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(74) Agents: **ROBERTS, Gwilym, Vaughan** et al, Kilburn & Strode, 20 Red Lion Street, London WC1R 4PJ (GB).

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(71) Applicant (for all designated States except US): **IMPERIAL INNOVATIONS LTD** [GB/GB], Electrical & Electronic Engineering Building, Level 12, Imperial College, Exhibition Road, London SW7 2AZ (GB).

(72) Inventors; and

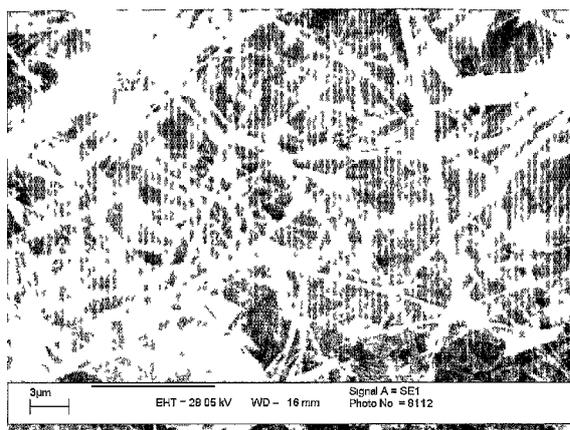
(75) Inventors/Applicants (for US only): **GREEN, Mino** [GB/GB], Imperial Innovations Ltd, Electrical & Electronic Engineering Building, Level 12, Imperial College, Exhibition Road, London SW7 2AZ (GB). **LIU, Feng-Ming** [CN/GB], 5 Jemmett Close, Kingston-upon-Thames, Surrey KT2 7AJ (GB).

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(54) Title: A METHOD OF FABRICATING HBRES COMPOSED OF SILICON OR A SILICON-BASED MATERIAL AND THEIR USE IN LITHIUM RECHARGEABLE BATTERIES



(57) Abstract: A method of fabricating fibres of silicon or silicon-based material comprises the steps of etching pillars on a substrate and detaching them. A battery anode can then be created by using the fibres as the active material in a composite anode electrode.

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A METHOD OF FABRICATING FIBRES COMPOSED OF SILICON OR A  
SILICON-BASED MATERIAL AND THEIR USE IN LITHIUM  
RECHARGEABLE BATTERIES.

5 The invention relates to a method of fabricating fibres composed of silicon or a silicon-based material and their use the active anode material in rechargeable lithium battery cells.

It is well known that silicon can be used as the active anode material of a  
10 rechargeable lithium-ion electrochemical cell (see, for example, Insertion Electrode Materials for Rechargeable Lithium Batteries, M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak in Adv. Mater. 1998, 10, No. 10). The basic composition of a conventional lithium-ion rechargeable battery cell is shown in Fig. 1 including a graphite-based anode electrode, the component to  
15 be replaced by the silicon-based anode. The battery cell includes a single cell but may also include more than one cell.

The battery cell generally comprises a copper current collector for the anode 10 and an aluminium current collector for the cathode 12 which are externally  
20 connectable to a load or to a recharging source as appropriate. A graphite-based composite anode layer 14 overlays the current collector 10 and a lithium containing metal oxide-based composite cathode layer 16 overlays the current collector 12. A porous plastic spacer or separator 20 is provided between the graphite-based composite anode layer 14 and the lithium containing metal  
25 oxide-based composite cathode layer 16 and a liquid electrolyte material is dispersed within porous plastic spacer or separator 20, the composite anode layer 14 and the composite cathode layer 16. In some cases, the porous plastic spacer or separator 20 may be replaced by a polymer electrolyte material and in

such cases the polymer electrolyte material is present within both the composite anode layer 14 and the composite cathode layer 16.

When the battery cell is fully charged, lithium has been transported from the lithium containing metal oxide via the electrolyte into the graphite-based layer where it reacts with the graphite to create the compound,  $\text{LiC}_6$ . The graphite, being the electrochemically active material in the composite anode layer, has a maximum capacity of 372 mAh/g. It will be noted that the terms "anode" and "cathode" are used in the sense that the battery is placed across a load.

It is generally believed that silicon, when used as an active anode material in a lithium-ion rechargeable cell, provides a significantly higher capacity than the currently used graphite. Silicon when converted to the compound  $\text{Li}_{21}\text{Si}$  by reaction with lithium in an electrochemical cell, has a capacity of 4,200 mAh/g.

Existing approaches of using a silicon or silicon-based active anode material in a lithium-ion electrochemical cell have failed to show sustained capacity over the required number of charge/discharge cycles and are thus not commercially viable.

One approach uses silicon in the form of a powder, in some instances made into a composite with optionally an electronic additive and containing an appropriate binder such as polyvinylidene difluoride coated onto a copper current collector. However, this electrode fails to show sustained capacity when subjected to charge/discharge cycles. It is believed that this capacity loss is due to partial mechanical isolation of the silicon powder mass arising from the volumetric expansion/contraction associated with lithium insertion/extraction into and from the host silicon. In turn this gives rise to agglomeration of the powder mass in electrically isolated "islands".

In another approach described by Ohara et al. in Journal of Power Sources 136 (2004) 303-306 silicon is evaporated onto a nickel foil current collector as a thin film and this structure is then used to form the anode of a lithium-ion cell.

5 However, although this approach gives good capacity retention, this is only the case for very thin films and thus these structures do not give usable amounts of capacity per unit area and increasing the film thickness to give usable amounts of capacity per unit area causes the good capacity retention to be eliminated.

10 In another approach described in US2004/0126659, silicon is evaporated onto nickel fibres which are then used to form the anode of a lithium battery. However this is found to provide an uneven distribution of silicon on the nickel fibres hence significantly affecting operation.

15 In another approach described in US 6,887,511, silicon is evaporated onto a roughened copper substrate to create medium-thickness films of up to 10  $\mu\text{m}$ . During the initial lithium ion insertion process, the silicon film breaks up to form pillars of silicon. These pillars can then reversibly react with lithium ions and good capacity retention is achieved. However, the process does not  
20 function well with thicker film and the creation of the medium-thickness film is an expensive process. Furthermore the pillared structure caused by the break up of the film has no inherent porosity such that issues may arise with long term capacity retention.

25 The invention is set out in the claims. Because the anode electrode structure uses fibres of silicon or silicon-based material, the problems of reversibly reacting these silicon or silicon-based fibres with lithium are overcome. In particular by arranging the fibres in a composite structure, that is a mixture of fibres a polymer binder and an electronic additive, the charge/discharge process

becomes reversible and repeatable and good capacity retention is achieved. In addition the manner in which the fibres are laid can provide advantages. By providing a dis-ordered non-woven mat of fibres, a fully reversible and repeatable charging capability is introduced without risk of significant  
5 mechanical isolation. For example the fibres may be deposited as a felt or felt-like structure. In the case of a composite structure this can be with the additional components, or the felt can be with a simple binder or, where structurally appropriate, loose.

10 Furthermore, a simplified method of fabricating fibres is provided comprising etching a substrate to produce pillars and detaching the pillars providing a robust and high-yield approach.

Embodiments of the invention will now be described, by way of example, with  
15 reference to the figures, of which: .

Fig. 1 is a schematic diagram showing the components of a battery cell;

Fig. 2 is a magnified photograph of an electrode according to the present invention;

20 Fig.3 shows a first cycle voltage plot for a silicon fibre/PVDF/Super P composite electrode.

In overview the invention allows creation of fibres or hairs of silicon or silicon-based material and the use of these fibres to create both a composite anode  
25 structure with a polymer binder, an electronic additive (if required) and a metal foil current collector and a felt-like electrode structure. In particular it is believed that the structure of the silicon elements that make up the composite overcomes the problem of charge/discharge capacity loss.

## 5

By laying down the fibres in a composite or felt or a felt-like structure, that is a plurality of elongate or long thin fibres which crossover to provide multiple intersections, for example by being laid down in a random or disordered or indeed ordered manner, the problem of charge/discharge capacity loss is reduced.

Typically the fibres will have a length to diameter ratio of approximately 100:1 and hence in an anode layer such as a composite anode layer, each fibre will contact other fibres many times along their length giving rise to a configuration where the chance of mechanical isolation arising from broken silicon contacts is negligible. Also, the insertion and removal of lithium into the fibres, although causing volume expansion and volume contraction, does not cause the fibres to be destroyed and hence the intra-fibre electronic conductivity is preserved..

The fibres may be manufactured by detaching pillars from a substrate. In addition the manner of fabrication of the pillars may be provided by a simple repeatable chemical process.

One manner in which the pillars can be made is by dry etching, for example deep reactive ion etching of the type, for example, described in US application number 10/049736 which is commonly assigned herewith and incorporated herein by reference. The skilled person will be familiar with the process such that detailed description is not required here. Briefly, however, a silicon substrate coated in native oxide is etched and washed so as to give a hydrophilic surface. Caesium chloride (CsCl) is evaporated on the surface and the coated substrate is transferred under dry conditions to a chamber of fixed water vapour pressure. A thin film of CsCl develops into an island array of hemispheres whose dimensional characteristics depend on initial thickness,

water vapour pressure and time of development. The island array provides an effective mask after which etching is carried out for example by reactive ion etching leaving an array of pillars corresponding to the hemispherical islands. The CsCl resist layer is highly soluble in water and can be readily washed  
5 away.

Alternatively the pillars can be made by wet etching/using a chemical galvanic exchange method for example as described in our co-pending application GB 0601318.9 with common assignees and entitled "Method of etching a silicon-  
10 based material", incorporated herewith by reference. A related method which may also be used has been disclosed in Peng K-Q, Yan, Y-J Gao, S-P, Zhu J., Adv. Materials, 14 (2004), 1164-1 167 {"Peng"}; K. Peng *et al*, Angew. Chem. Int. Ed., 44 2737-2742; and K. Peng *et al*, Adv. Funct. Mater., 16 (2006), 387-394.

15 In the preferred embodiment pillars of for example 100 microns in length and 0.2 microns in diameter are fabricated on and from a silicon substrate. More generally pillars of length in the range of 20 to 300 microns and diameter or largest transverse dimension in the range of 0.08 to 0.5 microns may be used to  
20 provide the fibres. According to the process the silicon substrate may be n- or p- type and, according to the chemical approach, and may be etched on any exposed (100) or (110) crystal face. Since the etching proceeds along crystal planes, the resulting fibres are single crystals. Because of this structural feature, the fibres will be substantially straight facilitating length to diameter  
25 ratio of approximately 100: 1 and, when in a composite anode layer, allowing each fibre to contact other fibres many times along their length. The etching process can also be carried out either on very large scale integration (VLSI) electronic grade wafers or rejected samples of the same (single crystal wafers). As a cheaper alternative, photovoltaic grade polycrystalline material, as used

for solar panels, may also be used.

In order to detach the pillars to obtain the fibres, the substrate, with pillars attached, is placed in a beaker or any appropriate container, covered in an inert liquid such as ethanol and subjected to ultra-sonic agitation. It is found that within several minutes the liquid is seen to be turbid and it can be seen by electron microscope examination that at this stage the pillars have been removed from their silicon base.

It will be appreciated that alternative methods for "harvesting" the pillars include scraping the substrate surface to detach them or detaching them chemically. One chemical approach appropriate to n-type silicon material comprises etching the substrate in an HF solution in the presence of backside illumination of the silicon wafer.

Once the silicon pillars have been detached they can be used as the active material in a composite anode for lithium-ion electrochemical cells. To fabricate a composite anode, the harvested silicon is filtered from solution and can be mixed with polyvinylidene difluoride and made into a slurry with a casting solvent such as n-methyl pyrrolidinone. This slurry can then be applied or coated onto a metal plate or metal foil or other conducting substrate for example physically with a blade or in any other appropriate manner to yield a coated film of the required thickness and the casting solvent is then evaporated from this film using an appropriate drying system which may employ elevated temperatures in the range of 50 degrees C to 140 degrees C to leave the composite film free or substantially free from casting solvent. The resulting mat or composite film has a porous and/or felt-like structure in which the mass of silicon fibres is typically between 70 percent and 95 percent. The composite

film will have a percentage pore volume of 10-30 percent, preferably about 20 percent.

5 An SEM of a composite electrode structure obtained by the method set out above is shown in Fig. 2. Alternatively a felt or felt-like structure may be produced as a sheet material (not necessarily on a current collector) and act as its own current collector.

10 Fabrication of the lithium-ion battery cell thereafter can be carried out in any appropriate manner for example following the general structure shown in Fig. 1 but with a silicon or silicon based active anode material rather than a graphite active anode material. For example the silicon fibres-based composite anode layer is covered by the porous spacer 18, the electrolyte added to the final structure saturating all the available pore volume. The electrolyte addition is  
15 done after placing the electrodes in an appropriate casing and may include vacuum filling of the anode to ensure the pore volume is filled with the liquid electrolyte.

Please see the following examples:

20

0.0140 g of silicon fibres were weighed out into a 2 cm<sup>2</sup> Eppendorf centrifuge tube, and 0.0167 g of Super P conductive carbon was added. N-methyl pyrrolidinone (NMP) was then pipetted into the tube, until all the materials were dispersed (0.92 g). Previously, PVDF had been dissolved in NMP, at 7.8  
25 wt % PVDF. A quantity of this solution was added to the tube, containing 0.0074 g of PVDF. The mix composition was thus Si : PVDF : Super P = 85.3 : 4.5 : 10.1 wt%.

The tube was placed in an ultrasonic bath for one hour, to homogenise the mixture, and then stirred for a further hour. The slurry was then coated onto 14  $\mu\text{m}$  copper foil, using a doctor blade with a blade gap of 0.8 mm. The coating was then dried in an oven at  $100^{\circ}\text{C}$  for one hour, to evaporate the NMP solvent.

5 After drying, the thickness of the coated layer was 30 - 40  $\mu\text{m}$ . Figure 2 shows an SEM of a similar mix and coating, with no Super P carbon.

The coating was lightly rolled, and then electrode disks were cut out with a diameter of 12 mm. These were assembled into electrochemical cells in an

10 argon filled glove box. The counter electrode and reference electrode were both lithium metal. The electrolyte was  $\text{LiPF}_6$  in a mixture of organic carbonates. The cell was tested on a VMP3 device. After a thirty minute soak, the cell was held at - 0.1 mA for one hour, and then at - 0.2 mA until the required lithiation capacity was achieved. The electrode was then delithiated at + 0.2 mA, up to a

15 voltage of 1.0 V vs.  $\text{LiZLi}^+$ . Figure 3 shows the cell voltage during this first cycle.

A particular advantage of the approach described herein is that large sheets of silicon-based anode can be fabricated, rolled if necessary, and then slit or

20 stamped out subsequently as is currently the case in graphite-based anodes for lithium-ion battery cells meaning that the approach described herein can be retrofitted with the existing manufacturing capability.

A further advantage of the arrangement described herein is that the structural

25 strength in fact increases with each recharging operation. This is because the fibres are found to "weld" to one another as a result of the disrupted crystalline structure at the fibre junctions creating an amorphous structure. This in turn reduces the risk of capacity loss over multiple cycles as there is less risk of

## 10

mechanical isolation of the fibres once the fibres become connected in the manner described above.

5 It will be appreciated, of course, that any appropriate approach can be adopted in order to arrive at the approaches and apparatus described above. For example the pillar detaching operation can comprise any of a shaking, scraping, chemical or other operation as long as pillars are removed from the substrate to create fibres. Reference to silicon-based material includes silicon where appropriate. The fibres can have any appropriate dimension and can for  
10 example be pure silicon or doped silicon or other silicon-based material such as a silicon-germanium mixture or any other appropriate mixture. The substrate from which pillars are created may be n- or p- type, ranging from 100 to 0.001 Ohm cm, or it may be a suitable alloy of silicon, for example  $\text{Si}_x\text{Ge}_{1-x}$ . The fibres can be used for any appropriate purpose such as fabrication of electrodes  
15 generally including cathodes. The cathode material can be of any appropriate material, typically a lithium-based metal oxide or phosphate material such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_x\text{Ni}_x\text{Co}_{1-2x}\text{O}_2$  or  $\text{LiFePO}_4$ . The features of different embodiments can be interchanged or juxtaposed as appropriate and the method steps performed in any appropriate order.

## 11

Claims

1. A method of fabricating fibres of silicon or a silicon-based material comprising the steps of etching a silicon substrate or a silicon-based substrate to make pillars and detaching the pillars from the substrate.  
5
2. A method as claimed in claim 1 in which the fibres have transverse dimensions in the range 0.08 to 0.5 microns, preferably 0.2 microns and a length in the range 20 to 300 microns preferably 100 microns.  
10
3. A method as claimed in claim 1 in which the fibres have an aspect ratio of about 100:1.
4. A method as claimed in claim 1, claim 2 or claim 3 in which the fibres have a substantially circular cross-section.  
15
5. A method as claimed in claim 1, claim 2 or claim 3 in which the fibres have a substantially non-circular cross-section.
6. A method as claimed in any preceding claim in which the pillars are created by reactive ion etching.  
20
7. A method as claimed in any preceding claim in which the pillars are created by chemical reaction etching.  
25
8. A method as claimed in claim 7 in which the pillars are created by galvanic exchange etching.
9. A method as claimed in any preceding claim in which the pillars are detached by one or more of scraping, agitating or chemical etching.  
30

## 12

10. A method as claimed in any preceding claim in which the silicon or silicon-based material comprises one of undoped silicon, doped silicon or a silicon germanium mixture.
- 5
11. A method as claimed in any preceding claim in which the fibre is single crystal silicon or silicon-based material comprises one of single crystal silicon or silicon germanium
- 10
12. A method of creating a cell electrode comprising depositing a slurry containing silicon-based fibres to form a layer of silicon-based fibres.
- 15
13. A method as claimed in claim 12 in which the fibres are single crystal fibres.
14. A method as claimed in claim 12 or claim 13 in which the fibres are deposited in a felt.
- 20
15. A method as claimed in claim 12, claim 13 or claim 14 in which the fibres are deposited in a composite.
16. A method as claimed in any one of claims 12 to 15 including depositing the fibres on a current collector.
- 25
17. A method as claimed in any one of claims 12 to 16 in which the fibres are fabricated by a method according to any of claims 1 to 11.

## 13

18. A method as claimed in any one of claims 12 to 17 in which the electrode is an anode.
19. A method as claimed in any one of claims 12 to 15 in which the felt  
5 has a percentage pore volume of about 10-30 per cent.
20. A method of fabricating a lithium rechargeable cell comprising the steps of creating an anode as claimed in any of claims 12 to 19 and adding a cathode an electrolyte.  
10
21. A method as claimed in claim 20 further comprising adding a separator between cathode and the anode.
22. A method as claimed in claim 20 or claim 21 further comprising  
15 providing a casing around the cell.
23. A composite electrode containing silicon-based fibres fabricated using any of the preceding claims as one of its active materials.
24. A composite electrode in claim 12 which uses copper as a current  
20 collector.
25. A composite electrode in claim 12 in which the electrode is an anode.  
25
26. An electrochemical cell containing an anode as claimed in any one of claims 12 to 14.

## 14

27. An electrochemical cell in claim 15 in which the cathode comprises a lithium-containing compound capable of releasing and reabsorbing lithium ions as its active material.
- 5 28. An electrochemical cell in claim 15 in which the cathode comprises lithium-based metal oxide or phosphate as its active material preferably  $\text{LiCoO}_2$  or  $\text{LiMn}_x\text{Ni}_x\text{Co}_{1-2x}\text{O}_2$  or  $\text{LiFePO}_4$ .
- 10 29. A lithium rechargeable cell anode comprising a layer of silicon-based single crystal fibres in which the fibres form a felt
30. An anode as claimed in claim 29 in which the fibres are part of a composite.
- 15 31. An anode as claimed in any one of claims 29 to 30 including amorphous silicon portions at intersections of the fibres.
- 20 32. A cell comprising an anode as claimed in any one of claims 29 to 30 and a cathode.
33. A cell as claimed in claim 32 in which the cathode comprises lithium-based material.
- 25 34. A cell as claimed in claim 33 in which the cathode comprises lithium cobalt dioxide.
35. A device powered by a cell as claimed in any one of claims 26 to 34.

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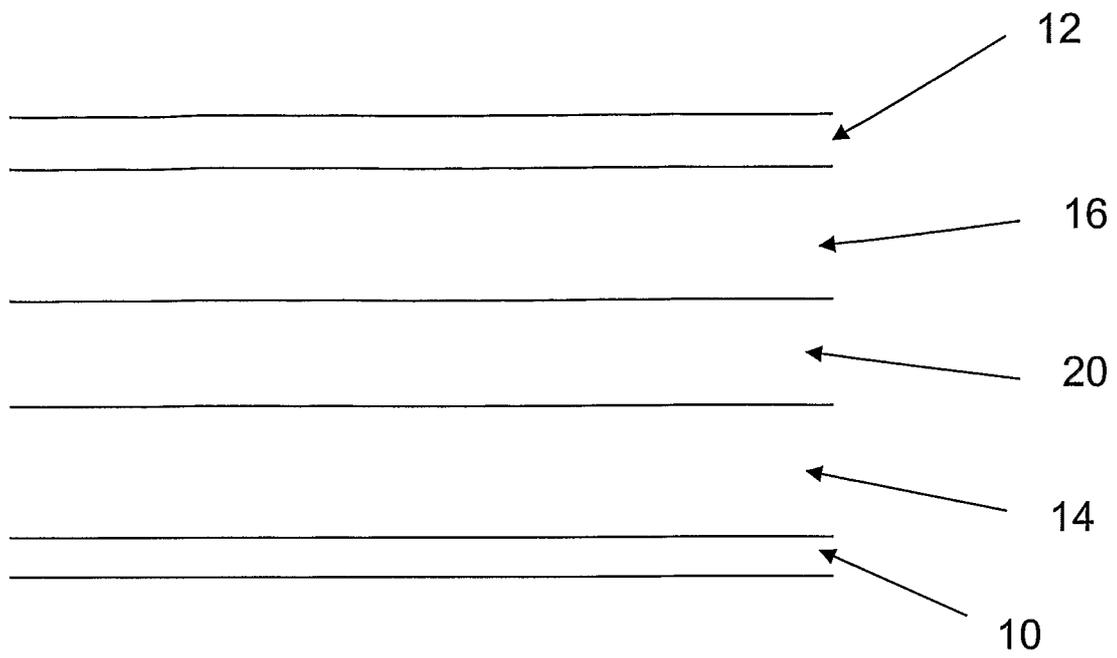
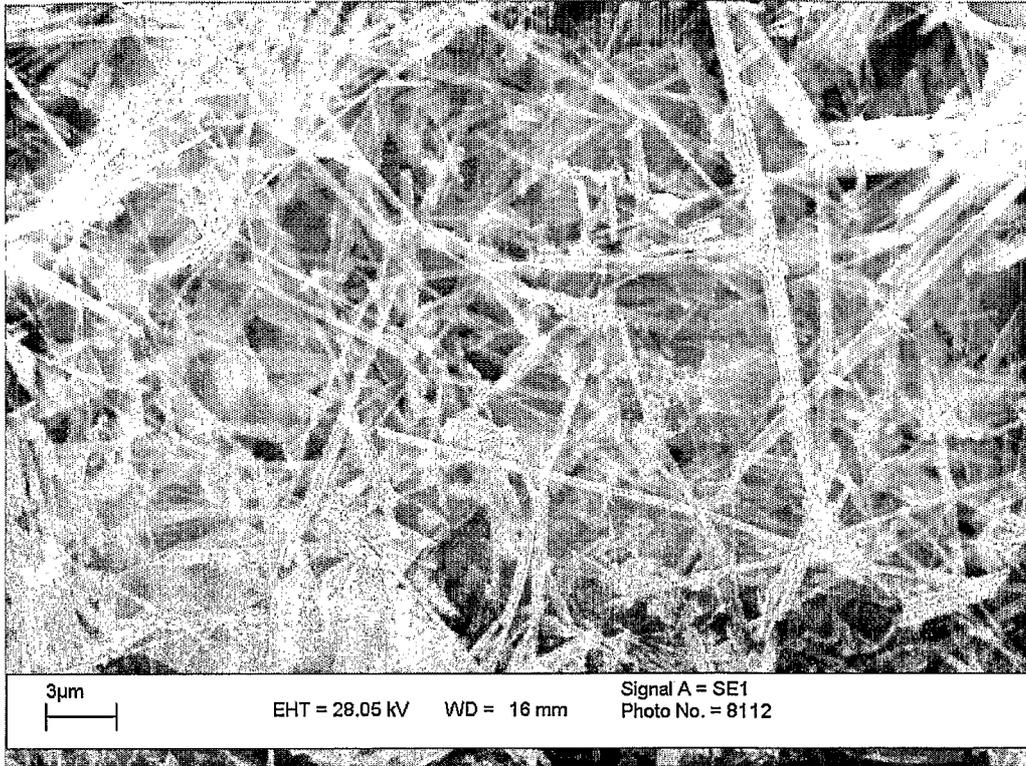


FIG. 1



**FIG. 2**

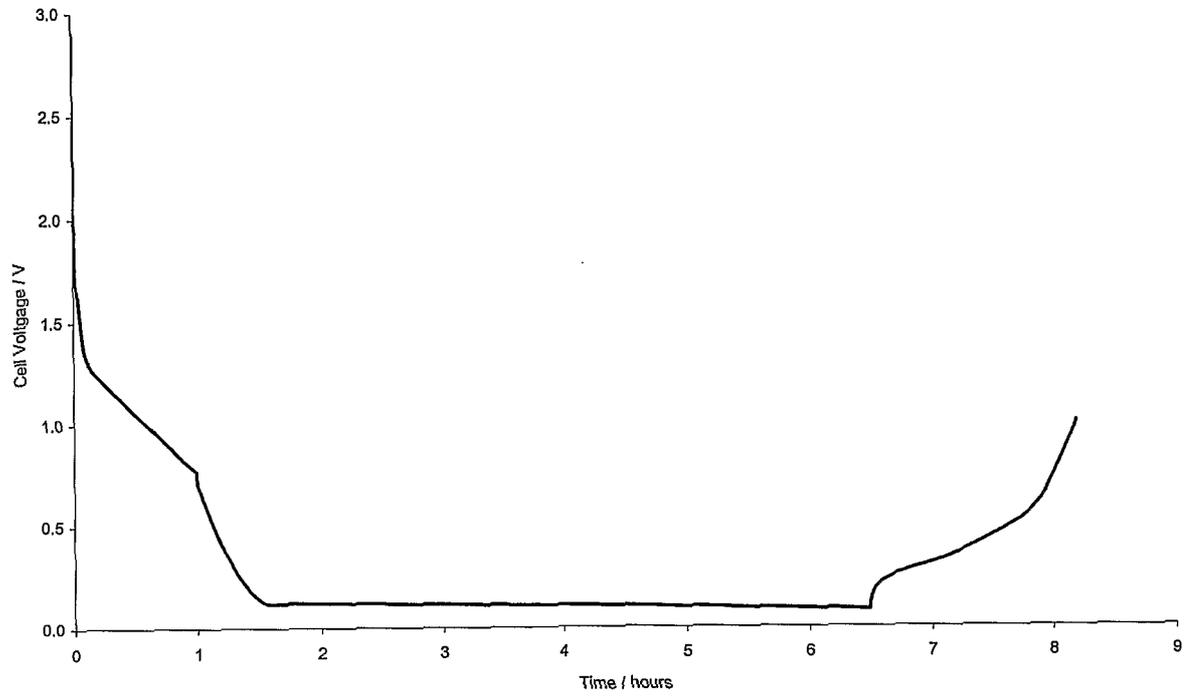


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No  
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A. CLASSIFICATION SUBJECT MATTER  
INV. H01M4/38 C30B29/06 C30B33/08

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)  
C30B HOIM

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 , INSPEC, 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	PENGE ET AL: ANGEW. CHEM. IND. ED, vol. 44, 6 April 2005 (2005-04-06), pages 2737-2742, XP002429289 Weinheim DE cited in the application page 2741	1, 4, 7-11
X	WO 01/96847 A (UNIV NORTH CAROLINA CHAPEL HIL [US]; ZHOU OTTO Z [US]; GAO BO [US]; SI) 20 December 2001 (2001-12-20) page 7 - page 9 ; figure 1	12-35
A	GB 2 395 059 A (IMP COLLEGE INNOVATIONS LTD [GB]) 12 May 2004 (2004-05-12) page 6 - page 8 ; figure 1	1-35
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Further documents are listed in the continuation of Box C

See patent family annex

\* Special categories of cited documents

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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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"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
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NL - 2280 HV Rijswijk  
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2007/000211

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	"Battery, especially for portable devices, has an anode containing silicon" DERWENT, no. 2002-564237, 2002, XP002326426 NL 1015956 (University of Delft) -----	1-35

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Information on patent family members

International application No

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