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(54) **Title**: LITHIUM-ION BATTERY COMPRISING NANOWIRES

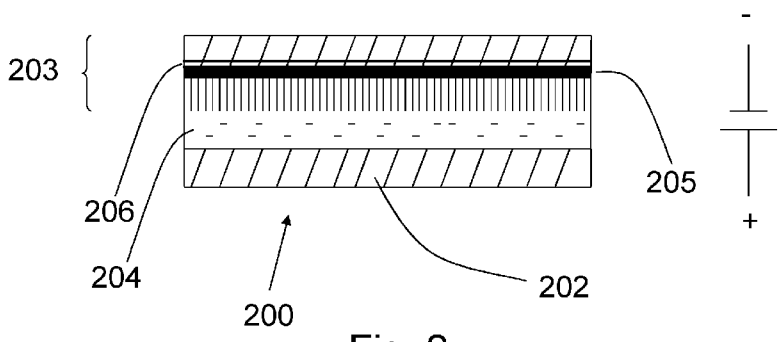

Fig. 2

(57) **Abstract**: The invention relates to a lithium-ion battery, comprising two electrodes and an electrolyte disposed between said two electrodes, wherein one of said electrodes comprises at least one elastic film that makes up outermost layer of said electrode such that said film abuts against the electrolyte. A plurality of gas-phase synthesized nanowires comprising silicon is partially immersed in said film and extend from said film into the electrolyte. Said plurality of nanowires is elastically deformable at least in the radial direction of the nanowires. The invention further relates to a method of manufacturing a lithium-ion battery.

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LITHIUM-ION BATTERY COMPRISING NANOWIRES

The present invention relates to a lithium-ion battery comprising nanowires.

Background of the Invention

A lithium-ion battery (sometimes Li-ion battery or LIB) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge. In this context, due to the ambivalent nature of cathode and anode in rechargeable batteries, we use the term cathode throughout the text to mean the negative pole during recharging, i.e., the electrode where the lithium ions are stored in a charged battery. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

Lithium-ion batteries are common in consumer electronics. They are one of the most popular types of rechargeable battery for portable electronics, with one of the best energy densities, no memory effect, and a slow loss of charge when not in use. Beyond consumer electronics, LIBs are also growing in popularity for military, electric vehicle, and aerospace applications. Research is yielding a stream of improvements to traditional LIB technology, focusing on energy density, durability, cost, and intrinsic safety.

The liquid organic electrolyte is usually a solution of an ion-forming inorganic lithium compound in a mixture of a high-permittivity solvent (eg. propylene carbonate) and a low-viscosity solvent (eg. dimethoxyethane).

Lithium ion batteries commonly use a carbon cathode (graphite), to collect lithium ions. The theoretical capacity of graphite cathodes is 372 mA • h / g. In contrast the theoretical capacity of silicon is 4212 mA • h / g. However silicon will swell up to 420% from its normal volume at full lithium insertion. The characteristic impedance of silicon nanowires varies widely with the amount of

lithium: low impedance for both low and high concentrations of lithium, but high for intermediate concentrations.

Obviously, a strain generated during a complete charge-discharge cycle under these circumstances causes significant fatigue and plastic deformation of the constituting materials of the battery. This leads to performance deterioration and, ultimately, an inoperative battery.

In spite of this, silicon-based nanowires have been proposed for electrodes in battery applications, e.g. by Ruffo et al in J. Phys. C., Vol 113, N0. 26 2009, pages 11390-11698, where they were used in the cathode of a lithium ion battery. Choice of Si-based nanowires for battery electrodes is owed to silicon's low discharge potential as well as its extremely high theoretical charge capacity.

Thus, in view of the above, an objective of the present invention is to improve the performance of lithium batteries comprising silicon-based nanowires.

Summary of the Invention

The above stated objective is achieved by means of a lithium-ion battery and a method of manufacturing thereof according to the independent claims, and by the embodiments according to the dependent claims.

A first aspect of the present invention provides a lithium-ion battery comprising two electrodes (a cathode and an anode) and an electrolyte disposed between said two electrodes, wherein at least one elastic film makes up outermost layer of one of said electrodes such that said film abuts against the electrolyte. Said battery further comprises a plurality of gas-phase synthesized nanowires comprising silicon that are partially immersed in said film and extend from said film into the electrolyte, wherein said plurality of nanowires is elastically deformable at least in the radial direction of the nanowires.

A second aspect of the present invention provides a method of manufacturing a lithium-ion battery, said method comprising the steps of providing a first electrode, providing catalytic seed particles suspended in a gas, providing

gaseous precursors comprising constituents of nanowires to be formed, forming, in a gas-phase synthesis, the nanowires from the gaseous precursors and catalytic seed particles, while the catalytic seed particles are suspended in the gas, immersing, at or near room temperature, the nanowires into an elastic film that makes up outermost layer of said electrode, providing an electrolyte so positioned that the nanowires extend into said electrolyte, and providing a second electrode.

The above arrangement enables the lithium battery to accommodate large strain without deterioration of its performance, i.e. breaking of the nanowires, indirectly caused by their volume change upon insertion and extraction of lithium ions into the nanowire material, is avoided. More specifically, when nanowires, during a charging cycle, swell up, in radial but also longitudinal direction, due to intercalation of lithium ions, the elastic film into which these are immersed and, consequently, are connected with is, thanks to its inherent properties, elastically deformed. Analogously, during a discharge cycle, i.e. when lithium ions leave the nanowires, resulting in their girth and length reduction, the elastic film, once again, undergoes an elastic deformation. This deformation is of substantially equal magnitude as the deformation during the charging cycle. The ability of the elastic film to deform itself elastically as required by the expansion/contraction of the nanowires renders possible effective accommodation of large strain. Accordingly, the elastic properties of the nanowires and the film jointly contribute to greatly reduce material fatigue. As a consequence, the number of cracks in the nanowires and in the film is significantly reduced. Likewise, a downright rupture of nanowires or film is also avoided. Since ruptured nanowires caused by strain induced during the charging/discharging cycle is one of the major reasons behind degradation of performance of lithium batteries, it is clear how above-described reduction of material fatigue improves the performance of the entire battery.

In addition, the manufacturing method of the nanowires, i.e. gas phase synthesis, imparts that the battery itself may be assembled at or near room temperature. This offers significant advantages when it comes to choice of material for the film. In this context, provided that a chosen material is elastic, a plethora of different materials may be used.

The gas phase synthesis also renders possible continuous production of nanowires, preferably in a roll-to-roll process. Consequently, mass production of the components of a lithium ion battery is hereby greatly facilitated.

Furthermore, in battery applications, it is desirable to create a large interface area between the electrolyte and an electrode so that fast charging/discharging of the battery may be achieved. In the invention at hand this is realized by covering an electrode with nothing but a thin film, into which film the relatively long conductive nanowires have subsequently been immersed. Thus, the nanowires are kept in place by means of said elastic film only. Consequently, the electrode is, via the nanowires it comprises, in electrical contact with the electrolyte over a large interface area. An efficient battery is hereby achieved.

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter and the accompanying drawings which are given by way of illustration only, and thus not to be considered limiting on the present invention, and wherein

Fig. 1 schematically illustrates a battery electrode incorporating the nanowire structure according to the invention;

Fig. 2 schematically illustrates a lithium ion battery according to the invention.

Fig. 3 shows an embodiment wherein the nanowires are partly embedded in the elastic film;

Fig. 4 shows nanowires having dendrites.

Detailed Description of Preferred Embodiments

In Fig. 1 a battery electrode 102 according to the invention is schematically illustrated. Said electrode 102 is a part of a “double-layer structure” 101 also comprising protruding nanowires 103. The electrode comprises a film (not shown in Fig. 1) on which nanowires have been deposited. The electrode may

further comprise a suitable substrate (not shown in Fig. 1). In such a case, said substrate is positioned on the face of the film facing away from the nanowires. The nanowires of the present invention are synthesized in gas-phase by means of a process denominated aerotaxy. Said process is disclosed in applicant's published International patent application PCT/SE2011/050599, incorporated herein in its entirety by reference.

The method comprises following basic steps (the materials mentioned by way of example in the description below are the more commonly used ones, but should not be regarded as an exhaustive list):

- An aerosol of nanoparticles is produced, consisting of gold particles in the size range from 5 to 500 nm in diameter (typically 80 nm), suspended in a nitrogen carrier gas at a pressure in the range from 10 mbar to 10 bar (typically 1 bar)
- The aerosol is mixed with precursor molecules, typically SiH4, at a partial pressure sufficient to grow the desired amount of silicon nanowire material
- The aerosol is led through a reaction furnace in a continuous flow, where the precursor molecules crack on the catalytic Au particles, growing into nanowires

The resulting Au/Si nanowire aerosol is collected by any of the following means:

- Precipitation on a flat substrate by means of an electric field (charged wires)
- Deposition on a flat filter substrate, e.g., a track-etched membrane
- Collection in a filter for subsequent transfer to a liquid (colloidal) solution
- Directly into a liquid in a scrubber type device
- Any other known method for extracting particles from a gas stream

We here distinguish between two main cases, namely where the nanowires are deposited on the elastic film directly from the gas phase, and where the wires come from a liquid (offline, using liquid batches of nanowire colloids).

When depositing directly from the gas phase, either by means of electric fields or onto filter material, the wires may be co-deposited with polymers using chemical vapor deposition (CVD) type transport (or simply cold wall condensation). In this context, electric field alignment may be combined with a filter type deposition. For this to work, the filter e.g. a nucleopore, needs to be flat on the scale of the nanowires. More specifically, as regards the deposition of nanowires and polymers, the layer closest to the film may be made with a dense conducting polymer, ensuring good electrical contact. On this layer, in a second phase of deposition, another layer is deposited. Simultaneously, a layer of nanowires, , dense enough to form an electrically interconnected network, is deposited. During the second deposition phase, the (co)deposited polymer is frequently a porous polymer matrix, allowing an electrolyte to flow/diffuse into the pores. Alternatively, a solid electrolyte may be co-evaporated in the second phase of the deposition. In case the wires are well enough connected, the second layer may be omitted. An electric field may be employed to align the nanowires more or less vertically, which increases the packing density of wires.

The resulting structure is then a porous network of interconnected nanowires, where lowermost non-immersed portion of the nanowire is firmly embedded in a conducting polymer, and the thereto adjacent part of the nanowire is held in place by a material allowing transport of (lithium) ions such as a porous polymer matrix. The composite material achieved in this way is elastic, which is beneficial both for the nanowire expansion as they absorb lithium ions, and for producing a battery in a volume-efficient manner.

In the case where the nanowires are deposited from the liquid phase, most of the above is still applicable: electric field alignment will yield vertical wires also in the liquid case, and filter-based deposition is well known. However, CVD or cold-wall methods will not work in a liquid. To achieve a layered polymer embedding the nanowires, chemical processes would be needed, using a sequential switching of solvents, or other known methods for thin film

deposition. Both the gas-phase and liquid mediated nanowire deposition routes are ideally suited for roll-to-roll processes.

To take advantage of the continuous flow of wires, the wires may be deposited and/or aligned in a continuous process, such as the above-mentioned roll-to-roll process. The deposition and/or alignment can be assisted by an electric field applied over the electrode and further by charging the wires, and optionally also the film and the substrate, if present. By locally charging the film and the substrate, if present, in a predetermined pattern, nanowires can be deposited in predetermined positions on the film. Thus the present invention provides a continuous, high through-put, process for manufacturing aligned wires, optionally with "real-time" feed-back control to obtain high quality wires.

The wires produced by this method can be utilised to realise wire based semiconductor devices such as solar cells, field effect transistors, light emitting diodes, thermoelectric elements, etc which in many cases outperform conventional devices based on planar technology.

In one embodiment, the nanowires are aligned on the film onto which they are deposited. A method for aligning nanowires is disclosed in applicant's published International Patent Application PCT/SE2010/051461, the content of which is incorporated herein in its entirety by reference. Such alignment is achieved in general by a method of aligning nanowires on a film during manufacture of a nanowire structure, comprising the steps of:

providing a population of nanowires, and applying an electric field (E) over the population of nanowires (1), whereby an electric dipole in the nanowires makes them align along the electric field (E). Suitably, the positively charged end of each wire is forced in the direction of the electric field (E). Preferably, the electrical field induces an electrical dipole in the nanowires by separation of positive and negative charge carriers towards opposite ends of the nanowires, which contributes to the electrical dipole moment being formed along the nanowires.

In one embodiment, the immersed nanowires are randomly distributed and randomly oriented. Consequently, the catalytic particles associated with said nanowires (a catalytic particle is positioned at one end of each nanowire) are also substantially randomly distributed. A randomly oriented plurality of wires exhibits, if the density is sufficient, a very high degree of interconnectivity whereas perfectly vertically oriented nanowires may exhibit a lower degree of electrical interconnectivity, since perfect alignment requires all wires to touch the conducting part of the electrode. On the other hand, a certain degree of orientation (not random but not perfectly vertical) may exhibit acceptable interconnectivity, while providing a lower electrical resistance due to a more direct path from top to bottom.

Randomness, also in terms of nanowire width and length, is not desirable in itself, but certain randomness as regards nanowire width and length is a consequence of the manufacturing method. On the other hand, the randomness is not necessarily bad when speaking of device performance. Accordingly, for maximum benefit, device performance should be balanced against nanowire and process variables.

The nanowires are preferably made of silicon or silicon carbide, or silicon nanowires are combined with combination with carbon nanotubes, i.e. the carbon nanotubes are provided as a conductive core with a layer of silicon nanowires for the lithium absorption. Other semiconductor materials such as GaAs can also be used.

The nanowires are typically doped. By way of example B or P (p-type or n-type) are used as dopants, i.e. they are incorporated into the bulk in order to increase conductivity. The conductivity of the wires should be such that the electric resistance of the cathode as a whole meets the requirements of a functional battery structure.

In Fig. 1 an electrode 102 is shown, wherein the nanowires 103 are indicated as being single straight structures, but it is also possible to generate dendrite structures, i.e. structures having a branched character. An example of such

branched structures is shown in Fig. 4, taken from applicant's own WO 2005/054121, the content of which is incorporated herein in its entirety.

In one embodiment, the elastic film is made of polymer material. Preferably the polymer is sticky such that the nanowires when deposited become "immersed" into the polymer surface. Obviously, said polymer material must be stable in the electrochemical environment inside a battery structure. Also, it is suitable that the polymer is elastic in order to accommodate the swelling that may occur during the intercalation process where lithium is intercalated into the nanowire material. In another embodiment, the elastic film is made of metal having sufficient elasticity to withstand a permanent deformation. One example of a metal exhibiting this property is gold.

The nanowires 103 and the electrode 102 with the elastic film (not shown in Fig. 1) form a composite structure 101, which for structural stiffness may need a backing (not shown in Fig. 1) that also serves for current collection.

According to the invention this nanowire structure is usable as a cathode in a lithium ion battery, replacing the standard manganese dioxide or carbon cathode (graphite) cathode.

Fig. 2 schematically illustrates a battery 200 comprising a nanowire structure 203 according to the invention.

This battery comprises an anode 202, typically made of lithium or a lithium containing compound or alloy. Several possible compositions are known in the art such as lithium cobalt oxide, polyanions, such as lithium iron phosphate, spinel, such as lithium manganese oxide, LiCoO2, LiMn2O4 , LiNiO2, LiFePO4, Li2FePO4F, LiCo1/3Ni1/3Mn1/3O2, Li(LiaNixMnyCoz)O2. Obviously, the invention is not particularly restricted to the choice of anode material as long as it is a functioning lithium containing anode.

As a cathode the electrode structure shown in Fig. 1 can be used, suitably having some backing 206 for structural stiffness. By way of example, said backing 206 is a layer made of metal such as copper, aluminium or steel, or a

solid, conductive substrate and is, in a non-limiting embodiment, positioned on the face of the elastic film facing away from the electrolyte.

Between the anode and cathode there is an electrolyte 204 confined. The electrolyte 204 suitably comprises a lithium salt in an organic solvent. The electrolyte 204 may furthermore be dissolved in a matrix material (not shown in Fig. 2), such as porous plastic or cellulose. However, numerous other electrolytes are possible as long as they contain lithium ions and meet the requirements imposed by the material choices for the other components. Consequently, the invention is not particularly restricted as regards electrolyte material and/or state.

An elastic film 205 that makes up outermost layer of said electrode is arranged such that it abuts against the electrolyte. In one embodiment, said elastic film 205 is conductive. In another embodiment, said elastic film 205 is non-conductive and is therefore complemented by a further, thereto adjacent conductive film (not shown in Fig. 2). A plurality of gas-phase synthesized nanowires comprising silicon is partially immersed in said film 205 and extends from said film into the electrolyte 204. The nanowires comprise silicon for its excellent ability to absorb lithium ions. In one embodiment nanowires are made of pure silicon, whereas, in an alternative embodiment, they are made in silicon carbide. In this context, other material compositions and shapes are also possible. It is equally conceivable that nanowires with different structural properties are immersed in the same elastic film. These nanowires are, thanks to their intrinsic properties, elastically deformable in their radial as well as longitudinal direction.

The process for making the nanowires i.e. the fact that they are separately made and deposited allows to position wires on thin films with small heat budget, e.g. on a thin polymer film that optionally is conductive. There is no intrinsic limit to film thickness. If substrate is part of the electrode, the film should ideally be thicker than the substrate.

A film with nanowires deposited on/into the film has better elastic resistance than if nanowires are grown, epitaxially or in any other way, on or to a film.

Moreover, grown nanowires frequently break after only a few charge/discharge cycles. This stands in sharp contrast with the durability of gas-phase synthesized nanowires of the present invention. Furthermore, in order to achieve large contact area it is possible to fabricate dendrite nanostructures. This improves fast charging/discharging of the battery due to large interface area between the electrode and the electrolyte. For high capacity, large absorption volume is needed.

The central core may be of other material than the protruding nanowires, which reduces potential impedance problems with longer nanowires (example multi walled carbon nanotubes (MWCNT) based core and silicon nanowires).

It is also possible to deposit separate populations, one for conductive properties, one for lithium insertion (or intercalation). The inventors have published silicon branches grown on III-V nanowire trunks.

A porous electrolyte-confining matrix material (e.g. paper) where one side is saturated with nanowires gives a high lithium ion absorption volume. In practice, the nanowires may be applied in the form of a colloidal suspension, as a gel or powder, or be deposited directly from the gas phase. In any case, use of aerotaxy nanowires allows deposition of large amounts of wires, including the possibility to mix different kinds of wires to optimize both conductivity and ion capacity.

In another embodiment, shown in Fig. 3, the wires 103 are first deposited on and immersed in the elastic film 205, whereupon the wires may be embedded into a conducting polymer (not shown in Fig. 3) in order to achieve good electrical contact. Subsequent nanowire deposition will then be tailored to maximize ion absorption.

It is easy to extend the structure to sandwich film structures to increase the operating voltage of the battery.

Furthermore, it is possible to increase packing density by wide variation of nanowire diameter without compromising material durability.

The electrode structure according to the invention, i.e. silicon-based nanowires immersed in and protruding from the elastic film, can also be used in fuel cells, which is also an aspect of the invention and is encompassed in the inventive scope.

CLAIMS

1. A lithium-ion battery, comprising two electrodes and an electrolyte disposed between said two electrodes, wherein at least one elastic film makes up outermost layer of one of said electrodes such that said film abuts against the electrolyte, said battery further comprising

a plurality of gas-phase synthesized nanowires comprising silicon (Si) that are partially immersed in said film and extend from said film into the electrolyte,

said plurality of nanowires being elastically deformable at least in the radial direction of the nanowires.

2. A lithium-ion battery according to claim 1, wherein the immersed nanowires are randomly distributed and randomly oriented.

3. A lithium-ion battery according to any of the preceding claims, wherein said elastic film is conductive as well.

4. A lithium-ion battery according to any of the preceding claims, wherein said elastic film comprises polymer material.

5. A lithium-ion battery according to any of the preceding claims, wherein said electrode in addition to said elastic film comprises a conductive film that is adjacent to said elastic film.

6. A lithium-ion battery according to any of the preceding claims, wherein said plurality of nanowires is made of silicon or silicon carbide (SiC).

7. A lithium-ion battery according to any of the preceding claims, wherein said plurality of nanowires comprises nanowires with different structural properties.

8. A lithium-ion battery according to any of the preceding claims, wherein each of said plurality of nanowires is grown from a catalytic particle, the catalytic particles being substantially randomly distributed when said plurality of nanowires extend from said film.

9. A lithium-ion battery according to any of the preceding claims, wherein said plurality of nanowires is elastically deformable in the length direction of the nanowires.

10. A lithium-ion battery according to any of the preceding claims, wherein a backing is provided on the face of the elastic film facing away from

the electrolyte, said backing preferably being made of a metal, such as copper, aluminium or steel.

11. A lithium-ion battery according to any of the preceding claims, wherein a dense and conductive polymer material is deposited on the face of the film that faces the electrolyte.

12. A lithium-ion battery according to claim 11, wherein a porous polymer material is deposited on the face of the dense and conductive polymer material that faces the electrolyte.

13. A lithium-ion battery according to any of the preceding claims, wherein said plurality of nanowires is arranged so that at least one substantially dendrite-shaped structure is obtained.

14. A method of manufacturing a lithium-ion battery, said method comprising the steps of:

- providing a first electrode
- providing catalytic seed particles suspended in a gas,
- providing gaseous precursors comprising constituents of nanowires to be formed,
- forming, in a gas-phase synthesis, the nanowires from the gaseous precursors and catalytic seed particles, while the catalytic seed particles are suspended in the gas,
- immersing, at or near room temperature, the nanowires into an elastic film that makes up outermost layer of said electrode,
- providing an electrolyte so positioned that the nanowires extend into said electrolyte, and
- providing a second electrode.

15. A method according to claim 14, said method further comprising the step of:

- depositing a polymer material on said elastic film while said nanowires are being immersed into said elastic film.

16. A method according to claim 15, wherein said depositing of polymer material is achieved through a chemical vapor deposition method.

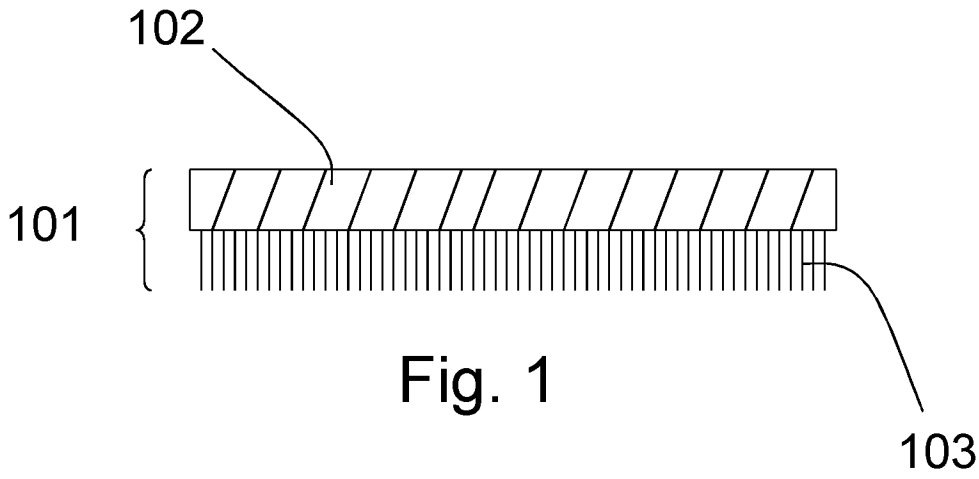

Fig. 1

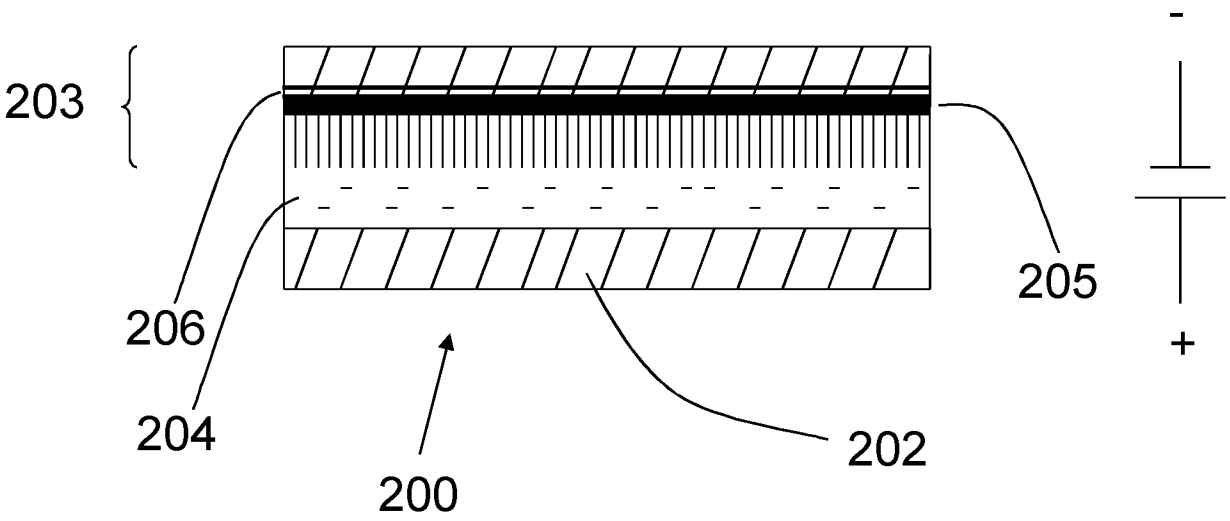

Fig. 2

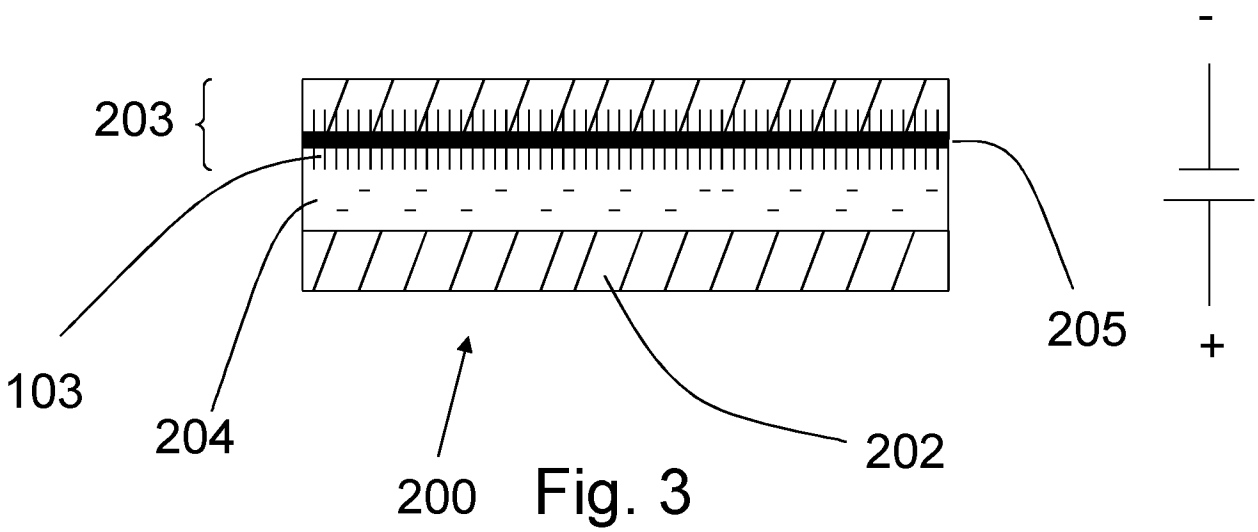

Fig. 3

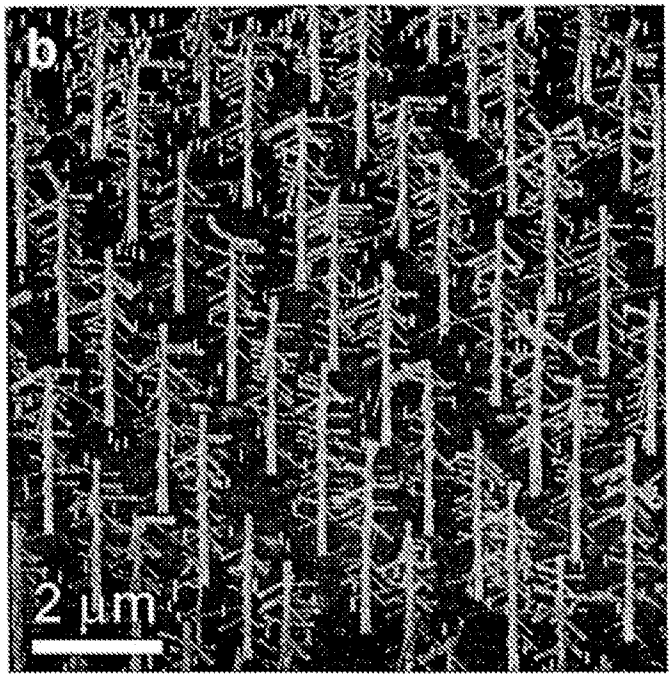

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/SE2012/050099

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/62 H01M4/134 H01M10/052 H01M4/1395
ADD. H01M2/16

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

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FÖLL H ET AL: "Si Nanowire arrays as anodes in Li ion batteries", PHYSICA STATUS SOLIDI (RRL) - RAPID RESEARCH LETTERS, WILEY-VCH VERLAG GMBH & CO. KGAA, WEINHEIM, vol. 4, no. 1-2, 1 February 2010 (2010-02-01), pages 4-6, XP002609036, ISSN: 1862-6270, DOI: 10.1002/PSSR.200903344 [retrieved on 2009-10-23] the whole document ----- -/--	1-3,5-9, 13

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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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)

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Date of the actual completion of the international search	Date of mailing of the international search report
23 April 2012	04/05/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Standaert, Frans

INTERNATIONAL SEARCH REPORT

International application No
PCT/SE2012/050099

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KATHERINE E. PLASS ET AL: "Flexible Polymer-Embedded Si Wire Arrays", ADVANCED MATERIALS, vol. 21, no. 3, 19 January 2009 (2009-01-19), pages 325-328, XP55025236, ISSN: 0935-9648, DOI: 10.1002/adma.200802006 the whole document	1,2, 4-11, 13-16
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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