to 280°C and dwelled under an argon atmosphere. After that it was kept at a constant temperature for 10 hours, and then cooled at ambient temperature. The cathode material thus prepared had a sulfur content of 45 wt%.

Embodiment 3

0.15g multi-wall carbon nanotubes with a diameter of 40-60nm were mixed with 1g acrylonitrile-butadiene-styrene copolymer (wherein the molar percentage of butadiene unit is 5%, and the molar percentage of styrene unit is 5%) in a ball mill for 15 hours, using ethanol as a dispersant.

15g sulfur was added into the ball mill, and the mixing was continued for another 15 hours. The mixture thus obtained was dried under vacuum to remove ethanol.

The mixture was then heated to 400°C and dwelled under an argon atmosphere. After that it was kept at a constant temperature for 5 hours, and then cooled at ambient temperature. The cathode material thus prepared had a sulfur content of 35 wt%.

Embodiment 4

0.1g single wall carbon nanotubes with a diameter of 40-60nm were mixed with 1g acrylonitrile-butadiene- methyl methacrylate copolymer (wherein the molar percentage of butadiene unit is 5%, and the molar percentage of methyl methacrylate unit is 10%) in a ball mill for 5 hours, using ethanol as a dispersant.

6g sulfur was added into the ball mill, and the mixing was continued for another 5 hours. The mixture thus obtained was dried under vacuum to remove ethanol.

The mixture was then heated to 450°C and dwelled under an argon atmosphere. After that it was kept at a constant temperature for 3 hours, and then cooled at ambient temperature. The cathode material thus prepared had a sulfur content of 50 wt%.

Performances of cathode materials prepared in Examples 2-4 were measured in a similar way as in Example 1. Results of these measurements showed that these cathode materials were as good as those made of polyacrylonitrile in terms of charge and discharge performances.

Beside the aforementioned advantages, acrylonitrile copolymers also allow better control of the morphology of cathode materials. In the present

invention, commercially available acrylonitrile copolymers with micrometer scale particle sizes may be ground by a ball mill to form particles with particle sizes of hundreds of nanometers, so as to improve the electrochemical activity of cathode materials and increase their energy density.

Also, when being mixed with carbon nanotubes in a ball mill, the acrylonitrile copolymer used in the present invention forms a homogeneous mixture with carbon nanotubes. Carbon nanotubes play important roles in the inventive cathode materials. As conductive materials they improve the rate capability of cathode materials. Also the framework formed of carbon nanotubes buffers the expansion of cathode materials during charge and discharge cycles, and hence extends the cycle life of batteries. As a result, the inventive cathode material can work at power rate as high as 7C and achieve stable charge and discharge cycles, which meets the requirement for commercial utilization in lithium-sulfur (Li-S) batteries.

What is claimed is:

1. A cathode material for Li-S battery, comprising a dehydrogenized acrylonitrile copolymer, sulfur and carbon nanotubes, wherein the weight percentages of these components are as below: $20\% \leq \text{dehydrogenized acrylonitrile copolymer} \leq 70\%$, $20\% \leq \text{sulfur} \leq 80\%$, $0\% \leq \text{carbon nanotubes} \leq 20\%$.

2. The cathode material for Li-S battery according to claim 1, wherein the acrylonitrile copolymer is acrylonitrile-butadiene copolymer, acrylonitrile-vinyl chloride copolymer, acrylonitrile-methyl acrylate copolymer, acrylonitrile-methyl methacrylate copolymer, or acrylonitrile-styrene copolymer, and molar percentage of acrylonitrile unit in the acrylonitrile copolymer is 90%-99%.

3. The cathode material for Li-S battery according to claim 1, wherein the acrylonitrile copolymer is 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%.

4. The cathode material for Li-S battery according to claim 1, wherein the carbon nanotubes are multi-wall carbon nanotubes or single wall carbon nanotubes, with outer diameters of 10nm-60nm and lengths of $1\mu\text{m}$ - $50\mu\text{m}$.

5. Cathode material for Li-S battery, which comprises the cathode material for Li-S battery according to anyone of claims 1-4.

6. A Li-S battery, which uses the cathode material for Li-S battery according to anyone of claims 1-4.

7. A Li-S battery according to claim 6, which comprises a negative electrode made of Li, EC-DMC-1M LiPF_6 as the electrolyte, and a porous

polyethylene membrane as a separator.

8. A method for preparing a cathode material for Li-S battery, including:
mixing carbon nanotubes and acrylonitrile copolymer in a ball mill,
wherein ethanol is used as a dispersant;
adding sulfur into the ball mill and further mixing;
drying the mixture under vacuum to remove ethanol;
heat treating and dwelling the mixture under a inert atmosphere; and
cooling at ambient temperature, so as to obtain a cathode material.

9. The method of claim 8, wherein the heat treating is conducted at a temperature of 200°C-450°C.

10. The method of claim 8, wherein the heat treated material is kept at a constant temperature for 1-20 hours after the heat treating step and before the cooling step.

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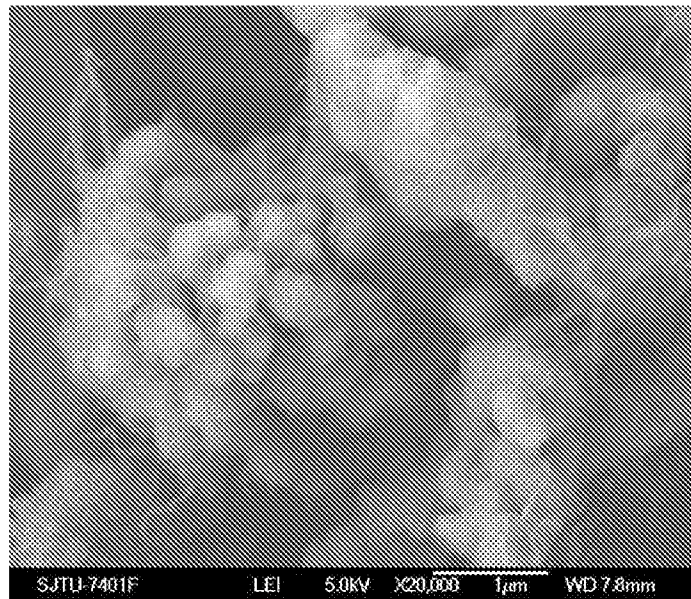


Fig. 1

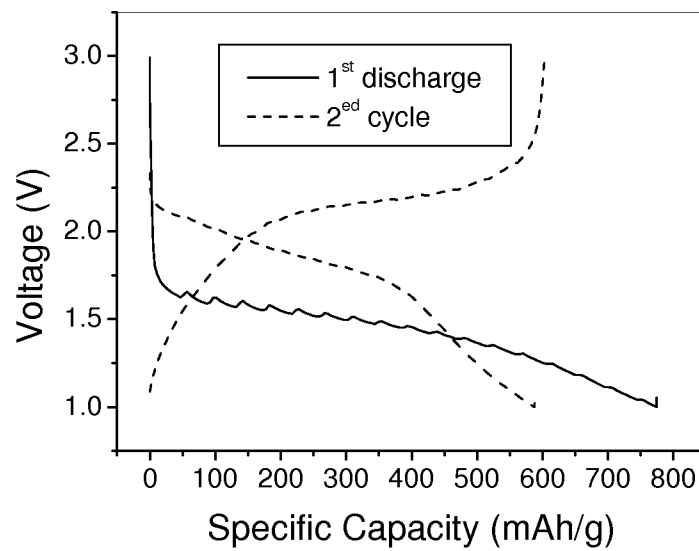


Fig. 2

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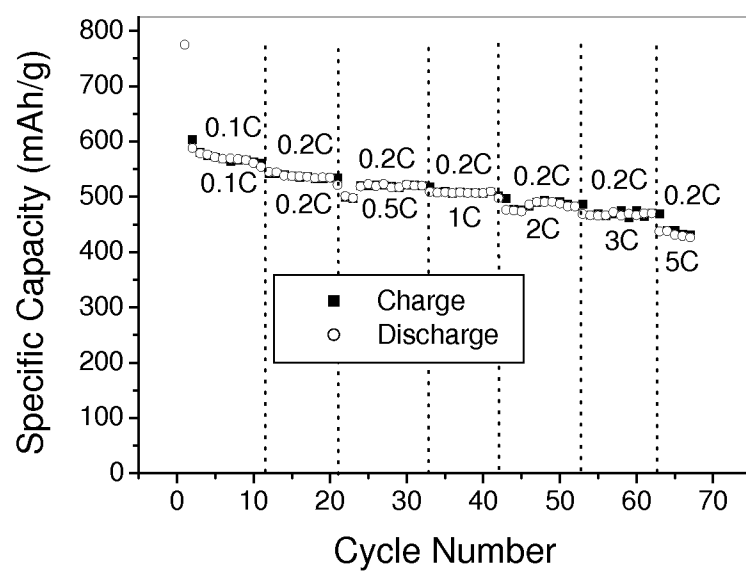


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2010/077530

A. CLASSIFICATION OF SUBJECT MATTER

See Extra Sheet

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, CNKI: cell, battery, lithium, sulfur, carbon, acrylonitrile, dehydrogen+, polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 101577323 A (SHANGHAI JIAO TONG UNIVERSITY) 11 Nov. 2009 (11.11.2009) claims 1-3 and 8, paragraph 2 of page 6	1-10
Y	CN 1337753 A (SHANGHAI METALLURGY INST. CHINESE ACAD. SC.) 27 Feb. 2002 (27.02.2002) claims 4 and 6	1-10
E	CN 101891930 A (SHANGHAI JIAO TONG UNIVERSITY) 24 Nov. 2010 (24.11.2010) claim 1, paragraph 0018	1, 5-6
A	CN 1495937 A (SAMSUNG SDI CO., LTD.) 12 May 2004 (12.05.2004) the whole document	1-10
A	WANG, Jiulin et al. Sulfur Composite Cathode Materials for Rechargeable Lithium Batteries. Advanced Functional Materials. Jun. 2003, Vol. 13, No. 6, 487-492	1-10

☐ 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
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"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	

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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 AI, Juan Telephone No. (86-10) 82245069

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2010/077530

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 101577323 A	11.11.2009	none	
CN 1337753 A	27.02.2002	CN 1252849 C	19.04.2006
CN 101891930 A	24.11.2010	none	
CN 1495937 A	12.05.2004	US 2004029014 A1	12.02.2004
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		KR 100454030 B	20.10.2004
		CN 1331252 C	08.08.2007

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2010/077530

Continuation of **A. CLASSIFICATION OF SUBJECT MATTER**

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