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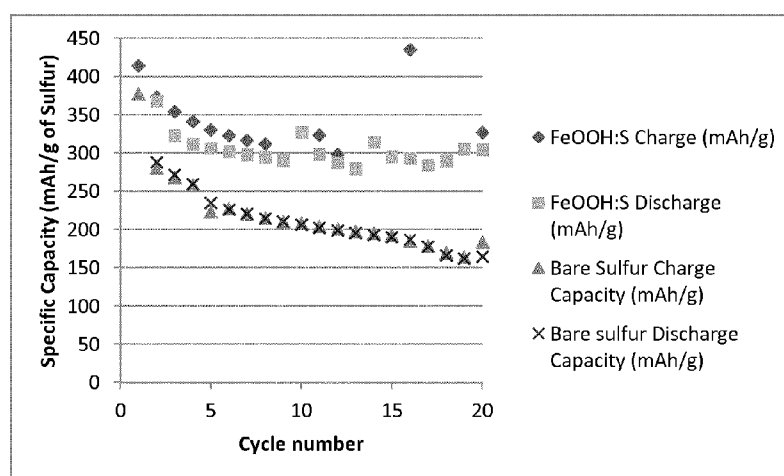
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(54) Title: POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM-SULFUR BATTERY

Figure 1A



(57) Abstract: The present invention relates to a sulfur-containing powder comprising iron (III) oxide-hydroxide, a method of preparing such powder, the use of such powder as positive active material for a rechargeable lithium-sulfur battery and a rechargeable lithium-sulfur battery comprising such powder.

WO 2017/109014 A1

Positive active material for rechargeable lithium-sulfur battery

This application claims priority to European application No.15307099.0 – filed on December 22, 2015-, the whole content of this application being incorporated herein by reference for all purposes.

**Technical Field**

5           The present invention relates to a sulfur-containing powder, a method of preparing such powder, the use of such powder as positive active material for a rechargeable lithium-sulfur battery and a rechargeable lithium-sulfur battery comprising such powder.

**Prior Art**

10           The lithium-sulfur battery is one of the most promising electrochemical technologies for "post-lithium-ion" batteries, owing to its high specific energy, along with its economic and environmental benefits. However, there are still a number of technical challenges hindering the commercialization of lithium-sulfur batteries, such as poor cycle life, low cycle efficiency, and severe self-discharge.  
15           These problems are related to a low electronic/ionic conductivity of sulfur and its reduction products and the solubility of active materials, particularly intermediate polysulfide ions in the liquid electrolyte.

          Over the years, efforts have been dedicated to addressing these technical issues. One of the main approaches to solve the problems has been to confine the  
20           active sulfur within conductive materials to trap the polysulfide species inside the electrode, and at the same time, facilitate the electron conduction through the conductive phase. Such an approach is described in US 2003/0082442 A1. This document discloses a positive active material for a rechargeable lithium-sulfur battery comprising a core of a sulfur compound and a surface-passivation layer  
25           formed on the core using a coating element, such as Al, B and Si. To prepare the positive active material the sulfur compound is encapsulated with a coating liquid including the coating material source. Thus, a multi-step solution process using organic solvents is required. Such process is time consuming, costly and environmentally questionable.

30           To overcome the problems associated with such multi-step solution process C. S. Kim, et al. suggest in Electrochemistry Communications 32 (2013) 35-38 a mechano-fusion technique to confirm the sulfur particles inside a stable

outer layer. It is said that this process only requires simple mixing of the dry powders with different particle size and has a short process time (a few minutes). It is therefore considered by the authors as appropriate to scale-up without adding much process cost. The authors suggest carbon-coated  $\text{LiFePO}_4$  as surface coating material for the sulfur particles.

While the mechano-fusion technique employed by C. S. Kim et al. constitutes an improvement over the prior art multi-step solution process for preparing the positive active material for a rechargeable lithium-sulfur battery, there is still a need for further improvements in particular with respect to the sulfur use, the energy density of the electrode and the capacity retention of the battery.

#### **Brief Description of the Invention**

The present inventors found that the above problems can be solved by using iron(III) oxide-hydroxide instead of  $\text{LiFePO}_4$  in the preparation of the positive active material.

The present invention therefore relates to a powder comprising elemental sulfur and/or a sulfur compound and iron(III) oxide-hydroxide.

In a further embodiment, the present invention relates to a method of preparing said powder.

In a further embodiment, the present invention relates to the use of said powder as positive active material for a rechargeable lithium-sulfur battery.

In a further embodiment, the present invention relates to a rechargeable lithium-sulfur battery comprising said powder as positive active material.

#### **Detailed Description of the Invention**

The present invention relates to a positive active material for a rechargeable lithium-sulfur battery having an improved power property, a high discharge voltage, improved sulfur use, improved energy density and high capacity retention. These results and others are achieved by providing a powder comprising elemental sulfur and/or a sulfur compound and iron(III) oxide-hydroxide.

The sulfur can be present in the powder in the form of elemental sulfur (such as  $\text{S}_8$ ) or in the form of a sulfur compound. Suitable sulfur compounds are  $\text{Li}_2\text{S}_n$  wherein  $n \geq 1$ , an organo sulfate compound, a carbon-sulfur polymer, and mixtures thereof. Suitable carbon-sulfur polymers are for example  $(\text{C}_2\text{S}_x)_n$  wherein  $x = 2.5$  to  $50$  and  $n \geq 2$ . In a preferred embodiment, the sulfur is present in the powder as elemental sulfur.

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Iron(III) oxide-hydroxide is also known as ferric hydroxide. Iron(III) oxide-hydroxide has the chemical formula  $\text{FeOOH}$ . It can be obtained for example by reacting ferric chloride with sodium hydroxide. Alternatively, iron(II) may be oxidized to iron(III) by hydrogen peroxide in the presence of an acid. Furthermore, ferric hydroxide can be prepared as described in  
5 WO 03/053560. Alternatively, commercially available iron(III) oxide-hydroxide may be used.

Iron(III) oxide-hydroxide occurs in anhydrous and hydrated forms. Furthermore, iron(III) oxide-hydroxide occurs in four different polymorphic  
10 forms, known as alpha-, beta-, gamma- and delta- $\text{FeOOH}$ . All these forms may be used in the present invention.

Applicants do not wish to be bound to any theory but it is believed that the iron(III) oxide-hydroxide modifies the surface morphology of the elemental sulfur or sulfur compound thereby improving the wetting property thereof to an  
15 electrolyte and increasing the electrochemical activity thereof. As such, the elemental sulfur or sulfur compound is modified on the surface thereof to improve the electrochemical activity and to prevent the dissolution of the elemental sulfur or sulfur compound powder during an electrochemical reaction.

In order to facilitate the above effects obtained by modifying the surface of  
20 the elemental sulfur or sulfur compound, it was found that it is advantageous if the elemental sulfur and sulfur compound is present in the form of particles having a median particle size being higher than the median particle size of the iron(III) oxide-hydroxide particles. In the context of the present invention, the median particle size D50 is according to a volume distribution. This and other  
25 particle sizes below are measured by laser diffraction methods according to ISO 13320.

In a preferred embodiment, the elemental sulfur and sulfur compound is present in the form of particles having a median particle size in the range of from about 5 to about 80  $\mu\text{m}$ , preferably from about 10 to about 70  $\mu\text{m}$ , more  
30 preferably from about 20 to about 60  $\mu\text{m}$  and even more preferably from about 30 to about 50  $\mu\text{m}$ , such as for example about 40  $\mu\text{m}$ . Depending on the specific particle size of the elemental sulfur and sulfur compound particles, the iron(III) oxide-hydroxide particles preferably have a median particle size below that of the elemental sulfur and/or sulfur compound. For example, the iron(III) oxide-  
35 hydroxide particles may have a median particle size in the range of from about 1 to about 3,000 nm, preferably about 5 to about 2,000 nm, more preferably from

about 10 to about 700 nm, even more preferably from about 50 to about 500 nm, such as in the range of from about 100 to about 400 nm.

The ratio of elemental sulfur and/or sulfur compound to iron(III) oxide-hydroxide is not particularly limited. However, the iron(III) oxide-hydroxide should be present in an amount sufficient to ensure covering of the elemental sulfur or sulfur compound particles. More preferably, all the iron(III) oxide-hydroxide should be used to form a uniform surface layer on the elemental sulfur or sulfur compound particles. This can be achieved, for example, when the weight ratio of elemental sulfur and/or sulfur compounds to iron(III) oxide-hydroxide in the powder of the present invention is in the range of from about 50:50 to about 95:5, preferably from about 70:30 to about 90:10, such as about 80:20 or about 70:30.

In a preferred embodiment, the powder of the present invention comprises a composite which comprises particles of elemental sulfur and/or a sulfur compound covered by a layer of iron(III) oxide-hydroxide. In this regard "composite" is to be understood as an agglomeration of iron(III) oxide-hydroxide around particles of elemental sulfur or sulfur compound wherein the iron(III) oxide-hydroxide covers the elemental sulfur or sulfur compound particles forming a coating around these particles. Such composite can be obtained by high-energy mixing as described further below.

If the powder is present in the form of a composite, the above particle sizes relate to the particles prior to the formation of the composite. For example, by high-energy mixing sulfur particles can be densified or several smaller sulfur particles can agglomerate to one larger particle which is then coated by the iron(III) oxide-hydroxide. Therefore, the size of the composite particles can be different from the size of the single elemental sulfur, sulfur compound and iron(III) oxide-hydroxide particles.

The present invention furthermore relates to a method of preparing the above powder by mixing particles of elemental sulfur and/or a sulfur compound with particles of iron(III) oxide-hydroxide. In a preferred embodiment, the mixing is conducted as a high-energy mixing. High-energy mixing can be conducted for example in a ball mill, such as a SPEX<sup>®</sup> miller. High-energy mixing can for example be conducted during 5 to 10 minutes with 10 stainless steel balls having a diameter of for example 0.5 cm. High-energy milling is also described by C. S. Kim, et al. in *Electrochemistry Communications* 32 (2013) 35-38.

High-energy mixing results in a powder comprising elemental sulfur and/or a sulfur compound and iron (III) oxide-hydroxide wherein the two components are fused to each other in a certain physical configuration being different to a mere mixture of the two components and also being different to a powder wherein the elemental sulfur or sulfur compound particles are coated by a coating material via a solution process. Thus, the present invention also relates to a powder comprising elemental sulfur and/or a sulfur compound and iron(III) oxide-hydroxide obtainable by high-energy mixing particles of elemental sulfur and/or a sulfur compound with particles of iron(III) oxide-hydroxide.

The above described powder is particularly suitable for use as positive active material for a rechargeable lithium-sulfur battery.

A rechargeable lithium-sulfur battery includes a positive active material including a sulfur-based compound having a sulfur-sulfur bond, and a negative active material including lithium metal or a carbonaceous material. The sulfur-based compound may be elemental sulfur or a sulfur compound as described above. The carbonaceous material is a material in which intercalation chemistry occurs, examples of which include graphite intercalation compounds, carbonaceous materials, and carbonaceous materials inserted with lithium. Upon discharge (electrochemical reduction), a sulfur-sulfur bond breaks, which results in a decrease in the oxidation number of S. Upon recharging (electrochemical oxidation), a sulfur-sulfur bond forms, which leads to an increase in the oxidation number of S. However, known lithium-sulfur batteries have the disadvantage of a low electrochemical activity which results from the fact that  $S_8$  is electrochemically inactive and that a passivation layer is formed on the surface of lithium metal, which results in a battery having a poor discharge voltage at a high C-rate and a poor cycle-life characteristics. These problems are dealt with by C. S. Kim, et al. in *Electrochemistry Communications* 32 (2013) 35-38 by providing an inner sulfur domain covered by an outer  $LiFePO_4$  layer. Such composite showed higher utilization of active sulfur compared to pristine sulfur. The present inventors now found that the utilization of sulfur can be surprisingly further enhanced by using sulfur/ferric hydroxide composites instead of the known sulfur/ $LiFePO_4$  composite.

The present invention therefore also relates to a lithium-sulfur battery comprising

a positive electrode including a positive active material, the positive active material comprising:

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a core of elemental sulfur and/or a sulfur compound, and  
a surface-passivation layer formed on the core, the surface-passivation  
layer comprising iron(III) oxide-hydroxide;  
a negative electrode comprising a negative active material, preferably  
5 including lithium metal or carbonaceous material; and  
an electrolyte disposed between said positive and negative electrodes.

Preferably, said lithium-sulfur battery comprises the above described  
powder as the positive active material.

Should the disclosure of any patents, patent applications and publications  
10 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 shall take precedence.

The invention will now be further described by the following examples,  
which are not intended to be limiting.

#### 15 **Example 1**

##### 1.1 Preparation of the iron(III) oxide-hydroxide powder:

A feed-solution was prepared from  $\text{Fe}(\text{NO}_3)_3$  and acetic acid with the  
following concentrations: 1.5 mol/L in Fe and 1.5 mol/L in acetic acid. A basic  
solution was prepared from ammonia 28 wt% with a final concentration of  
20 4 mol/L. The reactor was filled with 800 mL of water. The two feed solutions  
were introduced with speeds in order that pH was constant and adjusted to 6.9. In  
the same time the mixture was pumped with a speed in order to work at constant  
volume. After 40 min all the volume was renewed. The first collected batch was  
not kept. The second was kept. The product was then filtered and dried in an  
25 oven.

##### 1.2 Preparation of the sulfur-containing powder:

4 g of elemental sulfur powder having a particle size of about 40  $\mu\text{m}$   
(obtained from Sigma Aldrich) and 1 g of iron(III) oxide-hydroxide were mixed  
for 5 to 10 minutes in a high-energy SPEX<sup>®</sup> miller with 10 stainless steel balls  
30 (diameter 0.5 cm).

1.3 The thus obtained composite was used as positive active material for a  
rechargeable lithium-sulfur battery as follows:

An electrode was prepared by mixing N-methyl-2-pyrrolidone (NMP) with  
the composite prepared above, carbon black SP C65 from TIMCAL as  
35 conductive additive and polyvinylidene fluoride (PVDF) binder (Solef 6020  
from Solvay) in a weight proportion of 85/10/5. The amount of NMP is 400 %

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relative to the total mass of composite + carbon black + PVDF. The resulting ink was deposited by coating using a doctor blade micrometer (deposit 150  $\mu\text{m}$  thickness leading to 10 mAh loadings) on an aluminum foil of 20  $\mu\text{m}$  thickness. The coating was then dried at 55°C for 24 hours in air.

5 Electrochemical cells were prepared as coin cells in an argon filled glove box as follows:

Cathode: electrode prepared above

Separator: Celgard 2400 (from Celgard) + Viledon kind FS 2206-14 (from Freudenberg)

10 Electrolyte: 1M LiTFSI (Bis(trifluoromethane)sulfonimide lithium salt)) + 0,1M LiNO<sub>3</sub> in a 50/50 (in volume) mixture of TEGDME (TetraethyleneGlycolDimethylether)/DIOX (1,3-dioxolane)

Anode: Lithium foil 140 micrometers thick.

15 Tests were conducted at C/10 between 1.5-3.0 V vs. Li<sup>+</sup>/Li<sup>0</sup>; after 1h rest, C/10 meaning the application of a steady current chosen for a complete charge of the battery in 10 hours. The discharge is also done at this current (in the opposite sign).

The testing device was an "ARBIN BT2000" from ARBIN INSTRUMENTS

20 Capacity retention curves of i/ cathode containing only sulfur as active material (triangles for charge capacity; cross for discharge capacity) and ii/ the cathode containing S:FeOOH (80:20 in weight) (lozenges for charge capacity; squares for discharge capacity) composite as active material during a C/10 cycling are shown in Figures 1A and 1B. Results are depicted both in terms of sulfur use (figure 1A) and in terms of electrode gravimetric capacity (figure 1B).

### **Comparative Example**

Example 1 was repeated except that iron(III) oxide-hydroxide was replaced with LiFePO<sub>4</sub>.

30 Corresponding capacity retention curves are shown in Figure 2. It can be seen that capacity retention in terms of sulfur use is significantly lower compared to the capacity retention obtained with iron(III) oxide-hydroxide.

CLAIMS

1. Powder comprising elemental sulfur and/or a sulfur compound and iron(III) oxide-hydroxide.
2. Powder according to claim 1, wherein the sulfur compound is selected  
5 from the group consisting of  $\text{Li}_2\text{S}_n$ , wherein  $n \geq 1$ , an organo sulfur compound, a carbon-sulfur based polymer and mixtures thereof.
3. Powder according to claim 1 or 2, wherein the elemental sulfur and/or sulfur compound is present in the form of particles having a median particle size being higher than the median particle size of the iron(III) oxide-hydroxide  
10 particles.
4. Powder according to any of the preceding claims, wherein the elemental sulfur and/or sulfur compound is present in the form of particles having a median particle size in the range of from about 5 to about 80  $\mu\text{m}$ , preferably from about 10 to about 70  $\mu\text{m}$ , more preferably from about 20 to about 60  $\mu\text{m}$   
15 and even more preferably from about 30 to about 50  $\mu\text{m}$ .
5. Powder according to any of the preceding claims, wherein the weight ratio of elemental sulfur and/or sulfur compound to iron(III) oxide-hydroxide is in the range of from about 50:50 to about 95:5, preferably from about 70:30 to about 90:10.
- 20 6. Powder according to any of the preceding claims, comprising particles of elemental sulfur.
7. Powder according to any of the preceding claims, comprising a composite which comprises particles of elemental sulfur and/or a sulfur compound covered by a layer of iron(III) oxide-hydroxide.
- 25 8. Method of preparing the powder according to any one of claims 1 to 7, comprising mixing particles of elemental sulfur and/or a sulfur compound with particles of iron(III) oxide-hydroxide.
9. Method according to claim 8, wherein the mixing is conducted as high-energy mixing.

10. Powder comprising elemental sulfur and/or a sulfur compound and iron(III) oxide-hydroxide obtainable by the method of claim 9.

11. Use of the powder according to any one of claims 1 to 7 and 10 as positive active material for a rechargeable lithium-sulfur battery.

5 12. Lithium-sulfur battery comprising

a positive electrode including a positive active material, the positive active material comprising:

a core of elemental sulfur and/or a sulfur compound, and

10 a surface-passivation layer formed on the core, the surface-passivation layer comprising iron(III) oxide-hydroxide;

a negative electrode comprising a negative active material, preferably including lithium metal or carbonaceous material; and

an electrolyte disposed between said positive and negative electrodes.

15 13. Lithium-sulfur battery according to claim 12 wherein the positive active material is the powder mixture according to any one of claims 1 to 7 and 10.

Figure 1A

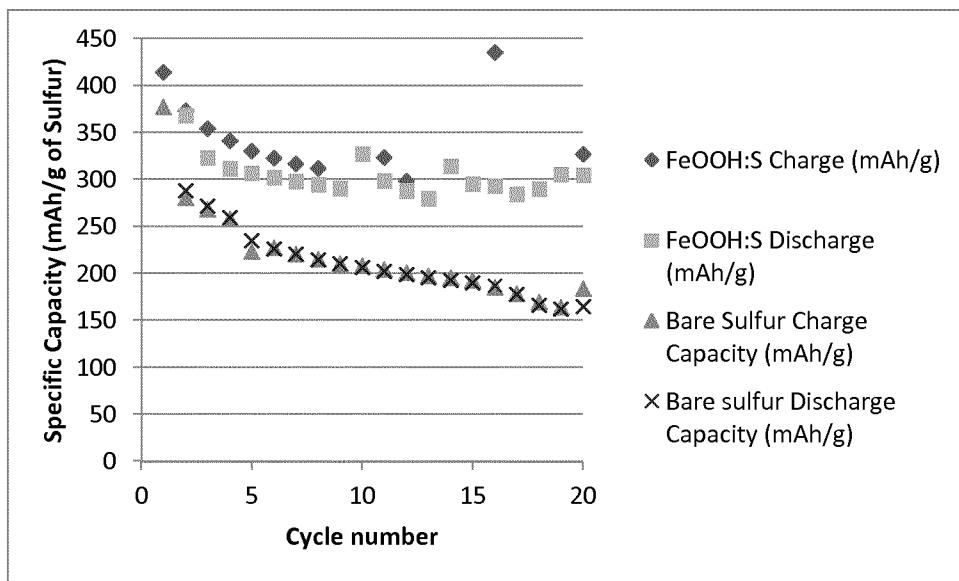


Figure 1B

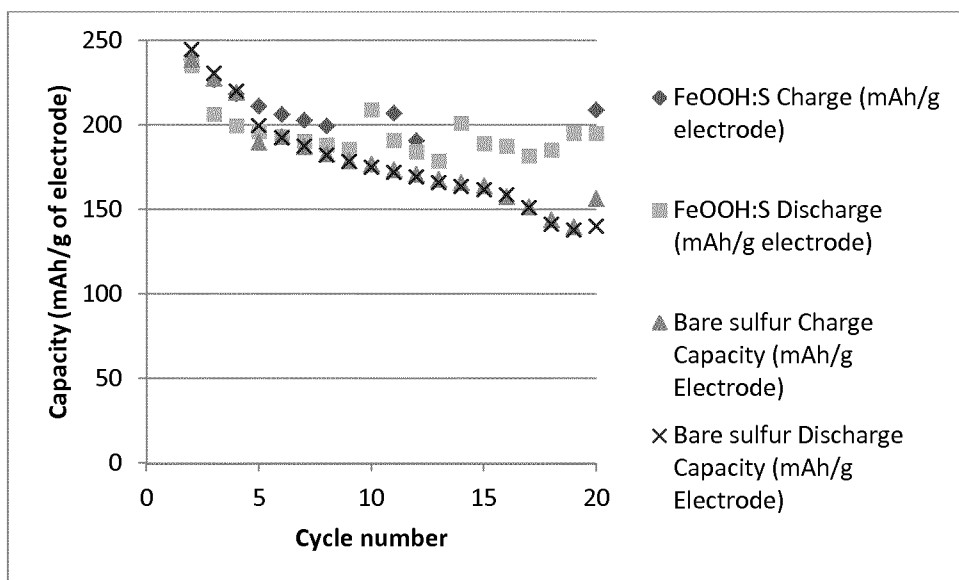
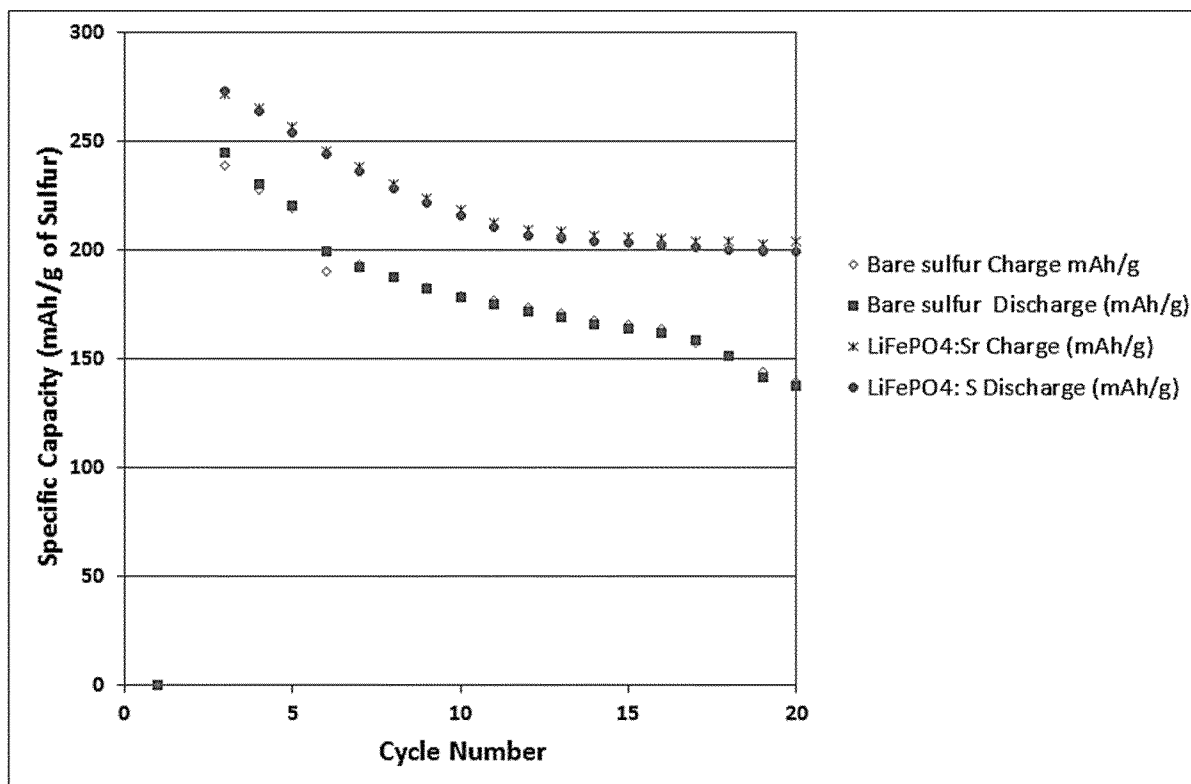


Figure 2



**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2016/082271

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. H01M4/36 H01M4/58 H01M4/62 H01M10/052 C01G49/00  
 C01B17/00  
 ADD. H01M4/02 H01M4/38  
 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 C01G C01B

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, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2008 176981 A (TOYOTA MOTOR CORP) 31 July 2008 (2008-07-31) abstract; figures 1, 5, 6 paragraph [0023] - paragraph [0026] paragraph [0049] - paragraph [0050] paragraph [0076] paragraph [0091] paragraph [0088] - paragraph [0089] -----	1-5,8-11  6,7,12, 13
X A	DE 197 55 351 A1 (JANSEN WALTER PROF DR [DE]; HELMS HARTMUT [DE]) 17 June 1999 (1999-06-17) page 2, lines 10-15 page 2, line 41 - line 50 page 4, line 1 - line 55 page 6, line 5 - line 32 ----- -/--	1,6,8, 10,11  2-5,7,9, 12,13

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

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  18 January 2017	Date of mailing of the international search report  27/01/2017
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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  Maxisch, Thomas
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/082271

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104 087 339 B (BEIJING BAOTASANJU ENERGY TECHNOLOGY CO LTD) 18 November 2015 (2015-11-18)	1,5,6,8, 10
A	paragraph [0021] - paragraph [0022]; example 2	2-4,7,9, 11-13
A	----- XIAO-QING NIU ET AL: "Nickel Hydroxide-Modified Sulfur/Carbon Composite as a High-Performance Cathode Material for Lithium Sulfur Battery", ACS APPLIED MATERIALS AND INTERFACES, vol. 7, no. 30, 9 July 2015 (2015-07-09), pages 16715-16722, XP055275465, US ISSN: 1944-8244, DOI: 10.1021/acsami.5b04408 the whole document	1-13
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A	----- JIAN JIANG ET AL: "Encapsulation of sulfur with thin-layered nickel-based hydroxides for long-cyclic lithium-sulfur cells", NATURE COMMUNICATIONS, vol. 6, 16 October 2015 (2015-10-16), page 8622, XP055275435, United Kingdom ISSN: 2041-1723, DOI: 10.1038/ncomms9622 the whole document -----	1-13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/082271

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2008176981	A	31-07-2008	NONE
DE 19755351	A1	17-06-1999	NONE
CN 104087339	B	18-11-2015	NONE