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.

The use of silicon as an active anode material in secondary batteries such as lithium ion batteries is well known. Early forms of these lithium ion batteries were prepared using bulk silicon electrodes, thin film silicon electrodes and silicon powder electrodes. Subsequently, silicon comprising electrodes including silicon comprising pillars, rods, fibres and wires have been prepared. Silicon comprising particles having a surface array of pillars have also been used in the fabrication of lithium ion batteries. US 2008/0241647discloses a cylindrical lithium battery comprising silicon or silicon alloy particles having dimensions in the range 5µm to 15µm. According to US 2008/0241647, batteries including silicon particles having dimensions outside this range exhibit inadequate performance; particles with diameters of less than 5µm give batteries with inadequate capacity, whereas batteries including particles having diameters greater than 15µm exhibit inadequate mechanical properties due to stresses arising from the expansion and contraction of the silicon material during the charge and discharge cycles of the battery. The particles used in the cylindrical batteries of US 2008/0241647 are prepared by chemical vapour deposition of silane onto seeded polycrystalline silicon. These particles are characterised by the presence of crystallites with dimensions of between 30 and 100nm. The polycrystalline nature of these particles means that each particle includes a large number of grain boundaries.

US 2009/0253033 discloses an anode active material suitable for use in lithium ion secondary batteries. The anode material comprises silicon or silicon alloy particles with dimensions of between 500nm and 20µm. These particles are manufactured using techniques such as vapour deposition, liquid phase deposition or spraying techniques.

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, rods or wires having nanoscale dimensions. Rods or wires having diameters in the range 1 to 50nm and lengths in range 500nm to 10µm can be prepared by laser ablation using an iron catalyst. Other techniques such as solution synthesis and chemical vapour deposition are also disclosed as being useful. Iron Germanium alloy nanostructures comprising a mixture of particles having a dimension in the range 1 to 50 nm and micron length rods having a diameter in the range 5 to 30nm can also be prepared using laser ablation. Similar nanostructures are disclosed in US 6334939 and ~~ZL~~CN1447916A.

~~01814166.8.~~ 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.

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 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 1000mA/g over 50 cycles are illustrated. The life of the battery is significantly increased if the battery is operated at a limited voltage level.

US 2010/0143798 discloses a solid nano-composite particulate composition for use in lithium ion batteries. The nano-composite particles comprise an electroactive material in the form of fine particles, rods, wires, fibres and tubes; nano-graphene platelets and a protective matrix. The electro-active material includes silicon comprising nano-structures having a typical diameter of 60nm. Solid nano-composite particles were prepared by dispersing a mixture of the electro-active material and nano-graphene platelets having an average diameter of 60nm in a polymeric matrix and spray drying the resulting mixture to produce nano-composite particles having an average diameter in the range 1µm to 5µm.

US 2008/0261112 discloses an electrode material including an electroactive material comprising a mixture of silicon comprising particles and nano-wires. The nano-wires are entangled to form a network, which is in contact with the particles. The electroactive composition is prepared by placing a silicon comprising material in a thermal plasma at a temperature of between 600 and 1500℃ to give a composition comprising a mixture of silicon comprising particles having a diameter of about 5µm and silicon comprising fibres having a diameter in the range 30 to 50nm. The components of the compositions become both entangled with and fused to adjacent components during the fabrication process. Further, the fabrication process means that the composition as a whole is fused to the current collector and anodes prepared in the way do not include additional components such as a binder or a conductive additive. Although it is alleged that these compositions are able to both accommodate silicon expansion during lithium intercalation and reduce the build up of an irreversible capacity over the lifetime of the cell, the diameter of the nano-wires present in the composition mean that they have a relatively high surface area and it is expected that the compositions of US 2008/0261112 will exhibit a relatively high first cycle loss as a result

carbon black, acetylene black, ketjen black, channel black; conductive fibres such as carbon fibres (including carbon nanotubes) and metallic fibre; metaellic powders such as carbon fluoride powder, aluminium powder and nickel powder; conductive whiskers such as zinc oxide and potassium titanate; conductive metal oxides such as titanium oxide and polyphenylene derivatives. Suitably the total amount of conductive carbon and electroactive carbon (such as graphite) comprises 4 to 85% of the total electroactive material by weight.

A filler is a further ingredient that may be present and can be used to inhibit anode expansion. There is no particular limit to the filler so long as it does not cause chemical changes in the fabricated battery and is a fibrous material. As examples of filler there may be used olefin polymers such as polyethylene and polypropylene and fibrous materials such as glass fibre and carbon fibres.

A coupling agent, if present, is a material used to increase adhesive strength between the active material and the binder and is characterised by having two or more functional groups. The coupling agent may be added in an amount of up to 0 to 30% by weight based on the weight of the binder. There is no particular limit to the coupling agent so long as it is a material in which one functional group forms a chemical bond via reaction with a hydroxyl or carboxyl group present on the surface of the silicon, tin or graphite-based active material, and the other functional group forms a chemical bond via reaction with the nanocomposite according to the present invention. Examples of coupling agents that can be used in the present invention include silane based coupling agents such as triethoxysilylpropyl tetrasulphide, mercaptopropyl triethoxysilane, aminopropyl triethoxysilane, chloropropyl triethoxysilane, vinyl triethoxysilane, methacryloxypropyl triethoxysilane, glycidoxypropyl triethoxysilane, isocyanopropyl triethoxysilane and cyanopropyl triethoxysilane.

An adhesive accelerator may be added in an amount of less than 10% by weight based on the weight of the binder. There is no particular limit to the nature of the adhesive accelerator so long as it is a material that improves the adhesive strength of the anode mix to the current collector. Examples of adhesive accelerators include oxalic acid, adipic acid, formic acid, acrylic acid and derivatives, itaconic acid and derivatives and the like. The silicon comprising 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; these materials suitably include one or more impurities selected from aluminium, boron or gallium as dopants.

The electrode materials can be characterised in relation to their density and their porosity. The electrode materials of the first aspect of the invention typically have density in the range 0.3 to 0.9g/cm^2, preferably 0.4 to 0.8g/cm^2. Electrode materials comprising a mixture of silicon-comprising fibres and silicon-comprising native particles in a ratio of 10:90 are characterised by a density of 0.79g/cm^2. Electrode materials comprising a mixture of silicon-comprising fibres and silicon-comprising native particles in a ratio of 90:10 are characterised by a density of 0.43g/cm^2. Further, the electrode materials of the first aspect of the invention typically have a porosity in the range 65 to 95%, preferably 65 to 85%. Electrode materials comprising a mixture of silicon-comprising fibres and silicon-comprising native particles in a ratio of 10:90 are characterised by a porosity of 69%. Electrode materials comprising a mixture of silicon-comprising fibres and silicon-comprising native particles in a ratio of 90:10 are characterised by a porosity of 83%.

The composition of the first aspect of the invention can be easily manufactured and a second aspect of the invention provides a method of preparing an electroactive material according to the first aspect of the invention, the method comprising the steps of mixing

a. a plurality of metal or semi-metal comprising elongate elements selected from one or more of the group comprising fibres, tubes, threads, ribbons and flakes with

b. a plurality of metal or semi-metal comprising particles ~~Selected~~ selected from one or more of the group comprising pillared particles, porous particles and porous particle fragments.

The method of the second aspect of the invention can be modified in that

a. the elongate elements are selected from one or more of the group comprising fibres or threads having a diameter in the range 100 to ~~200nm~~500nm, tubes, ribbons and flakes; and

b. the particles comprise native silicon particles.

A further modification of the method of the second aspect of the invention involves mixing an elongate element with a particulate element, wherein

a. the elongate element is a pillared particle having a an overall diameter in the range 20 to 30µm and pillar lengths of up to 10µm; and

b. the particles are selected from one or more of the group comprising native particles, porous particles and porous particle fragments.