pillars in the unetched regions, i.e. in the regions between the locations of the hemispheres.

An alternative, chemical approach is described in WO2007/083152 in the name of the present applicants. According to this method, silicon is etched using a solution containing HF and $AgNO_3$. The mechanism postulated is that isolated nanoclusters of silver are electrolessly deposited on the silicon surface in an initial stage. In a second stage, the silver nanoclusters and the areas of silicon surrounding them act as local electrodes that cause the electrolytic oxidation of the silicon in the areas surrounding the silver nanoclusters to form SiF_6 cations, which diffuse away from the etching site to leave the silicon underlying the silver nanocluster in the form pillars. The etched silicon can either be removed from the silicon substrate or used while still attached to the substrate.

The etching of silicon to form anode material is expensive to carry out and involves highly corrosive materials such as HF, which are difficult to handle.

Other methods for making the same type of high aspect ratio structures have also been presented in the literature including electrochemical etching of silicon, and deposition of fine Si structures using CVD, PECVD and sputtering, or SLS or VLS deposition such as VLS using Au catalysts. All these methods require varying levels of expense but all are above that of the method of the present invention.

Aluminium-silicon alloys are hard and wear-resistant with excellent cast-ability, weld-ability and low shrinkage and are used in very large quantities industrially wherever these properties are required, e.g. in car engine blocks and cylinder heads.

Disclosure of the invention

The present invention provides an alternative method of making silicon anode material with structural elements of suitable dimensions, which can be cheaper and use less expensive raw materials than the prior art proposals.

The inventors have recognised that crystalline silicon structures are precipitated within a matrix alloy when certain metal-silicon alloys are cooled; these alloys are those in which the solubility of silicon is low and in which the quantity of intermetallics formed on cooling are low or non-existent. Such silicon structures can have the physical and structure properties required to form anode material for use in lithium ion rechargeable cells.

The first aspect of the present invention provides a method of forming silicon anode material for rechargeable cells, which method comprises: providing a metal matrix, comprising no more than 30wt% silicon, including silicon structures dispersed therein, and etching the metal matrix to at least partially isolate or expose the silicon structures.

The claimed method provides a more economical process to obtain the anode material than is available in the prior art because the raw materials are relatively inexpensive and readily-available. It also provides a process to obtain anode material that is porous which helps to improve impregnation of the anode by the electrolyte.

Description of the drawings

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

Fig. 2 shows the Al-Si phase diagram.

Fig. 3a shows a Al-Si structure (12wt% Si) which has been etched in accordance with the claimed method;

Fig 3b is a higher magnification picture of part of the surface of the structure shown in Fig. 3a;

Fig. 4 shows a Al-Si particle (27.5wt% Si) which has been etched in accordance with the claimed method;

Fig. 5 shows full cell data with negative electrode made using Al-Si (12wt% Si) etched material; and

Fig. 6 shows half cell data with negative electrode made using Al-Si (12wt% Si) etched material.

Specific description of preferred embodiments

In overview, the present invention provides a method of producing silicon structures from using the growth of silicon precipitated within a metal-silicon alloy when cooled. The metal is then at least partially etched away to leave silicon-comprising structures. The metal is preferably aluminium because Al does not easily react with, or dissolve, Si and also because the Al-Si system provides a liquid eutectic without forming intermetallic compounds. Au-Si and Ag-Si are alternatives, but are too expensive unless a rigorous Au or Ag recovery regime is put in place. Tertiary alloys with eutectics and poor Si solubility/reactivity can also be used, e.g. aluminium alloys, such as Al-Mg-Si or Al-Cu-Si.

The structures may be discrete structural elements such as particles, flakes, wires, pillars or other structures. The structures may also be porous structures comprising structural elements, such as an agglomeration of structural elements in the form of, for example, a honeycomb structure. The structures may retain some of the metal. Although reference is made herein to silicon structures, it

should be understood that at least some metal may still be present in the structure. In fact, it may be advantageous to retain some metal. It should be understood that the structures may be (mono- or poly-) crystalline or amorphous and, when they are crystalline, each structure may be composed of one or more crystals.

The inventors have realised that the silicon structures contained in the solidified metal alloy are highly suitable as a lithium-ion anode material; some residual metal may remain after etching but this does not appear to interfere with the performance of the anode material.

Aluminium dissolves extremely little in silicon and silicon is not readily dissolved in solid aluminium when cooled to room temperature. The eutectic of an Al-Si melt is approx 12.6% Si, as can be seen from the Al-Si phase diagram is shown in Fig. 2. When cooling an aluminium-silicon alloy that contains more silicon than is soluble in solid aluminium, silicon structures can be precipitated with fine dimensions including spikes, stars and flakes.

Silicon can be obtained by two mechanisms; firstly, when a melt containing more silicon than is present in a eutectic mixture cools, it precipitates silicon structures until the composition of the melt reaches the eutectic point, where the melt solidifies. This precipitated silicon can be used as the silicon structures in the present invention. Secondly the solidified solid eutectic mixture itself includes segregated silicon that can also be used as the silicon structures in the present invention. There is an obvious economic benefit from the use of a melt containing higher silicon contents since the yield of silicon from the melt is higher. However, the shape and size of the silicon structures from these two types of mechanisms are important, as discussed below, and will depend on the process conditions (such as cooling rate) that are applied and that can be

anodes. For example, the expansion of the silicon matrix during lithiation to $Li_{13}Si_4$ at 3100mAh/g is around 205%, which means that the volume of the silicon when lithiated will be a factor of 3.05 times larger than its starting volume. An initial open porosity leaving 30% material and 60-70% voids (not including any binders or other additives) therefore partially allows for this expansion whilst minimising detrimental 'heave' of the anode, which would result in swelling of a battery. Not all of the void volume will be filled with the expanded silicon – there will still be some heave (or swelling) of the electrode mass and the remaining void space will retain good access for electrolyte into the body of the material. It will also allow sufficient expansion when there are higher orders of lithiation used which can theoretically go up to $Li_{22}Si_5$ at 4200mA/g. The inventors have recognised the interplay between all these factors and identified a range of silicon content which provides an advantageous metal matrix for use in a method for forming an improved silicon anode material.

The Al-Si process to form a metal matrix allows accurate control of the porosity of the porous structures, because it is possible to control the porosity by altering the amount of silicon incorporated in the initial Al-Si alloy by weight.

Common Al-Si alloys contain 7-18% Si and are used, for example, in car engines; they have fine structures and flakes of silicon (of the order of 0.5-1.0 μm thick and >10 μm long) in metallurgical specimens and such alloys may be used in the present invention especially when they have silicon towards the top of this silicon range.

The precipitated silicon can be isolated from the bulk alloy by etching away the bulk metal, provided the etching method does not etch the silicon structures but

does etch the metal. Etchants may be liquid or gaseous phase and may include additives or sub-processes to remove any by-product build up which slows etching. Etching can be done chemically, e.g. (in the case of Al) using ferric chloride, or electrochemically using copper sulphate/sodium chloride electrolytes. The vast majority of known aluminium etchants/methods do not attack the fine silicon structural elements, leaving them intact after the aluminium has been etched away. Any aluminium or aluminium silicide intermetallics remaining after etching, for example adhering to the crystalline silicon, can be tolerated when the silicon is used to form an anode as they are themselves excellent Li-ion anode candidates, and so long as any aluminium and intermetallic structures have comparable thickness to the silicon they can be expected to survive Li insertion cycling. In fact, aluminium and intermetallics may also aid in making electrical contact between the silicon and metal electrode.

In addition to the factors discussed above that dictate the length and thickness of the aluminium structures so that they are suitable for the application of Li-ion batteries (the amount of silicon in the melt, the solidification rate and any post-solidification heating and/or working, e.g. tempering), the silicon structures produced in the alloy can be controlled in fineness, length and structure by additives (e.g. Sb, Cu, Mg, Zn, Mn, Cr, Co, Mo, Ni, Be, Zr, Fe, Na, Sr, P). Some additives may be deleterious in effect to producing the high aspect ratio structures desired, whereas some may allow improved structure or ease of manufacture. The effects of these additives / contaminants is reportedly extensively in the literature, see Key to Metals Aluminium-silicon alloys, www.keytometals.com/Article80.

The invention provides an economical way of producing fine structured silicon for Li-ion battery anodes. The method is advantageous because aluminium is

Claims

1. A method of forming silicon anode material for rechargeable cells, which method comprises:

providing a metal matrix, comprising no more than 30wt% silicon, including silicon structures dispersed therein, and

at least partially etching the metal matrix to at least partially isolate the silicon structures.

2. A method according to claim 1 wherein the metal matrix including silicon structures dispersed therein is provided by solidifying a molten metal-silicon alloy.

3. A method according to claim 2, wherein the molten metal-silicon alloy comprises at least 7 wt%, e.g. 7– 25wt% silicon, for example 12 – 25 wt% or 7 – 18 wt% silicon.

4. A method according to any preceding claim wherein the metal is aluminium or an aluminium alloy, e.g. with magnesium or copper, containing at least 50 wt% aluminium.

5. A method according to claim 4 wherein the etching is performed chemically or electrochemically using an etchant comprising one or more acids, e.g. phosphoric, nitric, sulphuric, hydrofluoric or organic acids, or including one or more alkali, e.g. potassium hydroxide, sodium hydroxide, or using an ionic solution, optionally in combination with at least one acid or at least one alkali, such as one or more of ferric chloride copper sulphate and sodium chloride

6. A method according to any preceding claim wherein the silicon structures comprise crystalline and/or amorphous silicon.

7. A method according to any preceding claim, wherein the structures comprise structural elements and at least 80% of the structural elements have a size and shape such that they have an aspect ratio of at least 5 and optionally at least 10, and a minor dimension (i.e. the smallest dimension of the structural element) of 0.1-2μm and a major dimension (i.e. the largest dimension of the structural element) of at least 5μm.

8. A method according to claim 7 wherein the metal matrix containing the silicon structures that is etched is made by a cooling step and wherein the cooling step is controlled so that the matrix is cooled at a predetermined rate in order to provide silicon structures having the said size and shape.

9. A method according to claim 7 or 8 wherein the metal matrix including silicon structures dispersed therein also includes one or more modifiers, e.g. Sb, Cu, Mg, Zn, Mn, Cr, Co, Mo, Ni, Be, Zr, Fe, Na, Sr, P, to provide structural elements having the said size and shape.

10. A method according to any of claims 7 to 9 which comprises the step of tempering the matrix prior to etching to provide structural elements having the said size and shape.

11. A method according to any preceding claim further comprising the step of incorporating the silicon structures into a silicon anode for a rechargeable cell.

12. A method of forming silicon anode material substantially as hereinbefore described in the Examples.

13. An electroactive silicon anode material for rechargable Li-ion cells comprising silicon structures that have been at least partially isolated from a solidified metal silicon alloy.

14. An electroactive silicon anode material for rechargable Li-ion cells comprising silicon structures made by a method according to any of claims 1 to 13.

15. An electroactive silicon anode material according to claim 13 or claim 14 that includes aluminium and/or an aluminium-silicon intermetallic compound.

16. An electroactive silicon anode material according to any of claims 13 to 15, wherein the structures comprise structural elements and at least 80% of the structural elements have a size and shape such that they have an aspect ratio of at least 5 and optionally at least 10, and a minor dimension (i.e. the smallest dimension of the structure) of 0.1-2 μm and a major dimension (i.e. the largest dimension of the structure) of at least 5 μm.

17. An electrode for a lithium-ion battery comprising the silicon anode material according to any of claims 13 to 16.

18. An electrode according to any of claims 14 to 17 wherein the electrode is an anode.

19. An electrode according to any of claims 14 to 18 in which the silicon is part of a composite film.

20. An electrochemical cell comprising an electrode according to any of claims 17 or claim 19 and a cathode.

21. An electrochemical cell according to claim 20 in which the cathode comprises a lithium-containing compound capable of releasing and reabsorbing lithium ions as its active material.

22. A cell according to claim 21 in which the cathode comprises lithium-based material.

23. An electrochemical cell according to claim 22 in which the cathode comprises lithium-based metal oxide, sulphide or phosphate as its active material.

24. A cell according to claim 23 in which the cathode comprises lithium cobalt dioxide.

25. A device powered by a cell as claimed in any of claims 20 to 24.

pillars in the unetched regions, i.e. in the regions between the locations of the hemispheres.

An alternative, chemical approach is described in WO2007/083152 in the name of the present applicants. According to this method, silicon is etched using a solution containing HF and $AgNO_3$. The mechanism postulated is that isolated nanoclusters of silver are electrolessly deposited on the silicon surface in an initial stage. In a second stage, the silver nanoclusters and the areas of silicon surrounding them act as local electrodes that cause the electrolytic oxidation of the silicon in the areas surrounding the silver nanoclusters to form SiF_6 cations, which diffuse away from the etching site to leave the silicon underlying the silver nanocluster in the form pillars. The etched silicon can either be removed from the silicon substrate or used while still attached to the substrate.

The etching of silicon to form anode material is expensive to carry out and involves highly corrosive materials such as HF, which are difficult to handle.

Other methods for making the same type of high aspect ratio structures have also been presented in the literature including electrochemical etching of silicon, and deposition of fine Si structures using CVD, PECVD and sputtering, or SLS or VLS deposition such as VLS using Au catalysts. All these methods require varying levels of expense but all are above that of the method of the exemplary techniques disclosed herein.

Aluminium-silicon alloys are hard and wear-resistant with excellent cast-ability, weld-ability and low shrinkage and are used in very large quantities industrially wherever these properties are required, e.g. in car engine blocks and cylinder heads.

Disclosure of the invention

Implementation of the techniques disclosed herein provides an alternative method of making silicon anode material with structural elements of suitable dimensions, which can be cheaper and use less expensive raw materials than the prior art proposals.

The inventors have recognised that crystalline silicon structures are precipitated within a matrix alloy when certain metal-silicon alloys are cooled; these alloys are those in which the solubility of silicon is low and in which the quantity of intermetallics formed on cooling are low or non-existent. Such silicon structures can have the physical and structure properties required to form anode material for use in lithium ion rechargeable cells.

The invention is defined in the independent claims. Some of the optional features of the invention are defined in the dependent claims.

A first exemplary technique provides a method of forming silicon anode material for rechargeable cells, which method comprises: providing a metal matrix, comprising no more than 30wt% silicon, including silicon structures dispersed therein, and etching the metal matrix to at least partially isolate or expose the silicon structures.

The claimed method provides a more economical process to obtain the anode material than is available in the prior art because the raw materials are relatively inexpensive and readily-available. It also provides a process to obtain anode material that is porous which helps to improve impregnation of the anode by the electrolyte.

Description of the drawings

Fig. 1 is a schematic diagram showing the components of a battery cell; and Fig. 2 shows the Al-Si phase diagram.

Fig. 3a shows a Al-Si structure (12wt% Si) which has been etched in accordance with the claimed method;

Fig 3b is a higher magnification picture of part of the surface of the structure shown in Fig. 3a;

Fig. 4 shows a Al-Si particle (27.5wt% Si) which has been etched in accordance with the claimed method;

Fig. 5 shows full cell data with negative electrode made using Al-Si (12wt% Si) etched material; and

Fig. 6 shows half cell data with negative electrode made using Al-Si (12wt% Si) etched material.

Specific description of preferred embodiments

In overview, implementation of the techniques disclosed herein provides a method of producing silicon structures from using the growth of silicon precipitated within a metal-silicon alloy when cooled. The metal is then at least partially etched away to leave silicon-comprising structures. The metal is preferably aluminium because Al does not easily react with, or dissolve, Si and also because the Al-Si system provides a liquid eutectic without forming intermetallic compounds. Au-Si and Ag-Si are alternatives, but are too expensive unless a rigorous Au or Ag recovery regime is put in place. Tertiary alloys with eutectics and poor Si solubility/reactivity can also be used, e.g. aluminium alloys, such as Al-Mg-Si or Al-Cu-Si.

The structures may be discrete structural elements such as particles, flakes, wires, pillars or other structures. The structures may also be porous structures comprising structural elements, such as an agglomeration of structural elements in the form of, for example, a honeycomb structure. The structures may retain some of the metal. Although reference is made herein to silicon structures, it

should be understood that at least some metal may still be present in the structure. In fact, it may be advantageous to retain some metal. It should be understood that the structures may be (mono- or poly-) crystalline or amorphous and, when they are crystalline, each structure may be composed of one or more crystals.

The inventors have realised that the silicon structures contained in the solidified metal alloy are highly suitable as a lithium-ion anode material; some residual metal may remain after etching but this does not appear to interfere with the performance of the anode material.

Aluminium dissolves extremely little in silicon and silicon is not readily dissolved in solid aluminium when cooled to room temperature. The eutectic of an Al-Si melt is approx 12.6% Si, as can be seen from the Al-Si phase diagram is shown in Fig. 2. When cooling an aluminium-silicon alloy that contains more silicon than is soluble in solid aluminium, silicon structures can be precipitated with fine dimensions including spikes, stars and flakes.

Silicon can be obtained by two mechanisms; firstly, when a melt containing more silicon than is present in a eutectic mixture cools, it precipitates silicon structures until the composition of the melt reaches the eutectic point, where the melt solidifies. This precipitated silicon can be used as the silicon structures in the exemplary techniques disclosed herein. Secondly the solidified solid eutectic mixture itself includes segregated silicon that can also be used as the silicon structures in the exemplary techniques disclosed herein. There is an obvious economic benefit from the use of a melt containing higher silicon contents since the yield of silicon from the melt is higher. However, the shape and size of the silicon structures from these two types of mechanisms are important, as discussed below, and will depend on the process conditions (such as cooling rate) that are applied and that can be

anodes. For example, the expansion of the silicon matrix during lithiation to $Li_{13}Si_4$ at 3100mAh/g is around 205%, which means that the volume of the silicon when lithiated will be a factor of 3.05 times larger than its starting volume. An initial open porosity leaving 30% material and 60-70% voids (not including any binders or other additives) therefore partially allows for this expansion whilst minimising detrimental 'heave' of the anode, which would result in swelling of a battery. Not all of the void volume will be filled with the expanded silicon – there will still be some heave (or swelling) of the electrode mass and the remaining void space will retain good access for electrolyte into the body of the material. It will also allow sufficient expansion when there are higher orders of lithiation used which can theoretically go up to $Li_{22}Si_5$ at 4200mA/g. The inventors have recognised the interplay between all these factors and identified a range of silicon content which provides an advantageous metal matrix for use in a method for forming an improved silicon anode material.

The Al-Si process to form a metal matrix allows accurate control of the porosity of the porous structures, because it is possible to control the porosity by altering the amount of silicon incorporated in the initial Al-Si alloy by weight.

Common Al-Si alloys contain 7-18% Si and are used, for example, in car engines; they have fine structures and flakes of silicon (of the order of 0.5-1.0 μm thick and >10 μm long) in metallurgical specimens and such alloys may be used in the exemplary techniques disclosed herein especially when they have silicon towards the top of this silicon range.

The precipitated silicon can be isolated from the bulk alloy by etching away the bulk metal, provided the etching method does not etch the silicon structures but

does etch the metal. Etchants may be liquid or gaseous phase and may include additives or sub-processes to remove any by-product build up which slows etching. Etching can be done chemically, e.g. (in the case of Al) using ferric chloride, or electrochemically using copper sulphate/sodium chloride electrolytes. The vast majority of known aluminium etchants/methods do not attack the fine silicon structural elements, leaving them intact after the aluminium has been etched away. Any aluminium or aluminium silicide intermetallics remaining after etching, for example adhering to the crystalline silicon, can be tolerated when the silicon is used to form an anode as they are themselves excellent Li-ion anode candidates, and so long as any aluminium and intermetallic structures have comparable thickness to the silicon they can be expected to survive Li insertion cycling. In fact, aluminium and intermetallics may also aid in making electrical contact between the silicon and metal electrode.

In addition to the factors discussed above that dictate the length and thickness of the aluminium structures so that they are suitable for the application of Li-ion batteries (the amount of silicon in the melt, the solidification rate and any post-solidification heating and/or working, e.g. tempering), the silicon structures produced in the alloy can be controlled in fineness, length and structure by additives (e.g. Sb, Cu, Mg, Zn, Mn, Cr, Co, Mo, Ni, Be, Zr, Fe, Na, Sr, P). Some additives may be deleterious in effect to producing the high aspect ratio structures desired, whereas some may allow improved structure or ease of manufacture. The effects of these additives / contaminants is reportedly extensively in the literature, see Key to Metals Aluminium-silicon alloys, www.keytometals.com/Article80.

The implementation of the exemplary techniques disclosed herein provides an economical way of producing fine structured silicon for Li-ion battery anodes. The method is advantageous because aluminium is

Claims

1. A method of forming silicon anode material for rechargeable cells, which method comprises:

providing a metal matrix, comprising no more than 30wt% silicon, including silicon structures dispersed therein, wherein said silicon structures have an aspect ratio of at least 5; and

at least partially etching the metal matrix to at least partially isolate the silicon structures.

2. A method according to claim 1 wherein the metal matrix including silicon structures dispersed therein is provided by solidifying a molten metal-silicon alloy.

3. A method according to claim 2, wherein the molten metal-silicon alloy comprises at least 7 wt%, e.g. 7– 25wt% silicon, for example 12 – 25 wt% or 7 – 18 wt% silicon.

4. A method according to any preceding claim wherein the metal is aluminium or an aluminium alloy, e.g. with magnesium or copper, containing at least 50 wt% aluminium.

5. A method according to claim 4 wherein the etching is performed chemically or electrochemically using an etchant comprising one or more acids, e.g. phosphoric, nitric, sulphuric, hydrofluoric or organic acids, or including one or more alkali, e.g. potassium hydroxide, sodium hydroxide, or using an ionic solution, optionally in combination with at least one acid or at least one alkali, such as one or more of ferric chloride copper sulphate and sodium chloride

6. A method according to any preceding claim wherein the silicon structures comprise crystalline and/or amorphous silicon.

7. A method according to any preceding claim, wherein the structures comprise structural elements and at least 80% of the structural elements have a size and shape such that they have an aspect ratio of at least 5 and optionally at least 10, and a minor dimension (i.e. the smallest dimension of the structural element) of 0.1-2μm and a major dimension (i.e. the largest dimension of the structural element) of at least 5μm.

8. A method according to claim 7 wherein the metal matrix containing the silicon structures that is etched is made by a cooling step and wherein the cooling step is controlled so that the matrix is cooled at a predetermined rate in order to provide silicon structures having the said size and shape.

9. A method according to claim 7 or 8 wherein the metal matrix including silicon structures dispersed therein also includes one or more modifiers, e.g. Sb, Cu, Mg, Zn, Mn, Cr, Co, Mo, Ni, Be, Zr, Fe, Na, Sr, P, to provide structural elements having the said size and shape.

10. A method according to any of claims 7 to 9 which comprises the step of tempering the matrix prior to etching to provide structural elements having the said size and shape.

11. A method according to any preceding claim further comprising the step of incorporating the silicon structures into a silicon anode for a rechargeable cell.