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(54) **LITHIUM CONTAINING TRANSITION
METAL SULFIDE COMPOUNDS**

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(57) **ABSTRACT**

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§ 371 (c)(1),
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The present invention provides a convenient process for making lithium-containing transition metal sulfides involving heating at least one transition metal sulfide with lithium sulfate or any material that is a precursor for lithium sulfate, under reducing reaction conditions, wherein the oxidation state of the transition metal is not reduced during the reaction process.

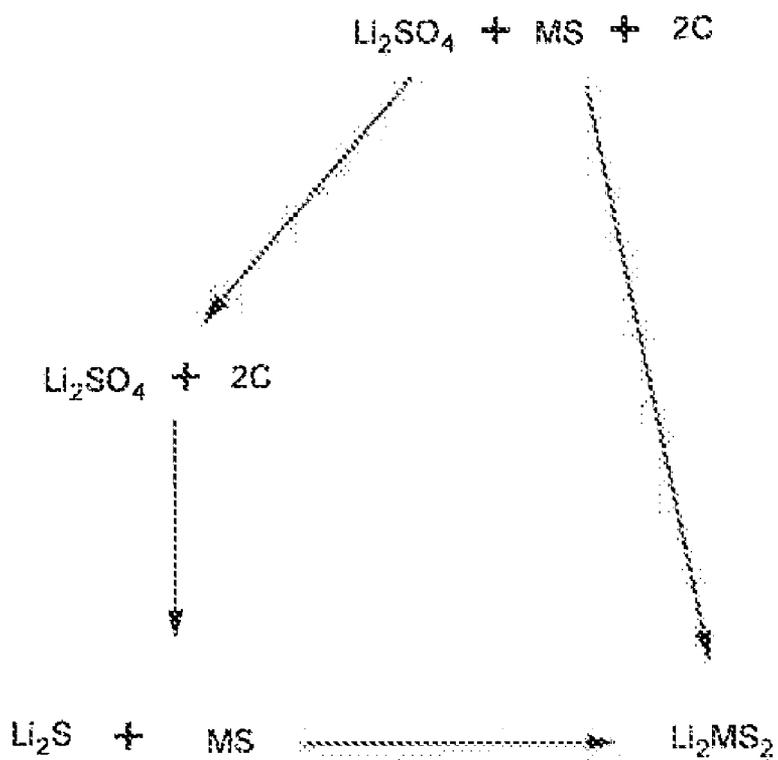


Figure 1

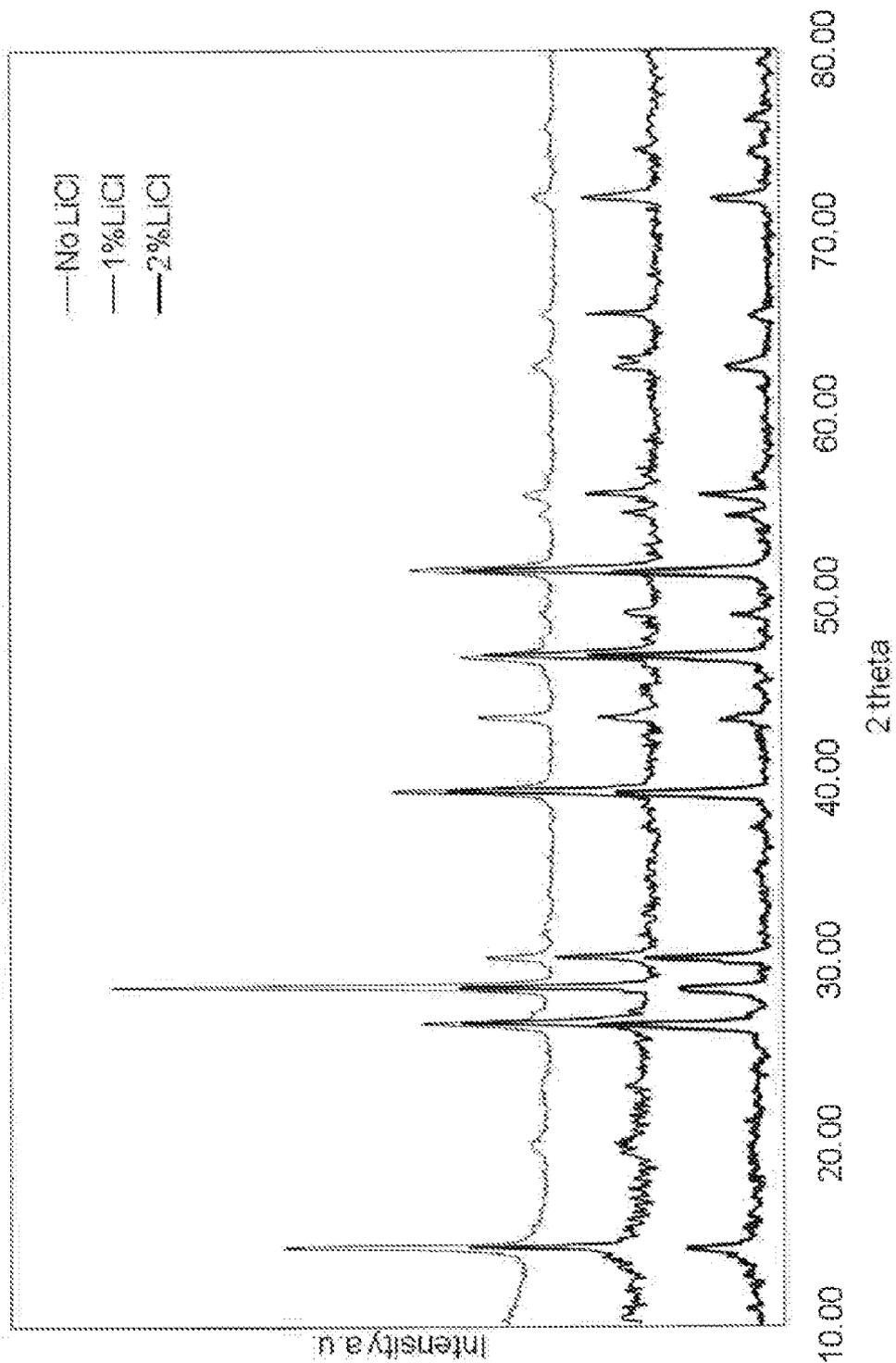


Figure 2

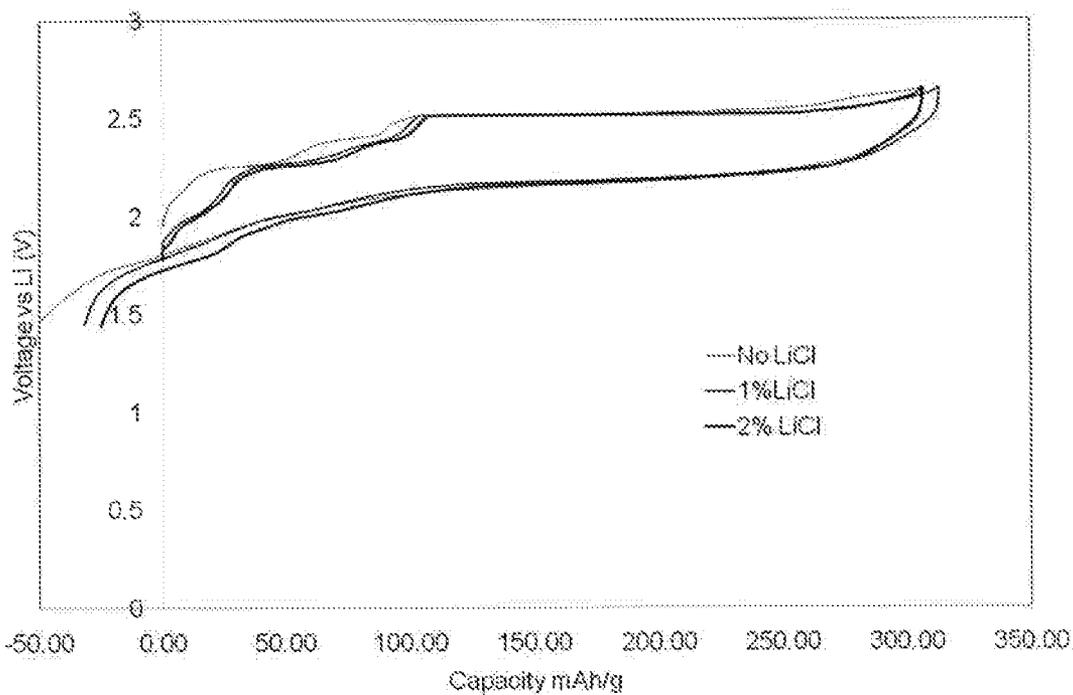


Figure 3

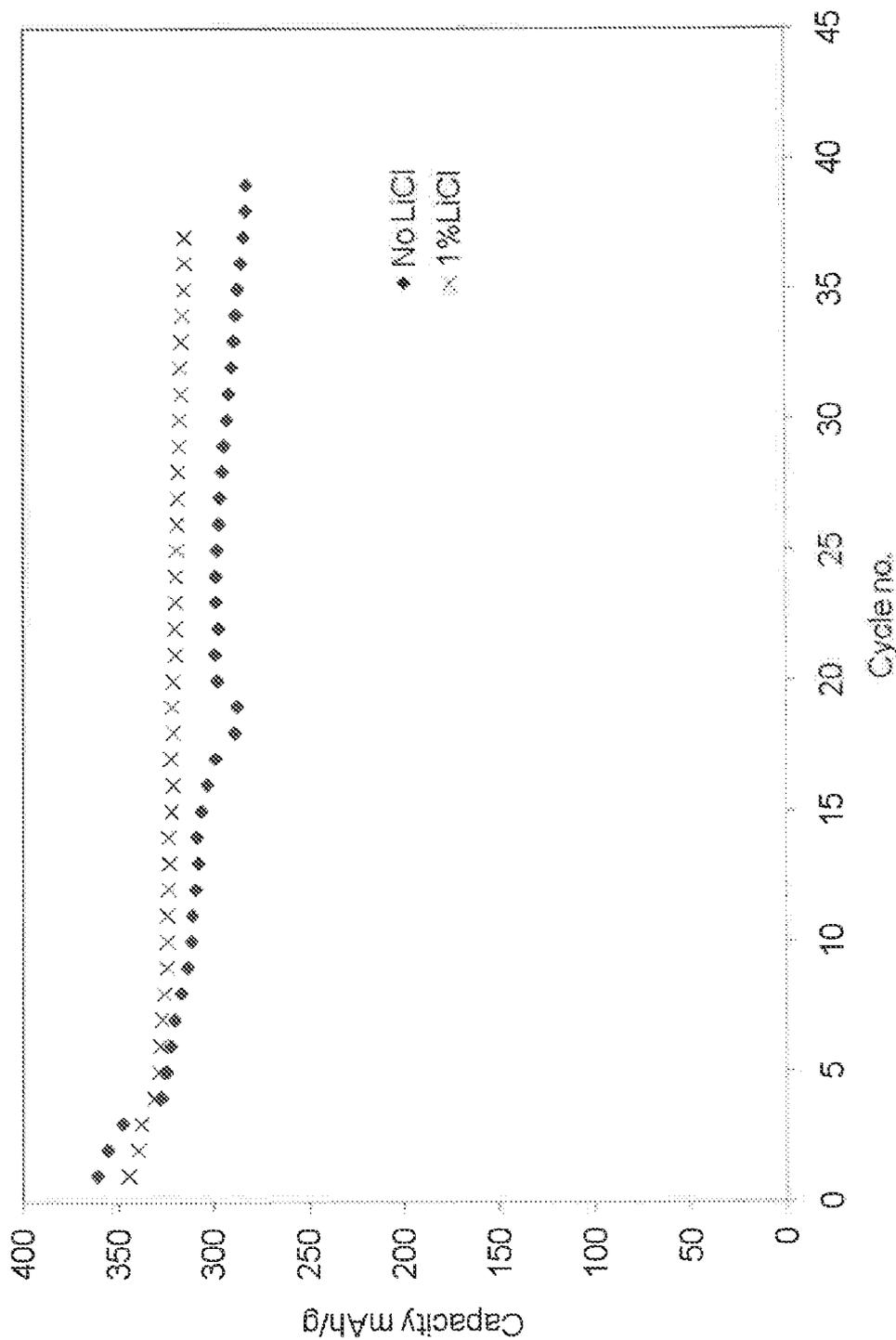


Figure 4

LITHIUM CONTAINING TRANSITION METAL SULFIDE COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a United States national phase application under 35 U.S.C. §371 of International Patent Application No. PCT/GB2009/051314 filed on Oct. 6, 2009, and claims the benefit of Great Britain Patent Application No. 0818758.5 filed on Oct. 14, 2008 and Great Britain Patent Application No. 0906601.0 filed on Apr. 17, 2009, all of which are herein incorporated in their entirety by reference. The International Application was published as International Publication No. WO 2010/043886 on Apr. 22, 2010.

FIELD

[0002] The present invention relates to lithium-containing transition metal sulfide compounds, a method of manufacturing lithium-containing transition metal sulfide compounds, the use of lithium-containing transition metal sulfide compounds in electrode materials in the manufacture of lithium ion cells or batteries and the use of such cells or batteries in commercial products.

BACKGROUND

[0003] Lithium ion batteries are secondary batteries that comprise an anode (negative electrode), a cathode (positive electrode) and an electrolyte material. They operate by the transfer of lithium ions between the anode and the cathode, and they are not to be confused with lithium batteries, which are characterised by containing metallic lithium. Lithium ion batteries are currently the most commonly used type of rechargeable battery and typically the anode comprises an insertion material, for example carbon in the form of coke or graphite. An electroactive couple is formed using a cathode that comprises a lithium-containing insertion material. Typical lithium-containing insertion materials are lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2) and lithium manganese oxide (LiMn_2O_4). In its initial condition, this type of cell is uncharged, therefore to deliver electrochemical energy the cell must be charged to transfer lithium to the anode from the lithium-containing cathode. Upon discharge, the lithium ions are transferred from the anode back to the cathode. Subsequent charging and discharging operations transfers the lithium ions back and forth between the cathode and the anode over the life of the battery. A review of the recent developments and likely advantages of lithium rechargeable batteries is provided by Tsutomu Ohzuku and Ralph Brodd in *Journal of Power Sources* 2007.06.154.

[0004] Unfortunately, lithium cobalt oxide is a relatively expensive material and the nickel compounds are difficult to synthesize. Not only that, cathodes made from lithium cobalt oxide and lithium nickel oxide suffer from the disadvantage that the actual charge capacity of a cell is significantly less than its theoretical capacity. The reason for this is that less than 1 atomic unit of lithium engages in the electrochemical reaction. Moreover, the initial capacity is reduced during the initial charging operation and still further reduced during each charging cycle. Prior art U.S. Pat. No. 4,828,834 attempts to control capacity loss through the use of a cathode mainly composed of LiMn_2O_4 . U.S. Pat. No. 5,910,382 on the other hand, describes another approach using lithium-mixed metal materials such as LiMPO_4 where M is at least

one first row transition metal. Preferred compounds include LiFePO_4 , LiMnPO_4 , LiCoPO_4 , and LiNiPO_4 and mixed transition metal compounds such as $\text{Li}_{1-2x}\text{Fe}_{1-x}\text{Co}_x\text{PO}_4$ or $\text{Li}_{1-2x}\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4$ where $0 < x < 1$.

[0005] The use of lithium ion rechargeable batteries is limited by the prohibitive cost of providing the lithium electrode material, particularly in the case of lithium cobalt oxide. Consequently, current commercialisation is restricted to premium applications such as portable computers and mobile telephones. However, it would be highly desirable to gain access to wider markets, for example the powering of electric vehicles and work has been ongoing in recent years to produce materials that maintain the high performance of lithium ion batteries, but which at the same time, are much cheaper to produce. To achieve this goal, it has been suggested, for example in JP Kokai No 10208782 and Solid State Ionics 117 (1999) 273-276, that sulfides may be used in place of oxides, as cathode materials. Although the use of many sulfides achieves less voltage, measured against lithium of the corresponding oxides, the capacity of some sulfide-based cathodes, measured in milliampere hours per gram, can be as much as about 3 times greater. Based on this, some sulfide-based cathodes achieve an overall advantage of about 1.5 times in terms of cathode energy density for batteries measured against a lithium metal anode, as compared against their oxide counterparts, and this makes the use of these sulfides a very attractive proposition. For example, in the case of lithium iron sulfide a theoretical capacity of 400 mAhg^{-1} may be obtained with an average operating voltage of 2.2V versus a lithium metal anode.

[0006] Thus, lithium-containing transition metal sulfides will be a convenient substitute material for the lithium metal oxides described above, with lithium iron sulfide being already described in the patent literature, for example in U.S. Pat. No. 7,018,603, to be a useful cathode material in secondary cells. The commercialisation of lithium-containing transition metal sulfides will depend largely on their cost of production. Taking lithium iron sulfide as a specific example, the conventional process for making this material is via a solid state reaction in which lithium sulfide (Li_2S) and ferrous sulfide (FeS), are intimately mixed together and heated under an inert atmosphere at a temperature of about 800°C . The starting materials ferrous sulfide (FeS) and iron disulfide (FeS_2) are relatively inexpensive as they are found as naturally occurring materials, and are dug out of the ground. However, a notable disadvantage of the reaction process is that the other starting material, Li_2S , is not only expensive but also highly moisture sensitive. The latter problem in particular has obvious implications for the complexity, and therefore the cost, of storing and handling the starting material, especially for large-scale commercial production. In addition, the kinetics of this reaction are reported in U.S. Pat. No. 7,018,603 to be very slow and it can apparently take up to one month to complete the reaction, thus this route is believed to be highly unfavourable in terms of energy costs and not commercially viable for the production of electrode materials.

[0007] As an alternative route for making lithium-containing transition metal sulfides, U.S. Pat. No. 7,018,603 discloses reacting a transition metal sulfide such as FeS with lithium sulfide in a reaction medium comprising molten salt or a mixture of molten salts at high temperature (temperatures of 450°C . to 700°C . are exemplified). The preferred molten salts are lithium halides. Whilst this reaction proceeds at a good rate there are still several issues that make it less than

ideal. Firstly, the fact it uses Li_2S as a starting material leads to the handling and storage problems described above. Secondly, it is very difficult to separate the reaction medium (molten lithium halide used in 1.5 molar excess) from the desired reaction product other than by solvent extraction, and this type of extraction is expensive. Further, even after rigorous purification as much as 8% of the reaction medium salt is still present in the reaction product, and this level of impurity is detrimental to the charge capacity per gram of lithium iron sulfide.

[0008] The authors of U.S. Pat. No. 7,018,603 also describe that the lithium sulfide used their molten salt process may be prepared via the reduction of lithium sulfate, for example by heating it to above 860°C . in the presence of carbon, and they suggest that this is more convenient for the large scale production of lithium iron sulfide, than buying lithium sulfide commercially. However, the handling, storage, and purification difficulties encountered with their molten salt method, as highlighted above, remain a problem.

[0009] Given the difficulties associated with the above synthetic routes to make lithium transition metal sulfides, it is highly desirable to find further alternative routes which rely on inexpensive and non-moisture sensitive starting materials, and which involve a simple, energy efficient reaction method to produce a clean product.

SUMMARY

[0010] Thus, in the first aspect of the above invention there is provided a method of producing a lithium-containing transition metal sulfide characterised in that it comprises heating at least one transition metal sulfide with lithium sulfate, or any material that is a precursor for lithium sulfate, under reducing conditions, wherein the oxidation state of the transition metal is not reduced during the reaction process. The reducing conditions preferably comprise a reducing agent such as carbon and/or performing the reaction process in a reducing atmosphere. Further preferably the transition metal sulfide made by the above method is of the formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ where $x=0$ to 1.5, preferably $x=0$ to 1, further preferably $x=0$ to 0.5 and particularly preferably $x=0$ to 0.3. Preferably, $y=0$ to 1; $z=0$ to 1, A is selected from one or more of silver (Ag), sodium (Na), copper (Cu(I)) and potassium (K) and M is a generic representation for one or more transition metals.

[0011] The reducing conditions used in the method of the present invention may be any well-known and used in the art of chemical reduction. Preferred examples involve one or more reducing gases, such as carbon monoxide, hydrogen, reforming gas (mixture of hydrogen and nitrogen), hydrogen sulfide, methane and other gaseous alkanes. One or more reducing agents such as carbon may also be used either alone or in combination with a reducing gas. In the present invention, it is highly preferred that the reducing conditions do not reduce the oxidation state of the transition metal ion.

[0012] The ideal reaction temperature used in the present invention is that which is sufficient to cause the lithium sulfate to be reduced to lithium sulfide and for this intermediate to react with the transition metal sulfide. If the reaction temperature is too high, the level and number of impurities, caused for example by the over-reduction of the transition metal ion to the zero oxidation or metallic state, is found to increase. The actual temperature used, therefore, will depend on the chosen transition metal sulfide. As a general rule the reaction temperature is conveniently from 650 to 950°C ., and preferably from 750 to 850°C . It is observed that the yield of target

material does not significantly increase when the reaction temperature is above 860°C . (the decomposition temperature of lithium sulfate). The reaction time varies according to reaction temperature and as one might expect, the higher the temperature, the faster the reaction. By way of example, a suitable reaction temperature/time profile that will produce the desired lithium-containing transition metal sulfide includes heating the reaction mixture for 12 hours at 750°C . Alternatively one could heat the reaction mixture for 9 hours at 800°C . The at least one transition metal sulfide used in the method of the present invention may be one or more sulfide compounds comprising one or more transition metals. This includes the use of single and/or mixtures of several transition metals in the sulfide. Preferably the reaction method uses mono-sulfides. Particularly suitable transition metals comprise one or more of manganese, iron, cobalt, nickel copper and zinc. Preferably, the transition metals are selected from magnesium, calcium, manganese, iron, cobalt and nickel. Particularly preferably the transition metals have an initial oxidation state of +2. Sulfides that comprise iron are the most preferred transition metal sulfides.

[0013] Although the starting materials are not air or moisture sensitive, and these positive attributes aid the storage and handling of these materials, the reaction product is itself reactive towards water. Therefore, it is advantageous to form and handle the lithium-containing transition metal sulfides under a dry and inert atmosphere such as argon or nitrogen.

[0014] Suitable reaction vessels comprise glassy carbon or graphite crucibles that generally have a loose fitting lid, however, a sealed pressurized vessel may also be used. For commercial scale production, it is advantageous to use a continuous process, for example, a rotary tube furnace, although a retort batch process may also be used.

[0015] The reaction of the present invention is a solid-state in situ process and this means that all reactants are in solid form and are without the need to use a reaction medium such as a solvent. Thus, the present reaction process is notably distinct from the process described in U.S. Pat. No. 7,018,603, for example the present invention uses lithium sulfate directly as a starting material and moreover, it does not involve a solvent comprising a molten salt or mixture of molten salts. The reactants are solid materials that are first ground using a ball mill to produce a fine powder that can either be used directly or first pressed into a pellet.

[0016] In the present invention, it is highly desirable that the reducing conditions in the process do not directly reduce the oxidation state of the transition metal ion. When carbon is used as a reducing agent, any amount of it may be used but it is convenient not to use too much to prevent it becoming a significant impurity in the reaction product, and thereby lowering its specific capacity. Having said this, it has been found to be of significant advantage, particularly to the conductivity of the target material, for at least a small amount of carbon to be present in the reaction product. Moreover, there are further specific advantages to be gained in the carbon being residual from the use of carbon in the present invention, as opposed to it merely being added later to a sample of the target lithium-containing transition metal sulfide material; during the process, the carbon is considerably intimately mixed with the lithium-containing transition metal sulfide product. The degree of mixing described as "intimate" refers specifically to the chemical as opposed to physical mixing that is achieved when carbon is used, at least in part, to provide the reducing conditions in the process of the present invention. This "inti-

mate" mixing is quite different from the degree of mixing that would ever be achieved using ball milling or other physical mixing apparatus. In particular, the carbon is dispersed at the microscopic level on individual particles of the lithium-containing transition metal sulfide.

[0017] The ratio of reaction starting materials is typically 1 mole of transition metal sulfide: the equivalent of from 0.5 to 4 moles of lithium sulfate ion: from 0.25 to 5 moles of the one or more reducing agent. The preferred ratio of starting materials, that is transition metal sulfide: number of mole equivalents of lithium supplied by sulfate: number of moles of one or more reducing agent, is 1:0.5-1.5:0.5-4, further preferably 1:0.5-1:0.5-3. In the case where carbon is used as the reducing agent, the most preferred ratio of reactants, that is, transition metal sulfide: number of mole equivalents of lithium supplied by the lithium sulfate: carbon, is 1:1:2.

[0018] As a general rule, lower amounts of carbon are required when a reducing gas and/or another reducing agent is also used.

[0019] When present, the carbon used may be in any suitable form, for example, graphite, charcoal and carbon black, although it is preferred to use high surface area carbons that are typically used in electrode formulations, for example Super P, Denka Black, Ensaco etc.

[0020] An alternative source of carbon may be derived in situ from any suitable carbonaceous material, for example by the thermal decomposition of an organic material such as lithium acetate, dextrin, starch, flour cellulosic substance or sucrose or a polymeric material such as polyethylene, polyethylene glycol, polyethylene oxide, and ethylene propylene rubber. In fact, most carbon containing materials may be used, provided their thermal decomposition does not involve the production of detrimental by-products.

[0021] The target lithium-containing transition metal sulfide compound produced by the first aspect of the present invention has a formula in the range $\text{Li}_{1.5-2.0}\text{FeS}_2$, however, the reaction temperature and duration of the heating step, for example, will determine the precise reaction product formulation.

[0022] Although not critical to the performance of the present invention, the applicants have found it is possible reduce the quantity of impurities formed and to optimise the reaction conditions, by the addition of a flux agent, also known as a mineraliser, to the reaction mixture. Flux agents or mineralisers are commonly used in the ceramics industry to lower the reaction temperature and shorten reaction times. Mineralisers such as sodium chloride, borax, lithium chloride, lithium fluoride, sodium fluoride, lithium borate and sodium carbonate are known. The present applicant has found that using a very small amount of a mineraliser, in particular an alkali metal halide will result in a lithium-containing transition metal sulfide product that exhibits enhanced crystallinity with lower levels of impurities. Any alkali metal halide may be used but lithium chloride and lithium iodide are most preferred. Alternatively, sodium carbonate or sodium chloride may be used however in this case it is likely that at least some substitution of the lithium for sodium will occur in the target product. Thus, amount of mineraliser used in the

present invention is up to 5% by weight of the starting materials, preferably from 0.5 to 2% by weight and further preferably 1% by weight of the starting materials.

[0023] A typical electrode comprises 94% of a lithium-containing material, 3% of a binder and 3% of a carbon-containing material. In this aspect of the present invention the lithium-containing material is preferably a lithium-containing transition metal sulfide and further preferably one that is made by the method of the present invention described above. The binder can be any material known in the art to be suitable for use as a binder, usually a highly inert polymer such as polytetrafluoroethylene (PTFE), polymers of ethylene propylene diamine monomer (EPDM), polyethylene oxide (PEO), polyacrylonitrile and polyvinylidene fluoride. The Applicant's preferred binder is ethylene propylene diene monomer (EPDM). The key feature of the binder is that it needs to be able to form a slurry or paste with the lithium-containing transition metal sulfide, which in turn may be coated onto a current collector. Conveniently, mixing the binder with a solvent facilitates coating. Any solvent may be used, provided it is non polar and does not react with either the binder or the lithium-containing transition metal sulfide, and also provided it is dry. Desirably the solvent is reasonably volatile to facilitate its removal at room temperature. Suitable solvents might include low molecular weight halogenated compounds, particularly halogenated hydrocarbons such as methylene chloride or low molecular weight materials such as cyclohexane, trimethylbenzene (TMB), toluene, and xylene, or low molecular weight alcohols such as methanol, and mixtures of any of these compounds. Trimethylbenzene is a preferred solvent.

[0024] The binder/solvent/lithium-containing transition metal sulfide slurry/paste may also include additives adapted to modify the properties of the binder. The chosen additive must be naturally compatible with the binder, the lithium-containing transition metal sulfide and the electrolyte, and must not affect the performance of the finished cell.

[0025] The lithium-containing transition metal sulfide materials produced by the method of the present invention are useful in a wide variety of applications where a low voltage rechargeable battery power source may be used, for example, in mobile phones, vehicles, lap top computers, computer games, cameras, personal CD and DVD players, drills, screw drivers and flash lights and other hand-held tools and appliances.

[0026] In order for the lithium-containing transition metal sulfides of the present invention to be used in such applications it is necessary to construct them into an electrochemical cell. Different methods of making such cells are described in the literature, but one particularly convenient example is described in EP 1 295 355 B1. In this case, an electrochemical cell is assembled comprising a plurality of anode plates and a plurality of cathode plates, each comprising respective insertion materials for example graphite in the anode plates and the lithium-containing transition metal sulfides of the present invention in the cathode plates. In particular, the method involves forming a stack of discrete, separate cathode plates and discrete, separate anode plates stacked alternately, each comprising a layer of a respective ion insertion material

bonded to a metal current collector, and interleaving a continuous separator/electrolyte layer between successive plates so it forms a zig zag.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The invention will now be particularly described by way of example with reference to the following drawings in which:

[0028] FIG. 1 shows the overall reaction scheme for the process of the present invention when carbon is used to provide the reducing conditions. In this case, the reaction proceeds by the reduction of lithium sulfate to lithium sulfide followed by the reaction of the latter with the transition metal sulfide to produce the target lithium-containing transition metal sulfide.

[0029] FIG. 2 shows powder x-ray diffraction patterns for compounds with the formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ made according to Examples 1 to 3 of the present invention.

[0030] FIG. 3 shows 1st cycle data for $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ compounds made according to Examples 1 to 3 of the present invention.

[0031] FIG. 4 shows further cycle data for $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ compounds made according to Examples 1 to 3 of the present invention.

using X-ray diffraction and/or electrochemical techniques. A suitable furnace for carrying out the above process may be a graphite lined rotary furnace, a retort furnace or a static tube furnace.

B) General Laboratory Scale Method For Making Compounds With the Formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ Using A Reducing Gas To Provide the Reducing Conditions

[0033] The lithium sulfate and transition metal sulfide are weighed out into a ball mill pot, this mixture is milled for 1-12 hrs depending on the size of the precursor mix at a rate of 200-350 rpm. The precursor mix is then pelletised, and placed into a glassy carbon crucible. The carbon crucible is placed into the furnace under a gentle flow of a reducing gas, and heated between 500 and 800° C. for 1 -20 hours dwell. The crucible is allowed to cool under the inert gas flow and transferred directly into a glove box and processed and analysed as described above.

[0034] Compounds with the Formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ (x, y and z are as defined above) were prepared according to Examples 1 to 3 summarised in Table 1 below:

TABLE 1

| Example | Lithium sulfate | Transition metal sulfide | Reducing conditions | Mineraliser | Reaction conditions Temp/Time |
|---------|---|-------------------------------|---|-------------------------|---|
| 1 | Li_2SO_4 (110 g; 1.0 mole) | FeS (87.91 g; 1.0 mole) | Carbon Denka Black (24 g; 2.0 moles) | None | 800° C./9 hr under argon in small tube furnace |
| 2 | Li_2SO_4 (110 g; 1.0 mole) | FeS (87.91 g; 1.0 mole) | Carbon Denka Black (24 g; 2.0 moles) | LiCl (1.3 g; 1 wt %) | 800° C./9 hr under argon in small tube furnace |
| 3 | Li_2SO_4 (110 g; 1.0 mole) | FeS (87.91 g; 1.0 mole) | Carbon Denka Black (24 g; 2.0 moles) | LiCl (2.6 g; 2 wt %) | 800° C./9 hr under argon in small tube furnace |

DETAILED DESCRIPTION OF THE EMBODIMENTS

A) General Laboratory Scale Method For Making Compounds With the Formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ Using A Reducing Agent To Provide the Reducing Conditions

[0032] The lithium sulfate, transition metal sulfide and reducing agent are weighed out into a ball mill pot, this mixture is milled for 1-12 hrs depending on the size of the precursor mix at a rate of 200-350 rpm. The precursor mix is then pelletised, and placed into a glassy carbon crucible with or without a lid. The carbon crucible is placed into the furnace under a gentle flow of an inert gas, and heated between 500 and 1500° C. at a rate of 1 to 10° C. per minute over a period of 1 to 24 hours. The crucible is allowed to cool under the inert gas flow and transferred directly into a glove box. The resulting product is ground initially using a pestle and mortar and then milled more finely using a ball mill. The lithium-containing transition metal sulfide product may then be analysed

[0035] General Procedure To Obtain Cycle Data For the $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ Compounds Made According To the Present Invention

[0036] Composite cathode electrodes were made by coating a composite comprising 6% carbon black, 1% EPDM and 93% active material onto an aluminium current collector from which discs were cut. A cell stack was constructed by placing a glass filter paper separator between a lithium anode disk and a composite cathode disk then made into a small pouch type cell. Tags of aluminium one side and nickel on the opposing side were sealed into the sides of a pouch. Electrolyte was pipetted onto the separator and the end of the pouch was then vacuum sealed. Constant current tests were performed on a MACCOR between the voltage limits 2.65V and 1.45V using an initial rate of 10 mA g^{-1} , (e.g. as shown in FIG. 3) followed by a rate of 15 mA g^{-1} for subsequent cycles (e.g. as shown in FIG. 4).

Determination of X-Ray Diffraction Data

[0037] Powder X-ray diffraction data was obtained using a SIEMANS D5000 using a copper $\text{K}\alpha_1$ and $\text{K}\alpha_2$ source, fitted

with a monochromator. The sample was placed into an air sensitive holder, which consisted of a Perspex dome which was sealed over the sample, thus preventing degradation of the material during data collection. Phase analysis data were collected over a period of 4 hours $10-80^\circ 2\theta$, whilst high quality data were collected $10-90^\circ 2\theta$ over a period of 16 hours.

Cycling Data For $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ Compounds
Made Using Examples 1 To 3

[0038] Cells were made using the general method described above and were cycled vs lithium between the voltage ranges 2.65V and 1.45V. The first cycle was performed at a rate of 10 mA g^{-1} (see FIG. 3), subsequent cycles were performed at a charge rate of 15 mA g^{-1} (see FIG. 4) and a discharge rate of 75 mA g^{-1} . Initial charge capacity of 320 mAh g^{-1} were observed and a discharge capacity approximately 350 mAh g^{-1} . All 1st cycles were similar, however the samples made with no mineraliser exhibited slightly higher discharge capacities than that made with mineraliser addition.

[0039] Investigation of the Effect of Adding 1%/wt Mineraliser During the Preparation of $\text{Li}_{2-x}\text{FeS}_2$

[0040] The $\text{Li}_{2-x}\text{FeS}_2$ compound made according to Example 2 includes 1%/wt LiCl mineraliser in its formulation. The effect of this mineraliser on the capacity of $\text{Li}_{2-x}\text{FeS}_2$ is indicated by the 1st cycle data shown in FIG. 2, and the cycling data shown in FIG. 3. The cycling data shows that the discharge capacities obtained at 10 mA g^{-1} are slightly high for the sample with no mineraliser, however upon cycling the capacity of this material fades rapidly compared to that with 1% mineraliser. After 40 cycles the material with no mineraliser shows a 17% drop in capacity, whereas the sample made with mineraliser shows only an 8% drop in capacity.

1. A method of producing a lithium-containing transition metal sulfide, characterised in that it comprises heating at least one transition metal sulfide with lithium sulfate, or any material that is a precursor for lithium sulfate, under reducing reaction conditions, wherein the oxidation state of the transition metal is not reduced during the reaction process.

2. A method of producing a lithium-containing transition metal sulfide, characterised in that it comprises heating at least one transition metal sulfide with lithium sulfate, or any material that is a precursor for lithium sulfate, in the presence of carbon, wherein the oxidation state of the transition metal is not reduced during the reaction process.

3. A method of producing a lithium-containing transition metal sulfide according to claim 1 or 2 wherein the lithium-containing transition metal sulfide is of the formula $\text{Li}_{2-x-y}\text{A}_y\text{Fe}_{1-z}\text{M}_z\text{S}_2$ where $x=0$ to 1.5 , $y=0$ to 1 , $z=0$ to 1 , A is selected from one or more of silver (Ag), sodium (Na), copper (Cu(I)) and potassium (K) and M is a generic representation for one or more transition metals.

4. A method of producing a lithium-containing transition metal sulfide according to claim 1, 2 or 3 wherein the at least one transition metal sulfide and lithium sulfate, or precursor thereof, are heated at a temperature of from 650°C . to 950°C .

5. A method of producing a lithium-containing transition metal sulfide according to claims 1 to 4 wherein the at least one transition metal sulfide comprises one or more of magnesium, calcium, manganese, iron, cobalt, nickel, copper and zinc.

6. A method of producing a lithium-containing transition metal sulfide according to claim 5 wherein the at least one transition metal sulfide comprises one or more of manganese, iron, cobalt and nickel.

7. A method of producing a lithium-containing transition metal sulfide according to any preceding claim wherein the at least one transition metal sulfide comprises one or more monosulfide.

8. A method of producing a lithium-containing transition metal sulfide according to any preceding claim, wherein the molar ratio of transition metal sulfide:lithium sulfate, or precursor thereof, one or more reducing agent is $1:0.5$ to $4:0.25$ to 5.

9. A method of producing a lithium transition metal sulfide according to any preceding claim, wherein the molar ratio of transition metal sulfide:lithium sulfate, or precursor thereof, carbon is $1:1:2$.

10. A method of producing a lithium-containing transition metal sulfide according to any preceding claim, wherein the at least one transition metal sulfide and the lithium sulfate, or precursor thereof, are in powder form and/or pellet form.

11. A method according to any of claims 1 to 10, further comprising the addition of one or more mineralisers in a total amount of up to 5% by weight of the starting materials.

12. A method of claim 11 wherein the one or more mineralisers comprise an alkali metal halide.

13. A method according to claim 12 wherein the one or more mineralisers comprise one or more of lithium iodide, lithium bromide and lithium chloride.

14. Use of the lithium-containing transition metal sulfide produced according to the method in any of claims 1 to 13 in the preparation of an electrode.

15. Use according to claim 14 wherein the electrode is a cathode.

16. An electrode made according to either of claim 14 or 15 further comprising a binder that is used in conjunction with a solvent to form a slurry or paste with the lithium-containing transition metal sulfide.

17. An electrode according to claim 16 wherein the solvent comprises a non-polar hydrocarbon solvent.

18. An electrode according to any of claims 14 to 17 used, in conjunction with a counter electrode and an electrolyte, in a lithium ion battery.

19. An electrode according to claim 18 used, in conjunction with a counter electrode and an electrolyte, in a rechargeable battery power source.

20. A lithium ion battery comprising a cathode comprising one or more lithium-containing transition metal sulfides produced according to the method of any of claims 1 to 13.

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