



(86) **Date de dépôt PCT/PCT Filing Date:** 2012/06/14
(87) **Date publication PCT/PCT Publication Date:** 2012/12/20
(45) **Date de délivrance/Issue Date:** 2020/06/02
(85) **Entrée phase nationale/National Entry:** 2013/12/11
(86) **N° demande PCT/PCT Application No.:** EP 2012/061058
(87) **N° publication PCT/PCT Publication No.:** 2012/171888
(30) **Priorité/Priority:** 2011/06/14 (DE10 2011 077 478.5)

(51) **Cl.Int./Int.Cl. C01B 17/22** (2006.01),
H01M 2/16 (2006.01), **H01M 4/136** (2010.01),
H01M 4/58 (2010.01), **H01M 4/62** (2006.01)
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(54) **Titre : PROCÉDE DE PRODUCTION D'UN SULFURE DE LITHIUM A REVETEMENT CARBONE, ET SON UTILISATION**
(54) **Title: METHOD FOR PRODUCING A CARBON-COATED LITHIUM SULFIDE, AND USE THEREOF**

(57) **Abrégé/Abstract:**

The invention relates to a novel method for producing a carbon-doped lithium sulfide powder, according to which elementary lithium is reacted with elementary sulfur and/or a sulfur-containing compound selected from the group containing CS₂, COS, SO₂ and SO, in a liquid state, in an aliphatic or cycloaliphatic hydrocarbon solvent. The products of the method according to the invention are used to produce lithium battery electrodes or a lithium-ion-conducting solid.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG(19) Weltorganisation für geistiges
Eigentum

Internationales Büro

(43) Internationales
Veröffentlichungsdatum
20. Dezember 2012 (20.12.2012)(10) Internationale Veröffentlichungsnummer
WO 2012/171888 A3

(51) Internationale Patentklassifikation:

C01B 17/22 (2006.01) H01M 4/136 (2010.01)
H01M 2/16 (2006.01) H01M 4/58 (2010.01)
H01M 4/62 (2006.01)

(21) Internationales Aktenzeichen: PCT/EP2012/061058

(22) Internationales Anmeldedatum:
14. Juni 2012 (14.06.2012)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
10 2011 077 478.5 14. Juni 2011 (14.06.2011) DE(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme
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Trakehner Straße 3, 60487 Frankfurt am Main (DE).(81) Bestimmungsstaaten (soweit nicht anders angegeben, für
jede verfügbare nationale Schutzrechtsart): AE, AG, AL,
AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
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ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.(84) Bestimmungsstaaten (soweit nicht anders angegeben, für
jede verfügbare regionale Schutzrechtsart): ARIPO (BW,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ,
TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ,
RU, TJ, TM), europäisches (AL, AT, BE, BG, CH, CY,
CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT,
LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Erklärungen gemäß Regel 4.17:

— Erfindererklärung (Regel 4.17 Ziffer iv)

[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR PRODUCING A CARBON-COATED LITHIUM SULFIDE AND USE THEREOF

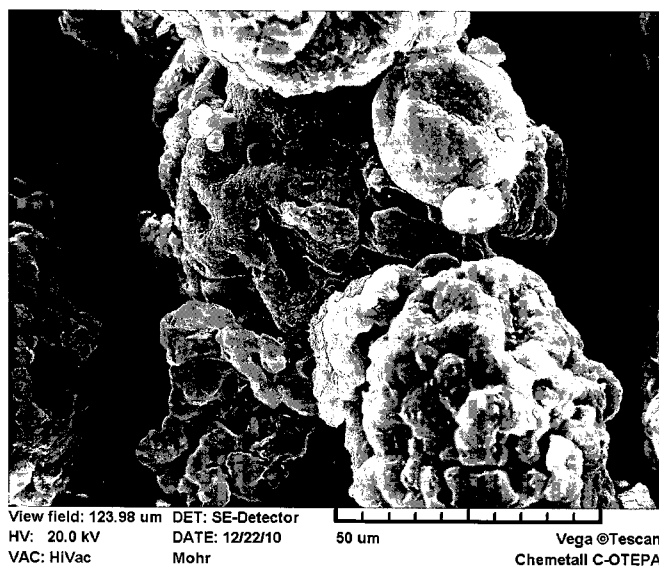
(54) Bezeichnung : VERFAHREN ZUR HERSTELLUNG EINES KOHLENSTOFFBESCHICHTETEN LITHIUMSULFIDS UND
DESSEN VERWENDUNG

Abb. 2

(57) Abstract: The invention relates to a
novel method for producing a carbon-
doped lithium sulfide powder, according to
which elementary lithium is reacted with
elementary sulfur and/or a sulfur-
containing compound selected from the
group containing CS₂, COS, SO₂ and SO,
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invention are used to produce lithium
battery electrodes or a lithium-ion-
conducting solid.(57) Zusammenfassung: Die Erfindung
betrifft ein neues Verfahren zur
Herstellung von einem kohlenstoffdotierten
Lithiumsulfidpulver, bei dem elementares
Lithium mit elementarem Schwefel
und/oder einer schwefelhaltigen
Verbindung ausgewählt aus der Gruppe
CS₂, COS, SO₂ und SO in flüssigem
Zustand in einem aliphatischen oder
cycloaliphatischenKohlenwasserstofflösungsmittel umgesetzt
wird. Die erfindungsgemäßen
Verfahrensprodukte werden für die

Herstellung von Lithiumbatterieelektroden oder die Herstellung eines lithiumionenleitfähigen Feststoffes verwendet.

WO 2012/171888 A3



Veröffentlicht:

- *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*
- *vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eingehen (Regel 48 Absatz 2 Buchstabe h)*

**(88) Veröffentlichungsdatum des internationalen
Recherchenberichts:**

30. Mai 2013

Method for producing a carbon-coated lithium sulfide, and use thereof

The invention relates to a method for producing a carbon-coated lithium sulfide, and use thereof.

Rechargeable electrochemical storage systems are presently becoming increasingly important in many areas of everyday life. In addition to the long-standing applications as automobile starter batteries and as an energy source for portable electronic devices, considerable growth is predicted in the future for electric automobile drives and for stationary energy storage. Traditional lead/sulfuric acid accumulators are not suitable for the new applications because their capacity is far too low, and they cannot be cycled frequently enough. In contrast, the best prospects are seen with lithium batteries.

However, lithium accumulators according to the prior art likewise have too little energy storage capacity for many applications. Present lithium-ion batteries have specific energy densities between approximately 100 and 250 Wh/kg. In addition, they usually contain costly elements such as cobalt and/or nickel. Lithium/sulfur and lithium/air systems have much higher (theoretical) energy densities:

Battery system	Theoretical energy density	
	Wh/L	Wh/kg
Li ion (LiC ₆ / Ni, Mn, Co oxide)	1710	510
Lithium / sulfur	2710	2450
Lithium / air		5830

The technical challenges in the development of Li/air systems are still so great that a marketable system is not expected for at least another 10–20 years (M. Jacoby, Chem. Eng. News Nov. 22 (2010) 29–31). The prospects for the lithium/sulfur system appear to be much more favorable. One drawback of this system is the use of lithium metal anodes. Lithium metal is relatively costly compared to saline materials or the graphite used in lithium-ion batteries. In addition, this battery has the further disadvantage that it loses capacity too rapidly during charging and discharging.

It has therefore been proposed to assemble the lithium/sulfur battery in the discharged state; i.e., a lithium-free (or low-lithium) material such as a tin/carbon composite is used as the anode, and lithium sulfide is used as the cathode (B. Scrosati, *Angew. Chem.* 2010, 122, 2421–2424). Unfortunately, this battery configuration has likewise proven to have insufficient cyclical stability. The main reason is that soluble oligosulfur compounds (Li_2S_3 and Li_2S_4 , for example) may form during cycling. As a result, the cathode loses redox-active material (Y. Li, *J. Power Sources* 195 (2010) 2945–2949; D. Aurbach, *J. Electrochem. Soc.* 156(8), A694–A702 (2009)). To improve the conductivity of the cathode material (sulfur or lithium sulfide), formation of a composite with carbon is often resorted to. Thus, T. Takeuchi has reported that commercially available sulfide powder may be coated with graphitic carbon in an arc plasma process (*J. Electrochem. Soc.* 157 (11) A1196–A1201 (2010)). However, such coating processes are energy-intensive and require expensive coating equipment and high-vacuum technology, and consequently entail high costs. Another approach to producing $\text{Li}_2\text{S}/\text{C}$ composites is to grind commercially available lithium sulfide powder in a ball mill, for example (B. Scrosati, *Angew. Chem.* 2010, 122, 2421–2424). Grinding processes likewise have a fairly complicated technology and require the availability of finished components. Lithium sulfide is obtainable from the chemical trade, but only at high cost, for example €560.00 for 50 g from Alfa Aesar (list price, 2011-2013 catalog edition). Lastly, it is known that the reaction of lithium with sulfur in boiling naphthalene results in a main product having the approximate composition of Li_2S and containing impurities of free metal (elemental lithium), carbides, and polysulfides (T.G. Pearson and P.L. Robinson, *J. Chem. Soc.* 1931, 413–420).

The object of the invention is to provide a simple method involving the cost-effective production of lithium sulfide in a pure phase, and the cost-effective formation of a composite of same with conductivity-increasing accompanying substances, preferably carbon.

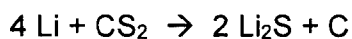
The object is achieved by a method which allows the simultaneous production of lithium sulfide and formation of a composite of same with a conductivity-increasing additive.

More particularly, according to another embodiment, the invention provides a method for producing a carbon-doped lithium sulfide comprising the step of reacting elemental lithium with elemental sulfur and/or at least one of a sulfur-containing compound selected from the group consisting of CS_2 , COS , SO_2 and SO , in a saturated

hydrocarbon solvent selected from the group consisting of aliphatic hydrocarbon solvents, cycloaliphatic hydrocarbon solvents and mixtures thereof, said saturated hydrocarbon solvent being liquid under the reaction conditions.

To this end, the raw materials lithium metal and sulfur and/or a sulfur-containing compound selected from the group comprising CS₂, COS, SO, SO₂ are reacted in a hydrocarbon-based solvent at temperatures above approximately 120°C to 300°C, preferably above 150°C to 250°C, particularly preferably above 180°C to 200°C. The solvent is preferably selected from the group of saturated hydrocarbons. It has surprisingly been found that when saturated hydrocarbons are used as the solvent, a product in a pure phase which is coated or doped with noncrystalline ("X-ray amorphous") carbon is obtained. In contrast, when aromatic or partially aromatic solvents are used, products containing lithium carbide or lithium hydride impurities often result. In addition, the reaction in aromatics or partial aromatics is sometimes inhibited, as shown by the residual content of elemental lithium. Solvents are preferably used which are liquid under the reaction conditions, i.e., which have boiling points of at least 120°C, more preferably at least 150°C, and particularly preferably boiling points > 180°C. Examples include octane, nonane, decane, undecane, dodecane, or any given mixtures of these compounds, whether they are linear, branched, or cyclic. Commercially available paraffin boiling fractions such as ShellSol®D70 or D100 are very particularly preferred.

The carbon content of the materials according to the invention is between 0.5 wt-% and 50 wt-%, preferably between 1 wt-% and 20 wt-%. The carbon content may be varied in a targeted manner by selecting the reaction conditions (primarily the temperature) and by selecting the sulfur raw material. Higher carbon contents are obtained in particular by using carbon-containing sulfur compounds, preferably carbon disulfide (CS₂) and/or carbonyl sulfide (COS). The reaction may proceed using only these compounds as the sulfur source according to



or



In one very particularly preferred embodiment, a mixture of elemental sulfur and carbon disulfide is used. The molar ratio to be selected depends on the desired C content. In general, the molar ratio of sulfur to carbon disulfide may vary between 99:1 and 1:99, particularly preferably between 50:50 and 95:5. It is preferred that the sulfur source is used at least in the stoichiometry necessary for complete reaction or in excess (1 mol-% to 30 mol-%).

The method according to the invention is preferably carried out as a one-step process, in particular as a one-vessel process.

The product according to the invention is characterized by a high specific surface area as the result of a cauliflower-like morphology. Since the achievable current density of electrode materials is scaled to the specific surface, among other factors, materials structured in this way are also suitable for achieving relatively high power, such as that necessary for automotive drive batteries, for example.

According to another embodiment, the invention relates to a lithium sulfide/carbon composite material which is prepared by a method comprising the step of reacting elemental lithium with elemental sulfur and/or at least one of a sulfur-containing compound selected from the group consisting of CS₂, COS, SO₂ and SO, in a saturated hydrocarbon solvent selected from the group consisting of aliphatic hydrocarbon solvents, cycloaliphatic hydrocarbon solvents and mixtures thereof, said saturated hydrocarbon solvent being liquid under the reaction conditions, wherein the composite material has a high specific surface area, has a cauliflower-like surface structure, and is a pure phase which is coated or doped with non-crystalline carbon .

The lithium sulfide/carbon composite materials according to the invention are used for the production of lithium battery electrodes or the production of lithium ion-conductive solids, for example for use as a separator in lithium batteries.

According to another embodiment, the invention relates to a use of the lithium sulfide/carbon composite material defined hereinabove as a separator in lithium batteries.

The invention is explained in greater detail below with reference to three examples, two

comparative examples, and ten figures.

The analyses of the crystalline structure and the assignments were conducted using the AXS (Discover D8) from Bruker; Cu K- α radiation, Sol X detector under the following conditions: Start: 5° – end: 75° (2 theta measuring range); 2 s measuring time / 0.02° measuring increment; temperature: 25°C

The figures show the following:

Figure 1 – UEL 10 153 (Li_2S from Li and S), crystalline phase – lithium sulfide (Li_2S) (red lines)

Figure 2 – Scanning electron microscope (SEM) recording from Example 1

Figure 3 – UEL 10 162 (Li_2S from Li and S), crystalline phase – lithium sulfide (Li_2S) (red lines)

Figure 4 – SEM recording from Example 2

Figure 5 – UEL 11 044 (gray sample), crystalline phase – lithium sulfide (Li_2S) (red lines)

Figure 6 – SEM recording from Example 3

Figure 7 – UEL 11 043 crystalline phase – lithium sulfide (Li_2S) (red lines); sulfur (S) (green lines); lithium hydride (LiH) (blue lines); lithium acetylide (Li_2C_2) (orange lines)

Figure 8 – SEM recording from Comparative Example 1

Figure 9 – UEL 11 042 (ochre sample) – lithium sulfide (Li_2S) (red lines); lithium (Li) (green lines); lithium hydride (LiH) (blue lines)

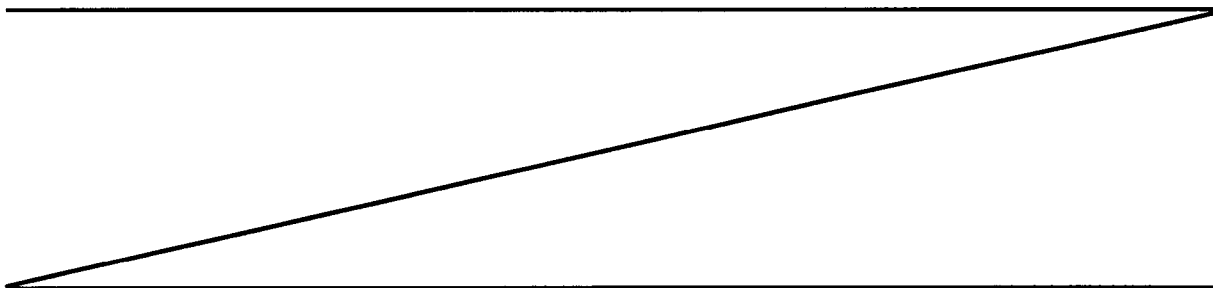


Figure 10 –SEM recording from Comparative Example 2

Example 1: Production of $\text{Li}_2\text{S/C}$ composite from sulfur and lithium powder at approximately 140°C in paraffin oil, receiving vessel containing sulfur

19.8 g powdered sulfur in 520 g Shellisol[®] D100 was placed in an inerted (i.e., free of water and air, filled with Ar) stainless steel double-shell reactor, and was melted/dissolved at a 140°C shell temperature, with stirring. 8.33 g lithium powder was then added in portions (1 g per mol) through a reactor opening. The reaction was exothermic, as shown by a rise in the internal temperature from 136°C to just under 140°C. After the last portion was added, stirring was continued for 1 h at 150°C, and the mixture was then cooled to 80°C and the suspension was pressed onto a filter frit using a Teflon immersion tube, washed (first with Shellisol[®], then three times with pentane), and dried to a constant weight at room temperature (RT). A quantitative product yield (99.8% of theoretical) was obtained. The powder was free-flowing with a grayish-brown tint.

XRD: Lithium sulfide in a pure phase (Figure 1)

SEM: Cauliflower-like surface structure (Figure 2)

Example 2: Production of $\text{Li}_2\text{S/C}$ composite from sulfur and lithium powder at approximately 190°C in paraffin oil, receiving vessel containing lithium

9.24 g lithium metal in 497 g Shellisol[®] D100 was melted in the reactor according to Example 1. 21.98 g powdered sulfur was metered in in portions over a period of approximately 1 h at an internal temperature of approximately 190°C, with stirring. After the addition was complete, stirring was continued for 2 h at 190°C and the mixture was then cooled. After filtration and vacuum drying, 32.1 g of a dark gray, very free-flowing powder was obtained.

XRD: Lithium sulfide in a pure phase (Figure 3)

SEM: Cauliflower-like surface structure (Figure 4)

C content: 4.7%

Li content: 41.1 mmol/g; S content: 20.5 mmol/g (→ 94% Li_2S content)

Example 3: Production of $\text{Li}_2\text{S/C}$ composite from sulfur/carbon disulfide and lithium powder at 190°C in paraffin oil, receiving vessel containing lithium, and secondary reaction at 190°C

9.98 g lithium in 504 g Shellsol[®] D-100 was melted in the reactor according to Example 1. 15.8 g powdered sulfur was metered in in portions at an internal temperature of 185°C , with good stirring. A 30% solution of 5.6 g carbon disulfide in Shellsol[®] D100 was then added dropwise over a period of 15 minutes. After the addition was complete, additional sulfur (8.0 g) was added. After stirring for 2 h at 190°C , the mixture was cooled and the product was isolated (35.1 g of an almost black powder).

XRD: Lithium sulfide in a pure phase (Figure 5)

SEM: Cauliflower-like surface structure (Figure 6)

C content: 7.2%

Li content: 39.9 mmol/g; S content: 20.0 mmol/g ($\rightarrow$ 92% Li_2S content)

Comparative Example 1: Production of $\text{Li}_2\text{S/C}$ composite from sulfur and lithium powder at approximately 190°C in biphenyl

7.67 g lithium in 450 g biphenyl was melted in the reactor according to Example 1. 18.25 g powdered sulfur was metered in in portions over a period of 1 h at an internal temperature of approximately 190°C . After metering was complete, stirring was continued for 2 h at 190°C . The mixture was cooled to 120°C , and 500 mL decane was added (to prevent solidification). The mixture was then hot-filtered and washed with heptane, and the filter residue was vacuum-dried. 25.8 g of a dark gray product was obtained.

XRD: Lithium sulfide with LiH and Li_2C_2 impurities (Figure 7)

SEM: Cauliflower-like surface structure (Figure 8)

C content: 6%

Li content: 40.0 mmol/g; S content: 10.0 mmol/g

Comparative Example 2: Production of $\text{Li}_2\text{S/C}$ composite from sulfur and lithium powder at 190°C in tetralin

8.92 g lithium in 556 g tetralin was melted in the reactor according to Example 1. 21.22 g powdered sulfur was metered in in portions over a period of approximately 1 h at an internal

temperature of approximately 190°C. After metering was complete, stirring was continued for 2 h at 190°C. The mixture was cooled to 80°C and then hot-filtered and washed with heptane, and the filter residue was vacuum-dried. 25.4 g of a yellow-ochre product was obtained.

XRD: Lithium sulfide with LiH and metallic lithium impurities (Figure 9)

SEM: Cauliflower-like surface structure (Figure 10)

C content: 1.1%

Li content: 41.5 mmol/g; S content: 12.0 mmol/g

The examples show that lithium sulfide powder in a pure phase with a large specific surface was formed when saturated hydrocarbon solvents were used. The carbon content in the product increased when CS₂ was used. The carbon was present predominantly in elemental form, presumably in a graphitic modification. When an aromatic solvent such as biphenyl was used, a C-doped lithium sulfide was likewise formed; however, this product had marked amounts of crystalline lithium carbide and lithium hydride impurities. When partially aromatic solvent such as tetralin was used, the reaction was not complete (elemental lithium remained in the product), and lithium hydride was formed as a by-product. The C content was much lower than when a saturated hydrocarbon solvent was used. The reaction may be brought to completion by longer reaction times and/or stoichiometric changes.

CLAIMS

1. A method for producing a carbon-doped lithium sulfide comprising the step of reacting elemental lithium with elemental sulfur and/or at least one of a sulfur-containing compound selected from the group consisting of CS₂, COS, SO₂ and SO, in a saturated hydrocarbon solvent selected from the group consisting of aliphatic hydrocarbon solvents, cycloaliphatic hydrocarbon solvents and mixtures thereof, said saturated hydrocarbon solvent being liquid under the reaction conditions.
2. A method according to claim 1, wherein the reaction is carried out at temperatures of 120°C to 300°C.
3. A method according to claim 1 or 2, wherein the saturated hydrocarbon solvent comprises at least one member selected from the group consisting of octane, nonane, decane, undecane and dodecane.
4. A method according to claim 1, wherein commercially available paraffin boiling fractions are used as the saturated hydrocarbon solvent.
5. A method according to claim 1, wherein a mixture composed of sulfur and carbon disulfide is used as a sulfur source.
6. A method according to claim 5, wherein the sulfur source is used at least in the stoichiometry necessary for complete reaction or in an excess of 1 mol-% to 30 mol-%.
7. A method according to claim 6, wherein a molar ratio of sulfur to carbon disulfide varies between 99:1 and 1:99.
8. A method according to any one of claims 1 to 7, wherein the method is carried out as a one-step process.
9. A method according to any one of claims 1 to 8, wherein the reaction is carried out at temperatures of 150°C to 250°C.
10. A method according to any one of claims 1 to 8, wherein the reaction is carried out at temperatures of 180°C to 200°C.
11. A method according to claim 5 or 7, wherein a molar ratio of sulfur to carbon disulfide varies between 50:50 and 95:5.

12. A method according to claim 8, wherein the method is carried out as a one-vessel process.
13. A method according to any one of claims 1 to 8, wherein the saturated hydrocarbon solvent has a boiling point of at least 120°C.
14. A method according to claim 13, wherein the saturated hydrocarbon solvent has a boiling point of at least 150°C.
15. A method according to claim 13, wherein the saturated hydrocarbon solvent has a boiling point >180°C.
16. A lithium sulfide/carbon composite material which is prepared by a method comprising the step of reacting elemental lithium with elemental sulfur and/or at least one of a sulfur-containing compound selected from the group consisting of CS₂, COS, SO₂ and SO, in a saturated hydrocarbon solvent selected from the group consisting of aliphatic hydrocarbon solvents, cycloaliphatic hydrocarbon solvents and mixtures thereof, said saturated hydrocarbon solvent being liquid under the reaction conditions, wherein the composite material has a high specific surface area, has a cauliflower-like surface structure, and is a pure phase which is coated or doped with non-crystalline carbon .
17. A lithium sulfide/carbon composite material according to claim 16, wherein the composite material has a carbon content of 0.5wt-% to 50wt-%.
18. A lithium sulfide/carbon composite material according to claim 16 or 17, wherein the composite material contains no crystalline phase besides lithium sulfide according to XRD measurements.
19. A lithium sulfide/carbon composite material according to claim 16, wherein the composite material has a carbon content of 1wt-% to 20wt-%.
20. Use of the lithium sulfide/carbon composite material according to any one of claims 16 to 19 for the production of lithium battery electrodes.
21. Use of the lithium sulfide/carbon composite material according to any one of claims 16 to 19 for the production of a lithium ion-conductive solid.
22. Use of the lithium sulfide/carbon composite material according to claim 21 as a separator in lithium batteries.

Figure 1

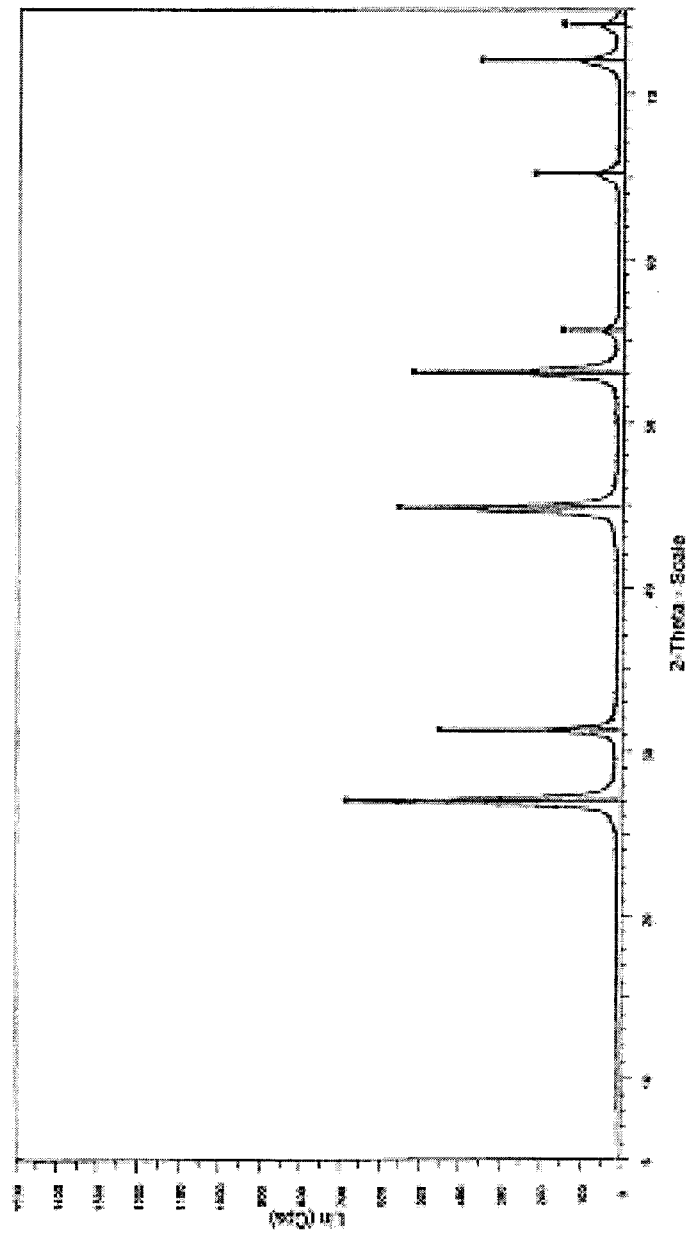


Figure 2

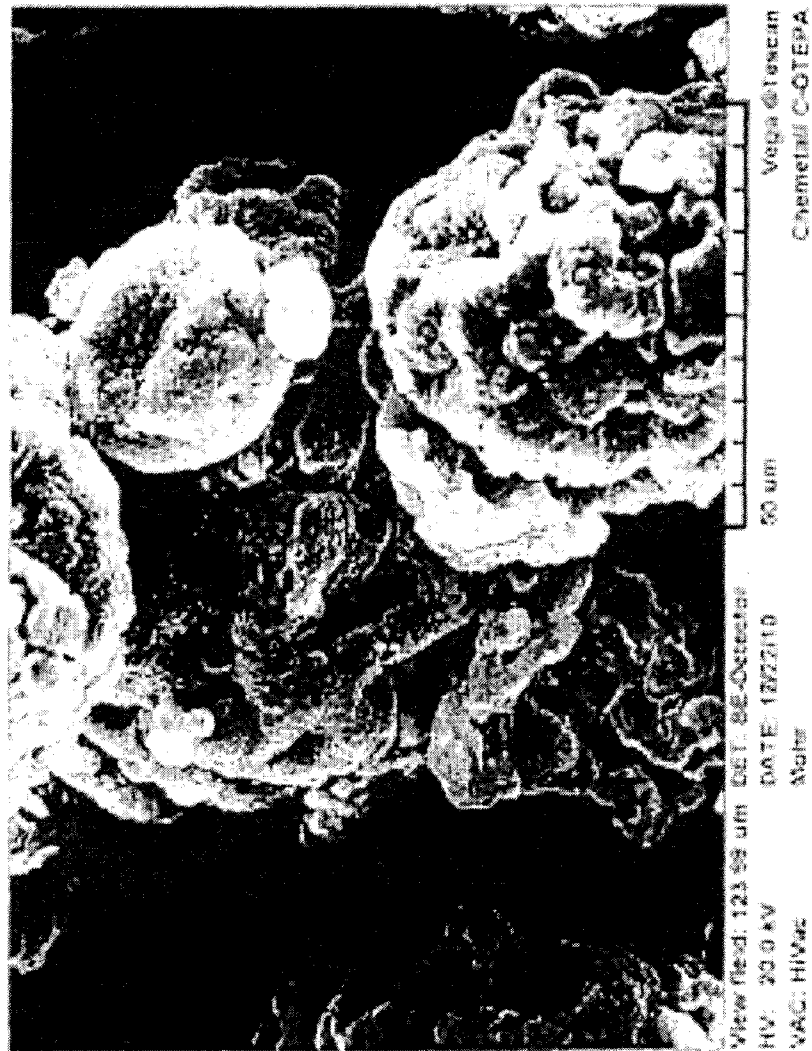


Figure 3

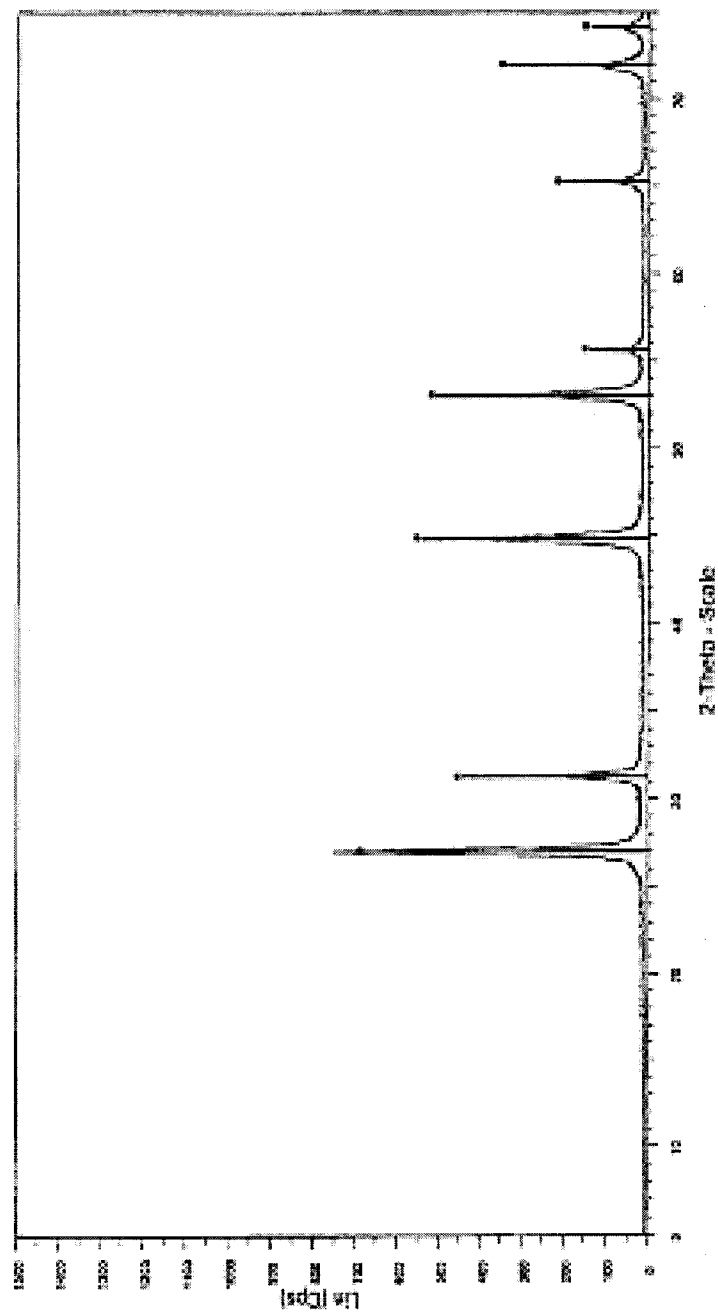


Figure 4

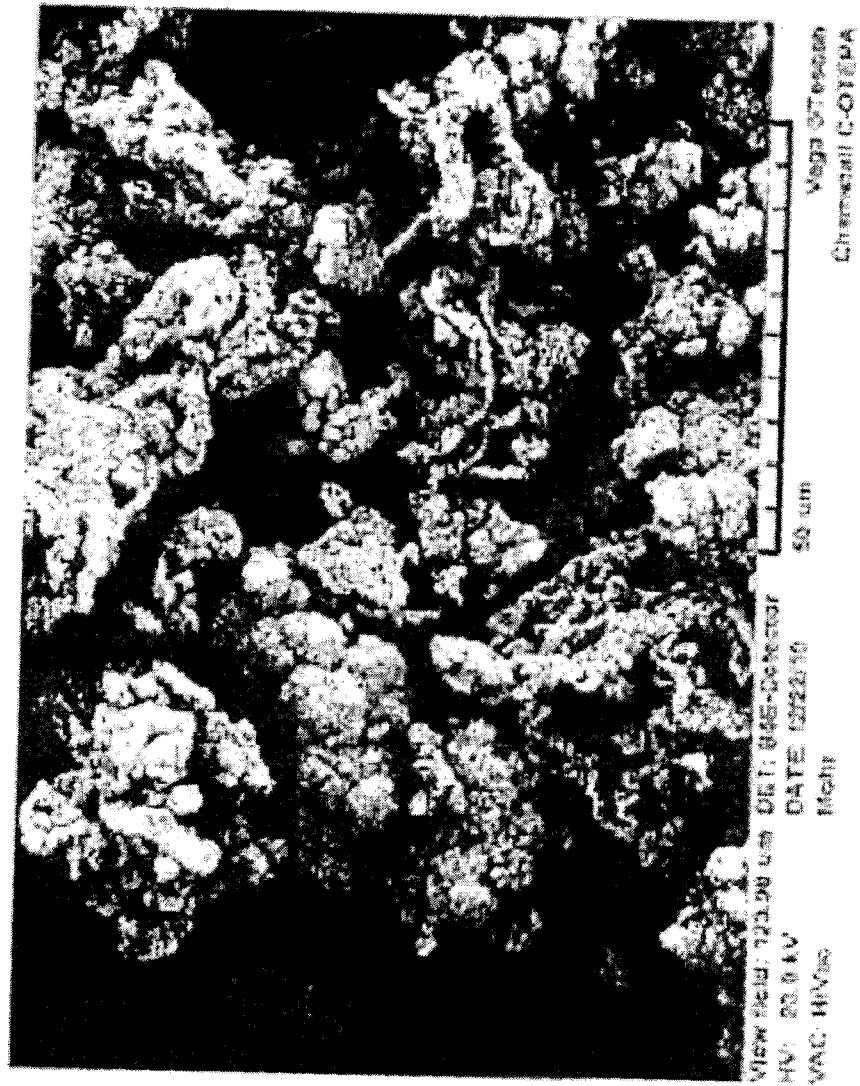


Figure 6

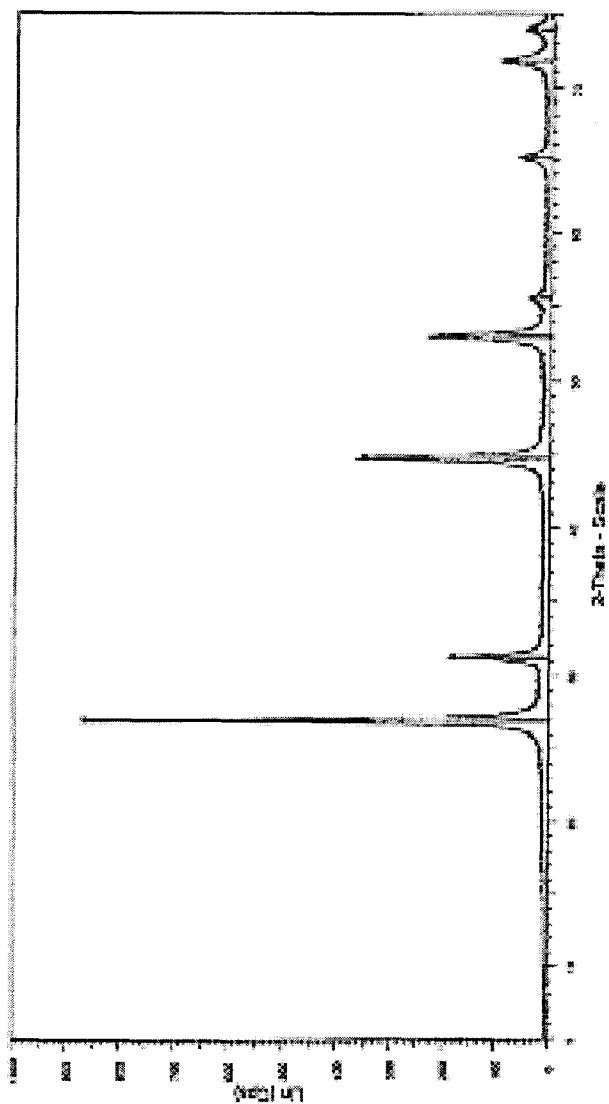


Figure 6

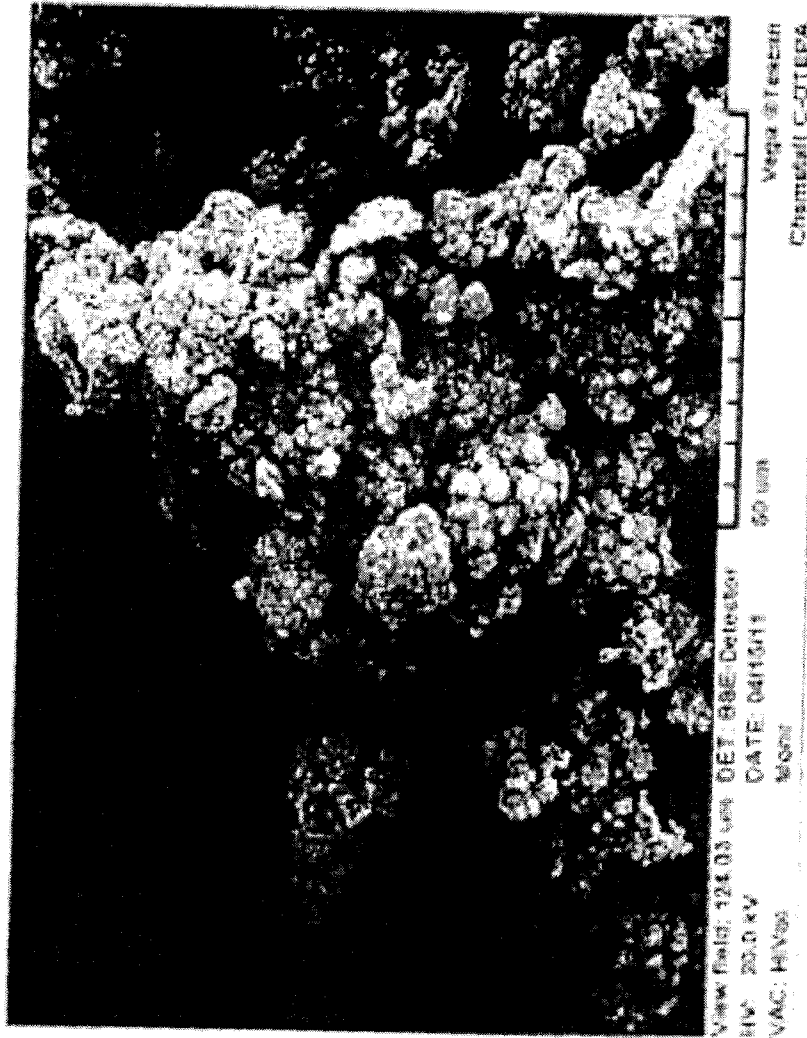


Figure 7

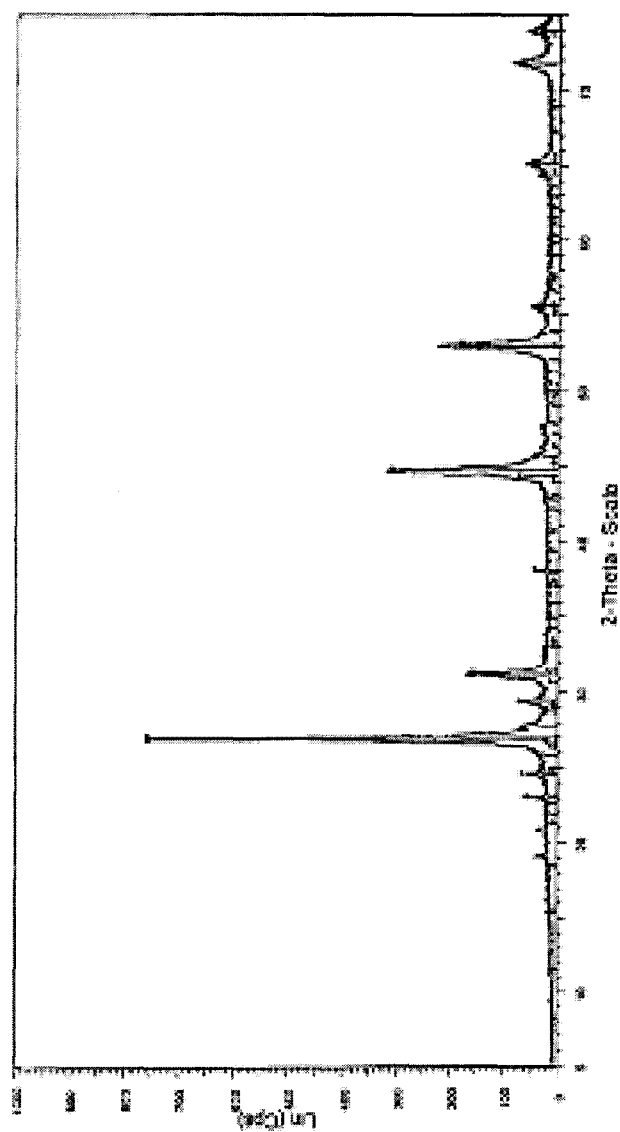


Figure 8

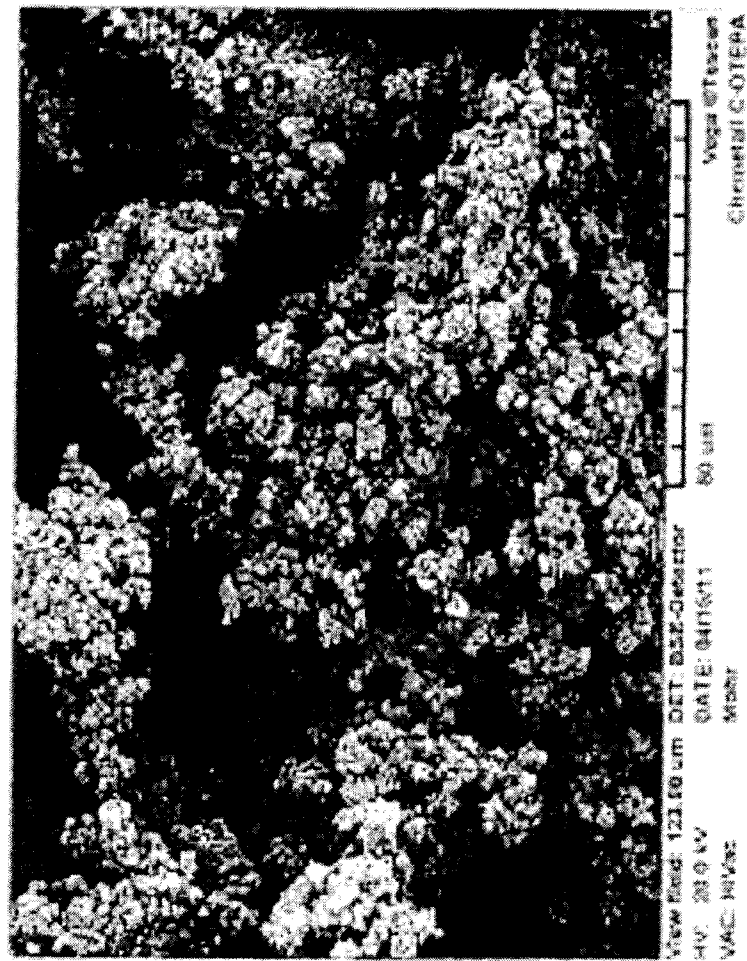


Figure 9

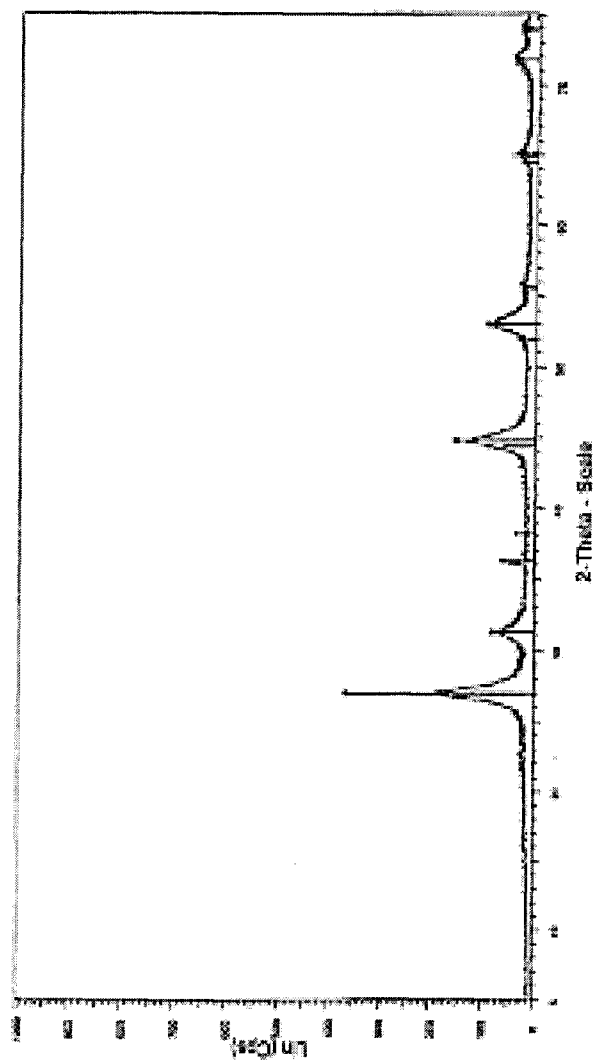


Figure 10

