Porous Electroactive Material

The present invention relates to an electroactive material comprising silicon; the use of such a material in the preparation of an electrode; an electrode including the electroactive silicon material of the invention; the use of an electrode in the preparation of an electrochemical cell and to an electrochemical cell or battery including such an electrode.

1.Background

Lithium ion rechargeable batteries are well known. The basic construction of a lithium ion rechargeable battery is shown in Figure 1. The battery cell includes a single cell, but may include multiple cells.

The battery cell generally comprises a copper current collector 10 for the anode and an aluminium current collector 12 for the cathode, which are externally connectable to a load or to a recharging source as appropriate. It should be noted that the terms "anode" and "cathode" are used in the present specification as those terms are understood in the context of batteries placed across a load, i.e. the term "anode" denotes the negative pole and the term "cathode" the positive pole of the battery. 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 a lithium containing metal oxide-based composite cathode layer 16: a liquid electrolyte material is dispersed within the 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 in the cathode via the electrolyte into the graphite-based anode where it is intercalated by reacting with the graphite to create a lithium carbon compound, typically LiC_6. The graphite, being the electrochemically active material in the composite anode layer, has a theoretical maximum capacity of 372 mAh/g.

The use of silicon as an active anode material in secondary batteries such as lithium ion batteries is well known (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 and also Wang, Kasavajjula et al, J. Power Source,s 163 (2007) 1003-

and anode structures for the fabrication of anodes for lithium ion batteries. Examples of silicon structures investigated include arrays of silicon pillars formed on wafers and particles, silicon fibres, rods, tubes or wires; and complete porous particles comprising silicon. Anode structures having pores or channels formed therein have also been investigated.

US 6,334,939 and US 6,514,395 each disclose silicon based nano-structures for use as anode materials in lithium ion secondary batteries. Such nano-structures include cage-like spherical particles and rods or wires having diameters in the range 1 to 50nm and lengths in range 500nm to 10μm. Similar nanostructures are disclosed in KR 1020027017125 and ZL 01814166.8. JP 04035760 discloses silicon based anode materials comprising carbon-coated silicon fibres having diameters in the range 10nm to 50μm for use in lithium ion secondary batteries. Batteries prepared using these nano-structures exhibited a total first cycle charging capacity of 1300 mAh/g and a reversible capacity of 800mAh/g.

US 2007/0281216 discloses an anode active material for a lithium secondary battery comprising a mixture of silicon nano-particles, graphite, carbon black and a binder. The silicon nano-particles comprise either thread-like aggregates (a chain of connected spheroidal particles) having a primary particle size in the range 20 to 200nm and a specific surface area of $11m^2/g$ or spherical particles having a primary particle size in the range 5 to 50nm and a specific surface area of $170m^2/g$. The silicon particles and threads are prepared using techniques such as chemical vapour deposition. Anodes exhibiting a capacity of up to 1000mAh/g over 50 cycles are illustrated. The life of the battery is significantly increased if the battery is operated at a limited voltage level.

Polycrystalline silicon nano-wires and wires having cross-sectional diameters in the range 20 to 500nm and aspect ratios of greater than 10, 50 or 100 and which have been prepared using epitaxial and non-epitaxial growth techniques are disclosed in US 7,273,732.

Single crystalline silicon fibres, pillars or rods having diameters in the range 0.1 to 1μm and lengths in the range 1 to 10μm can also be prepared using lithographic and etching techniques as disclosed in US 7,402,829. Alternative etching techniques such as those disclosed in WO 2007/083155, WO 2009/010758 and WO 2010/040985 can also be used.

The fibres, wires and rods described above are typically formed into a composite material containing, in addition to the silicon rods, wires and fibres, additional ingredients such as a binder, a conductive material and optionally a further electroactive material other than silicon. The composite material is also known as an anode mix and is typically used in the fabrication of anodes for lithium ion batteries. In accordance with the disclosure of the present inventors in WO 2009/010758 and WO 2009/010757 anode materials comprising

Rigid electrode structures such as those prepared by Shin et al tend to be associated with a build up of stress within the electrode structure on lithium intercalation or insertion as a result of the isotropic volume expansion of the entire electrode material. Providing the voids within the electrode structure are sufficiently open, the silicon mesh provides access for the electrolyte into the bulk of the electroactive anode. In contrast the more flexible meshed electrode structures including voids as described above are more able to accommodate expansion of the silicon material on lithium intercalation or insertion due the contraction and expansion of voids as described above. The overall expansion of a meshed electrode structure is therefore significantly less than that of the rigid channelled electrode structure described by Shin et al. This means that there will less build up of stress within meshed electrode structures compared to rigid electrode structures.

Porous silicon particles are also known and have been investigated for use in lithium ion batteries. The cost of manufacturing these particles is believed to be less than the cost of manufacturing alternative silicon structures such as silicon fibres, ribbons or pillared particles, for example. However, the life cycle performance of many of the composite electrodes prepared to date, which comprise porous silicon particles needs to be significantly improved before such electrodes could be considered to be commercially viable.

Porous silicon particles having dimensions in the range 4 to 11µm, an average pore sizes of 6 to 8Å and a BET surface area of from 41 to 143m^2/g have been prepared for use in fields such as drug delivery and explosive design (Subramanian et al, Nanoporous Silicon Based Energetic Materials, Vesta Sciences NJ 08852 Kapoor and Redner, US Army RDE-COM-ARDEC Picatinny Arsenal NJ 07806, Proceedings of the Army Science Conference (26^{th}) Orlando, Florida, 1-4 December 2008). There is no indication in Subramanian et al that their silicon containing porous particles would be suitable for use in the fabrication of lithium ion batteries.

Silicon nanosponge particles having a network of pores extending through the particle structure have also been prepared, US 7,569,202. Nanosponge particles having a diameter of 1 to 4µm and pore diameters of 2 to 8nm are prepared by stain etching metallurgical grade silicon powders to remove both silicon material and impurities. It is believed that the impurities in the metallurgical grade silicon are preferentially etched away to give particles having a network of pores distributed throughout. The nanosponge particles can be surface treated to introduce functional groups onto the silicon surface. US 7,569,202 teaches that the surface functional groups enable the nanosponge particles to be used for a broad range of applications from drug delivery to explosives. US 7,569,202 does not teach the application of nanosponge particles in lithium ion batteries.

releaseof lithium is fully compensated by the voids, the entire volume of the porous particle is maintained and the particles are not degenerated.

US 7,581,086 discloses an electrode material comprising porous silicon particles, which particles are prepared by quenching a eutectic alloy of silicon and another metal (typically aluminium) using a roll solidification method at a cooling rate of greater than 100K/s to give a thin film alloy sheet. The thin film is pulverised to give alloy particles having a typical diameter of 15µm, which are typically etched in HCl to give porous Si particles. Electrode materials prepared from these powder particles exhibited a capacity retention of approximately 68% at 10 cycles.

US 2009/0186267 discloses an anode material for a lithium ion battery, the anode material comprising porous silicon particles dispersed in a conductive matrix. The porous silicon particles have a diameter in the range 1 to 10µm, pore diameters in the range 1 to 100nm (preferably 5nm), a BET surface area value in the range 140 to 250m^2/g and crystallite sizes in the range 1 to 20nm. The porous silicon particles are mixed with a conductive material such as carbon black and a binder such as PVDF to form an electrode material, which can be applied to a current collector (such as a copper foil) to give an electrode. Although US 2009/0186267 suggests that these materials could be used for the manufacture of a battery, there is no data in this document to suggest that a battery has actually been manufactured.

Kim et al teaches the preparation of three-dimensional porous silicon particles for use in high performance lithium secondary batteries in Angewandte Chemie Int. Ed. 2008, 47, 10151-10154. Porous silicon particles are prepared by thermally annealing composites of butyl capped silicon gels and silica (SiO2) nano-particles at 900°C under an argon atmosphere and etching the silica particles out of the annealed product to give a carbon coated porous amorphous silicon particle having a pore wall thickness of 40nm, pore diameters of the order of 200nm and an overall particle size of greater than 20µm. Silicon crystallites having a diameter of less than 5nm were observed within the structure. Half cells prepared using these amorphous porous particles exhibited improved first cycling efficiency, which was thought to be due to the carbon coating. It was also suggested that an amorphous silicon structure could act as a buffer against the expansion of crystalline silicon upon intercalation or insertion.

Although anode structures comprising silicon fibres, rods and wires have been found to exhibit both a better capacity retention and an improved cycle life compared to bulk silicon and silicon powder anodes, an improvement in their absolute capacity and cycle life is still desired. Depending on the shape and dimension of the silicon elements, there can be a limit to the achievable packing density in the composite mix which can restrict the maximum

Many of the electrodes produced using the electro-active silicon materials discussed herein above are not able to exhibit the characteristics of uniform thickness, homogeneity and porosity. Such electrodes do not comprise a strongly connected network of active particles that are able to accommodate the expansion and contraction of the silicon material into its own volume without cracking or de-lamination during the charging cycles of the battery.

There is a need, therefore, for an electroactive material and an electrode structure that addresses the problems associated with the silicon based electrodes outlined above.

2. Compositions Comprising Porous Particle Fragments

A first aspect of the invention provides a composition comprising a plurality of electroactive porous particle fragments comprising an electroactive material selected from the group comprising silicon, tin, germanium, gallium, aluminium and lead. Preferably the porous particle fragments comprise silicon (which will hereafter also be referred to as silicon containing porous particle fragments). By the term "porous particle" it should be understood to include a particle comprising a plurality of pores, voids or channels within a particle structure, wherein each of the pores, voids or channels within the particle structure is defined, bound, partially bound or separated by the electroactive material from which the particle is formed. The term "porous particle" should also be understood to include a particulate material comprising a random or ordered network of linear, branched or layered elongate elements, wherein one or more discrete or interconnected void spaces or channels are defined between the elongate elements of the network; the elongate elements suitably include linear, branched or layered fibres, tubes, wires, pillars, rods, ribbons or flakes. Layered elongate elements include structures in which the elongate elements are fused together. The individual branched elongate elements typically have a smallest dimension in the range 50 to 100nm with branches every 100 to 400nm. The porous particles from which the porous particle fragments are derived can further be defined in terms of a smallest dimension (or pore wall thickness), this being the average thickness of material separating any one pore or void within a pore containing porous particle structure from an adjacent void, or where the particle comprises a network of elongate elements, the average thickness (this being the average smallest dimension) of an elongate element within the network. By the term porous particle fragment it should be understood to include all fragments derived from a porous particle, preferably a porous particle formed from an electroactive material such as silicon, tin, germanium, gallium, aluminium and lead. Silicon containing porous particles are especially preferred. Such fragments include structures having a substantially irregular shape and surface morphology, these structures being derived from the electroactive material originally defining, bounding, partially bounding or separating the pores or network

materials comprising electroactive compounds of silicon. Suitable silicon alloys include alloys of silicon with one or more metallic elements selected from aluminium, copper, titanium, strontium, nickel, iron, antimony, chromium, cobalt, tin, gold, silver, beryllium, molybdenum, zirconium and vanadium. These fragments will herein after be referred to as pore containing fragments. By the term "pore" or "channel" as defined in relation to the particles from which the fragments are derived as well as the porous particle fragments themselves, it should be understood to mean a void or channel enclosed or partially enclosed within the total volume of the particle as well as a channel extending into the interior of the particle from its surface. These pore and/or channel comprising porous particle fragments are also generally but not exclusively characterised by an irregular shape and surface morphology. In contrast, the particles from which the fragments are derived are generally but not exclusively characterised by a disc-like or substantially spherical shape and a relatively smooth outer surface morphology (inbetween the surface voids). Where the fractals and pore containing porous particle fragments are described together hereinafter they will collectively be referred to as either porous particle fragments or silicon containing porous particle fragments as appropriate. The network of pores and/or channels suitably comprises a three dimensional arrangement of pores and/or channels extending through the volume of the particle in which the pore and/or channel openings are provided on two or more planes over the surface of the pore containing porous particle fragment.

As indicated above, the porous particle fragments comprising the composition of the first aspect of the invention suitably comprise an electroactive material selected from the group silicon, tin, germanium, gallium, aluminium and lead and mixtures thereof as well as alloys of these elements with each other and/or with other electroactive or non-electroactive elements, providing the composition still exhibits electroactive properties. Silicon-containing electroactive materials are preferred. The silicon-containing porous particle fragments may be in the form of an alloy with or include additives such as Al, Sb, Cu, Mg, Zn, Mn, Cr, Co, Ti, V, Mo, Ni, Be, Zr, Fe, Na, Sr and P. Preferably the electroactive material is silicon, tin, aluminium or gallium. More preferably the electroactive material is an alloy of silicon and aluminium. Porous particle fragments comprising silicon or a silicon aluminium alloy are especially preferred. Porous silicon particle fragments prepared from porous particles, which porous particles were formed by etching particles of an aluminium silicon alloy comprising from 11 to 30wt% silicon, for example 12wt%, 26wt%, 27wt% and 30wt% silicon and fabricated using either a gas atomisation or melt spinning technique are especially preferred. The nature of the porous particles will in turn depend upon the technique used to fabricate the alloy particles and the processing conditions employed, the composition of the alloy and the particle size of the alloy droplets. Fragments prepared from porous particles formed by

the pore walls must not be too thick as this would lead to a build-up of stress within the structure, which can cause the particle to crumble, and an increased resistance to the passage of ions into the bulk of the silicon. In this respect, the facile fabrication of a good quality homogeneous coating or mat requires the use of silicon containing porous fragments having a maximum overall dimension in the range 1 to 40μm, preferably 1 to 20μm and especially 3 to 10μm. Porous particle fragments having diameters of less than 50nm are less preferred as particles of this size tend to agglomerate, which results in the formation of an inhomogeneous mat or coating. Suitably porous particle fragments having a maximum overall dimension in the range 1 to 40μm, preferably 1 to 20μm and especially 3 to 10μm comprise at least 10% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. Preferably porous particle fragments having a maximum overall dimension in the range 1 to 40μm, preferably 1 to 20μm and especially 3 to 10μm comprise at least 30% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. More preferably porous particle fragments having a maximum overall dimension in the range 1 to 40μm, preferably 1 to 20μm and especially 3 to 10μm comprise at least 50% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. It is especially preferred that porous particle fragments having a maximum overall dimension in the range 1 to 40μm, preferably 1 to 20μm and especially 3 to 10μm comprise at least 70% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. Where the silicon containing porous particle fragment is a pore containing fragment, each pore containing fragment comprises a three dimensional arrangement of pores having pore diameters in the range 60nm to 10μm, preferably 100nm to 5μm and especially 150nm to 2μm. The fractal material and the walls separating the pores within the porous particle fragments suitably have a thickness in the range 0.05 to 2μm, preferably 0.1 to 1μm, especially 100nm to 200nm.

Typically the ratio of pore diameter to wall thickness for pore containing fragments is suitably greater than 2.5:1 and is preferably in the range 3:1 to 25:1. The ratio of the volume of the pores to the volume of the fragment (otherwise known as particle porosity) is suitably in the range 0.2 to 0.8, preferably 0.25 to 0.75 and especially 0.3 to 0.7.

The porous particle fragments suitably have a BET surface area of greater than 0.5 m^2/g, preferably at least 5m^2/g. A higher surface area improves the electrical connectivity and ionic reactivity of the fragments as the active material in an electrode and generally increases the rate at which lithium can be inserted into the silicon. However a higher surface area leads to a larger amount of SEI layer being formed during charge and discharge of the electrode and consequently a higher lithium loss and reduced cycle life of the

components of the material is substantially retained over at least 100 charging and discharging cycles of a battery including the composite material. The cohesive mass of the composite electrode material may be provided in the form of a coating or layer, in which the porous particle fragments are arranged in a random or ordered fashion. The coating is typically applied or bonded to a current collector. Alternatively, the composite electrode material may be provided in the form of a felt or mat comprising silicon containing porous particle fragments and fibres of an electroactive or a conductive species which are randomly arranged in a composite material. The felt or mat is typically applied, adhered, bonded or connected to the current collector.

2.4.1 Additional Components of the Composite Electrode Material

The composite electrode material comprising porous particle fragments of the composition of the first aspect of the invention may optionally include, in addition to the silicon, tin, gallium, germanium, aluminium or lead containing porous particle fragments (first electroactive material) referred to herein above, additional components such as a binder, a conductive material and optionally a second electroactive material. Preferably the composition and/or structure of the second electroactive material is different to that of the first electroactive material. Examples of the second electroactive material include but are not limited to graphite, hard carbon, silicon, tin, gallium, germanium, aluminium and lead containing material. In a first preferred embodiment of the first aspect of the invention, the composition comprises a plurality of silicon containing porous particle fragments, a binder, a conductive material and optionally a non-silicon containing electroactive material. Alternatively, in a second preferred embodiment of the first aspect of the invention the composition may also contain, in addition to the components of the composition of the first embodiment, one or more silicon containing components having a minimal or negligible porosity, said components being selected from the group comprising native silicon containing particles; silicon containing tubes, wires, fibres, rods, sheets and ribbons and silicon containing pillared particles. By the term "minimal or negligible porosity" it should be understood to mean silicon structures having a porosity of less than 0.2. The terms "minimally porous silicon containing particles, wires, nano-wires, fibres, rods, sheets and ribbons" may include solid elongate elements such as wires, fibres, rods, sheets, ribbons and particles having a silicon-based core respectively as well as wires, fibres, rods, sheets, ribbons and particles having a silicon coating provided on a core other than silicon. Where the silicon containing elongate elements and particles comprise silicon coated elongate elements, tubes and particles, the cores of these coated elements can be selected from electronically and ionically conductive materials such as carbon, preferably hard carbon or graphite or a suitable metal. The silicon containing elongate elements, tubes and particles can be formed

suitably comprises up to 50wt%, for example from 5 to 40% by weight of the electrode or anode material or mix.

In a preferred embodiment of the first aspect of the invention, the composition comprises, in addition to the silicon containing porous particle fragments, an electroactive carbon material. These electroactive carbons may be present in an amount comprising 8 to 90% of the total weight of the electroacive material, preferably 8 to 80% and especially 8 to 50%. Examples of suitable electroactive carbons include graphite, hard carbon, carbon microbeads and carbon flakes, nanotubes and nanographitic platelets. Suitable graphite materials include natural and synthetic graphite materials having a particle size in the range 5 to 30μm. Electroactive hard carbon suitably comprises spheroidal particles having a diameter in the range 2 to 50μm, preferably 20 to 30μm and an aspect ratio of 1:1 to 2:1. Carbon microbeads having a diameter in the range 2 to 30μm can be used. Suitable carbon flakes include flakes derived from either graphite or graphene.

In a first more preferred embodiment of the first aspect of the invention, the composition comprises 5 to 40wt%, preferably 10 to 30wt% and especially 15 to 25wt% of silicon-containing electroactive material including silicon-containing porous particle fragments and 60 to 95wt%, preferably 70 to 90wt% and especially 75 to 85wt% of an electroactive carbon material. Preferably an electroactive composition comprising 20wt% of a silicon-containing electroactive material including silicon-containing porous particle fragments and 80wt% of graphite can be used to manufacture an electrode material. The silicon-containing electroactive material may include electroactive silicon-containing structures such as native particles, fibres, threads, tubes, wires, nano-wires, pillared particles and the like as well as porous particle fragments. Preferably the silicon-containing electroactive material comprises porous particle fragments.

A second more preferred embodiment of the first aspect of the invention, the composition comprises 60 to 80wt%, preferably 70 to 80wt% and especially 80wt% of silicon-containing porous particle fragments and 20 to 40wt%, preferably 20 to 30wt% and especially 20wt% of an electroactive carbon material. Preferably an electroactive composition comprising 80wt% of silicon-containing porous particle fragments and 20wt% of graphite can be used to manufacture an electrode material. The silicon-containing electroactive material may include electroactive silicon-containing structures such as native particles, fibres, threads, tubes, wires, nano-wires, pillared particles and the like as well as porous particle fragments. Preferably the silicon-containing electroactive material comprises porous particle fragments.

The binder is a component used to bind the components of the anode mix together either upon formation of the felt like mat or on application of the components to the current

collector. The binder helps to maintain the integrity of the anode mix according to the second aspect of the invention when used in battery cells. It also functions to help adhere the anode mix to the current collector. The binder can be added in an amount of 0 to 30% by weight based on the weight of the anode material. Examples of binders include, but are not limited to, polyvinylidene fluoride, polyacrylic acid, modified polyacrylic acid, carboxymethylcellulose, modified carboxymethylcellulose, polyvinyl alcohol, fluorocopolymers such as copolymers of hexafluoroethylene, polyimide, styrene butadiene rubber and thermo or photopolymerizable materials including, but not limited to, monomers, oligomers and low molecular weight polymers and mixtures thereof which are polymerizable by light irradiation and/or heat treatment. Examples of polymerizable monomers include epoxy, urethane, acrylate, silicon and hydroxyl based monomers and acrylic derivatives which may be used alone or in combination. Polymerisation of these materials is initiated with light irradiation or heat treatment. The polymerizable oligomer is a polymerisation product of from 2 to 25 monomers and may be formed into polymers having a higher degree of polymerisation by light irradiation or heat treatment. The term polymerisable low molecular weight polymer includes linear polymers and cross-linked polymers having a low degree of polymerisation or a low viscosity. Examples of such polymers include polyester acrylate, epoxy acrylate, urethane acrylate and polyurethane.

Preferably the binder is selected from one or more of a polyacrylic acid, a modified polyacrylic acid or alkali metal salts thereof. Lithium and sodium salts are preferred. Polyacrylic acid binders and sodium polyacrylic acid binders are able to bind to silicon materials containing impurities. The silicon-containing porous particle fragments according to the first aspect of the invention suitably have a silicon purity of between 75% and 100%. Preferably the silicon-containing porous particle fragments have a silicon purity of at least 80%, more preferably at least 95%. It is especially preferred that the silicon-containing porous particle fragments of the composition of the first aspect of the invention have a silicon purity of less than 99.99%, preferably less than 99.95% because these materials can be cheaper and the impurities can improve conductivity within the electrode structure. However if the level of impurities is too high the performance of the active material in the cell can be reduced and it has been found that a purity in the range 90% to 99.99% is preferred, more preferably 90% to 99.95%, especially 95% to 99.9%. It will be appreciated therefore, that the silicon containing porous particle fragments and other silicon containing components used in the preparation of compositions according to the first aspect of the invention may be derived from metallurgical grade silicon. Batteries including electrodes containing compositions of the first aspect of the invention, which include a binder comprising polyacrylic acid, a

range 10^3 to 10^5 K/s or faster: the use of cooling rates in this region results in the formation of alloy structures including regions of silicon comprising finely branched silicon structures. These finely branched silicon structures typically comprise tree like structures comprising branched rods of silicon having a diameter in the range 50 to 100nm, the rods including branches every 100 to 400nm. Where melt spinning techniques are used the rate of cooling depends on the rotational velocity of the cooled disc onto which the molten alloy particles impinge, the temperature of the disc, surrounding gas and its temperature and the alloy droplet size. Melt spinning techniques are generally associated with a cooling rate in the range 10^2 to 10^4K/s. The use of cooling rates in this region results in the formation of alloy structures including regions of silicon comprising both coarse and fine silicon structures. *Silicon structures having a minimum dimension of between 100nm and 500nm, preferably* between 100nm and 200nm and a length in the range 5 to 10μm have been observed. Alloy additives can also affect the shape and form of the silicon structures. A sodium additive may tend to spheroidise the silicon structures which is not preferred, whilst a combination of Ti and Sr additives may reduce the size of fibre-like structures. .Alloys of silicon with aluminium, in which the alloy comprises up to 30% silicon are preferred. Silicon aluminium alloys comprising 12%, 26% and 30% silicon can be used in the fabrication of the porous silicon particles from which the porous particle fragments are derived. The use of silicon aluminium alloys comprising 12% silicon are preferred. However, silicon alloys containing both 27% and 30% silicon as a constituent have also been observed to yield porous particle fragments that can be used in the manufacture of half cells having a capacity retention of almost 100% over more than 80 cycles when charged to 1200mAh/g or 1400mAh/g. As indicated above, the precipitated porous silicon structure can be isolated from the bulk alloy by etching away the some or all of 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 Si structures, leaving them intact after a sufficient amount of the aluminium (some or all) 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 porous silicon particles and metal electrode. Similar

WO2009/010758, WO2009/010759 and WO2009/010757, all incorporated herein by reference.

Although aluminium is preferred as the main component of the silicon alloy from which the silicon structures are precipitated, the skilled person will understand that other metals that will precipitate silicon during alloy cooling and can be etched may be used. Furthermore the skilled person will understand there are ways of foaming metals by injecting gases into the cooling molten mass and this can be applied to Si to create a 'foamed' Si matrix. One such method is described in *"Fabrication of lotus-type porous silicon by unidirectional solidification in hydrogen"* in Materials Science and Engineering A 384 (2004) 373–376. Using techniques such as this potentially allows a skilled person to avoid the need to etch away a sacrificial material to obtain the Si mesh or matrix. Solgel formation methods such as those used with silica to produce Aerogel may also be applied to silicon. The silicon containing components or structures of the composition of the first aspect of the invention suitably comprise a high purity polycrystalline silicon material as well as polycrystalline silicon materials comprising either n-type or p-type dopants as impurities. Polycrystalline silicon materials comprising n-type or p-type dopants are preferred because these materials exhibit a greater conductivity compared to that of high purity polycrystalline silicon. Polycrystalline silicon materials comprising p-type dopants are preferred and can be easily prepared from the aluminium silicon alloys referred to herein or using methods (such as ion implantation) known to a person skilled in the art; these materials suitably include one or more impurities selected from aluminium, boron or gallium as dopants.

4. Methods of Making Porous Particle Fragments

A second aspect of the invention provides a method for fabricating a composition according to the first aspect of the invention, the method comprising the steps of preparing a silicon containing porous particle and partially crushing that particle to give a silicon containing porous particle fragment. In a first preferred embodiment of the second aspect of the invention porous particles having a diameter in the range 10 to 1500μm, preferably 10 to 1000μm, more preferably 10 to 200μm, especially 10 to 100μm and which are prepared by etching a silicon aluminium alloy as specified above are partially crushed to give silicon containing porous particle fragments having a diameter in the range 1 to 40μm. The silicon containing porous particles used to prepare the silicon containing porous particle fragments suitably have a porosity in the range 0.2 to 0.8 and an pore wall thickness in the range 20 to 200nm, preferably 50 to 200nm. The etched particles are cleaned and placed in an ultra

The invention also provides silicon containing porous particle fragments prepared according to the method of the second aspect of the invention. A third aspect of the invention provides a composition comprising a plurality of silicon containing porous particle fragments prepared by partially crushing a plurality of silicon containing porous particles. The silicon containing porous particles from which the silicon containing porous particle fragments are derived suitably have a diameter of greater than 40µm, preferably greater than 60 µm, more preferably greater than 100µm and especially greater than 120µm. Typically the silicon containing porous particles from which the silicon containing porous particle fragments are derived suitably have a diameter in the range 40 to 200µm, preferably 50 to 150µm and especially 70 to 100µm. Preferably the porous particle fragments of the first aspect of the invention are prepared from porous particles (including porous particles comprising a network of elongate elements) having a diameter in the range 60 to 1500µm, more preferably 150 to 1000µm. These "starting particles" may be prepared by either etching a silicon aluminium alloy or by stain etching of a silicon particle using methods that are known to a skilled person as set out above.

In a first particularly preferred embodiment of the third aspect of the invention there is provided a composition comprising a plurality of silicon-containing porous particle fragments having a diameter in the range 1 to 40µm, preferably 1 to 20µm, more preferably 1 to 15µm and especially 1 to 10µm and an average smallest dimension (thickness) in the range 50nm to 2 µm, preferably 100nm to 1 µm, the porous particles being prepared by partially crushing porous silicon-containing particles having a diameter of at least 60µm, preferably at least 100 µm and especially at least 120 µm and having an average smallest dimension in the range 50nm to 2 µm, preferably 100nm to 1 µm. The silicon-containing whole porous particles are suitably prepared by etching a silicon alloy, preferably a silicon/aluminium alloy in a solution comprising a mixture of acetic acid, nitric acid and phosphoric acid to remove the bulk metal with which the silicon material is alloyed, washing and drying the particle.

A second preferred embodiment of the third aspect of the invention provides a porous particle fragment prepared by a method comprising the steps of:

a) Providing a molten silicon aluminium alloy composition comprising between 12 and 30wt% silicon;

b) Cooling the molten silicon aluminium alloy composition at between 10^2 and 10^5K/s to form a silicon aluminium particulate material having a diameter in the range 40 to 1500µm;

c) Etching the particulate material formed in (b) to form porous particles

d) partially crushing the porous particles formed in (c) to give porous particle fragments having a maximum diameter of less than 40µm

The molten alloy is suitably cooled in step (b) using either gas atomisation or melt spinning techniques. The etchants used in step (c) are well known to a person skilled in the art and are listed herein above. Where the alloy is a silicon aluminium alloy the amount of aluminium that can be removed from the alloy will depend on the etching conditions used.

The porous particle fragments according to the third aspect of the invention can be characterised by fractal or pore wall thicknesses in the range 50nm to 2µm. Porous particle fragments having a fractal thickness of 50 to 100nm can be used to make batteries. Fractal structures having a fractal or pore wall thickness in the range 100nm to 200nm can be used to prepare composite electrodes, which exhibit particularly good cycling behaviour.

5. Electrodes

The electroactive material according to the first aspect of the invention can be used in the manufacture of an electrode. The electrode is typically an anode. The electrodes are preferably used in the manufacture of a lithium secondary battery. A fourth aspect of the invention therefore provides an electrode comprising a composition according to the first aspect of the invention and a current collector. Preferably an electrode according to the fourth aspect of the invention comprises a composition according to the first aspect of the invention, a binder and a current collector. The electroactive material according to the first aspect of the invention is suitably provided in the form of an electrode or anode material, said electrode or anode material comprising in addition to the silicon containing porous particle fragments, a binder and optionally one or more components selected from the group comprising, a conductive material and a further electroactive material. Preferably the electrode or anode material comprises fractals as described above. The anode material can be in the form of a free-standing mat which can be connected or adhered to a current collector. Alternatively the anode mix can be provided in the form of a coating, which can be adhered to a current collector. The components of the anode mix from which the mat is formed are typically randomly arranged within the anode structure to provide optimum connectivity between the elements. The electrodes of the fourth aspect of the invention are easily prepared and a fifth aspect of the invention provides a method for fabricating an electrode comprising the steps of forming an electrode or anode mix, said electrode or anode mix comprising a slurry of a composition according to the first aspect of the invention and a solvent (herein after referred to as an electrode mix) and casting the electrode or

anode mix onto a substrate and drying the product to remove the solvent thereby to form the electrode or anode material on the substrate. The dried product (electrode material) is in the form of a cohesive mass which may be removed from the substrate, connected to a current collector and used as an electrode. Alternatively, where the composition according to the first aspect of the invention is adhered to the substrate as a result of casting and drying the slurry (electrode mix), the resulting cohesive mass will be connected or bonded to a current collector. In a preferred embodiment of the first aspect of the invention the composition is cast onto a substrate, which is itself a current collector. One or more components selected from the group comprising a conductive material, a viscosity adjuster, a filler, a cross-linking accelerator, a coupling agent and an adhesive accelerator may also be included in the slurry mixture (electrode mix). Examples of suitable conductive materials, viscosity adjusters, fillers, cross-linking accelerators, coupling agents and adhesive accelerators are provided above. Suitable solvents include N-methylpyrrolidone and water.

Suitable current collectors for use in electrodes according to the fourth aspect of the invention include copper foil, aluminium, carbon (including graphite), conducting polymers and any other conductive materials. The current collectors typically have a thickness in the range 10 to 50μm, preferably 10 to 20μm.. Current collectors can be coated with the electrode mix on one side or can be coated with the electrode mix on both sides. In a preferred embodiment of the fifth aspect of the invention a composition of the first aspect of the invention is preferably applied to one or both surfaces of the current collector to a thickness of between 1mg/cm^2 and 6mg/cm^2 , preferably between 1mg/cm^2 and 3mg/cm^2 per surface such that the total thickness of the electrode (current collector and coating) is in the range 25um to 1mm where only one surface of the current collector is coated or in the range 50μm to 1mm where both surfaces of the current collector are coated. In a preferred embodiment, the electrode or anode material is applied to a thickness of between 30 and 40μm onto one or both surfaces of a copper substrate having a thickness of between 10 and 15μm. The current collector may be in the form of a continuous sheet or a porous matrix or it may be in the form of a patterned grid or mesh defining metallised regions and non-metallised regions. Where the current collector comprises a continuous sheet, the electrode may be readily manufactured by applying a slurry of the anode mix directly to the current collector. Where the current collector comprises a metallised grid, this metallised grid may be formed onto a non-stick substrate such as PTFE to give a metallised non-stick surface (such as metallised PTFE) and the slurry of the anode mix is applied to the metallised non-stick surface and dried to give a metallised mat or felt. Alternatively the mesh or grid can be dipped into a solution or slurry to form a composite electrode.

In one embodiment of the fifth aspect of the invention, the electrode may be formed by casting the silicon containing mixture onto a substrate thereby to form a self supporting structure and connecting a current collector directly thereto.

The electrode of the fourth aspect of the invention can be used as an anode in the manufacture or formation of a lithium secondary battery. A sixth aspect of the invention provides a secondary battery comprising a cathode, an anode comprising a composition according to the first aspect of the invention and an electrolyte.

6.Cathode

The cathode is typically prepared by applying a mixture of a cathode active material, a conductive material and a binder to a cathode current collector and drying. Examples of cathode active materials that can be used together with the anode active materials of the present invention include, but are not limited to, layered compounds such as lithium cobalt oxide, lithium nickel oxide or compounds substituted with one or more transition metals such as lithium manganese oxides, lithium copper oxides and lithium vanadium oxides. Many such materials can be defined by the generic formula $Li_{1+x}(Ni_bCo_cAl_eMn_f)_{1-x}O_2$, where b, c, e, f and x have values of between 0 and 1. Examples of suitable cathode materials include $LiCoO_2$, $LiCo_{0.99}Al_{0.01}O_2$, $LiNiO_2$, $LiMnO_2$, $LiMn_2O_4$, $LiCo_{0.5}Ni_{0.5}O_2$, $LiCo_{0.7}Ni_{0.3}O_2$, $LiCo_{0.8}Ni_{0.2}O_2$, $LiCo_{0.82}Ni_{0.18}O_2$, $LiCo_{0.8}Ni_{0.15}Al_{0.05}O_2$, $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$, $Li_{1+x}(Ni_{0.333}Co_{0.333}Mn_{0.333})_{1-x}O_2$, $Li_{1+x}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{1-x}O_2$, $Li_{1+x}(Ni_{0.4}Co_{0.2}Mn_{0.4})_{1-x}O_2$, and $Li_{1+x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, phosphate-based cathodes such as $LiFePO_4$, non-lithiated cathode materials like V_6O_{13}, and sulphur / polysulphide cathodes. The cathode current collector is generally of a thickness of between 3 to 500μm. Examples of materials that can be used as the cathode current collector include aluminium, stainless steel, nickel, titanium and sintered carbon.

7. Electrolyte

The electrolyte is suitably a non-aqueous electrolyte containing a lithium salt and may include, without limitation, non-aqueous electrolytic solutions, solid electrolytes and inorganic solid electrolytes. Examples of non-aqueous electrolyte solutions that can be used include non-protic organic solvents such as N-methylpyrrolidone, propylene carbonate, ethylene carbonate, butylenes carbonate, dimethyl carbonate, diethyl carbonate, gamma butyro lactone, 1,2-dimethoxy ethane, 2-methyl tetrahydrofuran, dimethylsulphoxide, 1,3-dioxolane, formamide, dimethylformamide, acetonitrile, nitromethane, methylformate, methyl acetate, phosphoric acid trimester, trimethoxy methane, sulpholane, methyl sulpholane and 1,3-dimethyl-2-imidazolidione.

In a particularly preferred embodiment of the sixth aspect of the invention there is provided a battery comprising a cathode, an anode comprising a composition according to the first aspect of the invention and an electrolyte including an electrolyte solvent and an electrolyte salt, wherein the electrolyte solvent comprises a mixture of fluoroethylene carbonate (FEC) and ethylmethyl carbonate (EMC). It is particularly preferred that the electrolyte solvent includes a cyclic carbonate including a vinyl carbonate as an additive. In a most preferred embodiment of the sixth aspect of the invention the electrolyte solvent comprises 40 to 60vol%, preferably 50vol% FEC, 40 to 48vol%, preferably 46vol% EMC and 2 to 10vol%, preferably 4vol% VC.

Examples of organic solid electrolytes include polyethylene derivatives polyethyleneoxide derivatives, polypropylene oxide derivatives, phosphoric acid ester polymers, polyester sulphide, polyvinyl alcohols, polyvinylidine fluoride and polymers containing ionic dissociation groups.

Examples of inorganic solid electrolytes include nitrides, halides and sulphides of lithium salts such as Li_5NI_2, Li_3N, LiI, $LiSiO_4$, Li_2SiS_3, Li_4SiO_4, LiOH and Li_3PO_4.

The lithium salt is suitably soluble in the chosen solvent or mixture of solvents. Examples of suitable lithium salts include LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}C_{20}$, $LiPF_6$, $LiCF_3SO_3$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li and CF_3SO_3Li, lithium bis(oxatlato)borate (LiBOB) or a mixture thereof, dissolved in one or more cyclic and dialkyl carbonates referred to above. Examples of other electrolyte salts that can be used are found in JP 2008234988, US 7659034, US 2007/0037063, US 7862933, US 2010/0124707, US 2006/0003226, US 7476469, US 2009/0053589 and US 2009/0053589. Preferably the electrolyte salt is $LiPF_6$ or a mixture of $LiPF_6$ and lithium bisoxalate borate (LiBOB). A preferred electrolyte solution comprises 0.9 to 0.95M $LiPF_6$ and 0.05 to 0.1M LiBOB. The concentration of the lithium salt in the electrolyte solution is not limited but is preferably in the range of 0.5 to 1.5M. When larger amounts of additives are used it is preferable to increase the concentration of the lithium salt to prevent excessive depletion of lithium in the final electrolyte solution.

Where the electrolyte is a non-aqueous organic solution, the battery is provided with a separator interposed between the anode and the cathode. The separator is typically formed of an insulating material having high ion permeability and high mechanical strength. The separator typically has a pore diameter of 0.01 to 100μm and a thickness of 5 to 300μm.

The battery according to the sixth aspect of the invention can be used to drive a device, which relies on battery power for its operation. Such devices include mobile phones, laptop

computers, GPS devices, motor vehicles and the like. A seventh aspect of the invention therefore includes a device including a battery according to the sixth aspect of the invention.

The invention will now be described with reference to the following figures and non-limiting examples. Variations on these falling within the scope of the invention will be evident to a person skilled in the art.

8. Figures

Figure 1 shows a schematic view of a prior art battery.

Figure 2a shows an SEM image of a porous particle produced according to the procedure set out in the examples below. These porous particles were prepared by etching particles of an AlSi alloy comprising 12wt% silicon and having a diameter of 10 to 63µm, the alloy particles being formed through the use of a gas atomisation cooling technique. The silicon structures are characterised by a network of fine silicon structures.

Figure 2b shows a schematic diagram of the fine silicon fractal structures formed by partially crushing a porous particle illustrated in 2a.

Figure 2c shows an SEM of the silicon structures formed by partially crushing a porous particle illustrated in 2a.

Figure 2d shows an SEM image of a porous particle produced according to the procedure set out in the examples below. These porous particles were prepared from particles of an AlSi alloy comprising 27wt% silicon and having a diameter of 10 to 90µm, the alloy particles being formed through the use of a gas atomisation cooling technique. The porous particle is characterised by regions of particulate silicon interspersed within regions of finely branched silicon fibres.

Figure 2e shows an SEM image of a porous particle fragment obtained by partially crushing porous particles illustrated in Figure 2d.

Figure 2f shows an SEM of a porous particle fragment (fractal) produced by partially crushing the porous particles produced from AlSi(12wt%) alloy particles (formed using a gas atomisation technique) and having a diameter of 60 to 90µm, the porous particles being produced according to the procedure set out in the examples below.

Figure 3a shows an SEM image of a porous particle fragment produced according to the procedure set out in the examples below. These porous particle fragments were prepared by

Claims

1. A composition comprising silicon containing electroactive porous particle fragments, characterised in that the porous particle fragments are selected from the group comprising:

    a. A pore-containing porous particle fragment comprising a network of pores, cavities and channels, which pores, cavities and channels are separated and defined by silicon-containing walls within the particle structure;

    b. A fractal comprising a substantially irregular shape or surface morphology derived from the silicon material originally defining or bounding the pores or network of pores within the porous particle from which the fractals are derived without themselves comprising pores, channels or a network of pores or channels;

    c. A fractal having a substantially irregular shape or surface morphology derived from silicon material originally defining a random or ordered network of linear, branched or layered elongate elements, wherein one or more discrete or interconnected void spaces or channels are defined between the elongate elements of the network.

2. A composition according to claim 1, wherein the fractal and/or the silicon-containing walls of the pore-containing porous particle fragment have a thickness in the range 0.05 to 2μm, preferably 0.1 to 1μm.

3. A composition according to claim 1 or claim 2, wherein the ratio of the pore width to wall thickness in the pore-containing porous particle fragment is greater than 2.5:1

4. A composition according to any one of claims 1 to 3, wherein the silicon containing porous particle fragments have a maximum diameter in the range 1 to 40μm.

5. A composition according to any one of claims 1 to 4, wherein the silicon containing porous particle fragment has an aspect ratio (length (largest diameter) to width (smallest diameter) of particle) in the range 2:1 to 5:1.

6. A composition according to any one of the preceding claims, wherein the fractal structure comprises at least one peak or ridge disposed over the surface thereof.

7. A composition according to any one of the preceding claims, wherein the fractal structure has a spiky appearance or a ridged appearance.

8. A composition according to any one of claims 1 to 5, characterised in that the pore-containing porous particle fragments comprise pores having a width in the range 100nm to 10µm, preferably 150nm to 5µm.

9. A composition according to any one of claims 1 to 5 or 8, wherein the ratio of the total volume of the pores in the fragment to the total volume of the fragment is in the range 0.2 to 0.9, preferably 0.2 to 0.8, more preferably 0.25 to 0.75 and especially 0.3 to 0.7.

10. A composition according to any one of the preceding claims, wherein the particle fragments have a BET surface area greater than $4m^2/g$ preferably greater than $5m^2/g$.

11. A composition according to any one of the preceding claims, wherein the particle fragments have a BET surface area of less than $50m^2/g$, preferably less than $40m^2/g$, suitably less than $30m^2/g$.

12. A composition according to any one of the preceding claims, which further comprises one or more components selected from a binder, a conductive material and optionally a non-silicon containing electroactive material, such as graphite.

13. A composition according to any one of the preceding claims, which comprises an electroactive material, wherein the electroactive material comprises from 10 to 100% silicon containing porous particle fragments by weight.

14. A composition according to any one of the preceding claims, comprising 5 to 40wt% of a silicon-containing electroactive material including a silicon-containing porous particle fragment and 60 to 95wt% of an electroactive carbon material.

15. A composition according to claim 14, which comprises 50 to 90% of an electroactive material by weight, wherein the electroactive material comprises from 10 to 100% silicon containing porous particle fragments by weight.

16. A composition according to any one of the preceding claims, which further comprises one or more electroactive or non-electroactive silicon containing components selected from the group comprising native silicon containing particles having a minimal or negligible porosity; silicon containing wires, nano-

wires, fibres, rods, tubes, sheets, elongate bundles, substrate particles, scaffolds, ribbons and silicon containing pillared particles.

17. A composition according to any one of the preceding claims, wherein one or more of the silicon containing porous particle fragments and one or more silicon containing components include a coating selected from the group comprising a carbon coating or a coating comprising a lithium salt.

18. A composition according to any one of the preceding claims, which is an electrode material.

19. A composition according to any one of the preceding claims, which is in the form of a mat.

20. A method of making a composition according to any one of claims 1 to 19, the method comprising partially crushing a silicon containing porous particle and isolating the silicon containing porous particle fragment, wherein the silicon containing fragments are obtained by partially crushing silicon containing whole porous particles having a diameter greater than 40μm, a porosity in the range 0.2 to 0.8 and a pore wall thickness in the range 50nm to 2μm.

21 A method according to claim 20, which comprises the steps of:

a. forming a molten silicon aluminium alloy composition;

b. cooling the molten composition to give alloy particles;

c. etching the alloy particles to give silicon-containing porous particles;

d. partially crushing the silicon-containing porous particles from (c) to give silicon-containing porous particle fragments.

22, A method according to claim 21, wherein the molten alloy composition comprises from 11 to 35wt% silicon.

23. A method according to any one of claims 21 to 22, wherein the molten composition is cooled at a rate of between 10^2 and 10^5K/s.

24. A method according to any one of claims 21 to 23, wherein the cooled alloy particles have a diameter of from 40 to 1500μm.

25. An electrode comprising a current collector and a composition according to any one of claims 1 to 19.

26. An electrode according to claim 25, wherein the composition is in the form of a felt or mat having a mass per surface area of between 1mg/cm^2 and 6mg/cm^2 on one or both sides of the current collector to thereby give an electrode having a thickness of from 10 to 100µm.

27. A method of manufacturing an electrode according to any one of claims 25 to 26 comprising the steps of forming a slurry of the composition according to any one of claims 1 to 19 in a solvent, applying the slurry to a current collector and drying the product to remove the solvent.

28. A battery comprising a cathode, an anode comprising a composition according to any one of claims 1 to 19 and an electrolyte.

29. A device including a battery according to claim 28.

Porous Electroactive Material

The present invention relates to an electroactive material comprising silicon; the use of such a material in the preparation of an electrode; an electrode including the electroactive silicon material of the invention; the use of an electrode in the preparation of an electrochemical cell and to an electrochemical cell or battery including such an electrode.

1.Background

Lithium ion rechargeable batteries are well known. The basic construction of a lithium ion rechargeable battery is shown in Figure 1. The battery cell includes a single cell, but may include multiple cells.

The battery cell generally comprises a copper current collector 10 for the anode and an aluminium current collector 12 for the cathode, which are externally connectable to a load or to a recharging source as appropriate. It should be noted that the terms “anode” and “cathode” are used in the present specification as those terms are understood in the context of batteries placed across a load, i.e. the term “anode” denotes the negative pole and the term “cathode” the positive pole of the battery. 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 a lithium containing metal oxide-based composite cathode layer 16: a liquid electrolyte material is dispersed within the 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 in the cathode via the electrolyte into the graphite-based anode where it is intercalated by reacting with the graphite to create a lithium carbon compound, typically LiC_6. The graphite, being the electrochemically active material in the composite anode layer, has a theoretical maximum capacity of 372 mAh/g.

The use of silicon as an active anode material in secondary batteries such as lithium ion batteries is well known (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 and also Wang, Kasavajjula et al, J. Power Sources 163 (2007) 1003-

and anode structures for the fabrication of anodes for lithium ion batteries. Examples of silicon structures investigated include arrays of silicon pillars formed on wafers and particles; silicon fibres, rods, tubes or wires; and complete porous particles comprising silicon. Anode structures having pores or channels formed therein have also been investigated.

US 6,334,939 and US 6,514,395 each disclose silicon based nano-structures for use as anode materials in lithium ion secondary batteries. Such nano-structures include cage-like spherical particles and rods or wires having diameters in the range 1 to 50nm and lengths in range 500nm to 10µm. Similar nanostructures are disclosed in KR 100556305B and CN 1447916A. JP 04035760B discloses silicon based anode materials comprising carbon-coated silicon fibres having diameters in the range 10nm to 50µm for use in lithium ion secondary batteries. Batteries prepared using these nano-structures exhibited a total first cycle charging capacity of 1300 mAh/g and a reversible capacity of 800mAh/g.

US 2007/0281216 discloses an anode active material for a lithium secondary battery comprising a mixture of silicon nano-particles, graphite, carbon black and a binder. The silicon nano-particles comprise either thread-like aggregates (a chain of connected spheroidal particles) having a primary particle size in the range 20 to 200nm and a specific surface area of 11m^2/g or spherical particles having a primary particle size in the range 5 to 50nm and a specific surface area of 170m^2/g. The silicon particles and threads are prepared using techniques such as chemical vapour deposition. Anodes exhibiting a capacity of up to 1000mAh/g over 50 cycles are illustrated. The life of the battery is significantly increased if the battery is operated at a limited voltage level.

Polycrystalline silicon nano-wires and wires having cross-sectional diameters in the range 20 to 500nm and aspect ratios of greater than 10, 50 or 100 and which have been prepared using epitaxial and non-epitaxial growth techniques are disclosed in US 7,273,732. Single crystalline silicon fibres, pillars or rods having diameters in the range 0.1 to 1µm and lengths in the range 1 to 10µm can also be prepared using lithographic and etching techniques as disclosed in US 7,402,829. Alternative etching techniques such as those disclosed in WO 2007/083155, WO 2009/010758 and WO 2010/040985 can also be used. The fibres, wires and rods described above are typically formed into a composite material containing, in addition to the silicon rods, wires and fibres, additional ingredients such as a binder, a conductive material and optionally a further electroactive material other than silicon. The composite material is also known as an anode mix and is typically used in the fabrication of anodes for lithium ion batteries. In accordance with the disclosure of the present inventors in WO 2009/010758 and WO 2009/010757 anode materials comprising

Rigid electrode structures such as those prepared by Shin et al tend to be associated with a build up of stress within the electrode structure on lithium intercalation or insertion as a result of the isotropic volume expansion of the entire electrode material. Providing the voids within the electrode structure are sufficiently open, the silicon mesh provides access for the electrolyte into the bulk of the electroactive anode. In contrast the more flexible meshed electrode structures including voids as described above are more able to accommodate expansion of the silicon material on lithium intercalation or insertion due the contraction and expansion of voids as described above. The overall expansion of a meshed electrode structure is therefore significantly less than that of the rigid channelled electrode structure described by Shin et al. This means that there will be less build up of stress within meshed electrode structures compared to rigid electrode structures.

Porous silicon particles are also known and have been investigated for use in lithium ion batteries. The cost of manufacturing these particles is believed to be less than the cost of manufacturing alternative silicon structures such as silicon fibres, ribbons or pillared particles, for example. However, the life cycle performance of many of the composite electrodes prepared to date, which comprise porous silicon particles needs to be significantly improved before such electrodes could be considered to be commercially viable.

Porous silicon particles having dimensions in the range 4 to 11µm, an average pore sizes of 6 to 8Å and a BET surface area of from 41 to 143m^2/g have been prepared for use in fields such as drug delivery and explosive design (Subramanian et al, Nanoporous Silicon Based Energetic Materials, Vesta Sciences NJ 08852 Kapoor and Redner, US Army RDE-COM-ARDEC Picatinny Arsenal NJ 07806, Proceedings of the Army Science Conference (26^{th}) Orlando, Florida, 1-4 December 2008). There is no indication in Subramanian et al that their silicon containing porous particles would be suitable for use in the fabrication of lithium ion batteries.

Silicon nanosponge particles having a network of pores extending through the particle structure have also been prepared, US 7,569,202. Nanosponge particles having a diameter of 1 to 4µm and pore diameters of 2 to 8nm are prepared by stain etching metallurgical grade silicon powders to remove both silicon material and impurities. It is believed that the impurities in the metallurgical grade silicon are preferentially etched away to give particles having a network of pores distributed throughout. The nanosponge particles can be surface treated to introduce functional groups onto the silicon surface. US 7,569,202 teaches that the surface functional groups enable the nanosponge particles to be used for a broad range of applications from drug delivery to explosives. US 7,569,202 does not teach the application of nanosponge particles in lithium ion batteries.

release of lithium is fully compensated by the voids, the entire volume of the porous particle is maintained and the particles are not degenerated.

US 7,851,086 discloses an electrode material comprising porous silicon particles, which particles are prepared by quenching a eutectic alloy of silicon and another metal (typically aluminium) using a roll solidification method at a cooling rate of greater than 100K/s to give a thin film alloy sheet. The thin film is pulverised to give alloy particles having a typical diameter of 15µm, which are typically etched in HCl to give porous Si particles. Electrode materials prepared from these powder particles exhibited a capacity retention of approximately 68% at 10 cycles.

US 2009/0186267 discloses an anode material for a lithium ion battery, the anode material comprising porous silicon particles dispersed in a conductive matrix. The porous silicon particles have a diameter in the range 1 to 10µm, pore diameters in the range 1 to 100nm (preferably 5nm), a BET surface area value in the range 140 to 250m^2/g and crystallite sizes in the range 1 to 20nm. The porous silicon particles are mixed with a conductive material such as carbon black and a binder such as PVDF to form an electrode material, which can be applied to a current collector (such as a copper foil) to give an electrode. Although US 2009/0186267 suggests that these materials could be used for the manufacture of a battery, there is no data in this document to suggest that a battery has actually been manufactured.

Kim et al teaches the preparation of three-dimensional porous silicon particles for use in high performance lithium secondary batteries in Angewandte Chemie Int. Ed. 2008, 47, 10151-10154. Porous silicon particles are prepared by thermally annealing composites of butyl capped silicon gels and silica (SiO2) nano-particles at 900℃ under an argon atmosphere and etching the silica particles out of the annealed product to give a carbon coated porous amorphous silicon particle having a pore wall thickness of 40nm, pore diameters of the order of 200nm and an overall particle size of greater than 20µm. Silicon crystallites having a diameter of less than 5nm were observed within the structure. Half cells prepared using these amorphous porous particles exhibited improved first cycling efficiency, which was thought to be due to the carbon coating. It was also suggested that an amorphous silicon structure could act as a buffer against the expansion of crystalline silicon upon intercalation or insertion.

Although anode structures comprising silicon fibres, rods and wires have been found to exhibit both a better capacity retention and an improved cycle life compared to bulk silicon and silicon powder anodes, an improvement in their absolute capacity and cycle life is still desired. Depending on the shape and dimension of the silicon elements, there can be a limit to the achievable packing density in the composite mix which can restrict the maximum

Many of the electrodes produced using the electro-active silicon materials discussed herein above are not able to exhibit the characteristics of uniform thickness, homogeneity and porosity. Such electrodes do not comprise a strongly connected network of active particles that are able to accommodate the expansion and contraction of the silicon material into its own volume without cracking or de-lamination during the charging cycles of the battery.

JP 2005-310759 discloses a method of forming composite silicon particles and negative electrodes including such particles. The composite particles are prepared by sintering small silicon containing particles having a diameter of from 100nm to 10 µm in the presence of an organosilicon compound and to give a porous silicon-containing body. The porous body is then granulated to give silicon-containing particles having an inorganic silicon coating derived from the organosilicon compound. The composite porous particles thus prepared comprise non-porous coated silicon particles prepared by granulating a porous sintered body. They do not comprise fragments of a porous particle.

WO 2005/113467 discloses a method of forming a drug delivery device comprising a porous silicon body. The method involves consolidating silicon particles through the application of pressure to form a unitary consolidated porous body (as a result of the interstitial spaces between the particles) and anodising the consolidated body formed to increase its porosity. A beneficial substance may be trapped in the pores for subsequent release in a physioloigical environment. The unitary body may be fragmented to release the component particles, which now have a partially porous surface region – this partial porosity being generated as a result of the anodisaion of each of the particles comprising the unitary body. The fragmentation step therefore gives whole particles having partial porosity on their surface.

There is a need, therefore, for an electroactive material and an electrode structure that addresses the problems associated with the silicon based electrodes outlined above.

Aspects of the present invention are defined in the appended independent claims.

2. Compositions Comprising Porous Particle Fragments

A first aspect of the invention provides silicon containing electroactive porous particle fragments, characterised in that the porous particle fragments are selected from the group comprising: a pore-containing porous particle fragment comprising a network of pores, cavities and channels, which pores, cavities and channels are separated and defined by silicon-containing walls within the particle structure; a fractal comprising a substantially irregular shape or surface morphology derived from the silicon material originally defining or bounding the pores or network of pores within the porous particle from which the fractals are derived without themselves comprising pores, channels or a network of pores or channels; a fractal having a substantially irregular shape or surface morphology derived from silicon material originally defining a random or ordered network of linear, branched or layered elongate elements, wherein one or more discrete or interconnected void spaces or channels are defined between the elongate elements of the network. Preferably the porous particle fragments comprise silicon (which will hereafter also be referred to as silicon containing porous particle fragments). By the term “porous particle” it should be understood to include a particle comprising a plurality of pores, voids or channels within a particle structure, wherein each of the pores, voids or channels within the particle structure is defined, bound, partially bound or separated by the electroactive material from which the particle is formed. The term “porous particle” should also be understood to include a particulate material comprising a random or ordered network of linear, branched or layered elongate elements, wherein one or more discrete or interconnected void spaces or channels are defined between the elongate elements of the network; the elongate elements suitably include linear, branched or layered fibres, tubes, wires, pillars, rods, ribbons or flakes. Layered elongate elements include structures in which the elongate elements are fused together. The individual branched elongate elements typically have a smallest dimension in the range 50 to 100nm with branches every 100 to 400nm. The porous particles from which the porous particle fragments are derived can further be defined in terms of a smallest dimension (or pore wall thickness), this being the average thickness of material separating any one pore or void within a pore containing porous particle structure from an adjacent void, or where the particle comprises a network of elongate elements, the average thickness (this being the average smallest dimension) of an elongate element within the network. By the term porous particle fragment it should be understood to include all fragments derived from a porous particle, preferably a porous particle formed from an electroactive material such as silicon, tin, germanium, gallium, aluminium and lead. Silicon containing porous particles are especially preferred. Such fragments include structures having a substantially irregular shape and surface morphology, these structures being derived from the electroactive material originally defining, bounding, partially bounding or separating the pores or network

materials comprising electroactive compounds of silicon. Suitable silicon alloys include alloys of silicon with one or more metallic elements selected from aluminium, copper, titanium, strontium, nickel, iron, antimony, chromium, cobalt, tin, gold, silver, beryllium, molybdenum, zirconium and vanadium. These fragments will herein after be referred to as pore containing fragments. By the term “pore” or “channel” as defined in relation to the particles from which the fragments are derived as well as the porous particle fragments themselves, it should be understood to mean a void or channel enclosed or partially enclosed within the total volume of the particle as well as a channel extending into the interior of the particle from its surface. These pore and/or channel comprising porous particle fragments are also generally but not exclusively characterised by an irregular shape and surface morphology. In contrast, the particles from which the fragments are derived are generally but not exclusively characterised by a disc-like or substantially spherical shape and a relatively smooth outer surface morphology (inbetween the surface voids). Where the fractals and pore containing porous particle fragments are described together hereinafter they will collectively be referred to as either porous particle fragments or silicon containing porous particle fragments as appropriate. The network of pores and/or channels suitably comprises a three dimensional arrangement of pores and/or channels extending through the volume of the particle in which the pore and/or channel openings are provided on two or more planes over the surface of the pore containing porous particle fragment.

As indicated above, the porous particle fragments comprising the composition of the first aspect of the invention suitably comprise an electroactive material selected from the group silicon, tin, germanium, gallium, aluminium and lead and mixtures thereof as well as alloys of these elements with each other and/or with other electroactive or non-electroactive elements, providing the composition still exhibits electroactive properties. Silicon-containing electroactive materials are preferred. The silicon-containing porous particle fragments may be in the form of an alloy with or include additives such as Al, Sb, Cu, Mg, Zn, Mn, Cr, Co, Ti, V, Mo, Ni, Be, Zr, Fe, Na, Sr and P. Preferably the electroactive material is silicon, tin, aluminium or gallium. More preferably the electroactive material is an alloy of silicon and aluminium. Porous particle fragments comprising silicon or a silicon aluminium alloy are especially preferred. Porous silicon particle fragments prepared from porous particles, which porous particles were formed by etching particles of an aluminium silicon alloy comprising from 11 to 35wt% silicon, preferably 11 to 30wt% silicon, for example 12wt%, 25wt%, 26wt%, 27wt% and 30wt% silicon and fabricated using either a gas atomisation or melt spinning technique are especially preferred. The nature of the porous particles will in turn depend upon the technique used to fabricate the alloy particles and the processing conditions employed, the composition of the alloy and the particle size of the alloy droplets. Fragments prepared from porous particles formed by

the pore walls must not be too thick as this would lead to a build-up of stress within the structure, which can cause the particle to crumble, and an increased resistance to the passage of ions into the bulk of the silicon. In this respect, the facile fabrication of a good quality homogeneous coating or mat requires the use of silicon containing porous fragments having a maximum overall dimension in the range 1 to 40µm, preferably 1 to 20µm, more preferably 1 to 15 µm, most preferably 1 to 10 µm and especially 3 to 10µm. Porous particle fragments having diameters of less than 50nm are less preferred as particles of this size tend to agglomerate, which results in the formation of an inhomogeneous mat or coating. Suitably porous particle fragments having a maximum overall dimension in the range 1 to 40µm, preferably 1 to 20µm, more preferably 1 to 15 µm, most preferably 1 to 10 µm and especially 3 to 10µm comprise at least 10% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. Preferably porous particle fragments having a maximum overall dimension in the range 1 to 40µm, preferably 1 to 20µm, more preferably 1 to 15 µm, most preferably 1 to 10 µm and especially 3 to 10µm comprise at least 30% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. More preferably porous particle fragments having a maximum overall dimension in the range 1 to 40µm, preferably 1 to 20µm, more preferably 1 to 15 µm, most preferably 1 to 10 µm and especially 3 to 10µm comprise at least 50% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. In a particularly preferred embodiment, porous particle fragments having an overall maximum dimension in the name of 1 to 40 µm comprise 10 to 100 vol% of the composition of the first aspect of the invention. It is especially preferred that porous particle fragments having a maximum overall dimension in the range 1 to 40µm, preferably 1 to 20µm and especially 3 to 10µm comprise at least 70% of the volume of the porous particle fragments used in the composition of the first aspect of the invention. Where the silicon containing porous particle fragment is a pore containing fragment, each pore containing fragment comprises a three dimensional arrangement of pores having pore diameters in the range 60nm to 10µm, preferably 100nm to 5µm and especially 150nm to 2µm. The fractal material and the walls separating the pores within the porous particle fragments suitably have a thickness in the range 0.05 to 2µm, preferably 0.1 to 1µm, especially 100nm to 200nm. The porous particle fragments can also be defined by the length or largest diameter and the width (smaller diameter of the particle) as well as the material thickness. The ratio of the length of the width of the particle defines an aspect ratio. Preferably the porous particle fragments of the first aspect of the invention have an aspect ratio in the range of 2:1 to 5:1.

Typically the ratio of pore diameter to wall thickness for pore containing fragments is suitably greater than 2.5:1 and is preferably in the range 3:1 to 25:1. The ratio of the volume of the pores to the volume of the fragment (otherwise known as particle porosity) is suitably in the range 0.2 to 0.9, preferably 0.2

to 0.8, preferably 0.25 to 0.75 and especially 0.3 to 0.7.

The porous particle fragments suitably have a BET surface area of greater than 0.5 m^2/g, preferably at least $5m^2/g$. A higher surface area improves the electrical connectivity and ionic reactivity of the fragments as the active material in an electrode and generally increases the rate at which lithium can be inserted into the silicon. However a higher surface area leads to a larger amount of SEI layer being formed during charge and discharge of the electrode and consequently a higher lithium loss and reduced cycle life of the

components of the material is substantially retained over at least 100 charging and discharging cycles of a battery including the composite material. The cohesive mass of the composite electrode material may be provided in the form of a coating or layer, in which the porous particle fragments are arranged in a random or ordered fashion. The coating is typically applied or bonded to a current collector. Alternatively, the composite electrode material may be provided in the form of a felt or mat comprising silicon containing porous particle fragments and fibres of an electroactive or a conductive species which are randomly arranged in a composite material. The felt or mat is typically applied, adhered, bonded or connected to the current collector.

2.4.1 Additional Components of the Composite Electrode Material

The composite electrode material comprising porous particle fragments of the composition of the first aspect of the invention may optionally include, in addition to the silicon, tin, gallium, germanium, aluminium or lead containing porous particle fragments (first electroactive material) referred to herein above, additional components such as a binder, a conductive material and optionally a second electroactive material. Preferably the composition and/or structure of the second electroactive material is different to that of the first electroactive material. Examples of the second electroactive material include but are not limited to graphite, hard carbon, silicon, tin, gallium, germanium, aluminium and lead containing material. In a first preferred embodiment of the first aspect of the invention, the composition comprises a plurality of silicon containing porous particle fragments, a binder, a conductive material and optionally a non-silicon containing electroactive material. Alternatively, in a second preferred embodiment of the first aspect of the invention the composition may also contain, in addition to the components of the composition of the first embodiment, one or more silicon containing components having a minimal or negligible porosity, said components being selected from the group comprising native silicon containing particles; silicon containing tubes, wires, nano-wires, fibres, rods, sheets, elongate bundles, substrate particles, scaffolds and ribbons and silicon containing pillared particles. By the term “minimal or negligible porosity” it should be understood to mean silicon structures having a porosity of less than 0.2. The terms “minimally porous silicon containing particles, wires, nano-wires, fibres, rods, sheets and ribbons” may include solid elongate elements such as wires, fibres, rods, sheets, ribbons and particles having a silicon-based core respectively as well as wires, fibres, rods, sheets, ribbons and particles having a silicon coating provided on a core other than silicon. Where the silicon containing elongate elements and particles comprise silicon coated elongate elements, tubes and particles, the cores of these coated elements can be selected from electronically and ionically conductive materials such as carbon, preferably hard carbon or graphite or a suitable metal. The silicon containing elongate elements, tubes and particles can be formed

suitably comprises up to 50wt%, for example from 5 to 40% by weight of the electrode or anode material or mix.

In a preferred embodiment of the first aspect of the invention, the composition comprises, in addition to the silicon containing porous particle fragments, an electroactive carbon material. These electroactive carbons may be present in an amount comprising 8 to 90% of the total weight of the electroacive material, preferably 8 to 80% and especially 8 to 50%. Examples of suitable electroactive carbons include graphite, hard carbon, carbon microbeads and carbon flakes, nanotubes and nanographitic platelets. Suitable graphite materials include natural and synthetic graphite materials having a particle size in the range 5 to 30µm. Electroactive hard carbon suitably comprises spheroidal particles having a diameter in the range 2 to 50µm, preferably 20 to 30µm and an aspect ratio of 1:1 to 2:1. Carbon microbeads having a diameter in the range 2 to 30µm can be used. Suitable carbon flakes include flakes derived from either graphite or graphene.

In a first more preferred embodiment of the first aspect of the invention, the composition comprises 5 to 40wt%, preferably 10 to 30wt% and especially 15 to 25wt% of silicon-containing electroactive material including silicon-containing porous particle fragments and 60 to 95wt%, preferably 70 to 90wt% and especially 75 to 85wt% of an electroactive carbon material. Preferably an electroactive composition comprising 20wt% of a silicon-containing electroactive material including silicon-containing porous particle fragments and 80wt% of graphite can be used to manufacture an electrode material. The silicon-containing electroactive material may include electroactive silicon-containing structures such as native particles, fibres, threads, tubes, wires, nano-wires, pillared particles and the like as well as porous particle fragments. Preferably the silicon-containing electroactive material comprises porous particle fragments.

A second more preferred embodiment of the first aspect of the invention, the composition comprises 60 to 80wt%, preferably 70 to 80wt% and especially 80wt% of silicon-containing porous particle fragments and 20 to 40wt%, preferably 20 to 30wt% and especially 20wt% of an electroactive carbon material. Preferably an electroactive composition comprising 80wt% of silicon-containing porous particle fragments and 20wt% of graphite can be used to manufacture an electrode material. Compositions comprising 70wt% of silicon-containing porous particle fragments and 30wt% of graphite can also be used. The silicon-containing electroactive material may include electroactive silicon-containing structures such as native particles, fibres, threads, tubes, wires, nano-wires, pillared particles and the like as well as porous particle fragments. Preferably the silicon-containing electroactive material comprises porous particle fragments.

The binder is a component used to bind the components of the anode mix together either upon formation of the felt like mat or on application of the components to the current

collector. The binder helps to maintain the integrity of the anode mix according to the second aspect of the invention when used in battery cells. It also functions to help adhere the anode mix to the current collector. The binder can be added in an amount of 0 to 30% by weight based on the weight of the anode material. Examples of binders include, but are not limited to, polyvinylidene fluoride, polyacrylic acid, modified polyacrylic acid, carboxymethylcellulose, modified carboxymethylcellulose, polyvinyl alcohol, fluorocopolymers such as copolymers of hexafluoroethylene, polyimide, styrene butadiene rubber and thermo or photopolymerizable materials including, but not limited to, monomers, oligomers and low molecular weight polymers and mixtures thereof which are polymerizable by light irradiation and/or heat treatment. Examples of polymerizable monomers include epoxy, urethane, acrylate, silicon and hydroxyl based monomers and acrylic derivatives which may be used alone or in combination. Polymerisation of these materials is initiated with light irradiation or heat treatment. The polymerizable oligomer is a polymerisation product of from 2 to 25 monomers and may be formed into polymers having a higher degree of polymerisation by light irradiation or heat treatment. The term polymerisable low molecular weight polymer includes linear polymers and cross-linked polymers having a low degree of polymerisation or a low viscosity. Examples of such polymers include polyester acrylate, epoxy acrylate, urethane acrylate and polyurethane.

Preferably the binder is selected from one or more of a polyacrylic acid, poly(ethylene-maleic anhydride) a modified polyacrylic acid or alkali metal salts thereof. Lithium and sodium salts are preferred. Polyacrylic acid binders and sodium polyacrylic acid binders are able to bind to silicon materials containing impurities. The silicon-containing porous particle fragments according to the first aspect of the invention suitably have a silicon purity of between 75% and 100%. Preferably the silicon-containing porous particle fragments have a silicon purity of at least 80%, more preferably at least 95%. It is especially preferred that the silicon-containing porous particle fragments of the composition of the first aspect of the invention have a silicon purity of less than 99.99%, preferably less than 99.95% because these materials can be cheaper and the impurities can improve conductivity within the electrode structure. However if the level of impurities is too high the performance of the active material in the cell can be reduced and it has been found that a purity in the range 90% to 99.99% is preferred, more preferably 90% to 99.95%, especially 95% to 99.9%. It will be appreciated therefore, that the silicon containing porous particle fragments and other silicon containing components used in the preparation of compositions according to the first aspect of the invention may be derived from metallurgical grade silicon. Batteries including electrodes containing compositions of the first aspect of the invention, which include a binder comprising polyacrylic acid, a

range 10^3 to 10^5 K/s or faster: the use of cooling rates in this region results in the formation of alloy structures including regions of silicon comprising finely branched silicon structures. These finely branched silicon structures typically comprise tree like structures comprising branched rods of silicon having a diameter in the range 50 to 100nm, the rods including branches every 100 to 400nm. Where melt spinning techniques are used the rate of cooling depends on the rotational velocity of the cooled disc onto which the molten alloy particles impinge, the temperature of the disc, surrounding gas and its temperature and the alloy droplet size. Melt spinning techniques are generally associated with a cooling rate in the range 10^2 to 10^4K/s or 10^3 to 10^4 K/s. The use of cooling rates in this region results in the formation of alloy structures including regions of silicon comprising both coarse and fine silicon structures. Silicon structures having a minimum dimension of between 100nm and 500nm, preferably between 100nm and 200nm and a length in the range 5 to 10µm have been observed. Alloy additives can also affect the shape and form of the silicon structures. A sodium additive may tend to spheroidise the silicon structures which is not preferred, whilst a combination of Ti and Sr additives may reduce the size of fibre-like structures. .Alloys of silicon with aluminium, in which the alloy comprises up to 30% silicon are preferred. Silicon aluminium alloys comprising 12%, 26% and 30% silicon can be used in the fabrication of the porous silicon particles from which the porous particle fragments are derived. The use of silicon aluminium alloys comprising 12% silicon are preferred. However, silicon alloys containing both 27% and 30% silicon as a constituent have also been observed to yield porous particle fragments that can be used in the manufacture of half cells having a capacity retention of almost 100% over more than 80 cycles when charged to 1200mAh/g or 1400mAh/g. As indicated above, the precipitated porous silicon structure can be isolated from the bulk alloy by etching away the some or all of 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 Si structures, leaving them intact after a sufficient amount of the aluminium (some or all) 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 porous silicon particles and metal electrode. Similar

WO2009/010758, WO2009/010759 and WO2009/010757.

Although aluminium is preferred as the main component of the silicon alloy from which the silicon structures are precipitated, the skilled person will understand that other metals that will precipitate silicon during alloy cooling and can be etched may be used. Furthermore the skilled person will understand there are ways of foaming metals by injecting gases into the cooling molten mass and this can be applied to Si to create a "foamed" Si matrix. One such method is described in *"Fabrication of lotus-type porous silicon by unidirectional solidification in hydrogen"* in Materials Science and Engineering A 384 (2004) 373–376. Using techniques such as this potentially allows a skilled person to avoid the need to etch away a sacrificial material to obtain the Si mesh or matrix. Solgel formation methods such as those used with silica to produce Aerogel may also be applied to silicon. The silicon containing components or structures of the composition of the first aspect of the invention suitably comprise a high purity polycrystalline silicon material as well as polycrystalline silicon materials comprising either n-type or p-type dopants as impurities. Polycrystalline silicon materials comprising n-type or p-type dopants are preferred because these materials exhibit a greater conductivity compared to that of high purity polycrystalline silicon. Polycrystalline silicon materials comprising p-type dopants are preferred and can be easily prepared from the aluminium silicon alloys referred to herein or using methods (such as ion implantation) known to a person skilled in the art; these materials suitably include one or more impurities selected from aluminium, boron or gallium as dopants.

4. Methods of Making Porous Particle Fragments

A second aspect of the invention provides a method for fabricating a composition according to the first aspect of the invention, the method comprising partially crushing a silicon containing porous particle and isolating the silicon containing porous particle fragment, wherein the silicon containing fragments are obtained by partially crushing silicon containing whole porous particles having a diameter greater than 40µm, a porosity in the range of 0.2 to 0.8 and a pore wall thickness in the range 50nm to 2µm. In a first preferred embodiment of the second aspect of the invention, the porous particles having a diameter greater than 40µm are prepared by etching a silicon aluminium alloy as specified above are partially crushed to give silicon containing porous particle fragments having a diameter in the range 1 to 40µm. The etched particles are cleaned and placed in an ultra

The invention also provides silicon containing porous particle fragments prepared according to the method of the second aspect of the invention. There is therefore provided a composition comprising a plurality of silicon containing porous particle fragments prepared by partially crushing a plurality of silicon containing porous particles. The silicon containing porous particles from which the silicon containing porous particle fragments are derived suitably have a diameter of greater than 40pm, preferably greater than 60 pm, more preferably greater than 100pm and especially greater than 120pm. Typically the silicon containing porous particles from which the silicon containing porous particle fragments are derived suitably have a diameter in the range 40 to 200pm, preferably 50 to 150pm and especially 70 to 100pm. Preferably the porous particle fragments of the first aspect of the invention are prepared from porous particles (including porous particles comprising a network of elongate elements) having a diameter in the range 60 to 1500pm, more preferably 150 to 1000pm. These "starting particles" may be prepared by either etching a silicon aluminium alloy or by stain etching of a silicon particle using methods that are known to a skilled person as set out above.

There is provided a composition comprising a plurality of silicon-containing porous particle fragments having a diameter in the range 1 to 40pm, preferably 1 to 20pm, more preferably 1 to 15pm and especially 1 to 10pm and an average smallest dimension (thickness) in the range 50nm to 2 pm, preferably 100nm to 1 pm, the porous particles being prepared by partially crushing porous silicon-containing particles having a diameter of at least 60pm, preferably at least 100 pm and especially at least 120 pm and having an average smallest dimension in the range 50nm to 2 pm, preferably 100nm to 1 pm. The silicon-containing whole porous particles are suitably prepared by etching a silicon alloy, preferably a silicon/aluminium alloy in a solution comprising a mixture of acetic acid, nitric acid and phosphoric acid to remove the bulk metal with which the silicon material is alloyed, washing and drying the particle.

There is further provided a porous particle fragment prepared by a method comprising the steps of:

a) Providing a molten silicon aluminium alloy composition comprising between 12 and 30wt% silicon;
b) Cooling the molten silicon aluminium alloy composition at between 10^2 and 10^5K/s to form a silicon aluminium particulate material having a diameter in the range 40 to 1500pm;
c) Etching the particulate material formed in (b) to form porous particles

d) partially crushing the porous particles formed in (c) to give porous particle fragments having a maximum diameter of less than 40µm

The molten alloy is suitably cooled in step (b) using either gas atomisation or melt spinning techniques. The etchants used in step (c) are well known to a person skilled in the art and are listed herein above. Where the alloy is a silicon aluminium alloy the amount of aluminium that can be removed from the alloy will depend on the etching conditions used.

The porous particle fragments prepared according to the second aspect of the invention can be characterised by fractal or pore wall thicknesses in the range 50nm to 2µm. Porous particle fragments having a fractal thickness of 50 to 100nm can be used to make batteries. Fractal structures having a fractal or pore wall thickness in the range 100nm to 200nm can be used to prepare composite electrodes, which exhibit particularly good cycling behaviour.

5. Electrodes

The electroactive material according to the first aspect of the invention can be used in the manufacture of an electrode. The electrode is typically an anode. The electrodes are preferably used in the manufacture of a lithium secondary battery. A third aspect of the invention therefore provides an electrode comprising a composition according to the first aspect of the invention and a current collector. Preferably an electrode according to the third aspect of the invention comprises a composition according to the first aspect of the invention, a binder and a current collector. The electroactive material according to the first aspect of the invention is suitably provided in the form of an electrode or anode material, said electrode or anode material comprising in addition to the silicon containing porous particle fragments, a binder and optionally one or more components selected from the group comprising, a conductive material and a further electroactive material. Preferably the electrode or anode material comprises fractals as described above. The anode material can be in the form of a free-standing mat which can be connected or adhered to a current collector. Alternatively the anode mix can be provided in the form of a coating, which can be adhered to a current collector. The components of the anode mix from which the mat is formed are typically randomly arranged within the anode structure to provide optimum connectivity between the elements. The electrodes of the third aspect of the invention are easily prepared and a there is therefore provided a method for fabricating an electrode comprising the steps of forming an electrode or anode mix, said electrode or anode mix comprising a slurry of a composition according to the first aspect of the invention and a solvent (herein after referred to as an electrode mix) and casting the electrode or

anode mix onto a substrate and drying the product to remove the solvent thereby to form the electrode or anode material on the substrate. The dried product (electrode material) is in the form of a cohesive mass which may be removed from the substrate, connected to a current collector and used as an electrode. Alternatively, where the composition according to the first aspect of the invention is adhered to the substrate as a result of casting and drying the slurry (electrode mix), the resulting cohesive mass will be connected or bonded to a current collector. In a preferred embodiment of the first aspect of the invention the composition is cast onto a substrate, which is itself a current collector. One or more components selected from the group comprising a conductive material, a viscosity adjuster, a filler, a cross-linking accelerator, a coupling agent and an adhesive accelerator may also be included in the slurry mixture (electrode mix). Examples of suitable conductive materials, viscosity adjusters, fillers, cross-linking accelerators, coupling agents and adhesive accelerators are provided above. Suitable solvents include N-methylpyrrolidone and water.

Suitable current collectors for use in electrodes according to the third aspect of the invention include copper foil, aluminium, carbon (including graphite), nickel, conducting polymers and any other conductive materials. The current collectors typically have a thickness in the range 10 to 50µm, preferably 10 to 20µm. Current collectors can be coated with the electrode mix on one side or can be coated with the electrode mix on both sides. A composition of the first aspect of the invention is preferably applied to one or both surfaces of the current collector to a thickness of between 1mg/cm^2 and 6mg/cm^2 , preferably between 1mg/cm^2 and 3mg/cm^2 per surface such that the total thickness of the electrode (current collector and coating) is in the range 25um to 1mm where only one surface of the current collector is coated or in the range 50µm to 1mm where both surfaces of the current collector are coated. In a preferred embodiment, the electrode or anode material is applied to a thickness of between 30 and 40µm onto one or both surfaces of a copper substrate having a thickness of between 10 and 15µm. The current collector may be in the form of a continuous sheet or a porous matrix or it may be in the form of a patterned grid or mesh defining metallised regions and nonmetallised regions. Where the current collector comprises a continuous sheet, the electrode may be readily manufactured by applying a slurry of the anode mix directly to the current collector. Where the current collector comprises a metallised grid, this metallised grid may be formed onto a non-stick substrate such as PTFE to give a metallised non-stick surface (such as metallised PTFE) and the slurry of the anode mix is applied to the metallised nonstick surface and dried to give a metallised mat or felt. Alternatively the mesh or grid can be dipped into a solution or slurry to form a composite electrode.

In an embodiment of the invention, the electrode may be formed by casting the silicon containing mixture onto a substrate thereby to form a self supporting structure such as a free-standing felt or mat and connecting a current collector directly thereto.

The electrode of the third aspect of the invention can be used as an anode in the manufacture or formation of a lithium secondary battery. There is therefore provided a secondary battery comprising a cathode, an anode comprising a composition according to the first aspect of the invention and an electrolyte.

6.Cathode

The cathode is typically prepared by applying a mixture of a cathode active material, a conductive material and a binder to a cathode current collector and drying. Examples of cathode active materials that can be used together with the anode active materials of the present invention include, but are not limited to, layered compounds such as lithium cobalt oxide, lithium nickel oxide or compounds substituted with one or more transition metals such as lithium manganese oxides, lithium copper oxides and lithium vanadium oxides. Many such materials can be defined by the generic formula $Li_{1+x}(Ni_bCo_cAl_eMn_f)_{1-x}O_2$, where b, c, e, f and x have values of between 0 and 1. Examples of suitable cathode materials include $LiCoO_2$, $LiCo_{0.99}Al_{0.01}O_2$, $LiNiO_2$, $LiMnO_2$, $LiMn_2O_4$, $LiCo_{0.5}Ni_{0.5}O_2$, $LiCo_{0.7}Ni_{0.3}O_2$, $LiCo_{0.8}Ni_{0.2}O_2$, $LiCo_{0.82}Ni_{0.18}O_2$, $LiCo_{0.8}Ni_{0.15}Al_{0.05}O_2$, $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$, $Li_{1+x}(Ni_{0.333}Co_{0.333}Mn_{0.333})_{1-x}O_2$, $Li_{1+x}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{1-x}O_2$, $Li_{1+x}(Ni_{0.4}Co_{0.2}Mn_{0.4})_{1-x}O_2$, and $Li_{1+x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, phosphate-based cathodes such as $LiFePO_4$, non-lithiated cathode materials like V_6O_{13}, and sulphur / polysulphide cathodes. The cathode current collector is generally of a thickness of between 3 to 500µm. Examples of materials that can be used as the cathode current collector include aluminium, stainless steel, nickel, titanium and sintered carbon.

7. Electrolyte

The electrolyte is suitably a non-aqueous electrolyte containing a lithium salt and may include, without limitation, non-aqueous electrolytic solutions, solid electrolytes and inorganic solid electrolytes. Examples of non-aqueous electrolyte solutions that can be used include non-protic organic solvents such as N-methylpyrrolidone, propylene carbonate, ethylene carbonate, butylenes carbonate, dimethyl carbonate, diethyl carbonate, gamma butyrolactone, 1,2-dimethoxy ethane, 2-methyl tetrahydrofuran, dimethylsulphoxide, 1,3-dioxolane, formamide, dimethylformamide, acetonitrile, nitromethane, methylformate, methyl acetate, phosphoric acid trimester, trimethoxy methane, sulpholane, methyl sulpholane and 1,3- dimethyl-2-imidazolidione.

In an embodiment of the invention there is provided a battery comprising a cathode, an anode comprising a composition according to the first aspect of the invention and an electrolyte including an electrolyte solvent and an electrolyte salt, wherein the electrolyte solvent comprises a mixture of fluoroethylene carbonate (FEC) and ethylmethyl carbonate (EMC). It is particularly preferred that the electrolyte solvent includes a cyclic carbonate including a vinyl carbonate as an additive. In a further embodiment, the electrolyte solvent comprises 40 to 60vol%, preferably 50vol% FEC, 40 to 48vol%, preferably 46vol% EMC and 2 to 10vol%, preferably 4vol% VC.

Examples of organic solid electrolytes include polyethylene derivatives polyethyleneoxide derivatives, polypropylene oxide derivatives, phosphoric acid ester polymers, polyester sulphide, polyvinyl alcohols, polyvinylidine fluoride and polymers containing ionic dissociation groups.

Examples of inorganic solid electrolytes include nitrides, halides and sulphides of lithium salts such as Li_5NI_2, Li_3N, LiI, $LiSiO_4$, Li_2SiS_3, Li_4SiO_4, LiOH and Li_3PO_4.

The lithium salt is suitably soluble in the chosen solvent or mixture of solvents. Examples of suitable lithium salts include LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $_{LiB10C20,}$ $LiPF_6$, $LiCF_3SO_3$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li and CF_3SO_3Li, lithium bis(oxatlato)borate (LiBOB) or a mixture thereof, dissolved in one or more cyclic and dialkyl carbonates referred to above. Examples of other electrolyte salts that can be used are found in JP 2008234988, US 7659034, US 2007/0037063, US 7862933, US 2010/0124707, US 2006/0003226, US 7476469, US 2009/0053589 and US 2009/0053589. Preferably the electrolyte salt is $LiPF_6$ or a mixture of $LiPF_6$ and lithium bisoxalate borate (LiBOB). A preferred electrolyte solution comprises 0.9 to 0.95M $LiPF_6$ and 0.05 to 0.1M LiBOB. The concentration of the lithium salt in the electrolyte solution is not limited but is preferably in the range of 0.5 to 1.5M. When larger amounts of additives are used it is preferable to increase the concentration of the lithium salt to prevent excessive depletion of lithium in the final electrolyte solution.

Where the electrolyte is a non-aqueous organic solution, the battery is provided with a separator interposed between the anode and the cathode. The separator is typically formed of an insulating material having high ion permeability and high mechanical strength. The separator typically has a pore diameter of 0.01 to 100µm and a thickness of 5 to 300µm.

The battery according to embodiments of the invention can be used to drive a device, which relies on battery power for its operation. Such devices include mobile phones, laptop

computers, GPS devices, motor vehicles and the like. There is therefore provided a device including a battery according to embodiments of the invention.

The invention will now be described with reference to the following figures and non-limiting examples. Variations on these falling within the scope of the invention will be evident to a person skilled in the art.

8. Figures

Figure 1 shows a schematic view of a prior art battery.

Figure 2a shows an SEM image of a porous particle produced according to the procedure set out in the examples below. These porous particles were prepared by etching particles of an AlSi alloy comprising 12wt% silicon and having a diameter of 10 to 63µm, the alloy particles being formed through the use of a gas atomisation cooling technique. The silicon structures are characterised by a network of fine silicon structures.

Figure 2b shows a schematic diagram of the fine silicon fractal structures formed by partially crushing a porous particle illustrated in 2a.

Figure 2c shows an SEM of the silicon structures formed by partially crushing a porous particle illustrated in 2a.

Figure 2d shows an SEM image of a porous particle produced according to the procedure set out in the examples below. These porous particles were prepared from particles of an AlSi alloy comprising 27wt% silicon and having a diameter of 10 to 90µm, the alloy particles being formed through the use of a gas atomisation cooling technique. The porous particle is characterised by regions of particulate silicon interspersed within regions of finely branched silicon fibres.

Figure 2e shows an SEM image of a porous particle fragment obtained by partially crushing porous particles illustrated in Figure 2d.

Figure 2f shows an SEM of a porous particle fragment (fractal) produced by partially crushing the porous particles produced from AlSi(12wt%) alloy particles (formed using a gas atomisation technique) and having a diameter of 60 to 90µm, the porous particles being produced according to the procedure set out in the examples below.

Figure 3a shows an SEM image of a porous particle fragment produced according to the procedure set out in the examples below. These porous particle fragments were prepared by

Claims

1. A composition comprising a silicon containing electroactive porous particle fragments characterised in that the porous particle fragments are selected from the group comprising:

    a. A pore-containing porous particle fragment comprising a network of pores, cavities and channels, which pores, cavities and channels are separated and defined by silicon-containing walls within the particle structure;

    b. A fractal comprising a substantially irregular shape or surface morphology derived from the silicon material originally defining or bounding the pores or network of pores within the porous particle from which the fractals are derived without themselves comprising pores, channels or a network of pores or channels;

    c. A fractal having a substantially irregular shape or surface morphology derived from silicon material originally defining a random or ordered network of linear, branched or layered elongate elements, wherein one or more discrete or interconnected void spaces or channels are defined between the elongate elements of the network.

2. A composition according to claim 1, wherein the fractal and/or the silicon-containing walls of the pore-containing porous particle fragment have a thickness in the range 0.05 to 2µm, and/or,
wherein the ratio of the pore width to wall thickness in the pore-containing porous particle fragment is greater than 2:5:1.

3. A composition according to any one of claims 1 to 2, wherein the silicon containing porous particle fragments have a maximum diameter in the range of 1 to 40 µm, and/or,
an aspect ratio (length (largest diameter) to width (smallest diameter) of particle) in the range 2:1 to 5:1.

4. A composition according to any one of claims 1 to 3 which, comprises 10 to 100vol% of porous particle fragments having a maximum diameter of less than 40 µm.

5. A composition according to any one of the preceding claims, wherein the fractal structure comprises at least one peak or ridge disposed over the surface thereof,
and/or,
wherein the fractal structure has a spiky appearance,
and/or,
wherein the fractal structure has a ridged appearance.

6. A composition according to any one of claims 1 to 4, characterised in that the pore containing porous particle fragments comprise pores having a width in the range 60nm to 10µm, preferably 150nm to 2µm,
and/or,
wherein the ratio of the total volume of the pores in the fragment to the total volume of the fragment is in the range 0.2 to 0.9, preferably 0.2 to 0.8, more preferably 0.25 to 0.75 and especially 0.3 to 0.7.

7. A composition according to any one of the preceding claims, wherein the particle fragments have a BET surface area greater than $4m^2/g$, preferably greater than $5m^2/g$, and/or,
wherein the particle fragments have a BET surface area of less than 50 m^2/g, preferably less than $40m^2/g$, suitably less than $30m^2/g$.

8. A composition according to any one of the preceding claims, which further comprises one or more further silicon containing components selected from the group comprising native silicon containing particles having a minimal or negligible porosity; silicon containing wires, nano-wires, fibres, rods, tubes, sheets, elongate bundles, substrate particles, scaffolds, ribbons and silicon containing pillared particles.

9. A method of making a composition according to any one of claims 1 to 8, the method comprising partially crushing a silicon containing porous particle and lsolating the silicon containing porous particle fragments, wherein the silicon containing fragments are obtained by partially crushing silicon containing whole porous particles having a diameter greater than 40 µm, a porosity in the range 0.2 to 0.8 and a pore wall thickness in the range 50nm to 2µm.

10. A method according to claim 9, which comprises the steps of:
    a. forming a molten silicon aluminium allow composition;
    b. cooling the molten composition to give alloy particles;
    c. etching the alloy particles to give silicon-containing porous particles;
    d. partially crushing the silicon-containing porous particles from (c) to give silicon-containing porous particle fragments.

11. A method according to claim 10, wherein the molten alloy composition comprises from 11 to 35wt% silicon.

12. A method according to any one of claims 10 to 11, wherein the molten composition is cooled at a rate of between 10^2 and $10^5 K/s$.

13. A method according to any one of claims 10 to 12, wherein the cooled alloy particles have a diameter of from 40 to 1500 µm.

14. An electrode comprising a current collector and a composition according to any one of claims 1 to 8.

15. An electrode according to claim 14, wherein the composition is in the form of a mat or felt connected, adhered or applied to a current collector,
optionally,
wherein the composition is in the form of a free standing felt or mat to which a current collector is connected.