The invention provides a negative electrode material for use in a rechargeable battery, comprising a Si based material comprising a mixture of submicron sized Si particles and submicron sized Si wires, wherein the average particle size of the Si particles is at least twice the average width of the Si wires, preferably at least 5 times, and most preferably at least 10 times the average width of the Si wires. The process for manufacturing these Si based materials comprises the steps of: providing a Si based precursor, providing a gas stream at a temperature above the atomization point of the Si precursor, injecting the Si precursor in the gas stream, quenching the gas stream carrying the vaporized Si precursor, thereby obtaining a mixture of submicron sized Si particles and submicron sized Si wires, and separating the mixture from the gas stream.
Negative electrode material for lithium-ion batteries

TECHNICAL FIELD AND BACKGROUND

This invention relates to a negative electrode material for lithium-ion batteries and the synthesis of this powder using a gas phase technology.

Lithium-ion batteries are the most widely used secondary systems for portable electronic devices. Compared to aqueous rechargeable cells, such as nickel-cadmium and nickel metal hydride, Li-ion cells have higher energy density, higher operating voltages, lower self discharge and low maintenance requirements. These properties have made Li-ion cells the highest performing available secondary battery.

The worldwide energy demand increase has driven the lithium-ion battery community to search for new generation electrode materials with high energy density. One of the approaches is to replace the conventional carbon graphite negative electrode material by another better performing active material, being a metal, metalloid or metallic alloy based on silicon (Si), tin (Sn) or aluminum (Al). These materials can provide much higher specific and volumetric capacity compared to graphite. On top of the specific composition of the negative electrode material, also the morphology of the particles and the way they are ordered into a 3D (electrode) structure are playing a key role in the electrochemical behaviour of the resulting Li-ion battery. Therefore, it is of paramount importance to be able to optimize those parameters in order to enhance the electrochemical performance of the negative electrode.

The composite lithium-ion battery electrode needs to possess mixed conductivity with both ionic lithium and electrons. Such a complex medium is generally obtained by mixing together the active material particles with different additives such as a very fine powder of carbon black and a polymeric binder. The conductive additive can be a type of carbon black, but also graphenes, graphenes, carbon fibres or carbon nanotubes and combinations thereof. The binder additive has a complex role since it not only gives mechanical strength to the composite electrode but also allows for a good adhesion between the electrode layer and the current collector. The binder gives the composite electrode a sufficient liquid electrolyte uptake to provide internal ionic percolation. Suitable binders include, but are not limited to, carboxymethyl cellulose (CMC), polysaccharides, polyvinylidene fluoride (PVDF) polyolefins, florinated polyolefins, polyimides, polycrylates, natural or synthetic rubbers. Dispersants and additives known by those skilled in the art can be used to control the porosity or to optimize the distribution and contact of the active material within the 3D structure of the battery electrode. ‘Calendering’ is used to increase the density of the electrode or to increase contact between the different particles of the composite electrode.
As described above Si-based negative electrode materials could significantly enhance the energy density of the commercial lithium ion batteries. Silicon has the largest theoretical gravimetric capacity (3579 mAh/g) corresponding to the following reaction:

\[
15\text{Li} + 4\text{Si} \rightarrow \text{Li}_3\text{Si}_4
\]

and a large volumetric capacity (2200 mAh/cm\(^3\)). Unfortunately, it exhibits a poor capacity retention. This poor cycle life is due to several reasons, including loss of adhesion to the current collector and continuous electrolyte decomposition. The major reason is however that silicon shows a huge particle volume expansion over cycling (310%), resulting in the fact that the particles can break up, pulverize or become non-contacted.

Pulverization of the silicon particles can be minimized by using only a reversible part of the full theoretical capacity. The maximal volume expansion should be maintained below the point where the particles continue to break up.

A common approach to increase the electrochemical behaviour of Si based electrodes is to use (metal) wires/fibers, since in this way the current collectivity can be improved due to the formation of conductive paths among the anode active material particles. The concept of using wires in battery applications is technologically introduced in several ways. Carbon nanotubes can be incorporated as conductive material in the preparation of the silicon based electrode to prevent degradation of electron conductivity. A Si-based anode containing a plurality of metal fibers is disclosed in US2009-0269677. The metal fibers (e.g. Ti, Ni, Fe, ...) form a three-dimensional network structure that provides conductive paths for the silicon particles. Thus, compared to a general anode in which an active material layer is provided on a current collector made of a metal foil or the like, the current collectivity is improved. In another approach published in US2004-0126659 silicon is evaporated on nickel fibers. There however, a high weight percentage of inactive materials limit the application.

Another approach to solve the problems associated with silicon powder particles is to use pure silicon submicron sized fibers or wires. In this way not only the conductive paths are formed as mentioned above. Additionally, submicron sized wire anodes are believed to sustain larger strains during charging and discharging of the electrode (see for example Chan et al. in Nature Nanotech. 3 (2008) 31-35). The wires do not pulverize into smaller particles when cycled at high capacities. An important disadvantage of the use of such Si wires in battery electrodes is however that they are inherently fluffy and thus result in a low density in the deposited layer, due to the limited packing properties.

There are several production methods for silicon submicron sized wires. They can be prepared by etching a silicon-based substrate, where in a second step the pillars can be harvested. When the wires are grown on the current collector or attached to the current collector an efficient electron transport is maintained between current collector and the wires. Si fibers
can also be bonded together, prepared by wet or dry etching of a substrate and detaching the resulting fibers from the surface. High capacities at high currents are possible as disclosed in US2009-0042101, where submicron sized wires are growth-rooted from the substrate. The structures are produced using vapor-solid or vapor-liquid-solid growth.

As described above the use of submicron sized wires has the major intrinsic drawback of low density when applied in a coating. Additionally, the synthesis methods to obtain such wires are difficult to scale and of a high complexity (e.g. multi step process).

It is an aim of the present invention to improve or even overcome these problems, and to provide for better negative electrode materials that can be manufactured by a simple and economical process.

**SUMMARY**

Viewed from a first aspect, the invention can provide a negative electrode material for use as in a rechargeable battery, comprising a Si based material comprising a mixture of submicron sized Si particles and submicron sized Si wires, wherein the average particle size of the Si particles is at least 5 times the average width of the Si wires, and preferably at least 10 times the average width of the Si wires. The Si based material may be free-standing, that is, not grown on or attached to a substrate. In such an embodiment, the Si based material may be obtained in a plasma gas stream. The Si based material may also have a tap density of at least 0.25 g/cm³. In one embodiment, the submicron sized Si particles may have an average primary particle size greater than 10 nm and less than 500 nm. In another embodiment, the silicon powder may have an average particle size of between 0.04 and 0.3 μm, where the average particle size (d₅₀) can be derived from SEM or TEM analysis. The Si based material may also consist of pure Si.

The Si based material described above may have Si wires having a width between 1 and 100 nm. In one embodiment, their width is between 1 and 20 nm. The Si wires may also have an aspect ratio (length/width) of more than 5:1. In one embodiment, the aspect ratio may be more than 10:1, and in another embodiment, more than 20:1. In another embodiment, each of the submicron sized Si wires may be in contact with at least two submicron sized Si particles. In yet another embodiment, the Si based material may further comprise oxygen, with an oxygen content of less than 20 wt%.

Viewed from a second aspect, the invention can provide a process for manufacturing the Si based material described above, comprising the steps of:

- providing a Si based precursor,
- providing a gas stream at a temperature above the atomization point of the Si precursor,
- injecting the Si based precursor in the gas stream,
- quenching the gas stream carrying the vaporized Si based precursor, thereby obtaining a mixture of submicron sized Si particles and submicron sized Si wires, and
- separating the mixture from the gas stream. The temperature of the gas stream may be above 3500 K when injecting the Si based precursor, whereafter the gas stream may be quenched at a temperature between 1600 and 2500 K.

In one embodiment the Si based precursor is a micron-sized Si powder having an average particle size of less than 100 μm. In another embodiment the hot gas stream may be provided by means of either a gas burner, a hydrogen burner, an RF plasma, or a DC arc plasma. The gas stream may also be provided by means of a radio frequency inductively coupled plasma, and the gas stream may comprise a mixture of argon and nitrogen. Using a plasma device with a certain power expressed in kw, a quench rate of between 20 and 100 L/kg injected precursor. kw (liter per kg injected precursor and per kw) is indicated. A quench rate of between 40 and 80 L/kg.kw gives a good quantitative mix of Si particles and wires.

Viewed from a third aspect, the invention can provide an electrode composition for a rechargeable Li-ion battery comprising the Si based material described above and a carboxymethyl cellulose (CMC) binder material. The electrode can further comprise styrene butadiene rubber as binder material. In one embodiment, the electrode can consist of 20-60 wt% of the Si based material, 20-40 wt% binder material, the remainder being a compound consisting of carbon. The carbon compound can consist of acetylene black powder. In another embodiment, the electrode can consist of 50 wt% of the Si based material, 25 wt% binder material, and 25 wt% acetylene black powder.

Viewed from a fourth aspect, the invention can provide a process for preparing an electrode assembly for a rechargeable Li-ion battery comprising an electrode composition described before, comprising the steps of:

- dissolving a CMC salt in water so as to obtain an aqueous solution of binder material,
- dispersing the carbon compound in the aqueous solution, and thereafter
- dispersing the Si based material in the aqueous solution, thereby obtaining a slurry,
- spreading the slurry on a current collector, and
- curing the electrode assembly comprising the slurry at a temperature between 125 and 175°C.

Alternatively, the invention can provide a process for preparing an electrode assembly for a rechargeable Li-ion battery comprising an electrode composition described above, comprising the steps of:
- providing an aqueous solution of the binder material,
- dispersing the Si based material in the aqueous solution, and thereafter
- dispersing the carbon compound in the aqueous solution, thereby obtaining a slurry,
- spreading the slurry on a current collector, and
- curing the electrode assembly comprising the slurry at a temperature between 125 and 175°C.

In one embodiment of both these processes, the current collector is a copper foil. In another embodiment the aqueous solution of binder material has a concentration of 2-4 wt% of Na-CMC. In another embodiment the aqueous solution of binder material is aged under stirring for at least 5 hours, before dispersing either one of the silicon powder and the carbon compound in the aqueous binder solution. In yet another embodiment the pH of the aqueous solution of binder material is adjusted to a value between 3.5 and 6, preferably by addition of formic acid, before dispersing either one of the Si based material and the carbon compound in the aqueous binder solution.

DETAILED DESCRIPTION

An interesting approach to maintain the above mentioned advantages of the Si nanowires while at the same time increasing the density of the formulated layer is the ‘addition’ of particulate Si with improved packing behaviour compared to only wires. Ideally, there is a close interaction between the wires and the particles, thereby improving the electrical conductivity within the electrode. Si nanoparticles are here preferred because of their higher reactivity and moreover they will not pulverize if cycled below the maximum capacity and expansion (< 2000 mAh/g). The Si particle size may be larger than 10 nm, because otherwise the specific surface area and therefore the reactivity can be too high. Also, the density of the mixture of Si particles and wires may not be too close to the density of the pure Si wires, because this may lead to the disadvantage described before. Therefore it is provided that the average particle size of the Si particles is at least 5 times the average width of the Si wires, and preferably at least 10 times the average width of the Si wires. Too large particles (> 500 nm) may however break up upon cycling.

In Hu, L. et al., “Si nanoparticle-decorated Si nanowire networks for Li-ion battery anodes”, Chemical Communications, vol. 47, no. 1, p. 367-369 the particle size of the Si particles is nearly equal to the width of the Si wires, as can be seen in Fig. 1(a). The same is true in Yan X. Q. et al. in “H2-assisted control growth of Si nanowires”, Journal of Crystal Growth, vol. 257, no. 1-2, p. 69-74 - see Fig. 2(a). In EP2204867A1 a method is disclosed for preparing an electrode material by reacting silicon or tin with a metal oxide, reacting a silicon oxide or a tin oxide with a metal, or reacting a silicon compound or a tin compound with a metal compound. The reaction can take place in a plasma furnace. Metal core particles (e.g. silicon)
can be obtained formed into a network structure with fibrous substances, where the surface of the fibrous material is coated with at least an oxide. This core-shell fibrous structure may be composed of a silicon core and an amorphous silicon oxide shell. From the figures (especially 12A & B) it can be seen that the diameter of the particles is nearly the same as the width of the core-shell fibers.

An interesting method to prepare nanopowders is by plasma technology, as described in EP2086671 A1. The invention here includes a powder consisting of Si nanowires and Si nanoparticles, obtained by the optimization of the scalable high temperature plasma process. The developed powders combine the specific advantages of both submicron sized particles and wires.

It is appropriate to mention US2008-2611 12A1, where Si particles capable of absorbing and desorbing lithium are combined with nanowires. However, in this patent the Si particulate matter is in the micron-size range, inevitably leading to the problem of particle volume expansion as described above. The materials are also grown on a substrate, which makes their use less flexible.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: SEM (A) and TEM image (B) illustrating Si nanoparticles, no Si nanowires can be observed.
Figure 2: SEM (A) and TEM image (B) illustrating Si nanoparticles and Si nanowires.
Figure 3: Density versus applied pressure for a powder with only spherical particles (prismatic symbols - CEx A), a powder with spherical particles and nanowires (rectangles - Ex B) and a powder with only nanowires (triangles - CEx C).
Figure 4: SEM image illustrating Si nanowires, no Si nanoparticles can be observed.

The invention may be practiced, for example, by way of the different examples described below.

Comparative Synthesis Example A (CEx A)

The starting material (precursor) is a micron-sized Si powder (from ECKA - Austria, specified as being <75 \( \mu \text{m} \)). A 60 kW radio frequency (RF) inductively coupled plasma (ICP) is applied, using an argon plasma with 2.5 \( \text{Nm}^3/\text{h} \) argon gas. The solid silicon precursor is injected in the plasma at a rate of 800 g/h, resulting in a prevalent (i.e. in the reaction zone) temperature above 3500 K. In this first process step the Si precursor is totally vaporized followed by a nucleation into submicron sized Si powder. An argon flow of 90 L/min (expressed as function
of the power and the amount of injected precursor this corresponds to 112.5 L/kg.kW) is used as quench gas immediately downstream of the reaction zone in order to lower the temperature of the gas below 1600 K. After filtering a nano-sized Si powder is obtained, characterized by a cubic crystalline phase and a specific surface area of 20 ± 2 m²/g (BET), which corresponds to a mean primary particle size of about 130 nm. SEM and TEM characterization shows the presence of only Si nanoparticles (see Figure 1). The tap density equals to 0.4 g/cm³, while the pressed density is around 1.4 g/cm³.

The average particle size can be calculated from the specific surface area as the average primary particle size, assuming spherical particles of equal size, according to the following formula:

\[ d_{av} = \frac{6}{\rho \times BET} \]

Here \( \rho \) refers to the theoretical density of the powder (2.33 g/cc for pure Si) and BET refers to the specific surface area (m²/g) as determined by the N₂ adsorption method of Brunauer-Emmett-Teller.

The measured average particle size using the formula above corresponds to the observations with TEM and SEM.

**Synthesis Example B**

Again, the starting material (precursor) is the micron-sized Si powder of CEx A. A 60 kW radio frequency (RF) inductively coupled plasma (ICP) is applied, using an argon plasma with 2.5 Nm⁻³/h argon gas. The solid silicon precursor is injected in the plasma at a rate of 800 g/h, resulting in a prevalent (i.e. in the reaction zone) temperature above 3500 K. In this first process step the Si precursor is totally vaporized followed by a nucleation into nano-sized Si powder. An argon flow of 40 L/min (expressed as function of the power and the amount of injected precursor this corresponds to 50 L/kg.kW) is used as quench gas immediately downstream of the reaction zone in order to lower the temperature of the gas below 2000 K. In this way the metal nuclei are formed. After filtering a nano-sized Si powder is obtained, composed of a mixture of wires and particles, and characterized by a cubic crystalline phase. SEM and TEM characterization shows the presence of Si nanowires and Si nanoparticles (see Figure 2). From the TEM it can be derived that the nanoparticles have a diameter between 30 nm and 500 nm with an average around 130 nm, which corresponds to the observations of CEx A - as the Si particles obtained under the different process conditions are identical,
except for the presence or absence of additional wires. The diameter of the wires is between 15 and 20 nm. Hence the average particle size of the Si particles is at least 5 times the average width of the Si wires.

Tap density values of 0.3 g/cm$^3$ are measured for these powders, which is in the same range as for spherical silicon nanoparticles. On top of that the density is also measured as a function of the applied pressure. Here a probe cylinder is filled with the powder and ‘closed’ with a probe piston. Then pressure is applied and the resulting sample thickness is measured. This results in a ‘pressed density’ around $1.5$ g/cm$^3$ depending on the applied power (in Figure 3: rectangles for Ex B versus prismatic symbols for CEx A). This is again comparable to, and even higher than, the values obtained for spherical silicon nanoparticles. Based on the microscopy images it can be concluded that average aspect ratio is greater than 20:1, enabling a good interparticle connectivity.

**Comparative Synthesis Example C (CEx C)**

The apparatus according to Example B is operated in similar conditions using the same precursor. However, the conditions are modified in such a way that the quench is decreased to 10 L/min (equal to $12.5$ L/kg kW), and a quench temperature above $2500$ K is obtained. After filtering a nano-sized Si powder is obtained, characterized by a cubic crystalline phase and a specific surface area of $40 \pm 2$ m$^2$/g (BET). SEM characterization shows the presence of only Si nanowires (see Figure 4). The tap density is $0.024$ g/cm$^3$ and the pressed density is around $0.8$ g/cm$^3$ (see Figure 3: triangles) and thus much lower compared to the powders containing spherical nanoparticles.

**Electrode Example A**

An electrode with a composition of $50.0$ wt% of Silicon-particles/Silicon-wires powder (obtained in Synthesis Example B), $25$ wt% conductive additive acetylene black and $25$ wt% sodium-CMC is prepared as described in WO 201 1-035876. Formic acid is added to an aqueous solution of $2.0$ wt% CMC (Alfa Aesar) to obtain pH 5. In an alumina vessel with $5$ (1 cm) alumina balls, $12.3$ g of the binder solution is added to $0.5$ g of acetylene black. The vessel is mixed for $5$ minutes in a planetary mill (Fritsch Pulversisette 6, Fritsch Germany) at a speed set at 4. In a second mixing step $0.5$ g of the Silicon-particles + Silicon-wires powder is added and further mixing was done for $10$ minutes in the planetary mill at the speed setting 4. The slurry is coated onto a $17$ μm Cu-foil using a bar coater with a $320$ μm gap. The electrode is dried for $50$ minutes at $85^\circ$C in air and a second time for $180$ minutes in a Buchi vacuum dryer at $150^\circ$C.
Comparative Electrode Example B

An electrode with a composition of 50.0 wt% of Silicon powder (containing no nanowires, obtained in Comparative Synthesis Example A), 25 wt% conductive additive acetylene black and 25 wt% sodium-CMC is prepared as a comparative example following the same procedure as the Electrode Example B.

Coin cells are prepared from the Electrode Example A and Comparative Electrode Example B. Half-cell batteries (versus lithium metal) are prepared in a glove box. The electrolyte contains 1 M LiPF$_6$ in a solution of ethylene carbonate/dimethylene carbonate (1:1 volume/volume) and 2 wt% vinylene carbonate. The cells are cycled in an ARBIN 2000 by limiting the capacity at 1200 mAh/g silicon, this equals to 600 mAh/g for the electrode. The first lithiation and delithiation cycle is at C/20 with C = 3572 mA/g, all the following cycles are at C/10 (357.2 mA/g). The number of lithiation cycles at 1200 mAh/g is measured and presented in Table 1. The lithiation and delithiation cycle life (the number of cycles where it was possible to obtain 1200 mAh/g in de-lithiation) of Electrode Example A is much longer due to the presence of silicon wires. Silicon wires improve the long range connectivity between particles that are surrounded and electrically insulated by decomposed electrolyte.

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<th>Electrode Example</th>
<th>De-lithiation cycles at 1200 mAh/g</th>
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<tr>
<td>Example A</td>
<td>125</td>
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<td>Comparative</td>
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</table>

Comparative Electrode Example C

Using the same procedure as for the electrode examples above with the material obtained in CEx C, a paste can be obtained. However, no uniform homogeneous coating is possible and therefore no electrochemical results can be obtained.

While specific embodiments and/or details of the invention have been shown and described above to illustrate the application of the principles of the invention, it is understood that this invention may be embodied as more fully described in the claims, or as otherwise known by those skilled in the art (including any and all equivalents), without departing from such principles.
CLAIMS

1. A negative electrode material for use in a Li-ion battery, the electrode material comprising a Si based material comprising a mixture of submicron sized Si particles and submicron sized Si wires, wherein the average particle size of the Si particles is at least 5 times the average width of the Si wires, and preferably at least 10 times the average width of the Si wires.

2. The electrode material of claim 1, wherein the Si based material has a tap density of at least 0.25 g/cm³.

3. The electrode material of claim 1 or 2, wherein the submicron sized Si particles have an average primary particle size greater than 10 nm and less than 500 nm.

4. The electrode material of claim 3, wherein the submicron sized Si particles have an average primary particle size between 40 and 300 nm.

5. The electrode material of anyone of claims 1 to 4, wherein the Si wires have a width between 1 and 100 nm, preferably between 1 and 20 nm; and an aspect ratio (length:width) of more than 5:1, preferably more than 10:1, and most preferably more than 20:1.

6. The electrode material of any one of claims 1 to 5, wherein each of the submicron sized Si wires is in contact with at least two submicron sized Si particles.

7. A process for manufacturing a Si based material comprised in a negative electrode material according to any one of claim 1 to 6, comprising the steps of:
   - providing a Si based precursor,
   - providing a gas stream at a temperature above the atomization point of the Si based precursor,
   - injecting the Si based precursor in the gas stream,
   - quenching the gas stream carrying the vaporized Si based precursor, thereby obtaining a mixture of submicron sized Si particles and submicron sized Si wires, and
   - separating the mixture from the gas stream.

8. The process according to claim 7, wherein the gas stream is provided at a temperature above 3500 K before injecting the Si based precursor, whereafter the gas stream is quenched to a temperature between 1600 and 2500K.

9. The process according to claim 7 or 8, wherein the Si based precursor is a micron sized Si powder having an average particle size of less than 100 μm.
10. The process according to any one of claims 7 to 9, whereby the hot gas stream is provided by means of either one of a gas burner, a hydrogen burner, and a plasma device such as an RF plasma, or a DC arc plasma.

11. The process according to claim 10, wherein the gas stream is provided by a radio frequency inductively coupled plasma, and the gas stream comprises a mixture of argon and nitrogen.

12. The process according to claims 10 or 11, wherein the gas stream is provided by a plasma device having a given power expressed in kW, and the gas stream is quenched with a quench rate between 20 and 100 L/kg injected precursor, kw, and preferably between 40 and 80 L/kg.kw.

13. The electrode material according to any one of claims 1 to 6, further comprising a carboxymethyl cellulose (CMC) binder material.

14. The electrode material of claim 12, further comprising styrene butadiene rubber as binder material.

15. The electrode material of claims 13 or 14, wherein the electrode consists of 20-60 wt% of Si based material, 20-40 wt% binder material, the remainder being a compound consisting of carbon.

16. The electrode material of any one of claims 13 to 15, wherein the carbon compound consists of acetylene black powder.

17. The electrode material of any one of claims 13 to 16, wherein the electrode consists of 50 wt% of the Si based material, 25 wt% binder material, and 25 wt% acetylene black powder.

18. A process for preparing an electrode assembly for a rechargeable Li-ion battery comprising the electrode material according to any one claims 13 to 16, comprising the steps of:
- dissolving a CMC salt in water so as to obtain an aqueous solution of binder material,
- dispersing the carbon compound in the aqueous solution, and thereafter
- dispersing the Si based material in the aqueous solution, thereby obtaining a slurry,
- spreading the slurry on a current collector, preferably a copper foil, and
- curing the electrode assembly comprising the slurry at a temperature between 125 and 175°C.
19. A process for preparing an electrode assembly for a rechargeable Li-ion battery comprising the electrode material according to any one claims 13 to 16, comprising the steps of:
- providing an aqueous solution of the binder material,
- dispersing the Si based material in the aqueous solution, and thereafter
- dispersing the carbon compound in the aqueous solution, thereby obtaining a slurry,
- spreading the slurry on a current collector, preferably a copper foil, and
- curing the electrode assembly comprising the slurry at a temperature between 125 and 175°C.

20. A process for preparing an electrode assembly according to claims 18 or 19, wherein the aqueous solution of binder material has a concentration of 2-4 wt% of Na-CMC.

21. A process for preparing an electrode assembly according to claim 18 or 19, wherein the aqueous solution of binder material is aged under stirring for at least 5 hours, before dispersing either one of the silicon powder and the carbon compound in the aqueous binder solution.

22. A process for preparing an electrode assembly according to claim 18 or 19, wherein the pH of the aqueous solution of binder material is adjusted to a value between 3.5 and 6, preferably by addition of formic acid, before dispersing either one of the Si based material and the carbon compound in the aqueous binder solution.
Figure 3

Figure 4
**INTERNATIONAL SEARCH REPORT**

**International application No**

PCT/EP2011/060403

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. H01M4/38 H01M4/134 H01M10/0525 H01M4/04 C30B29/06 H01L29/12

**ADD.**

According to International Patent Classification (IPC) into both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01M C30B H01L

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, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>EP 2 204 867 AI (CANON KK [JP]) 7 July 2010 (2010-07-07) cited in the application on paragraphs [0054], [0057], [0059], [0069], [0072], [0074], [0081], [0093], [0099], [0103], [0125], [0126], [0128], [0129], paragraphs [0143], [0150], [0152], [0153], [0199], [0202], [0214], [0216], [0247]; figures 2c, 2d, 12a; tables 1, 2, 3</td>
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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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  - "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

3 October 2011

Date of mailing of the international search report

10/10/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Schwake, Andree

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